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One Hundred Years of the Fritz Haber Institute

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Dedicated to Professor Gerhard Ertl on the occasion of his 75th birthday

We outline the institutional history and highlight aspects of the scientific history of the Fritz Haber Institute (FHI) of the Max Planck Society, successor to the Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry, from its founding in 1911 until about the turn of the 21st century. Established as one of the first two Kaiser Wilhelm Institutes, the Institute began as a much-awaited remedy for what prominent German chemists warned was the waning of Germany's scientific and technological superiority relative to the United States and to other European nations. The history of the Institute has largely paralleled that of 20th century Germany. It spearheaded the research and development of chemical weapons during World War I, then experienced a "golden era" during the 1920s and early 1930s, in spite of financial hardships. Under the National Socialists it suffered a purge of its scientific staff and a diversion of its research into the service of the new regime, accompanied by a breakdown in its international relations. In the immediate aftermath of World War II it suffered crippling material losses, from which it recovered slowly in the postwar era. In 1952, the Institute took the name of its founding director and the following year joined the fledgling Max Planck Society, successor to the Kaiser Wilhelm Society. During the 1950s and 1960s, the Institute supported diverse research into the structure of matter and electron microscopy in its geographically isolated and politically precarious location in West Berlin. In subsequent decades, as Berlin benefited from the policies of détente *and later* glasnost *and the Max Planck Society continued to reassess its preferred model of a research institute, the FHI reorganized around a board of coequal scientific directors and renewed its focus on the investigation of elementary processes on surfaces and interfaces, topics of research that had been central to the work of Fritz Haber and the first "golden era" of the Institute. Throughout its one-hundred-year history, the Institute's pace-setting research has been shaped by dozens of distinguished scientists, among them seven Nobel laureates. Here we highlight the contributions made at the Institute to the fields of gas-phase kinetics and dynamics, early quantum physics, colloid chemistry, electron microscopy, and surface chemistry, and we give an account of the key role the Institute played in implementing the Berlin Electron Synchrotron (BESSY I and II). Current research at the Institute in surface science and catalysis as well as molecular physics and spectroscopy is exemplified in this issue [Angew. Chem.* ***2011****, 123, 10242; Angew. Chem. Int. Ed.* ***2011****, 50, 10064].*

1. Introduction

The Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry was established in 1911 as one of the first two institutes of the Kaiser Wilhelm Society (KWG). Its successor, the Fritz Haber Institute (FHI), is not only one of the oldest and most tradition-rich institutes of the Max Planck Society (MPG), but also one of the most distinguished, with the highest number of affiliated Nobel laureates of any KWG/MPG institute. These include Fritz Haber, the founding director, the later directors Max von Laue, Ernst Ruska, and Gerhard Ertl, and several scientists who served at the Institute in lesser capacities, such as James Franck, Eugene Wigner, and Heinrich Wieland (Table 1).

The Institute has been not only a hub of scientific excellence and productivity but also an active participant in the history of the 20th century. It played a central role in the German development of chemical warfare during World War I. It was particularly hard-hit by Nazi racial policies and was revamped into a "Nazi Model Enterprise" during the Third Reich; and finally, to remain productive during the Cold War, its directors had to find ways to assert its importance in the territorially insular and politically precarious city of West Berlin.

The shifting fortunes and socio-political roles of the Institute help to explain the striking breadth of topics that have been researched within its walls over the past century, but so too do the diverse abilities and personalities of the scientists who have made the Institute, however briefly, their

Table 1: Nobel laureates affiliated with the KWI for Physical Chemistry and Electrochemistry or later the Fritz Haber Institute of the Max Planck Society.

	Year of award and affiliation	Nobel prize winning work done at	Period at KWI-PChE/FHI-MPG	Capacity
Max von Laue (1879-1960)	1914, Munich (LMU)	Munich (LMU)	1951-1959	Director
Fritz Haber (1868-1934)	1918, Berlin (PChE)	Karlsruhe (THK)	1911-1933	Founding Director
James Franck (1882-1964)	1924, Göttingen (GAU)	Berlin (FWU)	1918-1920	Department Leader
Heinrich Wieland (1877-1957)	1927, Munich (LMU)	Freiburg (ALU), Munich (LMU)	1917-1918	Fellow, Army Officer
Eugene Wigner (1902-1995)	1963, Princeton	Berlin (PChE, THCh), Princeton	1923-1932	PhD Student, Fellow
Ernst Ruska (1906-1988)	1986, Berlin (FHI)	Berlin (THCh, Siemens, FHI)	1949-1974	Director of the Institute of Electron Microscopy
Gerhard Ertl (*1936)	2007, Berlin (FHI)	Munich (LMU), Berlin (FHI)	1986-2004	Director

ALU	Albrecht-Ludwig-Universität Freiburg
FWU/HU	Friedrich-Wilhelms-Universität/Humboldt-Universität zu Berlin
GAU	Georg-August-Universität Göttingen
KWI-PChE/FHI-MPG	KWI für Physikalische Chemie und Elektrochemie/Fritz-Haber-Institut der MPG
LMU	Ludwig-Maximilians-Universität München
THCh/TUB	Technische Hochschule Charlottenburg/Technische Universität Berlin
THK	Technische Hochschule Karlsruhe

intellectual home. Dozens of distinguished scientists, including the previously mentioned seven Nobel laureates, have shaped the pacesetting research in physical chemistry, chemical physics, and other areas, such as electron microscopy, performed at the Institute. Their interests have ranged from providing for the concrete needs of society, in times of peace or war, to plumbing the abstract depths of quantum mechanics, and from the apparent simplicity of hydrogen chemistry to the acknowledged complexity of nonlinear dynamics. Their investigations reflect a distinct, intellectual facet of 20th century history that is inextricable from social, cultural, and political history.

In order to do justice to the complex scientific and political history of the FHI, the Institute's Board of Directors, prompted by the approaching centenary of the Institute (and the KWG/MPG), offered support in 2007 for a broad historical investigation of the Institute from its inception to the present. The *Centennial Group*, established in response to the Board's initiative in the Fall of 2008 and comprised of Bretislav Friedrich, Dieter Hoffmann, Jeremiah James, and Thomas Steinhauser, launched a research project to examine the Institute's scientific and institutional history supported by archival evidence and set against the context of the rapid changes in the intellectual content of the sciences to which the Institute contributed and in the societies, both scientific and political, that supported it.

In writing the scientific and institutional history of the Institute, we have been frequently reminded of the words of a doyen of modern history of science research, Gerald Holton:[1] "*[The] science research project of today is the temporary culmination of a very long, hard-fought struggle by a largely invisible community of our ancestors. Each of us may be standing on the shoulders of giants; more often we stand on the graves of our predecessors.*" At times in the history of the Fritz Haber Institute, these struggles for the future of science have been as clearly political and social as "simply" intellectual and have, in themselves or through their outcomes, had profound, and even fatal, repercussions. The *Centennial Project* in general and its main outcome, the centennial volume,[2] in particular have aimed to highlight these struggles of the past and to pay tribute to those who, for the most part, persevered through them.

In this Essay, largely based on the centennial volume, we provide a brief survey of the institutional history of the Institute and highlight contributions from the Institute to the research areas that featured on its agenda with particular prominence: gas-phase kinetics, early quantum physics, colloid chemistry, electron microscopy, BESSY, and surface chemistry.

2. Outline of the Institutional History of the FHI

When the KWG was founded in 1911 it became the third in a series of institutional innovations during the "long 19th century"—after the founding of the Berlin University (1810) and of the Imperial Institute of Physics and Technology (1887)—which originated in Berlin but shaped the modern research establishment more broadly. The founding of the KWG in general and the Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry in particular came about in reaction to forewarnings by numerous prominent scientists and science policymakers about the waning of Germany's scientific and technological superiority relative to the United States and to other European nations, especially France and Britain.[3] In hindsight, these institutions appear to have been a successful answer to this perceived challenge, in that during the following decades the KWG established itself as one of the leading research organizations both domestically and internationally. The Institute supported the development of physical chemistry, which was—in comparison to the then dominant organic chemistry—not a well-established field in Germany at that time. At its founding it had more resources and better research equipment at its disposal than most laboratories at German universities, and it rapidly became one of the leading research institutions in its field, with its predominantly "pure" research endeavors reaching a first high-point during the Weimar era.

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Figure 1. The banker and entrepreneur Leopold Koppel. Illustration by David Vandermeulen.

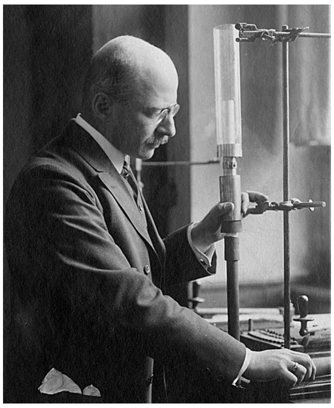


Figure 2. Fritz Haber in his laboratory in Karlsruhe, ca. 1905.

The establishment of the KWI for Physical Chemistry and Electrochemistry was made possible by an endowment from the Berlin Banker and philanthropist Leopold Koppel (1854–1933 Figure 1), granted on the condition that Fritz Haber (1868–1934; Figure 2), well-known for his discovery of a method to synthesize ammonia from its elements, be made its director.

Fritz Haber headed the Institute (Figure 3) from its inception up to his resignation in protest of National Socialist policies and emigration from Germany in 1933.[4] His aim was to establish a research institute for modern physical chemistry, whose research spectrum ranged from such classic topics as chemical processing technology and electrochemistry to reaction kinetics and colloid chemistry to aspects of quantum physics. He was, in this respect, akin to contemporaries such as Walther Nernst and Gilbert N. Lewis who helped pave the way for the transition from classical physical chemistry to chemical physics.

Figure 3. The Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry in Berlin-Dahlem, 1913; the Director's villa is on the far right.

Figure 4. The Kaiser Wilhelm Institute under Haber's direction with surrounding barracks during World War I.

The German entry into World War I in August of 1914 brought an end to the founding era of the Institute, since Haber not only took part in the widespread enthusiasm that accompanied German mobilization and entry into the war, but also promptly redirected the resources of his institute toward projects relevant to the war. After the war he would explain that "*in war, scientists belong to their Fatherland, like anyone, in peace, they belong to humanity.*"[5] The first war-related task of the Institute was to search for ways to economize or provide substitutes for so-called "war materials"—substances required for the operation of firearms, artillery, and other war machines. In the winter of 1914–1915 Haber proposed and began organizing the first gas cloud attack, which took place near Ypres on April 22, 1915. Shortly thereafter, at the request of the military, Haber redirected the research at the Institute toward the needs of gas warfare, focusing first on gas masks and defense but soon branching out into research and development of offensive measures. The Institute became the center of chemical warfare research and development in Germany (Figure 4). This brought about an unprecedented expansion of the Institute and its division into nine departments employing approximately 150 scientists and engineers and 1300 support staff, the latter composed largely of women. The Institute became a prototypical example of Big Science in the context of a military–industrial–academic complex, not only with respect to its sheer size but, above all, with respect to the complexity of its organizational structure and interdisciplinarity of its research methods. In the words of the historian Fritz Stern, Haber's Institute during the First World War became "*a kind of forerunner of the Manhattan Project*."[6]

After the German defeat in World War I the Institute had to withdraw rapidly from military involvement and a discussion ensued as to its future research direction. The following fourteen years are sometime referred to as the "golden era" of the Institute, since so much pioneering and outstanding research was done during the 1920s and early 1930s. The central research areas of the Institute during the "golden era," as set forth by Haber in 1923, were colloid chemistry and atomic structure.[7] These very broadly defined fields were meant to include investigations of surface energy, coagulation, photochemistry, reaction mechanisms, and even aspects of combustion—some details of which are provided below.

Figure 5. Farewell party for James Franck, Dahlem, 1920. Left to right, seated: Hertha Sponer, Albert Einstein, Ingrid Franck, James Franck, Lise Meitner, Fritz Haber, Otto Hahn; standing: Walter Grotrian, Wilhelm Westphal, Otto von Baeyer, Peter Pringsheim, Gustav Hertz.

Paradoxically, this period of thriving research was also marked by ongoing financial hardships owing to the hyperinflation of the early 1920s and the Great Depression that began at the turn of the 1930s. More than once, the continued existence of the Institute was called into question and staff members could not be paid or did not have their contracts or funding renewed. One consequence of these funding difficulties was that in 1923 the Institute left the administration of the Koppel Foundation and fully joined the KWG—only then becoming a standard Kaiser Wilhelm Institute. During the 1920s, about 50 scientists pursued research at the Institute; however, most of them were not employed by the KWG. They were instead paid by various "third-party" funds, in particular the Emergency Association of German Science (*Notgemeinschaft der Deutschen Wissenschaft*), the later German Research Association (*Deutsche Forschungsgemeinschaft*), industrial sponsors, and funds administered directly by Haber. Throughout the 1920s the Institute developed step by step into a more or less stable arrangement of four departments: the oldest department, for physical chemistry, under Haber; a department for colloid chemistry, guided by Herbert Freundlich; a physics department, established under James Franck in 1919 (Figure 5) and after 1924 led by Rudolf Ladenburg; and the department of Michael Polanyi, who moved from the next-door KWI for Fiber Chemistry to Haber's institute in 1923. Interspersed among these departments were a number of small "research groups" (*Arbeitskreise*), which were headed by highly qualified scholars, in general with a *Habilitation*, such as Karl Friedrich Bonhoeffer, Georg Ettisch, and Hartmut Kallmann, whom Haber expected to pursue independent research and direct their own assistants and graduate students (Figure 6).

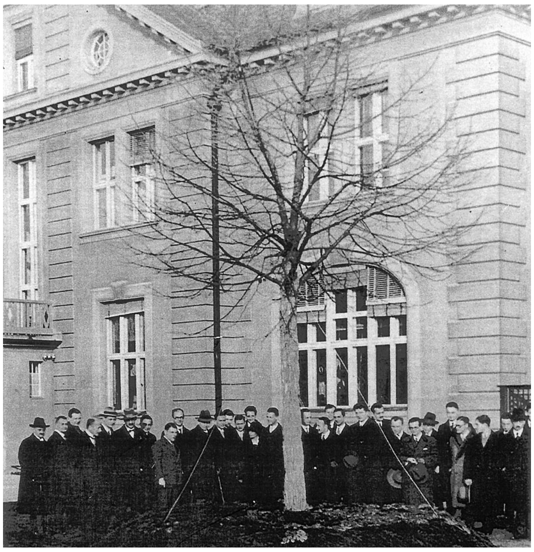


Figure 6. Planting of the Haber Linden Tree on the occasion of Fritz Haber's 60th birthday, December 9, 1928, with most of the academic staff members of the Institute present.

The unusual modes of financing at the Institute led to members of certain social groups, who were at a comparative disadvantage when competing for regular university appointments in Germany at the time, being disproportionately attracted by the professional opportunities offered at the Institute. This applied to the KWG in general, where foreigners, women, and above all scientists with Jewish ancestry were famously "over-represented" in comparison to university staffs. According to contemporaries, roughly half of the researchers active at Haber's institute during the 1920s had recognizably Jewish family backgrounds,[8] although many of the scientists or their families had officially converted to Christianity, including all of the scientific members of the Institute.

Not least of all because of these "Jewish" co-workers, the Institute came under pressure very soon after the seizure of power by the National Socialists on January 30, 1933 and the enactment of the first race laws, particularly the Law for the Restoration of the Professional Civil Service, promulgated on April 7, 1933. As a consequence of the government demand to dismiss his "Jewish" co-workers, Haber resigned his directorship with a letter to the ministry, in which he stated: "*My sense of tradition requires of me that, in the fulfillment of my scientific post, I only*

Figure 7. Farewell gathering in the Institute gardens, July 1933. First row standing on the right: Friedrich Epstein; seated from the right: Hartmut Kallmann, Michael Polanyi, Fritz Haber; seated in front of Haber: Rita Cracauer; two chairs left of Haber: Herbert Freundlich.

choose staff members according to their professional abilities and character, without regard to their racial composition. You will not expect of a man in the 65th year of his life that he change his way of thinking, one which has led him through the past 39 years of his university career. You will also understand that the pride with which he has served his native German soil throughout his life now requires him to request immediate retirement."[9] This was one of the very few documented instances of resistance by German academia to Nazi rule.

Freundlich and Polanyi were of a similar opinion and stepped down from their posts, shortly before Haber officially resigned (Figure 7). During the following months not only were the remaining Jewish members of the scientific and support staff expelled; the remaining non-Jewish scientific co-workers were also dismissed.[10] This was the first step in the total restructuring of the Institute by Nazi and military circles. At first, the plan was to turn the Institute into a center for research on the chemistry of war materials under the directorship of Gerhart Jander, but this plan failed. Instead, in 1935, Peter Adolf Thiessen, a recognized physical chemist but also a long-time member of the National Socialist party, was appointed director of the Institute by the Senate of the KWG "in an unusual manner"—as KWG President Max Planck described it. The appointment was proposed and strongly pushed by the ministries and the military, thus undermining the scientific and institutional autonomy of the KWG. Nevertheless, the KWG accepted this poltical imposition, and Thiessen, who would become one of the most prominent and successful science administrators in the Third Reich, was free during the following decade to develop the Institute into a "Nazi Model Enterprise."


Figure 9. Karl Friedrich Bonhoeffer at the unveiling of the Haber commemorative plaque on December 9, 1952.

Under Thiessen, research at the Institute moved away from the fundamental interests of the Haber era and focused on applied science. At the same time, for largely political reasons, the Institute experienced a breakdown in its international relations. Sincere efforts were made to achieve the research goals established by the Nazi government, to actively contribute to the drive toward German economic self-sufficiency, and to fulfill the demands of the National Socialist regime for new armaments, including chemical weapons.[11] These efforts established the framework for both applied and basic research at the Institute, so that no clear distinction can be made between exclusively military research and research into broader technical problems. Nevertheless, the Institute's achievements in applied research and the highly technical nature of the work done there were widely recognized and praised by the scientific community of the time. One focal point of research at the Institute was the structural analysis of fibers, glasses, synthetic materials, and metals. In this connection, pioneering work was done using modern analytical methods such as novel X-ray analysis techniques, electron diffraction, and electron microscopy.


Figure 8. Institute grounds circa 1939. The dedication to Haber around the Haber Linden has been removed.

In the immediate aftermath of World War II the Institute suffered crippling material losses, as it was given special priority in the dismantling and pillaging efforts of the Soviets. Its high-quality, cutting-edge equipment, was the best to be found among the institutes available for plundering in Berlin. Furthermore, Thiessen was "invited" to continue his research in the Soviet Union, where he worked on isotope separation as part of the Soviet atomic bomb project. Over and above the material losses, the resumption of research proved exceedingly difficult because scientific activities were effectively halted by Allied legal restrictions. Nevertheless, the Institute became a refuge for scientists in Berlin who lacked other institutional ties and needed to retool professionally. Among them was Hartmut Kallmann, who had survived the Holocaust living in Berlin thanks to a "privileged mixed marriage" and took up his research at the Institute very soon after the downfall of the Nazi regime. In 1948, he and some of his students were able to develop the first scintillation counter, a device that continues to play an important role in the detection of charged particles, particularly electrons.[12] The Institute, however, was struggling to survive. Given the nebulous future of the KWG and the precarious situation of the divided Berlin, its governmental and other institutional affiliations were highly unstable and hence its financing was also uncertain. Paradoxically, the Cold War helped to safeguard the Institute's existence, first as part of a newly founded German Research University—a kind of institute for advanced study—intended to contribute to American plans for the reform of the German research and education establishment, and then in 1953 as a bridge between West Berlin and West Germany through the Max Planck Society (MPG), the fledgling, Göttingen-based, successor to the Kaiser Wilhelm Society. After Karl Friedrich Bonhoeffer, who led the Institute from 1948 to 1951 (Figure 9), finally decided to depart for Göttingen to assume the directorship of a new MPI for Physical Chemistry, Max von Laue (1879–1960), already 72 years old at the time, took over as Director (Figure 10). Admission of the Institute into the MPG in 1953 coincided closely with Laue's appointment and with the renaming of the Institute for its founding director, making it the Fritz Haber Institute of the Max Planck Society.

Drawing upon his personal prestige as the Nobel prize winning member of the collaboration that discovered X-ray diffraction in crystals, as well as scientific and technical expertise at the Institute dating back to the end of the Thiessen era, Laue strove to develop the Institute into a center for research into the microstructure of matter, using primarily diffraction techniques. At his disposal among the scientific staff were Iwan Stranski (crystal structure and growth), Kurt Überreiter (macromolecular structure), Kurt Molière (electron diffraction), and his closest allies Gerhard Borrmann (X-ray diffraction and absorption) and Rolf Hosemann (small-angle X-ray diffraction). In addition, Ernst Ruska, who had previously been affiliated with the Institute only part-time, became head of the Department for Electron Microscopy—later to become a quasi-independent institute—shortly after the admission of the FHI into the MPG. Laue was a highly successful director in that he stabilized and expanded funding for the Institute and managed to keep it productive and relevant in spite of the challenges posed by its location in West Berlin, particularly with respect to attracting outside scientific staff. Laue did not succeed, however, in developing the kind of coherent focus on structure research at the Institute he had initially envisioned. Extensive research in fields related to material structure was conducted at the Institute, but in part thanks to the many rapid changes in leadership and staff that had accompanied the immediate postwar era (1945–1953), few collaborations and essentially no permanent organizational structures held together the various departments and research groups of the Institute.

Laue stepped down as director of the Institute in March of 1959, at almost 80 years old, to make way for Rudolf Brill, who had been trained in X-ray diffraction at the former KWI for Fiber Chemistry and made the field a mainstay of his research career thereafter, and therefore had the potential to steer the Institute deeper into structure research. However, Brill had at least as much trouble as Laue in unifying research in the various departments, and the Institute continued to operate much as it had before, divided into six largely independent departments whose research related more or less closely to the microstructure of matter. But Brill would oversee one of the single largest expansions in infrastructure in the history of the Institute, albeit as a result of an initiative begun under Laue. In part because of the special importance a prestigious research institute like the FHI had for West Berlin during its Cold War isolation, and inarguably in response to the growing prestige of Ernst Ruska (see below), the FHI received a large grant in 1957 for the construction of a new building for the Institute for Electron Microscopy, as well as a library, lecture hall, and administrative offices, which were inaugurated in 1963.

Figure 10. Max von Laue at an Institute outing, late 1950s.

For the future of the Institute though, the ways in which Brill broke with the tradition of Laue were more important than the ways in which he continued it. In particular, Brill chose surface catalysis, a field that had essentially vanished from the Institute with Haber, as the main topic of research in the department he led. He established two related research groups, headed by Hans Dietrich (structure of catalytic compounds) and Jochen Block (electron emission spectroscopy). This, coupled with the retirement of Stranski in 1967, reduced the emphasis on structure research and made research at the Institute appear less focused than it had before; however, in the end, it would turn out to be the first step toward the present incarnation of the FHI. As Brill's retirement in 1969 approached, the Chemical-Physical-Technical (CPT) Section of the MPG formed a committee to

Figure 11. Installation of Heinz Gerischer as FHI Director, December 9, 1968. From left to right, first row: A. Butenandt (with chain of office), H. Gerischer, R. Gerischer; second row: K. H. Herrmann, K. Überreiter, I. Stranski. Fourth row on the right: R. Hosemann.

Figure 12. Ernst Ruska (left) and Elmar Zeitler at the departmental Nobel Prize celebration on October 30, 1986.

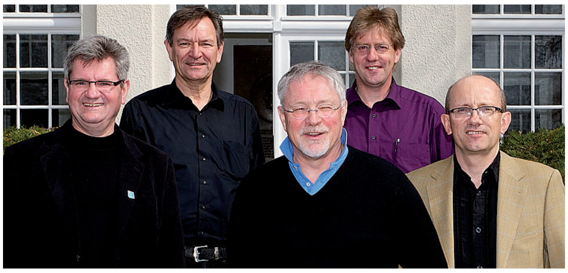


Figure 13. The current directors of the FHI in front of Haber Villa, 2011. From left to right: R. Schlögl, M. Scheffler, H.-J. Freund, G. Meijer, and M. Wolf.

Figure 14. A spontaneous gathering in the garden of the Fritz Haber Institute on October 10, 2007, after the announcement of the 2007 Nobel Prize in Chemistry.

consider the future of the FHI, as well as a committee to search for Brill's successor. Working in close contact, they decided to invite Heinz Gerischer (1919–1994) to become the new director of the Institute, in part because of his willingness to expand upon the lines of research introduced by Brill and develop the FHI into a center for surface physics and chemistry. Gerischer took office in November 1969 (Figure 11).

During Gerischer's directorship the Institute would not only transform into a center for research on surface science and catalysis, but would also make the transition to a collective scientific administration (*Kollegiale Leitung*), which was increasingly becoming the norm for MPG institutes. This intellectual and administrative restructuring would take considerable organizational efforts and most of the 1970s to complete. During the transition phase, from approximately 1974 to 1981, the FHI was divided into three subinstitutes: Physical Chemistry, Structure Research, and Electron Microscopy. The physical chemistry institute was somewhat deceptively named in that it included the core of researchers working on the new topics of surface science and catalysis, led by Gerischer, Molière, and Block. The structure institute housed the remainder of the researchers, Hosemann and Überreiter, who adhered more or less strongly to Laue's earlier vision of the FHI, and the electron microscopy institute remained under Ruska up to the end of 1974. Thereafter, careful consideration of how to integrate electron microscopy with the idea of the FHI as a center for surface science research resulted in the appointment in 1976 of Elmar Zeitler as Ruska's successor. Several important junior appointments also occurred during the 1970s, notably that of Alexander Bradshaw (see below); however, until the retirements of Überreiter, Molière, and Hosemann, all in 1980, no new positions were open for senior researchers, so that new lines of research that would come to define the FHI during the 1980s and beyond often developed within individual research groups rather than defining entire departments. The key exception was Gerischer's department, which was built around cutting-edge research into electrode processes, solar cells, and new methods of exploring surface structures, which were experiencing a boom thanks to advances in ultra-high-vacuum technologies. In addition, work in Block's department on electron emission methods also maintained a focus on the examination of surface structures and surface reactions.

As of January 1, 1981 the restructuring of the FHI was effectively complete, and the Institute took on the form it has essentially maintained ever since. A new charter established a Board of Scientific Directors, the earlier subinstitutes were eliminated in favor of a simpler department-based structure, and an Advisory Board (*Fachbeirat*) of internationally recognized experts was established to counsel the directors on questions of research policy. As of 1981, there were only four departments at the Institute: Physical Chemistry (Gerischer), Surface Reactions (Block), Surface Physics (Bradshaw), and Electron Microscopy (Zeitler). Surface science in general and heterogeneous catalysis in particular was a topic of research in all of these departments, albeit to a somewhat lesser degree under Zeitler than the others. With the structure of the Institute settled, the way was open for a number of key appointments that advanced existing fields and rounded out the research into surface science and catalysis. In 1985, in a somewhat surprising turn of events, the Institute managed to convince one of the main protagonists of modern surface chemistry research, Gerhard Ertl, to leave his post in Munich and move to the FHI as successor to his mentor Heinz Gerischer, who would soon retire. Three years later, a fifth division, the Theory Department, opened under the direction of Mathias Scheffler.

It was a new heyday for the FHI. In 1986, Ernst Ruska received half of a shared Nobel Prize in Physics, "*for his fundamental work in electron optics, and for the design of the first electron microscope*" (Figure 12). The presence of distinguished surface science and catalysis researchers, such as Gerhard Ertl, and the much improved conditions in Berlin made it easier for the Institute to again attract top-notch scientists, and the present board of directors gradually took shape as Robert Schlögl (1994), Hans-Joachim Freund (1996), Gerard Meijer (2002), and Martin Wolf (2008) joined Matthias Scheffler at the Institute (Figure 13). But before this process was quite complete the award of another Nobel prize would be celebrated at the Institute. In 2007, on Ertl's 71st birthday, his career was crowned with the award of an unshared Nobel Prize in Chemistry, "for his studies of chemical processes on solid surfaces" (Figure 14).

3. Key Scientific Contributions from the FHI

3.1. Gas-Phase Kinetics and Dynamics

Ammonia Synthesis. With the completion of his habilitation on “Experimental Investigations into the Decomposition and Combustion of Hydrocarbons” at the *Technische Hochschule Karlsruhe* early in 1896, Fritz Haber turned his attention to the still-young discipline of physical chemistry and distinguished himself as a rising star in the field. His work in applied thermochemistry, the thermodynamics of industrial gas reactions, and gas analysis attracted particular attention. Early in the summer of 1909, Haber made his greatest scientific achievement. Through a collaboration with BASF, Haber developed an industrially promising catalytic process for the synthesis of ammonia from its constituent elements. Carl Bosch and Alwin Mittasch at BASF then refined the process into a technology for the large-scale production of ammonia, thus capitalizing on its agricultural and military significance.[13]

Figure 15. Fritz Haber with his colleagues (left to right) Gerhard Just (?), Setsuro Tamaru, and Richard Leiser, circa 1913.

Research in the name of the Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry commenced in the autumn of 1911. As they lacked laboratories of their own in Berlin, Haber and his colleagues initially pursued their research as guests at various Berlin research centers, including the Imperial Institute of Physics and Technology in Berlin-Charlottenburg. The first scientific activities undertaken at the Institute were culminations of projects begun in Karlsruhe. Gerhard Just continued research begun with Haber into electron emission during gas–metal reactions, while F. Hillers followed Haber’s lead in research on the inner cone of hydrocarbon flames. Haber also reaffirmed his interest in electrochemistry through an investigation of the effects of currents passing through the walls of gas containers on the electrochemical behavior of gases. In the realm of gas chemistry, Haber and Fritz Kerschbaum collaborated in developing a general observation made by the American physical chemist Irving Langmuir into a specific method for measuring very low pressures using the oscillations of a quartz fiber.

Nevertheless, the bulk of Haber’s scientific publications in the years leading up to the First World War continued to relate to ammonia synthesis. In addition to an array of articles detailing new research on the subject, most of them co-written with Setsuro Tamaru, Haber also published the results of research projects undertaken with Robert LeRossignol, Haber’s chief assistant during initial development of the synthesis process, and Harold Cecil Greenwood, both of whom had returned to Britain rather than follow Haber to Dahlem. These articles concerned, primarily, the thermodynamics of the synthesis reaction and measurements of the specific heat of ammonia. In them, Haber broadened his initially applications-oriented perspective on ammonia synthesis, reexamining the reaction in light of fundamental questions in physical chemistry, such as the equilibrium constant and its relation to the heat capacities of the reactants and products. Haber also enlisted Albert Einstein, who arrived in Berlin shortly before the outbreak of the First World War, to aid the Institute in quantum theory research and provided office space for him (Figure 16).

Methane Detector (Firedamp Whistle). Similarly central to research at the Institute in its early years was the development of a firedamp (methane) detector for use in coal mines.[14] Up to that point, the safety lamp developed by Sir Humphry Davy at the beginning of the 19th century was the preferred safety and warning apparatus. However, the lamps themselves posed something of a risk, since a defective lamp could set off an explosion. The Kaiser witnessed the effects of one such disaster during a visit to Krupp at Villa Hügel in Essen in the summer of 1912, and he used the opportunity of the opening of the Kaiser Wilhelm Institutes to request that German chemists develop a safer, more reliable detector. Haber had been informed in advance of the Kaiser’s interest in such a device, and at the inauguration, he presented a gas interferometer he had developed in collaboration with the Zeiss company. However, the interferometer was a precision measurement device, not a rugged methane detector; hence the practical problem remained unsolved. Together with his assistant Richard Leiser, Haber dedicated himself during the next year to fulfilling the Kaiser’s request. In so doing, he was entering into competition with colleagues at numerous other chemical institutes, among them the Director of the neighboring KWI for Chemistry, Ernst Beckmann. Unlike his colleagues, who based their designs primarily upon spectroscopy or analytic chemistry, Haber began with acoustics, specifically the fact that the tone of a whistle depends upon the speed of sound in the gas that fills it. Using this fact, Haber and Leiser developed a firedamp whistle, whose pitch would change when filled with methane (Figure 17). However, the whistle required precision machining that made its production costly, and it was not robust enough to withstand long periods of uninterrupted use. Moreover, it could not be properly calibrated on site. But even though the device was neither a rousing practical success, nor a generator of great profits, it did add to Haber’s scientific reputation. Haber’s interest in firedamp detectors also illustrates the extent to

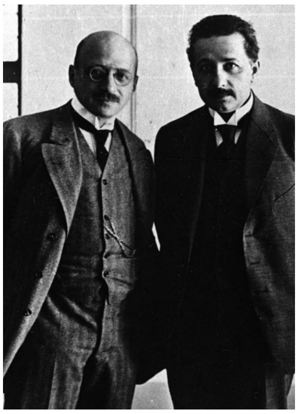


Figure 16. Albert Einstein and Fritz Haber in the stairwell of the KWI, 1914.

which he oriented his research around the technical problems of his times—a feature of his scientific activities that would take on particular significance during World War I.

Haber–Born Cycle. Haber spent some of the limited time he personally felt able to dedicate to pure research in the first years after the war developing new models of the structure of solids. The best known result of these efforts is the Haber–Born cycle, a thermodynamic analysis of the formation of ionic crystals into component steps corresponding to energies (ionization energy, electron affinity, etc.) whose sum gives the total energy of formation of the crystal; it was frequently used to calculate lattice energies, the one step in the cycle that cannot generally be measured directly. The Haber–Born cooperation resulted unexpectedly from the frequent trips Max Born made to Berlin to visit James Franck. Born was initially wary of Haber, as Born was opposed to chemical warfare, but Haber managed to win his confidence and arrange a brief collaboration with long-lasting results. The Born–Haber research had clear antecedents in the work of Born and Alfred Landé on crystal lattice energies, but Haber too made roughly contemporaneous attempts to calculate macroscopic properties of crystals on the basis of atomic scale models, albeit with a focus upon metal structure and markedly less lasting success.[15]

Chemiluminescence. Haber's definitive contribution to the research direction of the Institute in the early 1920s, however, would be an article with Walter Zisch on the emission of light during combustion reactions. Haber and Zisch studied the spectra emitted by ordinary flames, as well as those produced during reactions of alkali-metal and halide gases, in particular sodium and chlorine. They observed that these reactions emitted light that could not be ascribed to the heat of the reaction and that could be seen even when the reaction mixture was not hot enough to glow visibly according to the laws of blackbody radiation. To control the reaction temperature, Haber and Zisch allowed the gases to react only at very low pressures, creating "highly dilute flames". They posited that the process that produced this anomalous light, and which they took to be representative of chemiluminescence in general, was the inverse of a photochemical reaction. That is, they argued that light was emitted after electronic excitation of the reactants or products by the reaction, which then returned to their ground state, emitting light through a process analogous to fluorescence. The phenomenon was markedly more complex than fluorescence in that the nuclei and the electrons could interact in ways not fully understood at the time and the emitted light could originate from an electronic transition in any one of the reactants, intermediates, or products present in the reaction vessel. Hence, Haber and Zisch argued, one could not expect a one-to-one correspondence between the number of molecules of product formed and the number of light quanta emitted, as one might expect from a straightforward inversion of the photochemical decomposition mechanism, but one could very likely detect unstable intermediates and gain insights into reaction mechanisms by studying chemiluminescent spectra. Both the complexity of the reaction mechanisms suggested by the Haber and Zisch article and the possible insights one might gain into reaction mechanisms by careful spectral observations became launching points for new lines of research at the Institute. This would include research by Hans Kautsky on chemiluminescence in colloids and experimental work by the Polanyi group on reaction mechanisms in the gas phase, as well as Haber's own return to combustion research after 1926.[16]

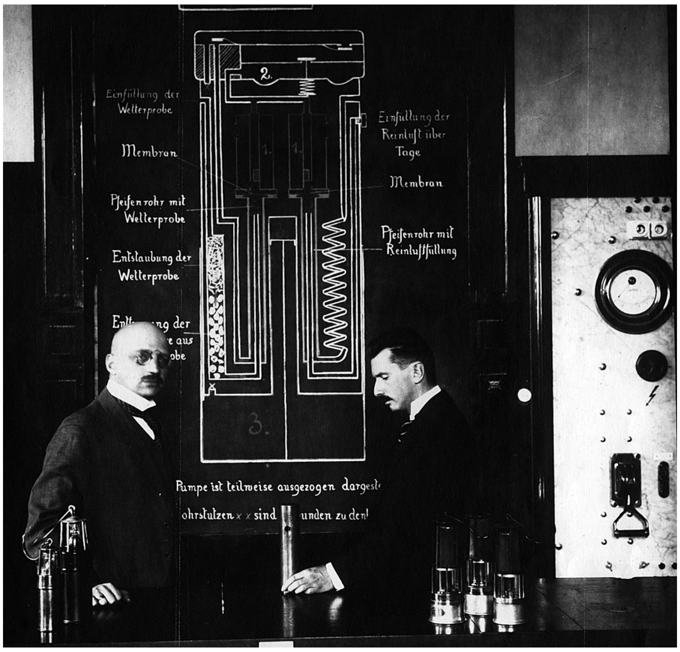


Figure 17. Fritz Haber and Richard Leiser with the firedamp whistle, 1913.

Several independent strands of research emerged within Haber's "physical chemistry" department while Haber was underway with Department M (the code name for the gold-from-seawater project). One of the most prestigious began with the arrival of Karl Friedrich Bonhoeffer at the Institute in 1923 and his subsequent investigations of the chemistry of activated, that is, atomic, hydrogen. Given that atomic hydrogen was the only substance for which physicists felt they might have an acceptable quantum theoretical model at the time, it was a topic with manifest, if nebulous, potential for bridging physics and chemistry. From the outset, Bonhoeffer took advantage of the expertise in low-pressure-gas chemistry available at the Institute. As he branched out to research on simple hydrogen-containing compounds, he also benefited from its spectroscopic facilities and from the assistance of Ladislaus Farkas, with whose help he established a connection between the diffuse bands in the electronic spectra of ammonia and predissociation, and interpreted the bands'

Figure 18. Fritz Haber amongst colleagues, standing: Paul Goldfinger, unknown; seated: Hans Dietrich Graf von Schweinitz, Ladislaus Farkas, circa 1930.

widths in terms of the energy–time uncertainty relation.[17] Bonhoeffer's research took a distinct turn, however, after the arrival of a new collaborator, Paul Harteck, in 1928. Harteck had habilitated under Max Bodenstein in Berlin, and then spent two years working as an assistant to Arnold Eucken in Breslau, at the time a center for experimental research on low-temperature specific heats, where first unsuccessful searches for the allotropic forms of hydrogen had been undertaken. Upon Harteck's arrival at the Institute, he and Bonhoeffer would adopt this line of research and achieve success (see below).

Combustion. After 1926, Haber returned personally to the study of combustion reactions. Inspired by a practical interest in improving existing combustion fuels and discovering new ones, his new research concentrated on the mechanism of combustion reactions rather than the light they emitted. In spite of the shift in focus, Haber and his collaborators continued to rely on many of the laboratory techniques and apparatus that had enabled the earlier Haber and Zisch research, including the use of spectroscopy to identify reaction intermediates. Karl Bonhoeffer joined him early in this research, followed by Ladislaus Farkas, Paul Goldfinger, Hans Dietrich Graf von Schweinitz, and Hubert Alyea (Figure 18). Their results demonstrated the importance of free radicals in combustion reactions and led, in the case of the combustion of hydrogen, to an interim reaction scheme, the so-called "Haber Chain." These insights attracted considerable interest from fellow chemists; however, they were not of immediate industrial importance. Instead, like Haber's original ammonia synthesis, they deepened scientists' understanding of the principles behind commercially significant chemical reactions, but left the practical application of these insights to industrial chemists and chemical engineers.[18]

3.2. Early Quantum Physics

Statistical Mechanics. In the wake of the First Solvay Conference (1911), many leading physicists had begun embracing the quantum hypothesis as a key to solving outstanding problems in the theory of matter. The quantum approach proved successful in tackling the thermal properties of the solid state, resulting in the nearly definitive theories of Debye (1912) and of Born and von Karman (1912–1913). However, the application of the old quantum theory to gases was hindered by conceptual difficulties, which were due in large part to the lack of a straightforward way of reconciling frequency-dependent quantization techniques with the aperiodic behavior of gas molecules. A breakthrough came from unlikely quarters. Otto Sackur (1880–1914; Figure 19) had been trained as a physical chemist but had been attracted to the new field of quantum physics. In 1911, he discovered an expression for the absolute translational entropy of a monoatomic gas. A Dutch high-school student, Hugo Martin Tetrode, obtained the same result at about the same time independently. The resulting Sackur–Tetrode equation rendered entropy as an extensive variable (in contrast to the classical expression, cf. the Gibbs paradox) and expressed the thermodynamically undetermined constant in terms of molecular parameters and Boltzmann's and Planck's constants. This result was of great heuristic value because it suggested the possibility of deriving the thermodynamic quantities of a gas quantum mechanically. At the same time, the Sackur–Tetrode equation offered a convenient means to evaluate the equilibrium constant of gas-phase reactions, thus foreshadowing a unification of quantum theory, thermodynamics, and physical chemistry.[19]

The key steps in the development of the Sackur–Tetrode equation were the partitioning of the phase space into elementary cells and the use of Planck's constant to fix the cells' volume. Following up on this feat, Sackur attempted to develop a general quantum theory of the ideal gas with, however, only partial success—and with a dose of naiveté. However, Sackur's bold attempt to deploy the quantum hypothesis in classical statistical mechanics prepared the path for Planck's later theory of a quantum gas. Sackur launched his research at the intersection of physical chemistry, thermodynamics, and quantum theory while a Privatdozent in Breslau, with hopes for a more senior academic appointment. His hopes were fulfilled at the end of 1913, when, thanks in part to mediation by Clara Immerwahr, Haber's first wife, Sackur received a call to Haber's institute. In 1914 he was promoted to the rank of department head. After the outbreak of World War I, Sackur was enlisted in military research at Haber's institute, but on the side succeeded to carry on with his experiments on the behavior of gases at low temperatures. He was killed in a laboratory accident in 1914 at the young age of 31.

Figure 19. Otto Sackur, circa 1913.

The Franck–Hertz and the Compton Effects. In the Physics Department, under the direction of James Franck, in the years immediately following the war Walter Grotrian, Paul Knipping, and Erich Einsporn concentrated primarily on the careful measurement of absorption spectra and ionization energies and the correlation of these measurements with the Bohr–Sommerfeld model of the atom. It was an extension of a line of research that Franck and Hertz had begun while at Berlin University before the war. There they devised the venerable "Franck–Hertz experiment," which demonstrated that electron collisions with mercury vapor atoms were elastic only up to a certain threshold energy, and that beyond this threshold inelastic collisions led to ionization and electronic excitation of the atoms.[20a] The specific ionization and excitation energies they observed corresponded with predictions based on Niels Bohr's quantum model of the atom, providing it strong experimental support. Though performed at an ostensibly chemical institute in the context of physical chemistry, their postwar efforts were similarly central to quantum physics, as their careful measurements of spectra and ionization energies "enabled the confirmation of Bohr's theory to a high degree of precision." Nevertheless, their results also formed part of the basis for several later investigations at the Institute, including, as already discussed, the pivotal 1922 study by Haber and Zisch,[16] as well as the work of Hans Beutler and others[20b] on the quantum mechanics of atomic collisions. In this respect, the focus of the Franck group on the spectra of mercury vapor was particularly important, as their exemplary results encouraged later researchers at the Institute to choose mercury vapor as a model system.

Figure 20. The Institute's hydrogen team, circa 1930. Left to right: Adalbert Farkas, Paul Harteck, Ladislaus Farkas, Karl Friedrich Bonhoeffer.

In an interregnum at the Physics Department between James Franck and Rudolf Ladenburg, Paul Knipping published retrospective articles on the discovery and practice of X-ray diffraction and descriptions of a new apparatus for ionization measurements.[20c] More importantly, the X-ray apparatus and spectroscopic equipment at the Institute offered members of the Physics Department the opportunity to branch out into research on the Compton effect, the shift in the wavelength of X-rays caused by inelastic scattering from an electron. The discovery of the Compton effect in 1923 caused quite a stir in the physics community, as it provided strong support for the particulate nature of X-rays and, by extension, of light.[21] However, Compton's results proved somewhat difficult to replicate. Noted Harvard X-ray physicist William Duane tried and failed, but Hartmut Kallmann of the Physics Department in collaboration with Hermann Mark, an expert on X-ray analysis at the neighboring KWI for Fiber Chemistry, were able to reproduce the phenomenon and to make careful measurements of the relationship between the scattering angle and the shift in wavelength.[22] Kallmann also performed a more rigorously physical analysis of the ongoing research at the Institute into the excitation of gas spectra through chemical reactions, cf. Haber and Zisch circa 1913.[23] Still, there is nothing to indicate that these were aspects of a department-wide line of research, and Kallmann, though nominally attached to the Physics Department, pursued his research interests essentially independently even before he became head of his own research group in 1928.

Allotropic Forms of Hydrogen. Bonhoeffer and Harteck set out together to confirm the existence of two recently posited, distinct forms of molecular hydrogen: *ortho*-hydrogen, with nuclear spins oriented parallel to one another, and *para*-hydrogen, with mutually opposing nuclear spins. Ever since Eucken first measured the specific heat of hydrogen gas at low temperatures in 1912, its anomalous temperature dependence had posed a challenge for quantum theories of specific heat. In 1927, working in close correspondence, Werner Heisenberg and Friedrich Hund, each independently published articles in which they suggested that hydrogen existed in distinct *ortho* and *para* allotropic forms. Furthermore, they argued that these two forms should exist in a ratio of 3 to 1 at high temperatures, but as Hund pointed out, should contribute differently to the specific heat of the gas. Later that year, David Dennison combined these insights into a theory that fully accounted for the observed specific heat of hydrogen, based in part on the premise that at low temperatures the *para* rather than the *ortho* form would be favored, but the transition between the two states would be slow.[24] It was this transition that would allow Bonhoeffer and Harteck to test the new theory, but it was a challenging task, Harteck's Breslau training in low-temperature methods notwithstanding. In a letter from October 28, 1928, Bonhoeffer wrote:[25a] "*we have set our minds upon an experiment that should show that ordinary hydrogen…is a mixture, as the theorists believe…but it isn't working at present, and I have lost half my hair to the futile drudgery*".

Fritz London, then an assistant to Erwin Schrödinger at the Berlin University, came to their aid and suggested keeping the hydrogen at low temperature as long as possible to facilitate the transition. In conjunction with Bonhoeffer's proposal that they measure the heat conduction rather than the specific heat of the gas, the former being proportional to the latter but easier to measure, they were able to overcome the technical challenges of the experiment. In March 1929 they published their results[25b] supporting the new theory, narrowly beating to press a nearly simultaneous announcement from Arnold Eucken. They also discovered, much to the benefit of later hydrogen research, that activated charcoal catalyzes the otherwise painfully slow conversion of *ortho*- to *para*-hydrogen. The importance of their research would be alluded to in the Nobel citation for Werner Heisenberg, who received the 1932 physics prize "*for the creation of quantum mechanics, the application of which has, inter alia, led to the discovery of two allotropic forms of hydrogen*." It also led to their being nominated at least once, in 1937, for the Nobel Prize in Chemistry. Adalbert and Ladislaus Farkas soon joined Bonhoeffer and Harteck in the investigation of hydrogen (Figure 20), using similar low-temperature methods to explore not only further properties of *ortho*- and *para*-hydrogen but also the properties of heavy hydrogen, that is, deuterium. This work distinguished the Institute as one of the world leaders in hydrogen research, and the results of investigations at the Institute formed the foundation for one of the first monographs on the subject, *Orthohydrogen, Parahydrogen and Heavy Hydrogen,* published by Adalbert Farkas in 1935[25c] following his emigration in 1933. In the case of Harteck, the hydrogen research also marked a first step in the direction of nuclear research, as he later recalled in connection with his choice to study with Rutherford at the Cavendish laboratory:[26] "*exactly like thermodynamics was and still is of importance for chemistry, similarly in the foreseeable future nuclear physics should open interesting and fundamental fields for a physical chemist.*"

Figure 21. Eugene Wigner (right) with Werner Heisenberg, 1928.

Later decisions concerning how he pursued this line of research would earn Harteck the dubious distinction of being interned at Farm Hall in England immediately after the Second World War, in connection with his participation in the German uranium project.[27]

Symmetry. Yet further afield from the Physics Department under Franck and Ladenburg, but still in keeping with the interest in spectroscopy at the Institute, were the enduring contributions of Eugen Wigner (1902–1995) to quantum theory (Figure 21). In 1926–1927, while still dividing his research efforts between Reginald Herzog's KWI for Fiber Chemistry and Haber's Institute, Wigner became the first scientist to employ group-theoretical considerations in the interpretation of the selection rules of atomic spectroscopy. He accomplished this by analyzing the transformation properties of energy eigenstates of a system with respect to operations that leave the system physically unchanged, for example, spatial rotations, mirror inversions, exchange of identical electrons. Wigner had developed his skills with group theory and symmetry transformations while working with Karl Weissenberg on crystallography, a field in which these mathematical tools had been commonplace since the end of the 19th century. Symmetry groups, however, had not yet made similar inroads into other branches of physics, and many physicists were initially hostile to their importation into quantum theory, even referring to them as the "*Gruppenpest*," the group plague.[28]

Nevertheless, the encounter Wigner arranged between group theory and the old quantum-theoretical notion of selection rules had a profound and long-lasting impact on quantum theory.[29] The connection between selection rules and group theory endowed quantum theory with a new type of symmetry argument, in which selection rules, rather than conservation laws, were regarded as the observable signature of an underlying physical symmetry. Interpreting experimental data in terms of selection rules, therefore, led to a redefinition of the traditional conserved quantities, notably angular momentum. In a brief paper published in 1927, Wigner drew attention to the new, quantum form of conservation laws, articulating what is today referred to as the quantum version of Noether's theorem. Wigner noted that in quantum mechanics one was only allowed to ask about the probability distribution of the values of physical quantities and concluded:[30] "*It is therefore necessary to formulate also the laws of conservation in this sense. They will then have the form, for example: The probability that the energy will have the value E does not change with time.*"

When asked in the early 1930s by Max von Laue what group-theoretical result derived so far was the most important one, Wigner replied: the explanation of the Laporte rule (the concept of parity) and the quantum theory of vector addition (angular momentum).[31] Partly in recognition of the power of these new theoretical devices, Wigner would receive the 1963 Nobel Prize in Physics "*for his contributions to the theory of the atomic nucleus and the elementary particles, particularly through the discovery and application of fundamental symmetry principles*".

Dispersion. While Wigner was taking the first steps to integrate group and quantum theory, a new line of experimental research was developing within the Physics Department, as Rudolf Ladenburg (1882–1952; Figure 22), in collaboration with Hans Kopfermann and Agathe Carst, undertook a series of experiments intended to test the new quantum theory of dispersion. Dispersion played a central role in the development of quantum theory in general, and in the formulation of the matrix mechanics by Werner Heisenberg in particular,[32a] and during his time in Breslau, Ladenburg had made important contributions to the transformation of classical dispersion theory into its quantum counterpart. In

Figure 22. Rudolf Ladenburg, circa 1930.

Breslau, Ladenburg was assisted in this research by his friend and colleague Fritz Reiche. In Dahlem, the task fell primarily to Hans Kopfermann (1895–1963; Figure 23), who arrived at the Institute in 1926, immediately after completing his habilitation in Göttingen under James Franck. Ladenburg and Kopfermann (and later Carst) compared the predictions of the latest versions of the quantum theory with novel experiments on dispersion in excited gases, and as Haber reported to a meeting of the Prussian Academy in June of 1926: "*Using the method of interference bands, anomalous dispersion was confirmed, and in some cases measured, in several lines of the He, Ne, Hg and H [spectra], when the gases were excited by a continuous current. On the basis of the quantum theoretical dispersion formula of Ladenburg and Kramers and the F-summation rule of Reiche–Thomas these measurements were used to determine the probabilities of various quantum transitions, as well as the number of atoms in the excited states and their dependence upon current and the temperature and pressure of the gas.*"

The continuation of this line of research also led to a series of articles publishedbetween 1928 and 1930,[32b] in which they presented the first evidence of "negative dispersion," what physicists now call stimulated emission. According to the quantum dispersion theory, as formulated independently by Ralph Kronig (1926) and Hendrik Kramers (1927), one could create a sample material that, when illuminated by light of the appropriate frequency, actually emitted more light of that frequency than it absorbed. This is now recognized as the crucial phenomenon behind the operation of lasers, and some historians of science have even argued that with just a bit more luck Ladenburg and Kopfermann might have observed the first laser pulse.[33a] After Günther Wolfsohn took over as Ladenburg's assistant in 1930, Kopfermann turned his attention to the hyperfine structure of atomic spectra. His investigations of the spectra of different isotopes during the following year contributed to the discovery of the "isotopic shift," the effects of the nucleus on the energy of the surrounding electrons. Exploring the properties of the nucleus through its interactions with electron orbitals would develop into Kopfermann's research specialty when he later moved to professorships at Kiel and then at Heidelberg, and he wrote in 1940 one of the standard early works on the topic, *Kernmomente*.[33b] As with Paul Harteck, this clear move toward nuclear studies laid the groundwork for his later participation in uranium research under the National Socialist regime.

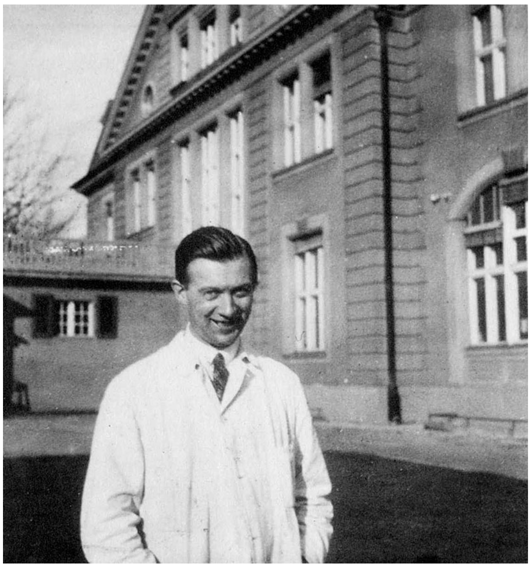


Figure 23. Hans Kopfermann, circa 1928.

Theoretical Chemistry. One of the research areas that has been pursued with particular vigor and success at both the Kaiser-Wilhelm-Gesellschaft and Max-Planck-Gesellschaft incarnations of the institute is Theoretical Chemistry. The theoretical work at the Kaiser-Wilhelm-Institut für physikalische Chemie und Elektrochemie during the 1920s and early 1930s was closely linked to Michael Polanyi's pioneering research in experimental chemical kinetics (Figure 24).[34] With his mutually "trusting but critical" team of young theorists, which included Eugene Wigner, Fritz London, and Henry Eyring, Polanyi laid conceptual foundations for kinetic theory consistent with the new quantum mechanics and foreshadowed the coming of chemical reaction dynamics, which would only arrive in the early 1960s in America.

Polanyi had puzzled over the implications of quantum mechanics for the kinetics of chemical reactions since about 1920. He recognized that the kinetic theories at hand could not be quite right, as the ratio of the forward and backward reaction rates failed to equal the equilibrium constant postulated by thermodynamics. In 1925, he and Wigner resolved the conundrum for two-body capture and its reverse, one-body decay, by invoking the uncertainty principle, in a form gleaned from spectroscopy by Niels Bohr.[35a] Their theory not only reconciled kinetics with thermodynamics for the capture/decay process but also foreshadowed what was later to become the Breit–Wigner formula (1936), which captures the kinetics of both molecular and nuclear near-resonant collisions.

Of paramount importance was the work on the dynamics of the simplest chemical exchange reaction, $H + H_2 \rightleftarrows H_2 + H$, which was prompted by the above-mentioned discovery at the institute of *para*-hydrogen and the study of its interconversion with *ortho*-hydrogen. This work established a way of looking at the process of making and breaking of chemical bonds which, for thermal and hyperthermal reactions, prevails until this day: a ball, representing the nuclei of the constituent atoms, rolls on the potential energy surface, given by the eigenenergy of the electrons (Figure 25). En route from the valley of the reactants to the valley of the products, the ball follows a path restricted by the reaction's energy disposal, comprising translational, vibrational, and rotational components. This view of the reaction entails a separation between the nuclear and electronic motions, known today as the Born–Oppenheimer approximation. The potential energy surface was calculated by Fritz London, who moved to Berlin from Zurich. There, in 1927, he and Walter Heitler invoked quantum mechanics to explain the baffling two-electron, covalent bond through the exchange interaction.[35b] Whereas London and Heitler's ground-breaking feat in quantum chemistry validated Gilbert Newton Lewis's 1916 hypothesis on the role of electron pairs in chemical bonding, London's tackling of the H_3 system breathed new life into Svante Arrhenius's 1889 concept of activation energy, by reinterpreting it as the summit-to-be-conquered between the electronic eigenenergy valleys of the reactants and products. Polanyi and Eyring subsequently enhanced the accuracy of London's calculations of the potential energy surface, by making use of data on the electronic energy obtained independently from spectroscopy. This approach, dubbed semiempirical, was yet another methodological advance which has since proved invaluable in a variety of contexts.

Figure 24. Polanyi's Physical Chemistry Department, 1933.

The rate at which the ball makes its transit over the summit—and hence the rate of the reaction—was evaluated in 1932 in Polanyi's group by Hans Pelzer and Wigner who made use of statistical mechanics and the London-Eyring-Polanyi semiempirical potential energy surface. This was the first take on the "transition-state" or "activated complex" theory of chemical reactions, which was later (1935) developed by Eyring and his collaborators at Princeton, and further refined by others.

Molecular Beams. Macroscopic reaction rates as observed, for example, in the experiments of Michael Polanyi and others during the 1920s and 1930s, represented averages over zillions of elementary collisions, whose identity and nature remained largely unknown—as did their relation to the molecular forces involved. This situation has been greatly remedied through the use of molecular beams whose deployment has made it possible to break with the bulk past and launch a new era in reaction kinetics based on the direct study of the dynamics of the underlying elementary collisions. Although the transition to the chemical/molecular dynamics era would materialize fully only three decades later and on the American continent, molecular beam methods have their roots in Europe, originating in part at Haber's institute. In 1921, Hartmut Kallmann and Fritz Reiche proposed a molecular beam experiment designed to determine whether individual polar molecules—as opposed to polar molecules in the bulk—carry an electric dipole moment.[37] A beam of polar molecules was to be sent through an inhomogeneous electric field and its deflection monitored. Kallmann and Reiche presumed that, while the beam's dilution would preclude any bulk interaction among the molecules, the directionality of the molecules in the beam would make their deflection, if any, measurable. Kallmann and Reiche thereby tapped into a key feature of the molecular beam method, as later characterized by Otto Stern, who extolled the method's "simplicity and directness", emphasizing that it "*enables us to make measurements on isolated neutral atoms or molecules with macroscopic tools .. [and thereby] is especially valuable for testing and demonstrating directly fundamental assumptions of theory*".[38a]

Kallmann and Reiche's paper prompted Stern to publish his proposal for what was to become the Stern–Gerlach experiment to test whether space quantization was real.[38b] Its demonstration, carried out in Frankfurt in 1922 by Stern and Walther Gerlach, ranks among the dozen or so canonical experiments that ushered in the heroic age of quantum physics.[39]

Kallmann's further molecular beam exploits include the production of keV cation and anion beams as well as of neutral beams obtained from ion beams by collisional electron transfer.[40] Kallmann also made use of electron transfer from multiply charged anions in his design of a multistage ion accelerator: an anion of initial charge of magnitude q was sent through an array of acceleration stages separated by the same voltage difference V. After being accelerated to an energy qV, the ion was passed through a thin foil where it lost an electron so that the magnitude of its charge dropped to $q' < q$. Although decelerated again on its flight out from the acceleration stage to the next, the ion gained a net energy $(q-q')V$. By repeating this process in subsequent acceleration stages (which entailed further stripping of the ion of its electrons), MeV energies could be attained with a voltage V on the order of only 100 kV.[41] This is a key element of the "tandem" principle which is at the core of accelerator physics.

Physisorption. Another key advance in molecular theory concerned physisorption. While at various stations during World War I, Polanyi proposed that there is an attractive force between gaseous atoms or molecules and a solid surface, whose spatial dependence he described empirically, in terms of a potential function. At the time, only two types of forces were admitted: electromagnetic and valence. However, each was believed to be able to adsorb only a single layer of atoms or molecules, a limitation which was not inherent to Polanyi's hypothesis. Opposed early on by, among others, Fritz Haber and Albert Einstein, Polanyi's theory was vindicated in 1930 by London, who showed that the hypothetical attraction is due to the dispersion forces. These arise from the mutual attraction of induced atomic or molecular dipoles generated

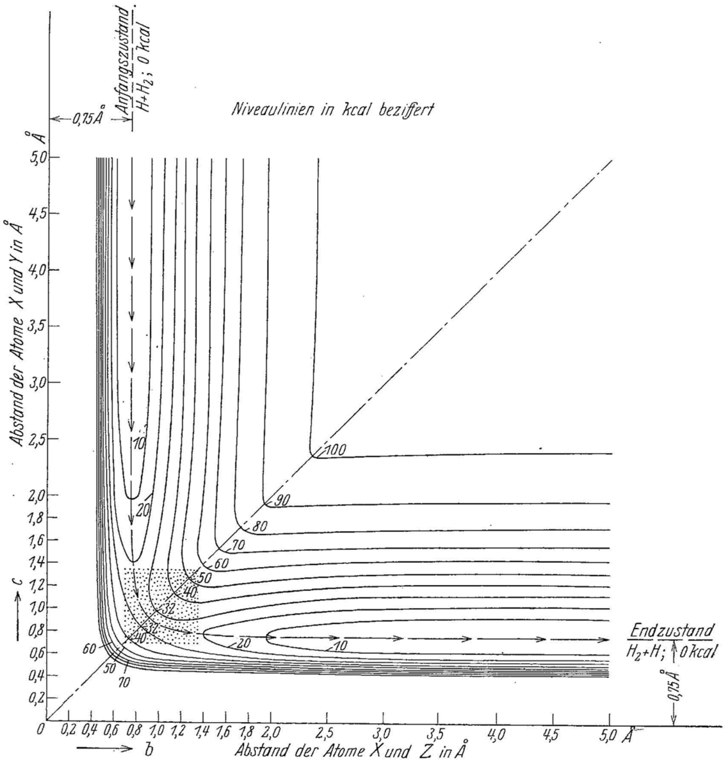


Figure 25. Potential energy surface of the $H+H_2 \rightleftarrows H_2+H$ reaction for a colinear collision geometry as reported by Henry Eyring and Michael Polanyi in 1931.[36]

by the fluctuations of the electron density and is demanded by quantum mechanics.[42a]

The interconnectedness of the research areas at the Institute notwithstanding, at times the topics of investigation may appear to have led members of the Institute beyond the bounds of physical chemistry, at least as we now see them. But disciplinary boundaries, however clear they may appear in pedagogy and funding practices, are often difficult to discern in ongoing research. For example, spectroscopy was, in very particular respects, of clear interest to chemists in the 1920s; it remains so today. But judging precisely in which respects spectroscopy is "chemistry" and in which respects "physics" requires a thorough understanding of the context, if it is possible at all. Haber, like many of his contemporaries in physical chemistry, did not feel it necessary to wait for and obey such clear disciplinary demarcations when choosing topics of research, and in the context of early 20th century physical chemistry this strategy often led to highly regarded results, as illustrated in the case of the Haber Institute, whose long-standing members often received enticing offers of faculty positions at prestigious universities.

3.3. Colloid Chemistry

Colloid chemistry, the unfailing mainstay of Herbert Freundlich's department during the Weimar years (Figure 26), traces its roots back to the discovery in the 1860s by the Scottish chemist Thomas Graham that certain aqueous solutions pass through a semipermeable membrane only with difficulty, if at all. These solutions he termed "colloids," to distinguish them from "crystalloids" which pass with ease through such a membrane.[42b] Graham presented his research on colloids as a fascinating aspect of the specialized field of solution chemistry. A more modern understanding of colloids, extending the definition of colloids to any substance in which one chemical compound is microscopically distributed through another regardless of the phases of either substance, and focusing on the role of surface forces in colloid behavior, only took shape some four decades later. It was largely the result of a campaign, spearheaded by Wolfgang Ostwald, son of the famous founder of physical chemistry, to establish colloid research as an independent and fundamental chemical discipline. Colloid chemistry was primarily an experimental endeavor, and in addition to redefining colloids with respect to both their material properties and their scientific significance, Ostwald and his allies developed and refined a host of instruments and techniques to advance the new discipline, many of which, such as the ultramicroscope and electrophoresis, remain familiar to chemists today.

Herbert Freundlich (1880–1941) belonged to the vanguard of the campaign for colloid chemistry. He completed his doctorate under Wilhelm Ostwald in Leipzig just a year before Wolfgang Ostwald did the same. Two years later Freundlich began publishing in the flagship journal of colloid chemistry, *Kolloid Zeitschrift*. The journal was edited by the younger Ostwald for over three decades and would host the overwhelming majority of publications by Freundlich and his collaborators during that period. Like many colloid chemists, Freundlich also emphasized the importance of colloids to biology, and he supported research in this vein in his department of the Institute. However, even when researching the properties of biological compounds, Freundlich framed his experiments as investigations into the general principles of colloid behavior, fully in keeping with the tenor of the Ostwald campaign.

Freundlich first made a name for himself in capillary and adsorption chemistry, investigating the thermodynamics of liquid–solid and gas–solid interfaces and the differences between various adsorption phenomena, in modern terms the distinction between chemisorption and physisorption. Following the broader definition of colloids proffered by Ostwald, Freundlich saw this research as bearing directly upon colloid chemistry, in that it aimed at clarifying the general principles of surface interactions. In his research on adsorption, Freundlich relied heavily upon the earlier work of the Yale University physicist Josiah Willard Gibbs to develop a quantitative account of the phenomena early researchers had only described qualitatively. Perhaps the most enduring legacies of this research are the Freundlich isotherm, relating gas adsorption to pressure at a given temperature, and Freundlich's textbook on capillary chemistry, which went through four editions and remained a standard reference in the field for many years. However, of greater immediate import for Freundlich's role at the Institute was his choice of experimental systems. Freundlich studied the adsorption of non-electrolytes and weak electrolytes on activated charcoal, which became a key component in German gas mask filters—hence his invitation to leave behind the *Technische Hochschule Braunschweig* and join Haber's Institute in 1916.

Immediately after the war, Freundlich had two primary assistants, Alexander Nathansohn and Hans Kautsky. Nathansohn was a rarity, an independent chemist who developed practical industrial applications. He worked with Freundlich on "wet metallurgy," that is, the application of knowledge concerning metal solutions and colloids to refining procedures. Together, they developed a patented method for separating lead from tin in mixed ores with high sulfur content. However, Nathansohn also encouraged, if not sparked, Freundlich's interest in the interaction of colloids with light. In addition to an article with Nathansohn on photochemical reactions in colloids,[43] Freundlich published an article on the electrocapillarity of colored solutions in collaboration with Marie Wreschner.[44] Freundlich and Wreschner included industrially significant dyestuffs in their research, but they maintained a focus on the general phenomena of electrocapillarity, using a technique Haber developed in collaboration with Klemensiewicz while at Karlsruhe to measure the potential of glass electrodes, then relating this potential to the migration of dyestuff ions in solution.

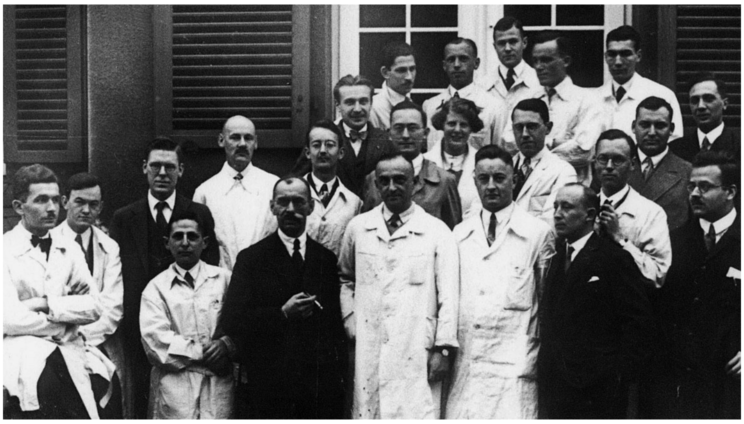


Figure 26. Herbert Freundlich's Colloid Chemistry Department, end of the 1920s.

Freundlich himself went on to attempt a general thermodynamic account of electrocapillarity, similar to his earlier work on adsorption. Further exploration of the optical properties of colloids devolved to Hans Kautsky, who was soon joined by Hans Zocher. Kautsky had begun work under Freundlich during the war, before completing his doctorate. Biochemistry would become the best acknowledged beneficiary of Kautsky's research. An extension of the experimental techniques Kautsky began developing at the Institute led to the first recognition of the Hirsch–Kautsky effect, the characteristic quenching of chlorophyll fluorescence. Hans Zocher's research, on the other hand, focused on optical and magnetic anisotropy in colloid systems, including the streaming or flow birefringence identified by Georg Quincke at the turn of the century. Zocher's recognition of the relation between the asymmetry of colloid particles, the anisotropy of their structure when stressed, and their birefringence is often cited as one of the earliest steps toward the development of liquid-crystal technologies. As with Kautsky and luminescence, Zocher published his most widely cited works in this field after his departure from Haber's institute, in Zocher's case while a professor at the Technical University in Prague during the 1930s. However, both lines of research clearly originated at Haber's institute and relied, in their formative stages, upon the work of institute colleagues. Kautsky drew, in particular, upon the work of Haber and Zisch on luminescence, while Zocher had immediate access to X-ray crystallographic studies of colloid structure, as well as a rudimentary theory of the structure of particulate colloids developed by Eugene Wigner and Andor Szegvari.

Upon his arrival in 1921, Georg Ettisch added a new facet to research in the Freundlich department. Ettisch, who remained at the Institute until forced to leave in 1933, embodied Freundlich's belief in the biological significance of colloid chemistry. Whereas Freundlich restricted himself to using biologically significant compounds in studies of general colloid phenomena, such as adsorption or coagulation, Ettisch endeavored to relate these general phenomena to specific biological functions. This was a widespread field of research during the 1920s, but its pursuit often led to tensions between chemists and medical researchers, as chemists frequently showed little respect for clinical research protocols and posited simple mechanisms to explain complex biological phenomena on the basis of exclusively laboratory research. Ettisch and his collaborators published careful studies of coagulation and the colloid behavior of blood serum and similar substances, but their research was not pivotal to the realization that proteins and other substances vital to the structure and sustenance of life were in fact macromolecules.

Instead, what colloid research at the Institute became widely known for, in addition to photochemistry and capillary chemistry, was the study of thixotropy, the reversible conversion of a semirigid gel to a fluid sol through shaking, stirring, or similar prolonged exposure to shearing forces. In the first years after the war, Freundlich returned to the study of coagulation only in passing, but he took a renewed interest in the topic after two junior researchers in his department, Emma Schalek and Andor Szegvari, observed reversible sol–gel transitions in iron oxide colloids. Freundlich coined the term thixotropy to describe the phenomenon and made the study of reversible transition phenomena a mainstay of his research for the remainder of his career. Initially, the iron oxide observations inspired several short-lived investigations that met with varying degrees of success, including a study of the structures of iron and aluminum hydroxides, both ingredients in thixotropic colloids, carried out by Johann Böhm, who married Emma Schalek in 1925.[45] Freundlich, however, soon embarked on a more systematic study of coagulation times and possible mechanisms for thixotropy. In

1928, Karl Söllner joined Freundlich in this research, and together they extended the study of thixotropy from transitions induced by mechanical stress to those induced by ultrasound. This research did not lead Freundlich and Söllner to fundamental new insights into cohesive forces, but it did lay the groundwork for our present understanding of a phenomenon vital to numerous industrial products including solder pastes and certain adhesives.

During the Nazi era, most of the departments of the Institute focused on the structural analysis of fibers, glasses, synthetic materials, and metals. The director himself, Peter Adolf Thiessen (1899–1990; Figure 27), headed a relatively large department where one of the main interests was the structure of soaps and soap gels, which acted as a model for the colloid properties of long-chain molecules. The intention was then to transfer these findings to a broad range of substances, such as higher carbohydrates, dyes, rubber, cellulose, and other high-molecular-weight polymers. Thiessen maintained: "*Once we have established the processes involved in gel formation, it will be possible to clarify and explain the behavior of technologically significant mixtures, and to cultivate those properties [of them that have] practical value*".[46] In addition to X-ray analysis and ultramicroscopy, the department also used optical and thermodynamic methods to study key interactions between the hydrophilic and hydrophobic parts of the rodlike molecular structures. Joachim Stauff observed a bilayer in soap films, which was held together by water molecules that forced themselves between the hydrophilic carboxyl groups, which were directed inward, toward one another, while the lipophilic hydrocarbon chains of the soap molecules formed an external barrier (Figure 28). He was thus the first to recognize clearly the fundamental principle behind the structure of cell membranes and many similar aggregates.

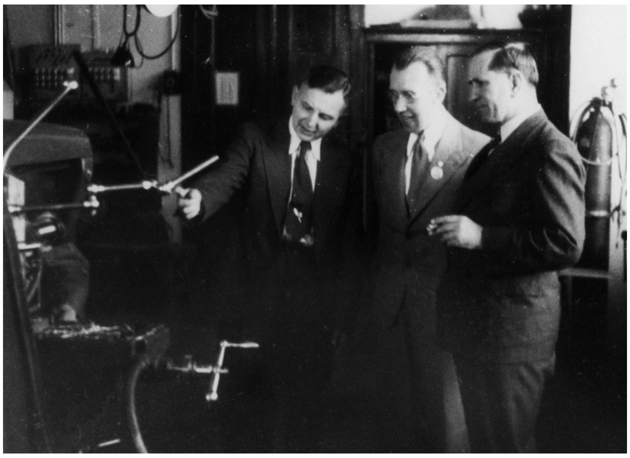


Figure 27. Peter Adolf Thiessen, standing on the left, points out construction details in one of the workshops, circa 1939.

A newly available Agfa color film was later used to document the formation of stable aggregates in soaps through color changes in polarized light. Here, too, Thiessen's group searched for relationships between the properties and the structure of the molecules, and between their spatial arrangement and the twisting, shifting, and stretching of their constituent parts. But the processes involved in aggregate and micelle formation are quite complex, and they were, therefore, unable to establish any universally applicable quantitative laws describing the phenomenon.

Beginning in 1934, August Winkel directed an independent Department for Colloid Chemistry, through which he furthered the research on aerosols, smokes, and fogs that he had previously pursued under Gerhart Jander, the first, albeit provisional, director of the Institute under the Nazis. Winkel emphasized the relevance of research on these mixed-phase systems to meteorology and to occupational health, for example, protection from inhaled particulates through the use of smoke and dust filters. He also noted, markedly more reticently, the possible military applications of such research, which, in addition to smoke screens, included distribution of poison gases, which were generally aerosols of toxic liquids. The Jander department also carried out research on filters to guard against chemical weapons and on filter-breaking compounds. Filtration research focused mainly on adsorption filters and porous materials, but also extended to industrial electro-filtering, which was important in the recovery of scarce raw and manufacturing materials.

Modern analytical methods were used to study particles as small as 0.1 μm; amongst the main methods were light absorption spectroscopy, X-ray crystallography, electron diffraction and, most important of all, ultramicroscopy. Conductivity measurements also ranked amongst the key analytical tools in Winkel's department, as they had under the leadership of his teacher, Jander. In this respect the polarography techniques developed by Jaroslav Heyrovsky in Prague were particularly important. These techniques were also used in analyses of the structures of organic molecules, in which differences in the reduction potential of individual functional groups, for example, keto, carbonyl, or carboxyl groups, were related to the chemical structures surrounding the group.[51]

3.4. Electron Microscopy

Two of the founding fathers of electron microscopy would direct departments at the Institute. Erwin W. Müller (1911–1977) would leave in 1951, but Ernst Ruska (1906–1988) would direct a department at the Institute for over twenty-five years (1949–1975), and thereby define a significant portion of its research profile. In his Diploma Thesis, completed under the direction of Max Knoll, Ernst Ruska worked on the focusing of electron beams in cathode ray tubes. By 1928, he had already obtained a magnification factor of 17.5 with an electron-optical arrangement, and in 1932 he published, jointly with Knoll, the first description of an electron microscope with electromagnetic lenses.[49] Its magnification came close to that of an optical microscope, which was first exceeded with the next prototype in late 1933. This marked the birth of the "ultra-microscopes".

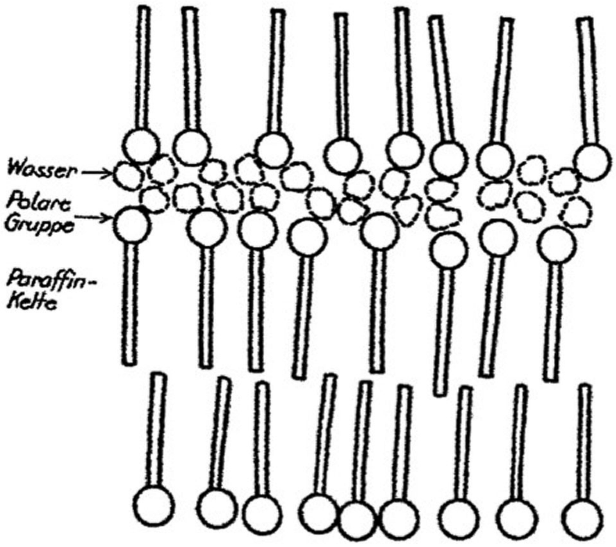


Figure 28. A bilayer in soap films as reported by Joachim Stauff, 1939.[47]

Four years later, Ruska persuaded Siemens AG to set up a laboratory dedicated to "ultra-microscopy." There he developed, jointly with his brother-in-law, Bodo von Borries, the first commercial magneto-optical electron microscope, with a magnification factor of over 30000 and a resolution of about 30 nm. By the end of World War II, 40 such transmission electron microscopes had been produced and put in the service of physical and biomedical research. Ruska's younger brother Helmut would be particularly important to the early development of the technique for biomedical research, and in 1938 the Ruskas (Figure 29) obtained the first images of viruses.

In 1949 a department was established for Ruska at the Institute, although he continued to work for Siemens and also held an honorary professorship at the Freie Universität and a lectureship at the Technische Universität Berlin, where he would become adjunct professor in 1959. Director Max von Laue agreed to expand Ruska's department in 1952, so that he might work full-time at the Institute, allowing him to focus on technical improvements in electron microscopes without regard to the economic factors that were of import to Siemens. Nonetheless, Ruska brought considerable funding from Siemens with him to the FHI;[50] from 1954 on, his department, and later the Institute, received no less than 150000 DM per year. He also brought several members of his scientific and technical staff with him from Siemens, including leading scientists Käthe Müller and Wolfgang Dieter Riecke.

The industrial origins of Ruska's methods and staff had a significant impact on the manner of work done in his department. The Ruska group did not focus so much on scientific issues, as the solving of problems related to the construction of ever more powerful electron microscopes. Their goal was to improve resolution up to the theoretically possible atomic scale. Up to 1951, Ruska pursued this goal in the context of a friendly competition with his fellow department head Erwin Müller. To improve resolution, department members investigated electrostatic as well as magnetic lens systems, and studied not only transmission electron microscopy, which was the center of most researchers' attention at the time, but also other applications of electron optics. One example of this broad line of investigation was the doctoral research of Wilfried Engel. In the years between 1960 and 1968, Engel developed a high-resolution, emission electron microscope in which the image-generating electrons could be produced either thermally, using UV light, or by bombardment with neutral gas atoms.[48]

Ruska's pet project was the development of a completely new, short-focal-length, electromagnetic, single-field condenser objective where the object lay at the focus of a magnetic lens—a now-standard arrangement in electron microscopy. Both the structural details and the adjustable parameters of the microscope had to be recalibrated to support this sensitive, high-performance system. The result was the DEEKO 100 (Figure 30). Completed in 1965, it was a transmission electron microscope with an accelerating voltage of 100 kV that enabled magnification of 800000:1. Its high performance was the result of a delicate technical precision that required highly stable and reliable voltage sources as well as electronic measurement and control instruments. The considerable length of the instrument also made it susceptible to vibrations. It could only achieve its highest resolution, 2.5 Ångström, during the night, when ground vibrations were at a minimum. In light of this problem, Riecke and his team conducted initial experiments on vibration-damping suspension systems. Meanwhile, Hans Günther Heide, one of Ruska's most talented construction technicians, took a different approach and disconnected the adjustment mechanism from the support table. This markedly improved the performance of the microscope, but ground vibrations would continue to be a troublesome source of "noise" to which Ruska and his colleagues had to attend when developing high-performance instruments.

Ruska was on the verge of retirement (January 1, 1975) when a new building was completed for his Institute for Electron Microscopy (IFE). Ruska's focus on ever higher resolutions continued to shape the IFE until the very end of his term of service. In 1972 construction was supposed to begin on a new microscope with a 250 kV single-field condenser objective. This DEEKO 250 was supposed to make possible a resolution of approximately 1 Ångström. However, sundry difficulties slowed its development, so that it only became operational under Ruska's successor in 1980. The potential of the DEEKO 100, on the other hand, was exploited to the very theoretical limits of its performance. Building on his experience at Siemens, Karl-Heinz Herrmann developed helpful image enhancement techniques.[52] Another landmark development of the early 1970s was the construction by Hans Günther Heide of a helium-cooled, cryogenic single-field condenser objective that could be used for temperature-stabilized observations in the range between 6 and 300 K. With cryo-electron microscopy one could sharply reduce thermal vibrations as well as radiation damage, so that even sensitive biological specimens could be effectively imaged. The first trials with bacteria were undertaken at the Institute in cooperation with veterinarian Siegfried Grund.[53]

Figure 29. Ernst (left) and Helmut Ruska at the electron microscope, circa 1957.

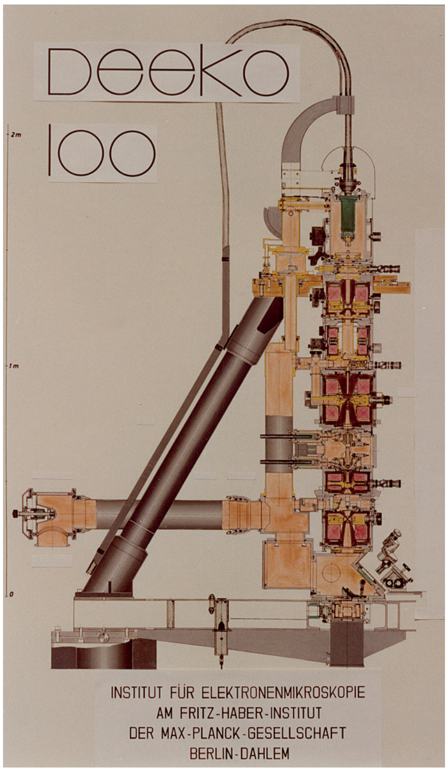


Figure 30. The DEEKO 100. Cross-section from the title page of a brochure.

A committee was established to search for a successor to Ruska who might steer the IFE toward experimental applications of electron microscopy. They eventually came to agree on Elmar Zeitler who was working in Chicago at the time. Zeitler had studied physics in Würzburg and received his doctorate in 1953 under Helmuth Kulenkampff. After some work in industry and a stint as a guest at the Karolinska Institute for Cell Research in Stockholm, Zeitler moved to Washington D.C. as Assistant Chief for Biophysics at the Armed Forces Institute of Pathology. Then, in 1971, he accepted an appointment at the University of Chicago as Professor of Physics and of Biophysics and member of the Enrico Fermi Institute.

Crucial to the decision in favor of Zeitler was his work on the quantitative interpretation of electron microscopy images and on the scanning transmission electron microscope (STEM), which was developed by Albert Crewe during Zeitler's time at Chicago. While Ruska understood electron microscopy by analogy to light microscopy, Zeitler saw it in the context of other measurement techniques. Shortly before his appointment to the FHI, he became the founding editor of the new journal *Ultramicroscopy*. His wide-ranging interests, which covered all aspects of electron microscopy from its fundamental theories to its subtlest applications, was seen as an indicator of his ability to integrate electron microscopy with ongoing research in the other subsections of the FHI. This was deeply desired and much discussed, but easier said than done.

One subject of particular interest to Zeitler was the study of the microstructures of biological samples. But heavy bombardment with electrons generally destroyed these structures before a satisfactory image could be generated. An array of novel methods that led to significant improvements in image generation helped. One of these improvements was the optimized adjustment procedure, developed by five former co-workers of Ruska, prominent among them theorist Peter Schiske, and jocularly dubbed the "*Fünf-Männer-Arbeit*" ("five-man paper"). In addition, Friedrich Zemlin developed a tableau that offered an overview of possible image frames and greatly simplified the calibration of optics for practical applications;[54] consulting such a tableau is now standard procedure when a microscope is operated near its performance limits, and the tableau bears Zemlin's name. With the image quality of the DEEKO 100 enhanced through such methods it was possible for the first time, in cooperation with Peter Ottensmeyer in Toronto, to generate a comparatively low-noise image of protamine proteins.[55]

When Zeitler arrived in Berlin, Heinz-Günter Wittmann, director of the newly founded MPI for Molecular Genetics in Berlin-Dahlem since 1964, was beginning to build up an international center for ribosome research. In 1979, Ada E. Yonath joined Wittmann at the MPI for Molecular Genetics. Wittmann wanted to take advantage of the electron microscopy expertise on hand at the IFE, since the crystallization procedure necessary for the X-ray analysis of ribosome proteins had proven a formidable challenge. However with the help of digital image processing and a peculiarity of the sample preparation process that guaranteed the ribosomes organized themselves into coplanar groups of four that could be arranged into "class average images," it became possible to generate images of the roughly 20 nm recognizable images of the ribosomes. Electron crystallographic data, much of it gathered with new low-temperature methods, would strengthen Yonath in her basic assumptions concerning the form and function of ribosomes. For example, in 1995, a ribosomal output channel for proteins could be discerned, an achievement in which Marin van Heel from Zeitler's department and his student Holger Stark played key roles.[56] In the end, even though it was X-ray analysis that enabled Yonath to finalize her structural explanation of ribosomes, for which she received the 2009 Nobel Prize in Chemistry, part of her achievement can be traced back to electron microscopy work done at the FHI.

Electron crystallography of the smallest specimens would be the special focus of the research group under Marin van Heel, who came to Berlin in 1982 from Groningen University and remained at the FHI until 1996, when he accepted a professorship at Imperial College London. Van Heel developed computer programs for the automatic classification of individual image frames, by use of which sequential views from multiple perspectives could be made the basis for tomographic representations[57] of single particles or molecules.[58] This enabled the elucidation of the structures of an array of receptors, enzymes, and functional protein complexes, such as the portal protein of the bacteriophage SPP1.

One key component for advancing this line of work was a superconducting lens developed in the research labs of Siemens AG in Munich by Isolde Dietrich's group.[59] With this new tool it would become possible to produce "molecular maps" of proteins. Installation of the lens brought with it a reduction in signal noise, as well as enabling the constant cooling of the sample to 4.2 K. This allowed the use of lower beam currents with longer exposure times, which reduced damage to specimens. The lens would be included in two different electron microscopes: first, the home-built "Suleika" (*Supraleitender Kühlapparat*), then SOPHIE (Superconducting Objective in a Philips electron microscope), built with the help of Philips and a special grant for international academic–industrial collaboration from the European Union.

Figure 31. Alexander Bradshaw, 1977.

At the same time, projects related to surface-sensitive methods supported stronger bonds between Zeitler's department and other departments at the Institute and contributed to its repertoire of surface science techniques, one example of which was the so-called "PEEMchen." In large part because of the inadequacy of UHV technology, Ernst Bauer of the Technische Hochschule Clausthal was only able to implement the long-familiar notion of a low-energy electron microscope (LEEM) in 1985.[60] This technique allowed the observation of adsorbate distribution on single-crystal surfaces in real time and at high contrast. Alexander Bradshaw investigated related phenomena, and a cooperation grew up, initiated by Bradshaw and Zeitler, between their respective co-workers Wilfried Engel and Marty Kordesch, aimed at recreating the revolutionary instrument with the help of Bauer. In the resulting instrument, a photoelectron emission microscope (PEEM), the photoelectric effect stimulates the emission of slow electrons from the specimen, which are then used to form an image of its surface. The dynamic nature of the images produced by the instrument impressed both Bradshaw and Gerhard Ertl;[61] for example, it enabled one to see the accrual of carbon in ethylene adsorbed on platinum. The decision was reached to build a more sophisticated, user-friendly "PEEMchen," at which point Ertl's co-worker Harm Hinrich Rotermund joined the PEEM group. Rotermund was able to develop impressive depictions of spatio-temporal changes in surface structures.[62] The "PEEMchen" would be patented on behalf of Engel by the MPG and offered for sale by STAIB Instruments, making it widely available for the study of surface reactions. This line of work is still being continued through the SMART project at BESSY II.

Another quite successful project of this sort was the introduction of electron energy loss spectroscopy (EELS) into the Electron Microscopy Department. When Zeitler arrived at the Institute, many of the microscopes were either obsolete or inoperable. Making the best use of what *was* available, he encouraged the inclusion of a radiation source already at hand in the construction of an energy loss spectrograph, in which a sector magnet spectrally resolved the electron beam and a system of lenses projected this energy distribution without rotation across the entire breadth of spectra which could be selected from different energy ranges.[63] The arrangement proved to be a high-performance EELS apparatus; in 1982, Zeitler, Engel, and Herman Sauer achieved an unrivaled lateral resolution of 0.2 nm with an energy resolution of 0.2 eV. Since it provided a means for spatially resolved chemical analysis of minimal samples of substances adsorbed on solid surfaces, EELS was a valuable surface science technique.

Rik Brydson, a student of John Meurig Thomas, one of the fathers of modern heterogeneous catalysis research, traveled to Dahlem regularly for several years after 1986 so that he could carry out high-resolution EELS analyses of the structures of minerals such as rhodizite,[64] rutile, and anatase.

3.5. BESSY

In addition to leading a research group at the FHI, London- and Munich-trained Alexander Bradshaw (*1944; Figure 31) took on a distinctive, public role in forwarding new lines of research in the late 1970s; he championed efforts to make synchrotron radiation more accessible to researchers at the Institute and in Berlin generally. Around the time of Bradshaw's move to the FHI, users of synchrotron radiation worldwide were considering plans for new "dedicated" sources. Late in 1976, in part in response to plans for a new 300 MeV synchrotron presented by Burkhard Wende of the Berlin branch of the Federal Institute of Physics and Technology (*Physikalisch-Technische Bundesanstalt*, PTB), Bradshaw, together with Helmut Baumgärtel of the Freie Universität and with the support of FHI Director Heinz Gerischer, began lobbying for a larger storage ring that could offer beam time to regional users, including the FHI, for experiments in solid-state and surface sciences as well as in gas-phase spectroscopy. Shortly thereafter, an Expert Committee under the direction of Manuel Cardona was set up to evaluate proposals for dedicated synchrotron radiation sources in Germany. The commission considered a proposal by Ernst-Eckhart Koch, Christoph Kunz, and Gottfried Mülhaupt from the DESY accelerator center to build a 700 MeV storage ring at DESY and a recommendation from a working group within the Federal Ministry of Research and Technology (BMFT) that was studying the potential use of X-ray lithography in microchip production, as well as the Berlin proposals. The commission advised that two storage rings would be optimal, an X-ray facility in Hamburg and a separate ultraviolet

Figure 32. BESSY I in Berlin-Wilmersdorf, 1986.

source, originally slated for Bonn. Political and funding considerations, however, tipped the balance in favor of the second site being Berlin, and just over two years later the Berlin Electron Synchrotron (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung, BESSY) was established as a limited-liability company (GmbH) for the construction and operation of an 800 MeV electron storage ring in Berlin. BESSY had eight original shareholders, four electronics companies: Siemens, Telefunken, Eurosil, and Valvo (Philips); and four research organizations: the Max Planck Society, the Fraunhofer Society, the Hahn Meitner Institute, and DESY, but the majority of funds for its construction came from the German federal government.

In light of the special interest in synchrotron radiation shown by Bradshaw and Gerischer, the CPT Section of the MPG agreed to a proposal from the Board of the FHI in February of 1978 that the Scientific Director of BESSY should also be appointed a scientific member of the FHI. A search committee formed within the CPT Section and chose Bradshaw for the post, and he took over as Scientific Director at the beginning of 1981, 18 months before the facility began normal operations, and just after he was promoted to Scientific Member of the FHI and head of the Department of Surface Physics. Bradshaw remained Scientific Director at BESSY until the end of 1985, then returned to the post for roughly a year in 1988, following the death of his successor Ernst-Eckhard Koch. Bradshaw credits the success of user operation at BESSY in the early years to a small but extremely capable in-house group, headed by William Peatman.

The challenges of administering BESSY occupied much of Bradshaw's time during the early 1980s. Nevertheless, Bradshaw and his FHI group managed to make several significant scientific contributions during the 1980s, in particular to synchrotron instrumentation. Together with Eberhard Dietz and Walther Braun, Bradshaw built a high-flux, high-energy toroidal grating monochromator (HE-TGM-1) for BESSY that began operation in 1984. In collaboration with Manuel Cardona, among others, Bradshaw also developed a VUV ellipsometer that enabled novel research into the optical properties of solids and surfaces. The first experiments with the infrared component of synchrotron radiation, to which Erhard Schweizer and Ernst Lippert were key contributors, were also made at this time. At the close of the decade, the Bradshaw group, in particular Josef Feldhaus, then took a leading role in the construction of the X1B undulator beamline at the National Synchrotron Light Source in Brookhaven, New York.

Bradshaw also remained active in promoting new synchrotron facilities. Even before his first term as scientific director at BESSY came to an end, he had begun lobbying for the construction of a new "third-generation" synchrotron in Berlin. Since the construction of BESSY (hereafter BESSY I; Figure 32), physicists had developed "wigglers" and "undulators" that could increase the spectral brilliance of synchrotron radiation several orders of magnitude by inducing periodic, "sideways" oscillations of the electron beam in the otherwise straight sections of the storage ring. Just three years after BESSY I became operational, Bradshaw and colleagues Gottfried Mülhaupt, William Peatman, Walter Braun, and Franz Schäfers sent a proposal to the BESSY Supervisory Board for a 1.5 GeV storage ring at the site in Berlin-Wilmersdorf using BESSY I as the injector.[65] The idea behind "BESSY II" was to cover roughly the same soft X-ray spectral range of the BESSY I bending magnets but with the much brighter undulator radiation. The first published proposal for BESSY II appeared at the end of the year and included among its contributors not only Alexander Bradshaw and Ernst-Eckhard Koch, but also Karsten Horn, Dieter Kolb, and Josef Feldhaus of the Fritz Haber Institute and Hans-Joachim Freund, who was then at Erlangen but would join the FHI as Director of the Department of Chemical Physics in 1996. In 1989, when the Berlin Wall fell and German reunification quickly followed, a whole host of possible new sites for the accelerator became available. An alternative site was chosen in Berlin-Adlershof (Figure 33), home of many institutes of the former Academy of Sciences of the German Democratic Republic, and the plan to use BESSY I as an injector was abandoned.[66] No parallel appointments similar to those spanning the FHI and BESSY I were made, but the ties between synchrotron radiation sources and research at the FHI remained firmly intact, above all through the efforts of Bradshaw and members of his Department of Surface Physics, but also through the work of Hans-Joachim Freund and Robert Schlögl and their respective departments.

Bradshaw embarked upon at least three new lines of research that specifically took advantage of the availability of synchrotron radiation sources. The first, a long-running application of "energy scan" photoelectron diffraction to the study of adsorbed molecules and molecular fragments in collaboration with Phillip Woodruff of the University of Warwick. Although photoelectron diffraction had been known for more than 15 years when Bradshaw and Woodruff began their collaboration, they were able to provide novel quantitative structural information for over a hundred adsorption systems (to date) by taking full advantage of synchrotron radiation and efficient, innovative simulation codes written by Volker Fritzsche. So-called direct methods were also pioneered in the group at this time, particularly by Philip Hofmann. The second line of research undertaken by

Bradshaw and his colleagues involved a series of photoionization studies of free molecules in the core-level region at hitherto unavailable spectral resolution. This research made extensive use of the previously mentioned X1B beamline at Brookhaven. Among other novelties, these investigations demonstrated the importance of vibronic coupling in molecules containing equivalent cores and provided the first measurements of the influence of shape resonances and double excitations on the vibrational fine structure of core level lines of various small molecules. Bradshaw's third major area of research in the 1990s was in low-energy electron microscopy and photoelectron microscopy with Winfried Engel and Elmar Zeitler of the Department of Electron Microscopy. After extensive laboratory studies on, among other things, reaction-diffusion fronts in heterogeneous reactions, this work resulted in a proposal for a photoelectron spectro-microscope for BESSY II (the SMART project) presented together with Eberhard Umbach, then of University of Würzburg and later an external member of the FHI, and with Hans-Joachim Freund.

These areas of research were, however, only the latest expressions of a long-standing tradition of pursuing atomic and molecular physics using synchrotron radiation within the Department of Surface Physics. The group of Ulrich Heinzmann performed pioneering studies of photoionization processes using circularly polarized radiation and spin-polarized detection of the photoelectrons, before Heinzmann was appointed to a Chair in Bielefeld in 1985. Ernst-Eckhard Koch, Heinzmann's successor at the FHI, also undertook seminal experiments on molecular crystals before his untimely death in 1988.

3.6. Surface Science

Electrons penetrate less deeply into a sample than X-rays, and soon after the diffraction of electrons by crystals was first recognized, in 1927, scientists realized that this limited penetrating power made electron diffraction analysis a particularly powerful tool for analyzing surface structures. However, the expensive equipment and elaborate mathematical methods required by the technique meant it was rarely used in chemical research. Beginning in the National Socialist period, researchers at the Institute performed electron diffraction studies using fast electrons (HEED), whose diffraction patterns were not as exclusively dependent upon surface features but which gave rise to fewer experimental difficulties. They developed both new sample preparation techniques and new methods of diffraction pattern analysis which allowed them to translate their data into an atomic or molecular structure. Since surface structures play a substantial role in the adsorption processes involved in heterogeneous catalysis, Theodore Schoon and his colleagues used the new technique to investigate microcrystalline platinum catalysts and similarly active iron(III) oxide. Parallel research focused on the porosity and gas permeability of catalytic materials and on the systematic collection of data relating to industrial catalysts. Beginning in 1941, Schoon had access to the new electron microscope developed at Siemens by Ernst Ruska,[67] who was in personal contact with Peter Adolf Thiessen.[68] Schoon also used the new instrument to study the size and shape of the particles in rubber fillers, especially soots, and the effects of the fillers on the properties of the rubber mixtures. But Schoon's studies were just a beginning. Electron diffraction analysis would remain a standard research technique at the Institute for over forty years, largely thanks to the efforts of Kurt Molière, who first arrived at the Institute in the late 1930s and was a department head from the time the FHI joined the MPG until his retirement in 1980.

Figure 33. BESSY II in Berlin-Adlershof.

In 1964, FHI Director Rudolf Brill created a research group dedicated to field electron emission spectroscopy. It was initially headed by Werner A. Schmidt, who moved to Brill's department from the remainder of Erwin Müller's group, which had been integrated into Gerhard Borrmann's department. In 1966, Jochen H. Block took over the group, joining what would become a 50-year tradition of field electron emission spectroscopy at the Institute spanning from end of the 1940s well into the 1990s (Figure 34). Brill sought to groom Block for leadership, recognizing that the latter was interested primarily in spectroscopic methods, especially field-ion mass spectroscopy, that could be used for surface analysis, and hence might complement Brill's work on heterogeneous catalysis.

Block had completed his doctorate in 1954 under the direction of Georg-Maria Schwab, the father of German catalysis research, and he remained in Munich through 1960 to complete his habilitation. He worked subsequently for the European Research Association in Brussels and spent a year in the United States as a consultant for Union Carbide. Block and his group conducted experiments with field electron microscopes and mass spectrometers, seeking both to develop more advanced research techniques and to explain the mechanisms of surface catalytic reactions. For example, their mass spectrometer findings, together with infrared spectra, appeared to support Brill's hypothesis that during the Haber–Bosch process higher nitrogen hydrides are formed on the catalyst surface that then break down into ammonia before desorption.[69]

Later, under Gerischer, Block was able to form the core of what would become the Department for Surface Reactions using the resources available from his earlier research group. Soon Kurt Becker and his research group also joined Block in the new department. Becker persisted in his research into heterogeneous catalysis with catalysts such as zeolites. One prominent application of these aluminosilicates was as catalysts in the petrochemical industry. Studies at the Institute concentrated primarily on their structure, stability, and reactivity. However, in addition to seeking a better understanding of mechanisms of catalysis, members of the Institute also carried out experiments on reaction kinetics and catalyst poisoning. Becker's group found that the limits on the lifespan of petrochemical zeolite catalysts were set by self-poisoning with polymerized olefins, a product of the reactions they catalyzed.[70] Hellmut G. Karge, who retired in 1996, was one of the exceptionally productive members of this group. He modified zeolites and other catalysts using ion-exchange methods and thereby improved their longevity and selectivity.

The main focus of Block's interests was the behavior of surfaces in strong electric fields, which he explored using field emission phenomena, especially field-ion microscopy and field-ion mass spectrometry. Field desorption permitted inferences regarding the electronic properties of surfaces and surface adsorbates, and the atomic-scale resolution of the technique allowed very precise local analysis of crystallographically well-defined surfaces. However, it required that the substrate be manufacturable in the form of thin, sharp needles. Also, since the photoexcitation of field-ion formation using light, synchrotron radiation, or laser pulses (photo field-emission) evinced no penetrating power, it was treated as a technique that acted only at the surface. Institute members used this technique to study samples of tungsten, silver, and aluminum hydroxide, upon which H_2, O_2, H_2S, or ethylene had been adsorbed, across a range of temperatures.[71] Later experiments also examined superconductors. One of Block's abiding collaborators in these studies was Wolfgang Drachsel, who later led a research group in Hans-Joachim Freund's department and was active at the Institute until 2004.

Figure 34. From left to right: Jochen H. Block, Heinz Gerischer, Erwin W. Müller, October 1, 1976.

Another central and persistent focus of research in Block's department was heterogeneous catalysis, a field in which Block showed an early interest as cofounder and first chairman of the DECHEMA (*Gesellschaft für Chemische Technik und Biotechnologie*) section for catalysis. As a test of the applicability of field emission methods in catalysis research, the Block group examined simple systems such as the adsorption of noble gases or the chemisorption of CO, both of which manifested significant deviations, while in the apparatus, from their reactivity outside an electric field. Theoretical work based on models from "high-field chemistry" and completed, in part, through a close collaboration with Hans Jürgen Kreuzer, backed up these experiments. Kreuzer was Professor for Theoretical Physics at Dalhousie University in Halifax, Canada, and was named external member of the FHI in 1998. In later experiments, the surface-specific adsorption and chemisorption of various small molecules on metal surfaces were explored, phenomena that were of decisive import for heterogeneous catalysis. In order to study these systems, new methods were needed that increased the sensitivity of the apparatus. Hence, the field-ion microscope was equipped with a kind of atom probe and developed into a field-ion energy spectrometer that could generate data relating to the position and the energy of individual surface atoms at defined points on the microscope tip. One model system for induced field desorption studies was the formation of singly and multiply charged hydrogen ions. With linear H_3^+ ions in strong fields, it was shown that the H_{3ad} species was positioned upright and linearly against the probe surface.[72] Among the collaborators who worked extensively with Block on the kinetics of reactions on metal surfaces was Norbert Kruse, who had already been in Berlin and affiliated with the FHI almost 10 years in 1977, and who is now Professor for Chemical Physics at Université Libre in Brussels.

Block placed great weight on modern technical facilities, and in the Department for Surface Reactions several other instrumental methods were advanced, primarily ones related to electron field emission or ion emission. Pulse methods were developed that allowed for time-of-flight mass spectrometry,[73] including a variant of the technique in which a laser-stimulated photoemitter replaced the high-voltage pulse generator for exact mass determination;[74] for the necessary UV radiation Department members relied on HASYLAB at DESY and on BESSY (see above). Through the combination of pulsed desorption with time-of-flight mass spectrometry and digitally processed image displays it was possible to determine exactly the formation sites of various molecules.

In 1983, Elmar Zeitler, then the executive director of the FHI, traveled to Munich to sound out whether Gerhard Ertl (*1936) might accept an offer from the MPG to become a director at the FHI; this was an unlikely outcome in the eyes of many. Munich offered Ertl generous support for his research, and he was, and remains, a strong supporter of the universities and their students. However, Ertl accepted the offer, in part guided by what he later called an "emotional reason:" coming to the FHI enabled him to become the successor of his mentor Heinz Gerischer, who remained a scientific role model for Ertl (Figure 35). Moreover, his previous experiences in Stuttgart helped convince Ertl that an "optimal arrangement" was possible, in which a Max Planck Director works extensively with doctoral students and junior researchers, contributing in this way to the mission of the universities, but remaining free of routine teaching and administrative duties. It was this arrangement that Ertl set out to establish in Berlin. Ertl was appointed Scientific Member of the MPG and Director at the FHI as of April 1, 1985. Rather than immediately taking over from Gerischer, Ertl shared the Directorship of the Physical Chemistry Department with him for the next two years, while commuting between Berlin and Munich, to which he was still bound by previous commitments. The transition from Gerischer to Ertl was completed with Gerischer's retirement on April 1, 1987, at which point Ertl became the sole director of the Department.

Ertl had studied physics from 1956 to 1961 at the Technical University of his native city of Stuttgart where he wrote a Diploma Thesis on fast chemical reactions under the guidance of Heinz Gerischer, who was then at the Max Planck Institute for Metals Research in Stuttgart. His thesis, inspired by Manfred Eigen's relaxation technique and Gerischer's flash, presented a kinetic study of the recombination of protons and hydroxide ions induced by rapid heating of water with a microwave pulse. Ertl followed Gerischer to the *Technische Universität München* in 1961 as his PhD student, and it was there that he turned to the investigation of surface reactions, with Gerischer's blessing. At that time, the ultra-high vacuum needed in order to keep a surface clean long enough to study surface reactions could only be achieved with sealed-glass systems evacuated by mercury diffusion pumps and baked to 450 °C. Similarly, low-energy electron diffraction instruments (LEED) capable of providing information about the atomic structure of surfaces were still exceptional and large apparatus, and Ertl had to rely upon a grant from the German Science Foundation (DFG) to purchase the first such apparatus for the Munich laboratory in 1965. This investment launched what Ertl later called "*the real surface science era*."

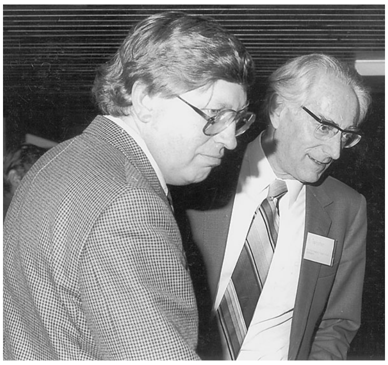


Figure 35. Gerhard Ertl (left) and Heinz Gerischer, 1981.

In his PhD and thereafter, Ertl combined structural information with thermodynamic and kinetic data to characterize and explain the course of chemical reactions on surfaces. In these early studies, one can already discern aspects of Ertl's characteristic approach to surface science. In his own words, he "*always attempted to tackle chemical questions with physical methods*." But unlike many of his colleagues, there was no one method to which Ertl remained devoted. There was, however, one question that engrossed him: "*How do chemical reactions proceed*."[75] In his investigations of the surface reactions of small molecules, Ertl introduced novel experimental techniques, such as scanning tunneling microscopy (STM) and photo-emission electron microscopy (PEEM), to systematically study the adsorption and chemisorption phenomena at well-defined, single-crystal surfaces. Such fundamental studies proved indispensible for our present understanding of heterogeneous catalysis. Key were Ertl's mechanistic studies relating to the Haber–Bosch process, carried out in Munich, as well as the investigations of the oxidation of CO on the platinum group metals from his FHI period. Under certain conditions, the latter reaction exhibits an oscillatory behavior that could be used to learn fundamental lessons about coupled systems in surface reaction kinetics and beyond. Many of Ertl's groundbreaking studies relied on experimental techniques that were matched to the particular needs and conditions of an experiment and were often deployed in novel combinations with other techniques.

The present and future of the Institute looked quite promising when Ertl arrived in Dahlem. Although the Department of Physical Chemistry under Gerischer was already fairly large, Ertl brought roughly two dozen additional co-workers with him from Munich, most of them doctoral students. Relatively autonomous were the research group on biophysical dynamics led by Josef Holzwarth, who came to the FHI along with Gerischer, and the group of Frank Willig, whose research dealt with the picosecond dynamics of photo-electrochemical systems. Both groups occupied new labs in one of the buildings of the Department of Electron Microscopy. In subsequent years, Ertl's department shrunk somewhat, but it remained the most populous at the Institute, and doctoral students continued to constitute the bulk of its scientific workforce. Throughout his tenure, Ertl developed a broad, multifaceted research program in his department that revolved around the model catalytic process of the oxidation of carbon monoxide on various catalysts. The bountiful results of Ertl's research made an indelible mark on surface science, catalysis, and studies of the dynamics of complex systems and self-organization. The main activities of Ertl's department, apart from further studies of the mechanisms of catalytic reactions (with Karl Jacobi and Herbert Over et al.) were:

- investigation of nonlinear dynamics and spatio-temporal pattern formation, including theory, in surface reactions (with Alexander Mikhailov and Harm Rotermund et al.);
- investigations of the above in electrochemical systems (with Markus Eiswirth and Katharina Krischer et al.);
- imaging of surface processes on the atomic scale by scanning tunneling microscopy (with Joost Wintterlin et al.);
- studies of the dynamics of fast surface processes by femtosecond pump–probe laser techniques (with Martin Wolf et al.);
- various aspects of electrochemistry (with Bruno Pettinger and Rolf Schuster et al.);
- exoelectron emission in surface reactions.

At a 1974 catalysis symposium, a doyen of the field, Paul Hugh Emmett, noted that: "*The experimental work of the past 50 years leads to the conclusion that the rate-limiting step in ammonia synthesis over iron catalysts is the chemisorption of nitrogen. The question as to whether the nitrogen species involved is molecular or atomic is still not conclusively* *resolved.*"[76] Emmett's lament spurred Gerhard Ertl's resolve to meet the challenge that it embodied.[77] Ertl recognized that the techniques of surface science then available in his laboratory at the University of Munich (*Ludwig-Maximillians-Universität*) might suffice to identify the elementary steps of nitrogen fixation, and thereby to provide a basis for a quantitative description of the reaction that is at the core of the Haber–Bosch process. The surface science approach to tackling problems in catalysis had been advocated already in the 1920s by Irving Langmuir, but could be implemented only in the 1960s, when ultrahigh vacuum technology and surface sensitive physical methods, such as low-energy electron diffraction (LEED), became available.

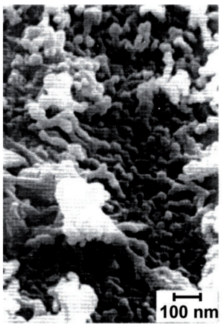
The need for Ertl's approach becomes evident once a sample of an industrial catalyst comes under closer scrutiny. Figure 36 shows a high-activity catalyst with a rather large specific surface area, composed of nanometer-sized active particles. Under reaction conditions, these are reduced into metallic iron covered by a submonolayer of potassium (and oxygen) which acts as an "electronic" promoter. The configuration of active particles is stabilized against sintering by a framework consisting of alumina (Al_2O_3) and quick lime (CaO), which act as "structural" promoters. The active component possesses a variety of crystal planes and defects, all of which bear on its reactivity.

Generally, atoms that make up the surface layer of a solid have fewer neighbors than atoms within the bulk, so they are chemically unsaturated. Therefore, surface atoms can form new bonds with molecules impinging on the surface from the gas or liquid phases (chemisorption), and modify and even break the existing bonds of the impinging molecules (dissociative chemisorption). The species formed on the surface may then jump from one site to an adjacent site and react there with other species. The products thus formed may subsequently detach from the surface (desorption) and leave. If the solid surface in question is that of a catalyst immersed in a flow reactor, it can partake in the chemisorption/desorption cycle continuously without being consumed.

At low surface concentrations, the chemisorbed species undergo a random walk; while at higher ones, the adsorbed particles separate into two ordered two-dimensional phases, a quasi-solid and a quasi-gas. Ertl and co-workers as well as others have found that the formation of such structured adsorbate phases with long-range periodicity is quite common and that their structural parameters can be determined by electron diffraction techniques, such as LEED. The dissociative chemisorption of nitrogen on various single-crystal surfaces of iron exemplifies the formation of such structured phases which, in this case, stem from chemisorbed nitrogen atoms. The probability of the dissociative chemisorption of nitrogen over iron is very low, typically on the order 10^{-6}, and puts a cap on the total rate of ammonia synthesis. Figure 37 shows how the surface concentration of nitrogen atoms chemisorbed on various iron single-crystal surfaces varies with the number of nitrogen molecules impinging on the surface per unit surface area and time at a given temperature. The influence of the surface structure is quite pronounced. The most densely packed (110) surface is least active, while the open (111) plane exhibits the highest dissociative chemisorption probability and is indeed responsible for the overall activity of the industrial catalyst. This activity is further enhanced by the presence of the potassium atoms in the role of the electronic promoter, which increases the dissociation probability of the adsorbed nitrogen molecules $N_{2,ad}$. The same behavior was also found for dissociative nitrogen adsorption at high pressure, indicating that the results are scalable in terms of pressure—there is no "pressure gap" in the case of this reaction.

After tackling the ammonia synthesis problem for about a decade, Ertl and co-workers were able to meet Emmett's challenge: They showed that a combination of the kinetic parameters associated with the individual reaction steps shown in Figure 38 furnishes a steady-state yield of ammonia from the elements that, for a range of conditions, accurately reproduces the real-life yields measured at industrial plants. This agreement has demonstrated that, in the case of the ammonia synthesis, the "surface science" approach to catalysis is capable of providing no less than a quantitative description of an industrial process.

Like the ammonia synthesis, catalytic oxidation of carbon monoxide is at the core of a major technological process, namely the removal of toxic substances from automobile



Technical conditions: $T \approx 400°C$, $p \approx 300$ bar
promoted iron catalyst

BASF S6-10 catalyst (atom %)

	Fe	K	Al	Ca	O
Bulk composition	40.5	0.35	2.0	1.7	53.2
Surface –					
unreduced	8.6	36.2	10.7	4.7	40.0
reduced	11.0	27.0	17.0	4.0	41.0
cat. active spot	30.1	29.0	6.7	1.0	33.2

Figure 36. Electron micrograph of a sample of an iron-based catalyst, developed by Alwin Mittasch around 1911, widely used in the Haber–Bosch process. The sample has a specific surface area of about 20 $m^2 g^{-1}$.

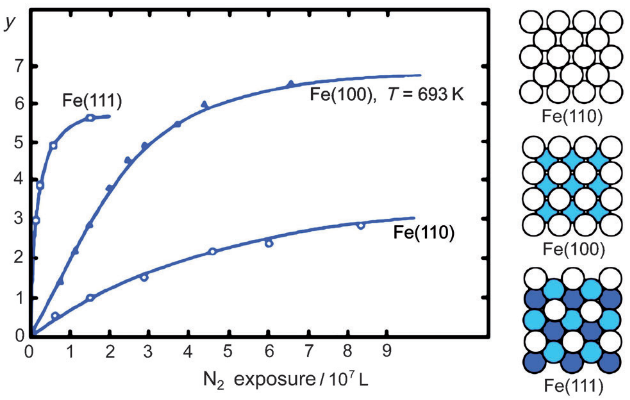


Figure 37. The variation of the relative coverage, y, of nitrogen atoms chemisorbed at 693 K on various iron single-crystal surfaces with exposure to gaseous N_2 (1 L = 1.33×10^{-6} millibar seconds is about the exposure which would suffice to form a complete monolayer if each incident molecule were adsorbed).

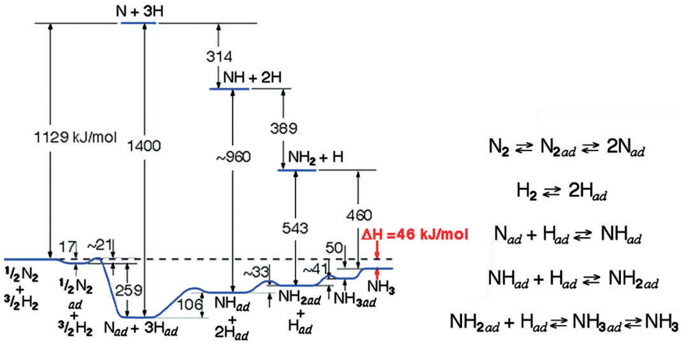


Figure 38. Mechanism and energy diagram of ammonia synthesis on iron.

exhaust fumes. In a catalytic converter, the exhaust fumes interact with the surface of fine-grained particles of metals from the platinum group. While the carbon monoxide (CO) molecules are adsorbed by the surface of the catalyst, the oxygen molecules (O_2) contained in the fumes are dissociatively chemisorbed, furnishing the O_{ad} species. These atoms react with the chemisorbed CO to form carbon dioxide molecules (CO_2), which instantaneously desorb into the gas phase.

Under typical steady-state flow conditions, the rate of product formation is time independent. However, as noted by Ewald Wicke and co-workers in 1970, if the reactants are rarefied, the rate of product formation may become time-dependent and exhibit temporal oscillations similar to those of a Belousov–Zhabotinsky reaction in solutions (see Figure 39). This behavior, explored beginning in the 1950s by Ilya Prigogine and by Hermann Haken in the framework of synergetics, is characteristic of open systems far removed from equilibrium, which may develop dissipative structures. Ertl: "*A particularly spectacular example of such a behavior is the variation with time of the number of furs from hares and lynxes delivered [by hunters] to the Hudson's Bay Company. The oscillating populations of both species are coupled to each other with a certain phase shift. The reason seems to be quite obvious: If the lynxes find enough food (=hares), their population grows, while that of the hares decays as soon as their birth rate cannot compensate for their loss any more. When the supply of hares drops, the lynxes begin to starve and their population also decays so that that of the hares can recover.*"[78]

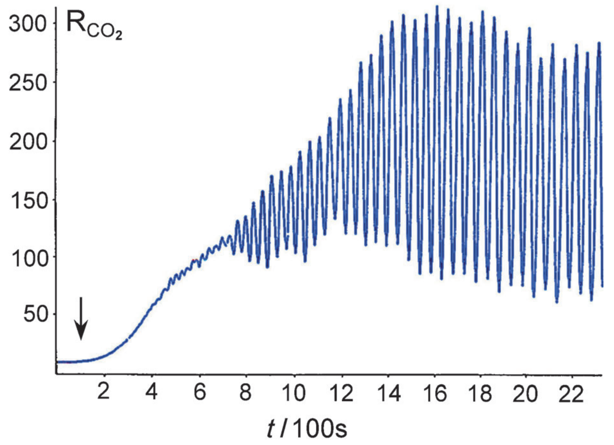


Figure 39. Temporal dependence of the CO oxidation rate over a well-defined platinum (110) surface. At the time marked by the arrow, the O_2 pressure was raised stepwise from 2.0 to 2.7×10^{-4} mbar. As a consequence, the rate slowly increased and then developed periodic variations with a large and constant amplitude.

Gerhard Ertl's research has demonstrated that a rather simple system (a chemical reaction occurring between two diatomic molecules on a well-defined single-crystal surface with fixed external parameters and well-established mechanism) can be used to study and model quite a complex behavior. The conclusions which it allows us to draw about open systems far from equilibrium transcend catalysis and surface science and provide clues about laws believed to govern the whole of nature.

We would like to thank the Board of Directors of the Fritz Haber Institute, who, in preparation for the 100th anniversary of the founding of the Institute, initiated the Centennial Project, amongst whose goals was the production of this article. The Institute and its Directors Hans-Joachim Freund, Gerard Meijer, Matthias Scheffler, Robert Schlögl, and Martin Wolf have generously supported the Centennial Project over the past three years and followed it with an abiding interest. Our thanks are also due to our numerous colleagues who provided indispensable help and assistance in the course of the Centennial Project. Thanks the Archive of the Max Planck Society and the Fritz Haber Institute for providing most of the photos used in this article. Our special thanks are due to David Vandermeulen for allowing us to use his rendition of L. Koppel (Figure 1). This aid and assistance notwithstanding, the material included in this article has been selected by the authors alone and presented in the manner we felt appropriate. We alone are answerable for the interpretations of historical events it offers, as well as any lacunas or inaccuracies that may have escaped our notice.

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