Surface Chemistry

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Molecules at Surfaces: 100 Years of Physical Chemistry in Berlin-Dahlem

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heterogeneous catalysis · history of chemistry · scanning probe techniques · surface chemistry

Preface

On 28 October 2011 the former Kaiser-Wilhelm Institut für Physikalische Chemie und Elektrochemie (now Fritz Haber Institute of the Max Planck Society) in Berlin-Dahlem celebrated its 100th anniversary. Its history had been described before in a monograph[1] as well as in an article by B. Friedrich et al.[2] The present Essay is a more personal account as presented as a lecture at the centenary celebration which is focused on some of the contributions from the institute to the understanding of the interactions of molecules with solid surfaces.

1. The Early Years

A number of years ago my predecessor Heinz Gerischer entered my room with some music in his hands: "I found this in my office, perhaps you may have some use for it." It was a "Rondo for two pianos" composed by H. Freundlich in 1916. Who has two pianos available? That is why most probably the first performance of this piece took place only now just before the century celebration event (for a video of the performance, see the Supporting Information). Herbert Freundlich (Figure 1) had at first intended to become a musician, but then instead studied chemistry with Wilhelm Ostwald in Leipzig. His work was concerned with adsorption from solution, that is, the interaction of molecules from a solution with the surface of a solid, and Freundlich established a relationship between the adsorbed amount and the concentration of the species in the solution,—the famous Freundlich isotherm.[3] At this time Ostwald did not yet believe in the existence of atoms, and therefore Freundlich proposed an interpretation in terms of a continuum model thereafter the adsorbate modifies the surface tension of the solid and thus causes interaction. A few years later, however, the existence of atoms was unequivocally demonstrated by Max von Laue (Figure 2) through the interference of X-rays.[4] In his later years von Laue was to become the director of the institute. In 1916 Freundlich joined our institute where soon later he became deputy director and one of the founders of colloid chemistry.

Figure 1. Herbert Freundlich (1880–1941; time at the institute: 1916–1933).

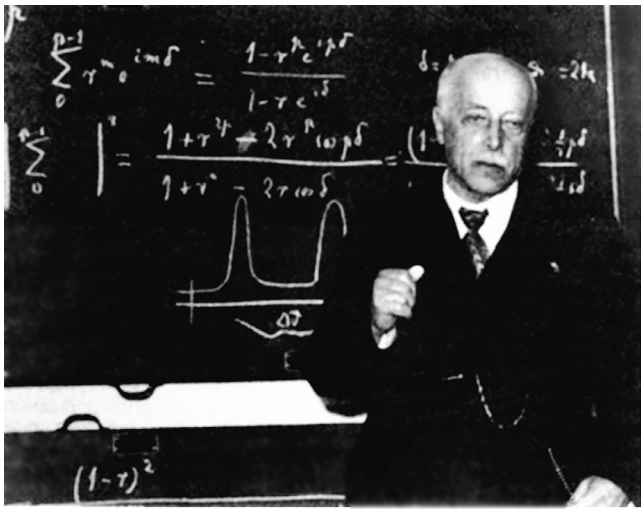

Figure 2. Max von Laue (1879–1960; time at the institute: 1951–1960).

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The "Rondo for two pianos" composed by H. Freundlich and the "Anniversary March" composed by T. Hennig can be heard in the Supporting Information, which is available on the WWW under http://dx.doi.org/10.1002/anie.201205401.

Figure 3. Fritz Haber (1868–1934; time at the institute: 1911–1933).

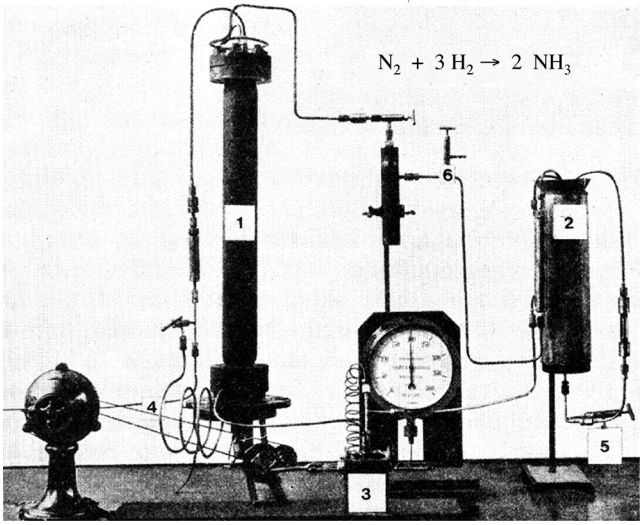


Figure 4. Apparatus for the catalytic formation of ammonia from nitrogen and hydrogen by Haber and Le Rossignol (1909).[5]

The first director was Fritz Haber (Figure 3) whose most important scientific achievement had been the realization of the catalytic transformation of nitrogen and hydrogen into ammonia. His laboratory apparatus developed while he was still in Karlsruhe (Figure 4)[5] was transformed by Carl Bosch into a large-scale industrial production, hence the name Haber–Bosch process. The first plant started operation as early as 1913, but it took nearly seven decades to elucidate the mechanism underlying this reaction.[6] It turned out that the decisive step consists in splitting the bond between the two atoms in the N_2 moleculeby interaction with the surface of the catalyst. In contrast to Freundlich, Haber was convinced that adsorption is not just an effect of variation of the surface tension but that such strong energetic changes were the consequence of the operation of chemical forces. This view is usually attributed to Langmuir, but was indeed already expressed in 1914 by Haber by referring to the discovery of von Laue.[7] But what is the origin of these chemical forces?

2. The Advent of Quantum Mechanics

The theory of quantum mechanics was developed in the mid-1920s by Heisenberg, Schrödinger, and others. The citation of the 1932 Nobel Prize in Physics for Werner Heisenberg reads "for the creation of quantum mechanics, the application of which has, *inter alia*, led to the discovery of the allotropic forms of hydrogen." Heisenberg's theory led to the conclusion that the nucleus of the H atom (that is, the proton) carries a certain angular momentum (spin) and that in the H_2 molecule these two nuclear spins are either antiparallel (para) or parallel (ortho) to each other (Figure 5). The total nuclear

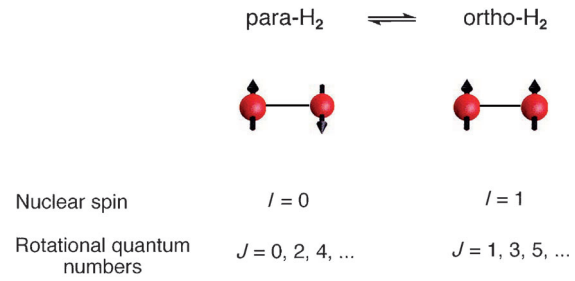


Figure 5. Para- and ortho-hydrogen molecules.

spin of the molecule is then 0 or 1, respectively, and the symmetry of the whole wavefunction requires that allowed rotations of the molecule are associated with even and odd quantum numbers J in the case of para- and ortho-H_2, respectively. As a consequence, a small difference in total energy and hence also in specific heat exists between these two allotropic modifications and the equilibrium concentrations vary with temperature. Several previous attempts to verify experimentally this effect through measurements of the specific heat had failed, mainly because the transition between these two states is quantum-mechanically forbidden and hence very slow. Two young researchers of the institute, K. F. Bonhoeffer and P. Harteck (Figure 6), were, however, successful. Instead of the specific heat they measured the heat conductance, and to accelerate the transition they used a catalyst, that is, the interaction of the hydrogen molecules with a solid surface.[8] In this way they were, for example, able to produce near 100% pure para-H_2 and to measure its physical properties, whereby the predictions of Heisenberg's theory could be experimentally verified.

Quantum mechanics provided also the tools for the theoretical description of the formation of chemical bonds between atoms and eventually even to follow the progress of a chemical reaction. Such an attempt was made by M. Polanyi and a young American postdoc, H. Eyring (Figure 7). (Eyring later developed the transition-state theory of absolute reaction rates which has since then become the most powerful concept for the description of chemical transformations.) In their work they used the simplest type of bimolecular chemical reaction, namely $H + H_2 \rightarrow H_2 + H$, and evaluated the variation of the potential energy as a function of the two nuclear distances (Figure 8).[9] This contour plot illustrates how the potential energy varies when the H atom approaches

Über Para- und Orthowasserstoff.

Von

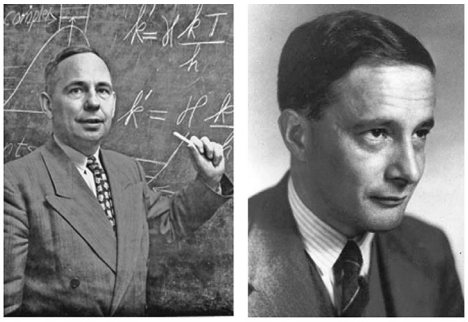
K. F. Bonhoeffer und P. Harteck.

(Aus dem Kaiser Wilhelm-Institut für physikalische Chemie und Elektrochemie, Berlin-Dahlem.)

(Mit 5 Figuren im Text.)

(Eingegangen am 22. 5. 29.)

Figure 6. K. F. Bonhoeffer (left; 1899–1957; time at the institute: 1923–1930, 1948–1949) and P. Harteck (right; 1902–1985; time at the institute: 1928–1933; time as an external scientific member of the institute: 1956–1985) and the title page of their seminal paper on para- and ortho-hydrogen.[8]



Über einfache Gasreaktionen.

Von

H. Eyring und M. Polanyi.

(Aus dem Kaiser Wilhelm-Institut für physikalische Chemie und Elektrochemie, Berlin-Dahlem.)

(Mit 17 Figuren im Text.)

(Eingegangen am 7. 2. 31.)

Figure 7. H. Eyring (left; 1901–1981; time at the institute: 1929–1930) and M. Polanyi (right; 1891–1976; time at the institute: 1923–1933) and the title page of their seminal paper "Über einfache Gasreaktionen"[9] [About Simple Gas Reactions].

the H_2 molecule. After overcoming an energy barrier (that is, the activation energy) the H_2 molecule combines with the incoming H atom whereby simultaneously its second atom is released. In this way the partitioning of energy between the different degrees of freedom during the course of a chemical reaction could be described. This work triggered the whole field of reaction dynamics, and in memory of this seminal paper a conference was held in the institute in 1981.[10] Among the participants of this meeting were four future Nobel Prize winners (Figure 9), namely D. Hershbach from Harvard, Y. Lee from Berkeley, J. Polanyi (the son of M. Polanyi) from Toronto, and the author who was then still in Munich.

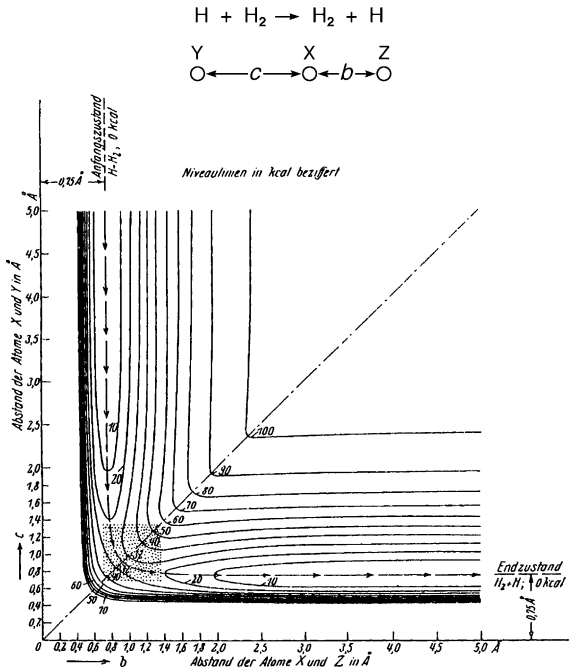


Figure 8. Potential-energy surface for the collinear reaction $H + H_2 \rightarrow H_2 + H$ as a function of the distances [Abstand] *b* and *c* from Ref. [9].

3. Molecules at Surfaces: Structure and Dynamics

Back to 1931: the existence of atoms was now without doubt firmly established, but so far nobody had yet 'seen' an atom. Their size (and mutual separation) was far below the wavelength of visible light and therefore no optical microscopy could provide the necessary spatial resolution. The solution of this problem came nearer through the invention of the electron microscope[11] by Ernst Ruska (Figure 10). With modern instruments indeed atomic resolution can be routinely achieved, and this technique is now widely applied to study the structure of catalysts. As an example, Figure 11 shows an image from a small Ag catalyst particle as investigated in the department directed by R. Schlögl.[12] It was, however, still a long way to reach this goal: Even in 1954 Ruska stated at a conference only that "the theoretical limit of transmission electron microscopy is such as to permit proving the existence of atoms." At that time another development in the institute had, however, already almost enabled the visualization of atoms. In 1951 a paper was published by E. W. Müller (Figure 12) in which the principle of field ion microscopy was presented.[13] (Soon later Müller left for a faculty position in the USA, but later became an external scientific member of the institute.) With this technique usually noble-gas atoms are ionized by the high electric field strength in front of a sharp metallic tip, and the ions are then accelerated onto a fluorescent screen where their points of impact mark the location of ionization.

Figure 9. Group photo of the conference "50 Years Dynamics of Chemical Reactions" in Berlin (October 12–15, 1981). The four future Nobel Laureates are indicated by the red stars.

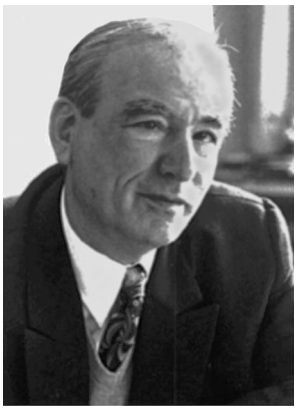


Figure 10. Ernst Ruska (1906–1988; time at the institute: 1949–1988).

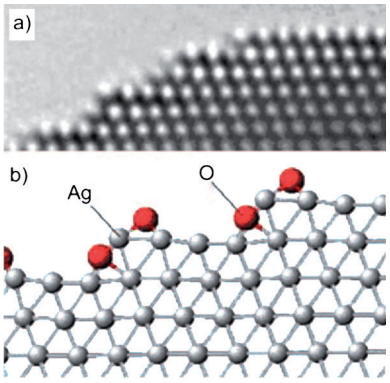


Figure 11. a) Transmission electron microscope (TEM) image from a small Ag catalyst particle with atomic resolution.[12] b) Schematic presentation of the structure.

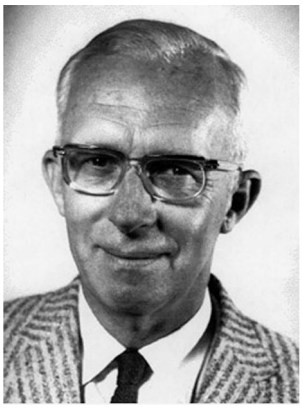


Figure 12. Erwin W. Müller (1911–1977; time at the institute: 1947–1951; time as an external scientific member of the institute: 1957–1977).

Thereby an image with atomic resolution is created (Figure 13). In this way in 1955 atoms at a surface could be made visible for the first time. Later this technique was widely used by J. H. Block (Figure 14) at the institute for studies on the progress of surface reactions.

Nowadays, however, scanning probe techniques instead are widely used to study the properties of solid surfaces with atomic resolution. As a recent example, Figure 15 shows an image of a vitreous SiO_2 surface as investigated by H. J. Freund and his co-workers[14] by means of scanning tunneling microscopy (STM). There ordered (right side) and amorphous (left side) areas become visible.

STM can also be used to image the result of the interaction of molecules with surfaces. Figure 16 shows a Pt-

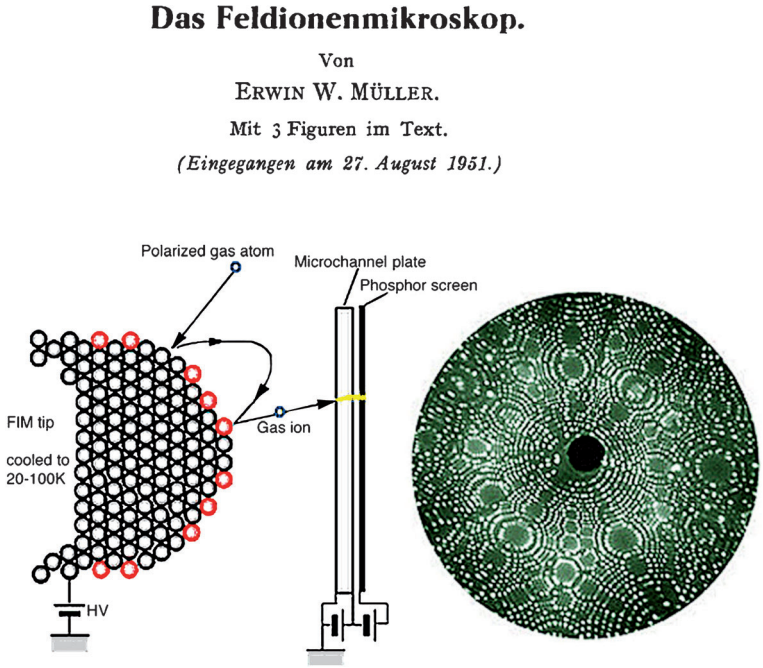


Figure 13. Title page of the publication of E. W. Müller on the field ion microscope[13] and its principle.

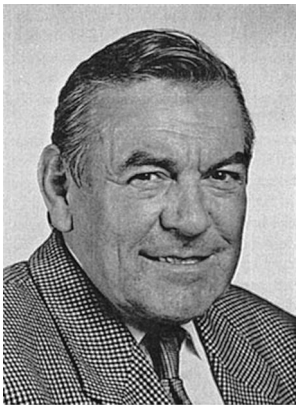


Figure 14. Jochen H. Block (1929–1995; time at the institute: 1966–1995).

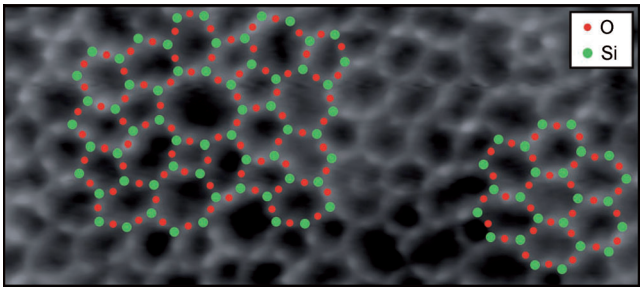


Figure 15. STM image from a vitreous SiO_2 surface with atomic resolution.[14]

(111) surface after exposure of a small amount of O_2 molecules at 165 K.[15] Apart from the Pt atoms of the substrate, pairs of adsorbed O atoms resulting from the dissociative adsorption are discernible. At this low temperature the adsorbed atoms are practically immobile. At elevated temperatures, they start to jump to neighboring sites. Their residence time at a certain site is however affected by neighboring adsorbates. These interactions may be repulsive as well as attractive and are responsible for the formation of configurations with long-range order which may be analyzed with the tools of surface crystallography.[16] As an example Figure 17 shows the ordered structures formed by adsorbed O and/or CO species on a Rh(111) surface.[17] While the CO molecules couple to the surface through the C atoms and occupy both 'on top' and bridge sites with a tendency for formation of a densely packed phase, the O atoms form a relatively open mesh and are located in threefold coordinated sites. This has consequences for the mechanism of catalytic CO_2 formation through reaction of CO with O: While CO molecules can still be adsorbed within

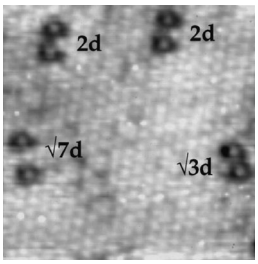


Figure 16. STM image from a Pt(111) surface (5.3 nm × 5.5 nm) after dissociative adsorption of a small amount of O_2 (2 L).[15]

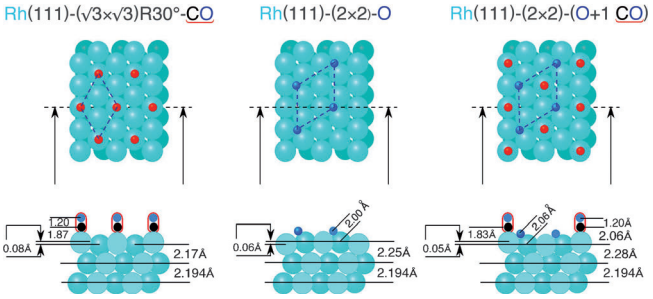


Figure 17. Ordered structures formed by adsorbed CO and/or O on a Rh(111) surface as determined by low-energy-electron diffraction (LEED).[17]

the open structure formed by the O atoms, dissociation of incoming O_2 molecules is inhibited if the CO coverage exceeds a critical value. Under continuous-flow conditions, in this case a steady-state rate of product formation can hence only be achieved if the temperature is high enough to enable continuous desorption of part of the adsorbed CO molecules.

In recent years theory made also enormous progress, and energy hypersurfaces as evaluated originally by Eyring and Polanyi[9] in a very crude approximate manner can now be calculated with sufficient accuracy by means of density functional theory (DFT). As an example, Figure 18 shows

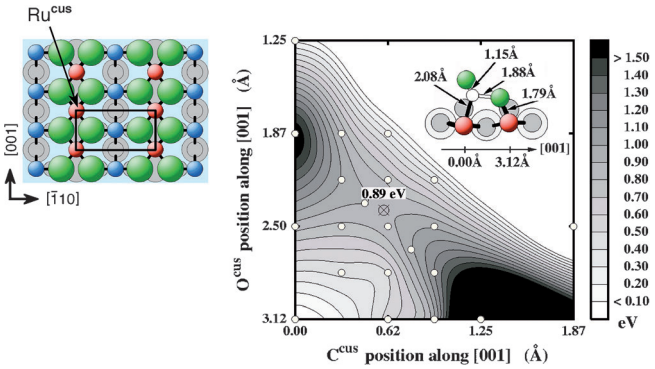


Figure 18. Theoretical potential-energy surface for O and CO co-adsorbed on a RuO_2(110) surface on coordinatively unsaturated surface atoms (cus) along the [001] direction.[18]

the potential surface for O and CO interacting with each other on a RuO_2(110) surface as evaluated by M. Scheffler and K. Reuter from the theory department.[18] Theory can go even one step further: With information about the elementary processes also modeling of the rate r of catalytic reactions becomes accessible. This task was solved with the steady-state kinetics of CO oxidation on a RuO_2(110) surface.[19] This rate depends on three external parameters: The temperature T and the partial pressures of O_2 and CO, p_{O_2} and p_{CO}, respectively. If the former two variables are kept fixed, the resulting variation of r with p_{CO} as calculated by theory[19] is shown in Figure 19 together with the corresponding experimental data.[20] These are absolute numbers in terms of turnover frequencies, that is, reactive events per surface site and second. The agreement is not perfect, but remarkably good. This result demonstrates that it is now in principle possible to rationalize the rate of a catalytic reaction on the basis of first principles.

Rates of chemical reactions are usually described in the framework of Eyring's transition-state theory of absolute-rate processes. This theory assumes that all elementary steps are in thermal equilibrium (except passage along the transition state) which implies that the transfer of energy between the different degrees of freedom of the system is faster than the chemical transformation in which the system passes the transition state. With a solid surface these degrees of freedom are the vibrations of the atoms (phonons) and excitation of the valence electrons. These processes may be studied experimentally by the use of ultrafast (that is, femtosecond) laser pulses. The light is absorbed by the valence electrons of the atoms near the surface and the excitation is then transferred to the other degrees of freedom. In the example represented in Figure 20[21] for CO and O coadsorbed on a Ru(0001) surface an infrared pulse of 60 fs duration is absorbed by the metal electrons which in turn excite the M–O bond which then can react with a neighboring adsorbed CO to CO_2 before CO may desorb as a consequence of the excitation of phonons. In this way indeed the time scale on which surface reactions proceed may be probed. Investigations of this type on the ultrafast dynamics of surface processes form one of the main topics of research of M. Wolf who is now director of the department of Physical Chemistry.

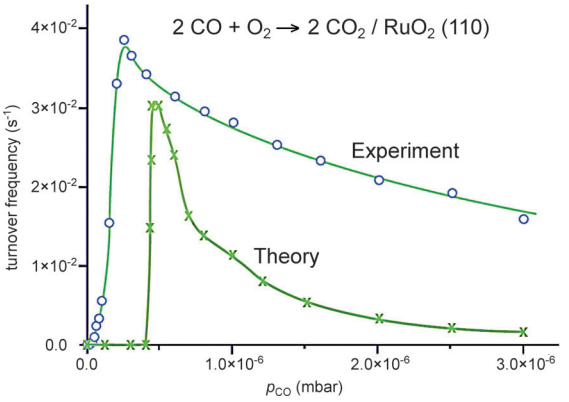


Figure 19. Steady-state rate of CO_2 formation on a RuO_2(110) surface as a function of CO partial pressure at fixed O_2 partial pressure (10^{-7} mbar) and temperature (350 K). Theory[19] and experiment.[20]

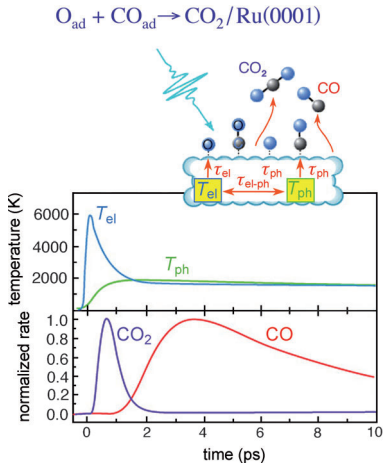
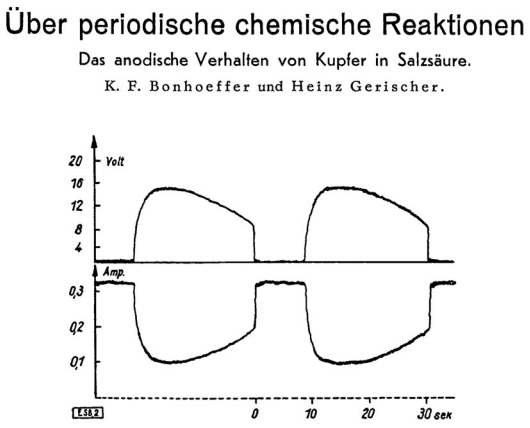


Figure 20. Evolution, as a function of time, of the electron and phonon temperatures, T_{el} and T_{ph}, respectively, and of the release of CO_2 and CO into the gas phase for CO + O co-adsorbed on a Ru(0001) surface following excitation with a femtosecond laser pulse.[21]

4. Complex Reactions and Nonlinear Dynamics

In 1948 K. F. Bonhoeffer returned to the institute for a short period. He was accompanied by his assistant H. Gerischer with whom he had worked on periodic reactions in electrochemical systems. As shown in Figure 21 the electrochemical dissolution of copper exhibits periodic variation with time of both the voltage and the current.[22] Phenomena of this type had already been reported in the 19th century and are observed in different areas. Gerischer (Figure 22) became director of the institute in 1969 and introduced electrochemistry as an important new field. Even one of his last research papers was concerned with periodic electrochemical reactions.[23] In the same year he published also an extended Review article on the use of light as a probe for electrochemical interface reactions on the occasion of the centenary of *Angewandte Chemie*.[24]


Über periodische chemische Reaktionen

Das anodische Verhalten von Kupfer in Salzsäure.

K. F. Bonhoeffer und Heinz Gerischer.

Figure 21. Title page of the publication of Bonhoeffer and Gerischer on temporal oscillations in the electrochemical dissolution of copper and graph from that paper.[22]

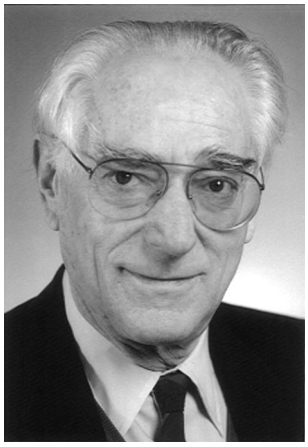


Figure 22. Heinz Gerischer (1919–1994; time at the institute: 1948–1949, 1969–1994).

Even with much simpler surface reactions, such as CO oxidation on flat single-crystal surfaces, periodic oscillations of the reaction rate under steady-state flow conditions may be observed. As an example, Figure 23 shows the variation of the rate of CO_2 formation R_{CO_2} at a Pt(110) surface with time

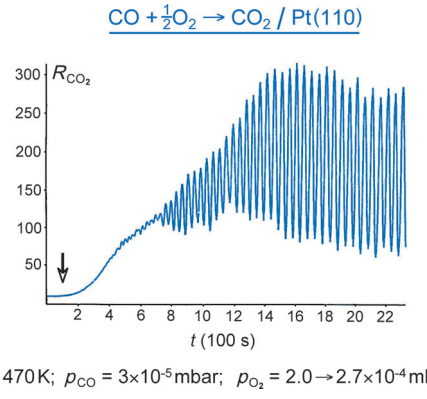


Figure 23. Temporal oscillations in the catalytic formation of CO_2 at a Pt(110) surface.[25]

when at the point marked by an arrow the partial pressure of O_2 is stepwise altered to another value:[25] R_{CO_2} slowly increases and then starts to oscillate with growing amplitude until a steady state is reached. If a macroscopic surface exhibits such an effect, the concentrations of the adsorbed species will necessarily also vary with time and will be coupled to each other in space. As a consequence, the formation of spatio-temporal concentration patterns is expected with length scales determined by the interplay of reaction and diffusion.

Imaging of these concentration patterns could be achieved by the development of a special photoemission electron microscope (PEEM) in a joint effort between members of three departments of the institute.[26] Characteristic patterns like the spirals developing during the CO oxidation on a Pt(110) surface, as shown in Figure 24, can be observed in real time.[27] In this case, dark areas are predominantly covered by adsorbed O atoms (where also the reaction occurs with co-adsorbed CO), while brighter areas covered by adsorbed CO are less reactive. A theoretical description may be achieved by solution of the associated partial differential equations in the framework of nonlinear dynamics, and extended studies of complex chemical systems of this type have been performed during recent years.

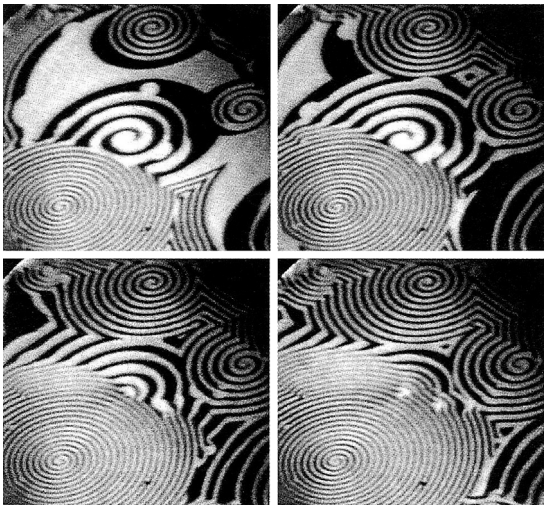


Figure 24. PEEM images of a Pt(110) surface during catalytic CO oxidation under steady-state conditions.[27] Diameter: 500 μm, $p_{O_2} = 4\times10^{-4}$ mbar, $p_{CO} = 4.3\times10^{-5}$ mbar, $T = 448$ K.

5. The Circle Closes

This survey started with Freundlich, who studied adsorption more or less without any clear underlying concepts, and his music. In contrast Fritz Haber proposed an explanation for the fact that a surface may affect even strong chemical bonds. His synthesis of ammonia is based on the ability of the surface of a catalyst to break even the very strong bond, with 10 eV energy between the two atoms, in a N_2 molecule. The weakest bond in a diatomic molecule, on the other hand, is that between two He atoms with a strength of the order of only 10^{-7} eV. We may now turn the question around: Is there

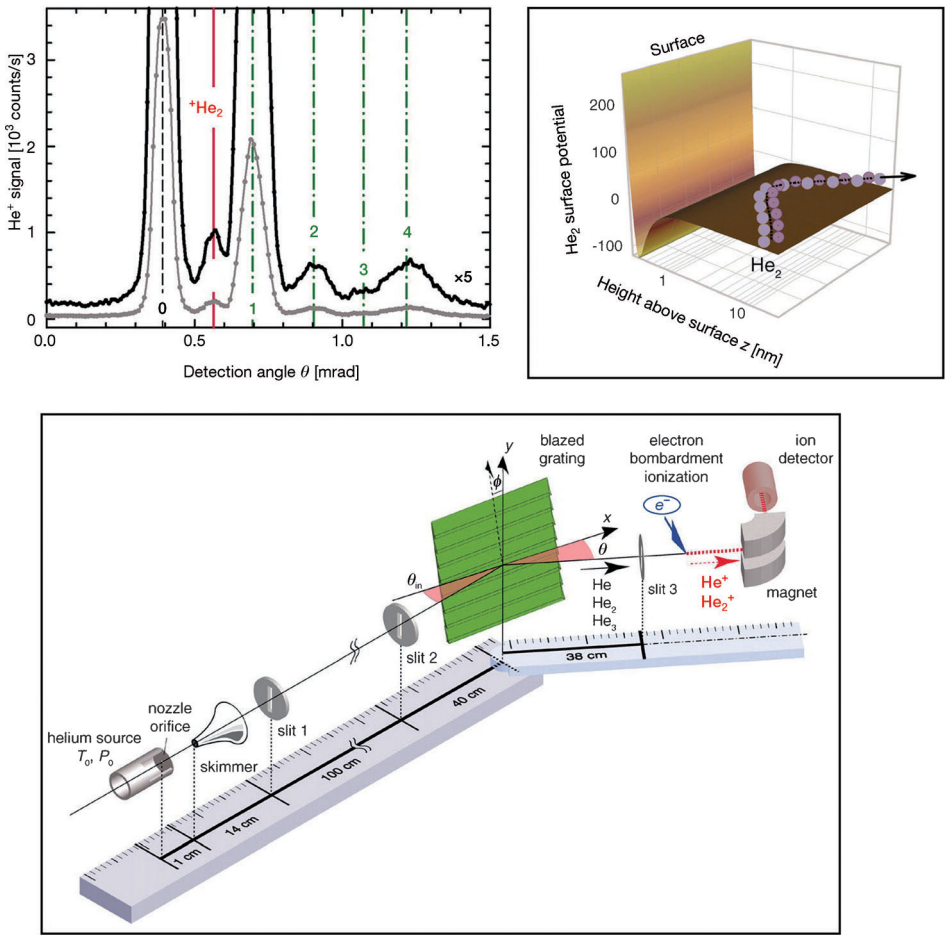


Figure 25. Angular distribution of helium scattered at a periodic grating demonstrating the partial survival of He_2 species.[31]

a finite probability that He_2 survives the interaction with a surface?

First of all, the temperature of such a species has to be extremely low. This may be achieved by expansion of the gas in a molecular beam. This technique had already been pioneered in the institute in the early 1920s.[28] By adiabatic expansion in this way the internal temperature of He_2 may be lowered down to about 1 mK. Then, how to detect that indeed a He_2 species has been reflected from a surface? Now quantum mechanics comes again into play. Such a molecular beam with a narrow velocity distribution also has the properties of a wave which can undergo diffraction at a periodic grating as first shown by O. Stern and I. Estermann[29] and, for example, discussed in a monograph by M. von Laue.[30] According to de Broglie, the wavelength depends on the mass and velocity of a particle, and if the angular distribution of diffracted particles coming off the surface at known velocity is recorded, their mass can be derived. Such an experiment has recently been performed in G. Meijer's department,[31] and the result reproduced in Figure 25 shows indeed that a small amount of the He_2 species does survive interaction with the surface. This is possible only again because of a quantum mechanical effect. The wavefunction of He_2 is so extended that reflection already partly takes place several nanometers above the surface, before the interaction potential comes into operation.

This Essay was intended to show that studies on the interaction of molecules with surfaces are continuing to be fascinating research topics in the institute and have been for more than one hundred years. This session of the centenary celebration started with a Rondo by H. Freundlich and ended with the first performance of a centenary march composed by T. Hennig on the theme f.h.a.b.e (Figure 26 and the Supporting Information).

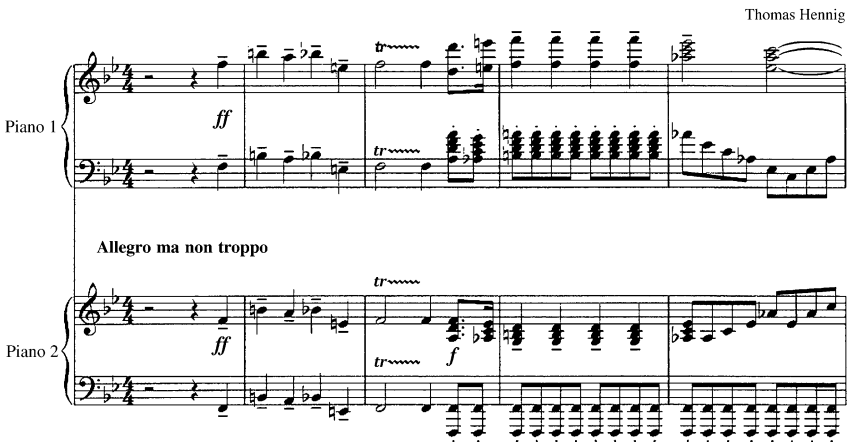


Figure 26. Score of the beginning of the anniversary march composed by T. Hennig on the theme f.h.a.b.e. (For a video of the performance, see the Supporting Information.)

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