

**Molecules at surfaces:
100 years of physical chemistry in Berlin-Dahlem**

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On 28 October 2011 the former Kaiser-Wilhelm Institut für Physikalische Chemie und Elektrochemie (now Fritz Haber Institut der Max-Planck-Gesellschaft) 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 focussed on some of the contributions from the institute to the understanding of the interactions of molecules with solid surfaces.

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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. 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, i.e. the interaction of molecules from a solution with the surface of the solid, and Freundlich established a relation 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 whereafter the adsorbate modifies the surface tension of the solid and thus causing 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 Laue was then 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.

The first director was then 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 was starting operation already in 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 molecule by 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 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-twenties 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 had concluded that the nucleus of the H atom (= the proton) carries a certain angular momentum (spin) and that in the H₂ molecule these two nuclear spins are either antiparallel (para) or parallel (ortho) to each other (Figure 5). The total nuclear spin of the molecule is then 0 or 1, and the symmetry of the whole wave function requires that allowed rotations of the molecule are associated with even and odd quantum numbers J in the case of para- and ortho-H₂, 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 in order to accelerate the transition they used a catalyst, i.e. 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-H₂ and to measure its physical properties, whereby the predictions of Heisenberg's theory could be experimentally verified.

Quantum mechanics provided now also the tools for 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). (The latter developed later the theory of absolute reaction rates which has since then become the most powerful concept for description of chemical transformations). In their work they used the simplest type of bimolecular chemical reaction, namely $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$, 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 varies when the H atom approaches the H₂ molecule. After overcoming an energy barrier (= the activation energy) the latter 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 (Figure 9) were four future Nobel Prize winners, 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.

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 *“the theoretical limit of transmission electron microscopy is such as to permit proving the existence of atoms.”* At this time another development in the institute had, however, already 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. 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. 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 SiO₂ surface as investigated by H. J. Freund and his coworkers [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(111) surface after exposure of a small concentration of O₂ 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 the presence of 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 analysed with the tools of surface crystallography. As an example Figure 17 shows the ordered structures formed by adsorbed O and 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 the 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 CO₂ formation through recombination of CO+O: While CO molecules can still be adsorbed within the open structure formed by the O atoms, dissociation of incoming O₂ molecules is, on the other hand, 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 the potential surface for O+CO interacting with each other on a RuO₂ (110) surface as evaluated by M. Scheffler and his coworkers 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 reaction becomes accessible. This task was solved with the steady-state kinetics of CO oxidation on a RuO₂(110) surface [19]. This rate depends on 3 external parameters: The temperature T and the partial pressures of O₂ and CO, p_{O_2} and p_{CO} , respectively. If the former two 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, i.e. 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 theory of absolute rate processes. This theory assumes that all elementary steps are in thermal equilibrium 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 (=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 by Figure 20 [21] for CO+O adsorbed on a Ru(0001) surface an infrared pulse of 60 fs duration is absorbed by the metal electrons which in turn excite the metal-O bond which then can react with a neighboring adsorbed CO to CO₂ 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 which is now director of the department of Physical Chemistry.

4. Complex reactions and nonlinear dynamics

In 1948 K. F. Bonhoeffer returned back 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 at the occasion of the centenary of *Angewandte Chemie* [24].

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 CO₂ formation R_{CO_2} at a Pt(110) surface with time when at the point marked by an arrow the partial pressure of O₂ 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 during the CO oxidation on a Pt(110) surface as shown in Figure 24 can be observed in real time [27]. Here, dark areas are predominantly covered by adsorbed O atoms (where also the reaction occurs with coadsorbed CO), while brighter areas covered by adsorbed CO are less reactive. 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.

5. The circle closes

This survey started with Freundlich and his music who studied adsorption more or less without any clear underlying concepts. By 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 even to break 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 a finite probability that a He_2 dimer 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 into a molecular beam. This technique has been pioneered in the institute already in the early twenties [28]. By adiabatic expansion in this way the internal temperature of He_2 dimer 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 has also the properties of a wave which can undergo diffraction at a periodic grating as first shown by O. Stern et al. [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 part of the He₂ species is surviving interaction with a surface. This is possible only again because of a quantum mechanical effect. The wave function of He₂ is so extended that reflection partly takes place already several nanometers above the surface before the interaction potential comes into operation.

This contribution was intended to show that studies on the interaction of molecules with surfaces are continuing to be fascinating research topics in the institute since over more than 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 Th. Hennig on the theme f..h..a..b..e (Figure 26).

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