Current Era

Ushering in the Institute's next hundred years

We define the current era by the present scientific structure of the institute, the arrival of its five incumbent Department Directors and their collective leadership of the Institute. As with any study of recent science, a dearth of archival sources limits our abilities to assess the present institute historically but direct access to the active researchers allows us considerable insight into their current activities. Therefore, we will focus on recent research endeavors at the five departments, offering a description, in lay language, of one or two projects representative of each department’s thrust, but we will also point out, whenever feasible, the connections between current research and that of previous eras, which in some cases extend back to the very beginnings of the Institute.

The five Departments and their directors, ordered chronologically by their year of appointment, are:

- Theory, headed, since 1988, by Matthias Scheffler
- Inorganic Chemistry, headed, since 1994, by Robert Schögl
- Chemical Physics, headed, since 1996, by Hans-Joachim Freund
- Molecular Physics, headed, since 2002, by Gerard Meijer
- Physical Chemistry, headed, since 2008, by Martin Wolf

Each of the following five sections of this chapter covers one of the departments.

It should be kept in mind, however, that these departments, though the heart of the Institute, do not encompass all of its activities. The Institute continues to be a crucible in which numerous advanced students refine their abilities. Currently, there are approximately 20 pre-doctoral and 100 doctoral students at the Institute working toward their degrees and about another 100 post-doctoral fellows are receiving further tutelage before taking their places in academic or industrial research. An international Max Planck Research School offers a range of lecture courses and workshops that are designed to augment the students’ training in topics pursued at the Institute. Visiting scholars greatly contribute to scientific life at the Institute, many of them supported by prestigious awards from the Alexander von Humboldt Foundation; the Institute hosts roughly 20 von Humboldt Fellows and 25 Awardees annually.

In addition to the scientific Departments, the Institute also comprises specialized workshops (electronic, mechanical and woodwork) as well as an information
technology group and library staff that provide technical support without which the scientific Departments could not function effectively. Similarly, the Joint Network Center (Gemeinsames Netzwerk Zentrum, GNZ) provides the necessary infrastructure to meet the Institute’s ever-growing computing needs. A separate, central administration handles fiscal and personnel affairs for the Institute as a whole, i.e. both the scientific and technical groups.

The present Institute operates on a flexible budget that allows it to draw funds from the coffers of the Max Planck Society as needed; over the period 2000–2010, these amounted to an average of about 20 million Euros per annum. This long-term, project-independent support has proved the key to the Institute’s success in endeavors which would hardly have been feasible on the basis of shorter-term, purpose-directed funding. However, more specialized grants from sources such as the Deutsche Forschungsgemeinschaft, the Federal Ministry of Education and Research and the European Commission, as well as industrial partners, lend the Institute even greater flexibility in its research projects. The Max Planck Society also provides the Institute with funds for special projects through peer-reviewed “project actions.” Most recently such funds have supported the construction of an infrared free electron laser at the Institute, slated to begin hosting researchers roughly on the date of the Institute’s centennial. This facility will provide a new nexus for many of the Institute’s current lines of experimental research.
Theory Department

Since 1987, computational physics and chemistry have been pursued at the Institute by Matthias Scheffler and his collaborators. Their principal aim has been to develop a predictive theory of materials, one capable of aiding in the design of new and the improvement of existing materials, in particular those materials used in semiconductor physics and in heterogeneous catalysis on metal and oxide surfaces. To be relevant to material design the theory needs to allow researchers to model materials subject to real-life environments, e.g. appropriate gas mixtures under realistic pressures and temperatures. Such a predictive theory requires a combination of an accurate description of atomic-scale processes with a treatment of their statistical interplay at meso- and macroscopic scales, which controls phenomena such as steady-state crystal growth and heterogeneous catalysis. This, in turn, requires attention to the behavior of matter on diverse scales, both spatial (from fractions of a nanometer to a millimeter) and temporal (from femtoseconds to hours), see Fig. 6.2. Among other results and insights, the work of the Theory Department has demonstrated that a “one-structure, one-site, one-mechanism” description is, in general, inadequate for understanding the function of materials at authentic ambient conditions.

The treatment of the atomic-scale processes is based on ab initio electronic structure theories suitable for treating both valence and dispersion forces. This entails tackling the many-body, i.e. many-electron problem, which requires the use of approximation techniques. The method of choice for Scheffler and coworkers is the density functional theory (DFT), whose development was initiated by Walter Kohn and coworkers circa 1964–65. Greatly enhanced by recent theoretical and

Fig. 6.2. Temporal and spatial scales involved in materials science applications, such as in heterogeneous catalysis. The elementary processes of bond breaking and bond making between atoms and molecules are described by the electronic-structure theory, from which the rest unfolds. The function of a catalyst is determined by an interplay among many molecular processes and only develops over meso- and macroscopic lengths and times.
computational advances, density-functional theory can now provide ‘chemical accuracy’ for sizable systems that contain hundreds of gaseous or condensed-phase atoms. Developing computational methods and computer codes that enable this new level of accuracy is among the core activities of the Theory Department.

On the next level of the hierarchy laid out in Fig. 6.2, electronic structure theory is linked to molecular-dynamics simulations that include energy dissipation and non-adiabaticity. A reduction of the computational cost of the electronic structure calculation per time step makes simulations over a longer time scale feasible without compromising accuracy. Simulations that extend over tens of picoseconds could thus be implemented for rapid processes in gases and solids, at interfaces and in solutions. An alternative approach, commonly used in molecular dynamics simulations, is based on empirical force fields. This approach often overlooks features that are critical to chemical reactions occurring in realistic probes and devices; although, “ab initio-on-the-fly” interatomic forces offer one possible remedy. Even though massively parallel computers alleviate some of the length scale problems and many of the accuracy issues encountered in this work, they are not necessarily beneficial in tackling the associated time scale problems, since time integration is sequential. Often a more effective way of dealing with time scale challenges is to employ long-term dynamics methods founded on the master equation of statistical mechanics. Numerical implementation of these methods, when linked with density-functional theory, is referred to as ab initio kinetic Monte Carlo (kMC), and is based on a set of rate constants calculated atomistically at the molecular dynamics level and tested for completeness via extensive molecular dynamics runs. As a result, the ab initio kinetic Monte Carlo approach has reached the point where processes can be tackled over time scales ranging from seconds to hours. However, beyond the scale of molecular dynamics and kinetic Monte Carlo the links to the mechanics of continua and to the rate equations become tenuous. Establishing robust links to these higher levels is a major challenge.

One concrete example of the research methods just described, is the multi-scale modeling of CO oxidation on the Ru/RuO₂ catalyst at realistic ambient conditions.
and the resulting description of the steady state of the catalytic conversion process. CO oxidation is a strongly exothermal reaction. Yet, in the gas phase, the CO + \( \frac{1}{2} \)O\(_2\) \( \rightleftharpoons \) CO\(_2\) reaction is spin-forbidden, since the reactants have a total spin \( S = 1 \) (due to the triplet ground state of O\(_2\)) while the reaction product (CO\(_2\)) has zero spin, \( S = 0 \). However, for dissociated O\(_2\), the individually adsorbed O atoms are in a spin zero state and so the reaction becomes spin-allowed. The reaction rate depends on an energy barrier determined by the properties of the adsorbent. But, obviously the adsorbed CO and O species must also occupy nearby positions. Thus, in order to predict the turn-over frequency, i.e. the number of CO\(_2\) molecules formed per unit area of the catalyst’s surface per unit time, one needs to take an appropriate statistical average over space and time.

Predictive modeling of heterogeneous catalysis must be able to represent the steady state of operation. Here the statistical mechanics of the various mutually interfering atomistic processes reveals the significance of instabilities and fluctuations; a catalyst is a “live” system, subject to incessant changes even in its steady state. As it turns out, these instabilities and fluctuations are crucial for the self-healing of locally poisoned areas of the catalyst and, hence, for its long-term operational stability and are particularly prominent at conditions of steady-state, high catalytic performance.

Catalysis on the Ru metal occurs at ambient conditions (pressure and temperature) where the bulk oxide, RuO\(_2\), is stable. However, this does not reveal much about the composition and structure of the surface. Under ultra-high vacuum conditions, the surface composition and structure of RuO\(_2\) has been predicted by the density-functional theory, Fig. 6.3. Here the surface is nearly perfect, with

![Calculated and measured CO\(_2\) turn-over rates as a function of CO pressure (top left); a snapshot of the surface occupancy under the conditions of optimal catalytic performance in the course of a kMC simulation (right); geometry of a transition state of the CO oxidation reaction (bottom left).](image-url)
almost no vacancies or other defects in the O-bridge rows and no adatoms at the coordinatively unsaturated sites (cus), Ru$_{\text{cus}}$. This prediction is in excellent agreement with scanning-tunneling microscopy results.

Moving pictures of the detailed atomic structure together with a “sensitivity analysis” reveal the importance of kinetics for understanding the conditions for high-performance catalysis: The dissociative adsorption of O$_2$ and the non-dissociative adsorption of CO compete for adsorption sites on the surface, specifically for the bridge and the coordinatively unsaturated sites, see Fig. 6.4. Here an important correlation is noted, owing to the fact that O$_2$ requires two nearby sites while CO needs just one. Hence after the catalytic reaction, O$_{\text{ad}}$ + CO$_{\text{ad}}$ $\rightarrow$ CO$_2$, has taken place, two empty sites are left behind. These can be occupied by two O adatoms (from the dissociated O$_2$) or by CO. However, as soon as one CO molecule has been adsorbed, the remaining empty site is no longer conducive to O$_2$ dissociation and so can only accommodate another CO molecule. As a consequence, kinetically-controlled, non-random structures form that disable some potentially active reaction pathways. In fact, the whole surface may become excessively CO-rich and thus catalytically inactive. Only if the pressure is chosen properly can the adsorbed CO desorb again at a rate sufficient to “heal” such “poisoned” regions. Alternatively, the surface may become O-rich, in which case it can only be healed if some desorption of oxygen takes place and/or chemical reactions erode away these regions from the edges. The calculated turn-over frequency of CO to CO$_2$ conversion as a function of O$_2$ and CO pressures identifies conditions where the steady state changes from an “O-poisoned” to a “CO poisoned” surface, see Fig. 6.5. The optimum, high performance conditions are found in between. In the active regime, the surface proceeds locally from an O-rich or a CO-rich to a catalytically highly-active composition and back to an inactive one. This is a clear-cut example of the sort of fluctuation and structural instability, referred to earlier in general terms, that is vital for sustained catalytic performance.

![Fig. 6.5. Map of calculated turn-over frequencies (TOFs) at a temperature of 600 K for the oxidation of CO on the Ru/Ru$_2$ catalyst. The plot is based on 400 kinetic Monte Carlo simulations for different CO and O$_2$ pressures.](image-url)
The Director of the Theory Department is Matthias Scheffler, born in 1951 in Berlin. He earned his PhD in Physics from the Technische Universität Berlin in 1978 with a thesis written at the FHI on “Theory of Angular Resolved Photoemission from Adsorbates.” His advisers were Kurt Molière (FHI), Kyozaburo Kambe (FHI) and Frank Forstmann (Freie Universität Berlin and FHI). Prior to his appointment as Director at the FHI in 1988, he was a staff scientist at the Physikalisch-Technische Bundesanstalt in Braunschweig. In 2004 he was appointed “Distinguished Visiting Professor for Computational Materials Science and Engineering” at the University of California Santa Barbara, where he spends up to a quarter of the year.

The following researchers previously or currently affiliated with the Theory Department over periods of several years had a noticeable impact on the Department’s work:

- Volker Blum (PhD in Physics 2001, Universität Erlangen-Nürnberg, adviser Klaus Heinz; at FHI since 2004)
- Jarek Dabrowski (PhD in Physics 1989, Polish Academy of Sciences, adviser Tadeusz Figielski; at FHI 1989–1992; at present staff scientist at Leibniz-Institut für innovative Mikroelektronik, Frankfurt/Oder, Germany)
- Kristen Fichthorn (PhD in Chemical Engineering 1989, University of Michigan, advisers Robert Ziff and Erdogan Güjarli; at FHI 1998–1999; at present Professor at The Pennsylvania State University, University Park, USA)
- Veronica Ganduglia-Pirovano (PhD in Physics 1989, Universität Stuttgart, adviser Peter Fulde; at FHI 1994–2001; at present Professor at the Universidad Autónoma de Madrid)
- Xavier Gonze (PhD in Applied Sciences/Engineering 1990, Université Catholique de Louvain, adviser Jean-Pierre Michenaud; at FHI 1998–1999; at present Professor at Université Catholique de Louvain, Louvain-la-Neuve, Belgium)
- Axel Groß (PhD in Physics 1993, Technische Universität München, adviser Wilhelm Brenig; at FHI 1993–1998; at present Professor at University of Ulm, Ulm, Germany)
- Bjørk Hammer (PhD in Physics 1993, Technical University of Denmark; adviser Karsten Jacobsen/Jens Nørskov; at FHI 1993–1994; at present Professor at Aarhus University, Aarhus, Denmark)
- Klaus Hermann (PhD in Physics 1974, Technische Universität Clausthal, advisers Ernst Bauer and Lothar Fritsche; at FHI since 1990)
- Joel Ireta Moreno (PhD in Physical Chemistry 1999, Universidad Autónoma Metropolitana-Iztapalapa, adviser Marcelo Galván; at FHI 1999–2007; at present Professor at Universidad Autónoma Metropolitana-Iztapalapa, Mexico City, Mexico)
- Hong Jiang (PhD in Physical Chemistry 2003, Peking University, adviser Xinsheng Zhao; at FHI 2006–2009; at present Professor at Peking University, Beijing, China)
Current Era

- Kyozaburo Kambe (PhD in Physics 1962, Freie Universität Berlin, adviser Kurt Molière; at FHI 1956–1991)
- Peter Kratzer (PhD in Physics 1993, Technische Universität München, adviser Wilhelm Brenig; at FHI 1997–2006; at present Professor at Universität Duisburg-Essen, Duisburg, Germany)
- Sergey Levchenko (PhD in Chemistry 2005, University of Southern California, adviser Anna I. Krylov; at FHI since 2008)
- František Máca (PhD in Physics 1983, Czechoslovak Academy of Sciences, adviser Igor Bartoš; at FHI 1988–1991; at present postdoctoral researcher at Academy of Sciences of the Czech Republic, Praha, Czech Republic)
- Michael Methfessel (PhD in Physics 1986, Katholieke Universiteit Nijmegen, advisers Jürgen Kübler and Alois Janner; at FHI 1989–1992; at present staff scientist at Leibniz-Institut für innovative Mikroelektronik, Frankfurt/Oder, Germany)
- Angelos Michaelides (PhD in Chemistry 2000, Queen’s University Belfast, adviser Peijun Hu; at FHI 2003–2006; at present Professor at University College London, London, United Kingdom)
- Jörg Neugebauer (PhD in Physics 1989, Humboldt Universität Berlin, adviser Rolf Enderlein; at FHI 1990–1993, 1996–2003; at present Director at Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany)
- Oleg A. Pankratov (PhD in Physics 1977, Moscow Physical-Technical Institute, adviser Evgeniy Maksimov; at FHI 1990–1995; at present Professor at Universität Erlangen-Nürnberg, Erlangen, Germany)
- Christian Ratsch (PhD in Physics 1994, Georgia Institute of Technology, adviser Andy Zangwill; at FHI 1995–1997, 2003; at present Professor at University of California, Los Angeles, USA)
- Karsten Reuter (PhD in Physics 1998, Universität Erlangen-Nürnberg, adviser Klaus Heinz; at FHI 2003–2009; at present Professor at Technische Universität München, München, Germany)
- Patrick Rinke (PhD in Physics 2002, University of York, adviser Rex Godby; at FHI since 2003)
- Angel Rubio (PhD in Physics 1991, University of Valladolid, adviser Carlos Balbas; at FHI (distinguished visiting scientist) since 2009; at present Professor at the University of the Basque Country, Donostia-San Sebastian, Spain)
- Paolo Ruggerone (PhD in Physics 1989, University of Milan, adviser Giorgio Benedek; at FHI 1994–1998; at present Professor at Università deglo Studi di Cagliari, Cagliari, Italy)
Since its inception in 1994, the Department of Inorganic Chemistry has advanced a research program focused on studying, and bridging, the gap between catalytic model systems of surface science and real heterogeneous catalysts. Originally housed on the premises of Elmar Zeitler’s Department of Electron Microscopy, the Department relocated five times before settling in the refurbished former IFE building, which provides it adequate space to house facilities ranging from high-resolution electron microscopes to synthetic-chemistry laboratories.

The current, functional understanding of heterogeneous catalysis relies on the work of Gerhard Ertl and Gabor Somorjai, who pioneered the single-crystal approach to modeling a metal catalyst. This approach led to a quantitative description of elementary processes relevant for catalytic transformations which, in turn, became a pre-requisite for the development of a theory of heterogeneous catalysis. However, despite the solid conceptual framework established by the theory, it remains nearly impossible to predict the catalytic properties of working catalysts developed by empirical or combinatorial methods. Finding the missing link between the conceptual and practical understandings of heterogeneous catalysis has become the long-term goal of the Department.

At the core of present research is analytic work aimed at determining the essential ingredients of the high-performance, complex catalytic systems encountered in chemical technology. This analysis is followed by a synthesis of the identified functional materials whose kinetic characteristics match those of the complex catalytic system. In order to probe the catalytic activity of the synthesized materials, the Department has developed a suite of in situ analytical techniques that mimic real-life conditions. This enables Department members to establish

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**Department of Inorganic Chemistry**

- Arno Schindlmayr (PhD in Physics 1999, University of Cambridge, adviser Rex Godby; at FHI 1998–2003; at present Professor at Universität Paderborn, Paderborn, Germany)
- Catherine Stampfl (PhD in Physics 1990, La Trobe University, Melbourne, adviser John D. Riley; at FHI 1990–2003; at present Professor at University of Sydney, Sydney, Australia)
- Alexandre Tkatchenko (PhD in Physical Chemistry 2007, Universidad Autónoma Metropolitana, Iztapalapa, adviser Marcelo Galván; at FHI since 2007)
- Chris van de Walle (PhD in Electrical Engineering 1986, Stanford University, adviser Richard M. Martin; at FHI 1999; at present Professor at University of California, Santa Barbara, USA)
- Byung Deok Yu (PhD in Physics 1992, Seoul National University, adviser Jisoon Ihm; at FHI 1994–1997; at present Professor at University of Seoul, Seoul, Korea)
quantitative relationships between the structure and the function of the materials involved.

Establishing such relationships is complicated by the dynamic response of a catalyst to its reaction environment, which leads to the formation of metastable surfaces containing the active sites as minority features. The active catalytic sites change their structure in a cycle which brings them back to their initial state after the completion of each reaction sequence. Since the sites are metastable with respect to the equilibrium state of the bulk catalyst phase, the catalyzed chemical reaction can proceed beyond its equilibrium. But if the cycles are interrupted by separating the catalyst from its reaction environment, for the purpose of analysis or static experimentation, the metastable active sites decay to stable products, thereby precluding their structural identification.

This creates gaps of understanding between surface science and the performance of complex catalytic systems. Indeed, the origin of the failure to predict the catalytic properties of complex systems lies in the conundrum that catalysts can either be rigorously analyzed in non-functioning forms or operated at high performance without knowing their active structure. In order to bridge this gap, Department members synthesize functioning models with minimal complexity and investigate their structural properties in situ. The Institute’s rich background in catalysis and its focus on model systems (cf. the Department of Chemical Physics) facilitate such interdisciplinary research on the interface between physical and inorganic chemistry. The development of the Department of Inorganic Chemistry can be characterized as a gradual adaptation to such an interdisciplinary effort – using the opportunities of the Institute’s existing infrastructure on the one hand and providing stimuli for the work of other Departments on the other.

When the Department was founded, it had already been realized that electron microscopy of catalysts could provide unique access to the non-translational aspects of their structure, but taking advantage of this realization required a full arsenal of microscopic techniques and cutting-edge instrumentation. Between 1995 and 2007, the Department replaced its outdated microscopes with a set of modern instruments. The know-how of Zeitler’s Department in constructing and operating electron microscopes has thus contributed to novel insights into the structure of real polycrystalline catalysts. The method of electron energy loss spectroscopy was also successfully adapted to the needs of catalysis research and augmented by a unique combination with its surface-sensitive counterpart – soft X-ray absorption spectroscopy – which has been implemented as an in situ method at the BESSY synchrotron. Another instrument of strategic importance to the Department’s research has been an ambient-pressure photoemission spectrometer (HP-XPS). A critical component of this instrument is a variable-energy “electron microscope” which transfers photoelectrons through a series of apertures into an electrostatic analyzer. The Department’s HP-XPS has a long history, going back to the work of Jochen Block. Its present incarnation was built in collaboration with the group of Miquel Salmeron at the Advanced Light Source in Berkeley and became operational in 2007.
Since no synthetic chemistry infrastructure was available at the Department (or, indeed, the Institute) before 2008, polycrystalline samples of catalysts had to be obtained from external, often industrial, partners. In order to produce model systems in house, researchers in the Department of Inorganic Chemistry developed a suite of instruments allowing the synthesis of metal oxides by physical vapor deposition of elements and by annealing procedures at ambient pressure. They chose the dehydrogenation of ethylbenzene to styrene on iron oxides as the subject of their first major study. Figure 6.6 summarizes the main results. The technical catalyst (A) is a complex convolution of phases, with the active sites located at the solid-solid interface. It was possible to synthesize well-ordered thin films (D) of the relevant ternary potassium iron oxide and to determine their chemical structure and reactivity. In parallel, Department members developed a micro-reactor device (B) allowing them to measure kinetic data (C) on such thin films. In this way, they were able to obtain experimental data needed for kinetic modeling under well-defined reaction conditions, which they could use to prove that the model reaction occurs in the same way as the reaction in the real-life system. Thin oxide
Film research moved to the newly established Department of Chemical Physics in 1998, but a strong synthesis group remains within the Department of Inorganic Chemistry.

This work enabled Department members to understand and control the details of catalyst synthesis with a new level of precision. This improved control of materials quality and catalytic performance could then be applied to the preparation of commercially relevant synthetic catalysts. Figure 6.7 shows as an example the preparation of a Cu-based catalyst used for methanol synthesis. After constructing a new device for computer-controlled synthesis group, its members were able to resolve the precipitation process of the solid into two phases, as can be discerned from the colors of the respective solids and the corresponding X-ray diffraction patterns. Time-resolved studies allowed them to answer a long-standing question regarding the best precursor phase for the active catalyst – in favor of the zincian malachite phase as opposed to the auricalcite phase; earlier attempts by a global industry consortium to settle the question of the best precursor phase had been unsuccessful. They were also able to explain the origin of the “chemical memory effect,” by recognizing that the non-translational structure of the Cu metal catalyst is controlled by the kinetics of the decomposition of the colored precursors.
shown in Fig. 6.7. By controlling the defect structure of the Cu nanoparticles, they were further able to demonstrate the relevance of precursor synthesis to the final performance of the catalyst.

Several complementary in situ methods and electron microscopy were employed in this effort. Its successful completion required the targeted application of a broad portfolio of experimental techniques and is a testament to the highly effective collaboration within the Department. The Department comprises six Research Groups, each of which covers a certain field of competence (see below). Group leaders are responsible for teams of post-docs, students and engineering support, as well as for the transfer of know-how from one generation of collaborators to the next. Research, however, is commonly carried out in Project Teams, consisting of members of multiple Research Groups who collaborate to advance a specific topic of research, moving from a phenomenological to an analytical understanding of the subject. This bi-level collaborative structure has been in place since 2005.

As mentioned earlier, visualization of the non-translational structure of active catalysts has turned out to be of enormous value in finding strategies for analyzing quantitative data, and electron microscopy has provided particularly perspicacious visualizations. The Department’s microscopes are stabilized by large masses of concrete in good contact with the native ground, which has turned out to be at least as good a method as the earlier, more complex approach based on active stabilization of platforms suspended in double-walled towers.

Figure 6.8 shows typical electron microscope images of catalysts. They demonstrate the need to understand structure on different length scales when analyzing the functioning of catalysts. The scanning electron microscope image shows a mesoporous silicate structure with hexagonal channels and their regular congestions. These unwanted long-range structures arise from the dynamics of the templating micelles. It is not possible to use transmission electron microscopy (TEM) to verify the homogeneity of the material, as the long-range channel modulation destroys the resolution of the TEM image by projecting the variable pore diameter onto the image plane. Whereas in the atomic domain aberration-corrected TEM is often an effective means to observe the dynamics of small objects, such as rafts of gold atoms anchored on purposely modified carbon nanotubes, which form highly effective catalysts for oxidations of biomass. The internal structure of the raft is fully dynamical at an observation time interval of 20 s, but the raft as a whole is firmly bound to its support and can even survive reactions in water and oxygen.

By following a research trajectory from overwhelmingly complex, high-performing catalysts to simplified model systems capable of maintaining a catalytic function of interest, work in the Department has shown repeatedly that complex solid structures are required to stabilize active phases, but that active phases are often chemically simple. In several cases, these active phases could be matched by model systems obtained through exacting physical preparation. The active species could then be identified and a theoretical description of the catalytic process in question provided whereby, in these instances, the gap between surface science and high-performance catalysis could be closed.
Fig. 6.8. Electron microscopy in catalysis. Plate (A) shows a mesoporous silicate SBA 15 sample at different magnifications. The hexagonal mesopores of 7 nm average diameter exhibit fluctuations with congestions every few hundreds of nanometers. Plate (B) shows a raft of gold atoms supported by carbon nanotubes. The top and bottom images attest to a fluctuation of the internal structure, observed over an interval of 20 s (given by the image recording time). The same atoms forming a three-dimensional nanoparticle appear static when observed under the same conditions.

The Director of the Department of Inorganic Chemistry is Robert Schlögl, born in 1954 in Munich. He studied chemistry at the Ludwig Maximilians University in Munich, where he also completed his PhD on graphite intercalation compounds in 1982 under Gerhard Ertl. Prior to his appointment as Director at the FHI in 1994, he held a Professorship in Inorganic Chemistry at the University of Frankfurt (1989–1994).

The following researchers previously or currently affiliated with the Department of Inorganic Chemistry served as research group leaders:

- In situ Diffraction and Synthesis, led by Malte Behrens (PhD in Chemistry 2006, Christian-Albrechts-Universität Kiel, advisor Wolfgang Bensch; at FHI since 2006)
- Geometric Structure, led by Josef Find (PhD in Chemistry in 1998, Technische Universität Berlin, supervisor Robert Schlögl; at FHI from 1994 until 1999)
- Geometric Structure, led by Daniel Herein (PhD in Chemistry in 1995, Johann Wolfgang Goethe-Universität, supervisor Robert Schlögl; at FHI from 1994 until 1998)
- Emmy Noether Research Group on High Temperature Catalysis, led by Raimund Horn (PhD in Chemistry 2003, Technische Universität Berlin, advisor Robert Schlögl; at FHI since 2007)
• Functional Characterization, led by Friederike C. Jentoft (PhD in Chemistry in 1994, Ludwig-Maximilians-Universität München, supervisor Helmut Knözinger; at FHI from 1996 until 2008)


• Inorganic chemistry, surface organometallic chemistry, led by Klaus Köhler (PhD in Chemistry in 1988, Universität Leipzig, supervisor Reinhard Kirmse; at FHI from 1994 until 1996)

• Heterogeneous Catalysis, led by Gerhard Mestl (PhD in Chemistry in 1994, Ludwig-Maximilians-Universität München, supervisor Helmut Knözinger; at FHI from 1997 until 2002)

• Preparation, led by Dirk Niemeyer (PhD in Chemistry in 2001, University College London, supervisor David E. Williams; at FHI from 2002 until 2004)

• Model Catalysis, led 2000–2006 by Wolfgang Ranke (PhD in Physics in 1973, Technische Universität München, supervisor Heinz Gerischer; at FHI from 1970 until 2006)

• Geometric Structure, led by Thorsten Ressler (PhD in Chemistry in 1995, Universität Hamburg, supervisor Wolfgang Metz; at FHI from 1999 until 2005)

• Electronic Structure, led by Thomas Schedel-Niedrig (PhD in surface science physics 1992, Technische Universität Berlin, supervisor Alexander M. Bradshaw; at FHI from 1988 until 1998)

• Electron Microscopy and Carbon Science, led by Dangsheng Su (PhD in Physics 1991, Technische Universität Wien, advisor Peter Schattschneider; at FHI since 1999)

• Synthesis an In Situ Structural Spectroscopy, led by Annette Trunschke (PhD in Chemistry 1990, Akademie der Wissenschaften Berlin, advisor Hans Miessner; at FHI since 2004)

• Electron Microscopy, led by Yuji Uchida (PhD in Applied Physics in 1969; at FHI from 1978 until 2002)

• Nanoparticles, led by Joachim P. Urban (PhD in Physics in 1970, Freie Universität Berlin, supervisor Prof. Hosemann; at FHI from 1975 until 2005)

• Model Catalysis, led by Werner Weiß (PhD in Chemistry in 1993, Universität Tübingen, supervisor Wolfgang Göpel; at FHI from 1995 until 1999)

• Heterogeneous Catalysis, led by Harald Werner (PhD in Chemistry in 1994, Johann Wolfgang Goethe-Universität, supervisor Robert Schlögl; at FHI from 1994 until 1998)

• Electron Microscopy, led by Marc Willinger (PhD in Chemistry 2005, Technische Universität Berlin, advisor Robert Schlögl; at FHI since 2011)
Department of Chemical Physics

The reorientation of the institute toward surface science was bolstered by the appointment in 1996 of Hans-Joachim Freund, whose prior research had progressively come to focus on the study of model systems in heterogeneous catalysis.

By the late 1980s, oxide surfaces had emerged as a key alternative to single crystal metal surfaces and shown promise as a basis for the study and utilization of more complex combinations of materials. Freund and his coworkers developed an atomistic approach to the understanding of oxide surfaces, as well as oxide surface supported nanoparticles, aimed at a full characterization of their functionalities and properties. This approach has enabled a rational design of new systems whose applications range from catalysis (which will be our focus here) to energy production.

Real-life, dispersed-metal catalysts consist of particles of varying sizes that are distributed nonuniformly over a supporting surface. Using a well-ordered oxide film as a supporting surface results in a system which captures some of the complexity of the technologically employed dispersed-metal catalysts while allowing the application of a whole toolbox of surface science techniques to investigate the systems at the atomic level. The Department’s experimental work on oxide surfaces and oxide-surface-supported nanoparticles has been supported not only by the Institute’s Theory Department, but also by the theoretical work of Paul Bagus, Hannu Häkkinen, Gianfranco Pacchioni and Joachim Sauer, an External Member of the FHI.

In addition to exploring and exploiting the properties of oxide films of macroscopic thickness (∼ 10 nm), Freund and coworkers have recently turned their attention to producing systems containing ultra-thin oxide films (≤ 1 nm) consisting of a few epitaxially grown atomic layers supported by metal substrates. Ultra-thin films have characteristics that allow investigators to control the status, organization, and charge state of metal atoms and nanoparticles via the thickness of the film that supports them and can thus be engineered into catalysts with preordained properties.

In what follows, we will describe three case studies exemplifying the surface chemistry and catalyst modeling enabled by oxide films. The first concerns the exchange reactions of hydrogen on metallic catalysts, the mechanism for which was advanced in the early 1930s by Juro Horiuti and Michael Polanyi at Haber’s institute and at Manchester. In its present incarnation, the process is catalyzed by palladium (Pd) nanoparticles deposited on a thick magnetite (Fe₃O₄) film. The other two case studies concern the control of the charge state of gold (Au) atoms as well as gold clusters, and the enhancement of carbon monoxide (CO) oxidation over ultrathin oxide films. We will also highlight the development of key instrumentation undertaken by the Department.

At first blush, one might think that hydrogenation, e.g. of cis-butene, on well faceted palladium particles would proceed in the same way as the catalytic
conversion on metal single crystals explored earlier by Gerhard Ertl and Gabor Somorjai. However, research in the Department of Chemical Physics has shown that, in contrast to a single crystal, the flexible lattice of nanoparticles and its finite interior space lead to the active participation of adsorbed hydrogen and adsorbed carbon in the hydrogenation reaction, see Fig. 6.9(a,b).

A schematic of the Horiuti-Polanyi mechanism, which captures the elementary steps of the reaction, is drawn for cis-butene in Fig. 6.9(c). The key intermediate is a butyl whose C–C double bond is half-hydrogenated on one end and bound to the surface on the other. The butyl may either dehydrogenate again and subsequently desorb as trans-2-butene (the stable isomer of cis-2-butene) or become fully hydrogenated and desorb as butane. Alternatively, the original hydrocarbon may fully dehydrogenate and stick to the surface as a carbonaceous deposit. While both the isomerization and dehydrogenation are observed on a palladium single crystal, the fully sustained hydrogenation reaction is not. However, on the nanoparticles, all three reactions take place. Moreover, only the nanoparticles afford a sustained catalytic activity, which is connected with the presence of carbonaceous species and their moderating effect on the diffusivity of hydrogen from the surface to the immediate sub-surface of the metal, see Fig. 6.9(a,b). Indeed, it is the sub-surface hydrogen which is key to the hydrogenation reaction. Sub-surface hydrogen was previously considered crucial for hydrogenation on both palladium single crystals and palladium nanoparticles. However, while the bulk of the Pd single crystal favors an entropy-driven dissolution of hydrogen, in a nanoparticle the hydrogen is forced to linger near the surface, owing to the particle’s size and the diffusion barrier of the oxide. How much hydrogen is present in the nanoparticle is determined by its pressure in the gas phase. A quantitative grip on the content of the sub-surface hydrogen was obtained through resonant-nuclear reaction analysis (multiple scattering of variable-kinetic energy $^{15}$N by H to yield $^{12}$C, an $\alpha$ particle, and an easily detectable $\gamma$ photon).

Introducing some of the real-life complexities of a working catalyst into more abstract models has been a distinguishing feature of work in the Department of Chemical Physics to date. In the above case study, it was the size of the nanoparticle and the presence of its oxide support that were key to developing an understanding of the elementary processes involved. A metal single crystal was too simple a model.

Thin oxide films formed by oxidation of metal surfaces have been center stage in semiconductor research since Walter Schottky formulated his ideas on electronic barriers in solids during the 1920s and 30s. In 1948, Nevill Mott and Nicolas Cabrera embraced these same ideas, in attempts to describe and explain the elementary processes involved in oxide layer formation. Scientists at the Department of Chemical Physics have made use of Schottky’s ideas to approach a variety of seemingly disjunct problems, two of which will be outlined below.

The first concerns the control of the charge state of Au clusters on oxide surfaces. By choosing, e.g., a bi-layer of magnesia (MgO) in (100) orientation grown
on a silver (Ag) single (100) crystal, charge transfer becomes facile due to a drop in the interfacial work function. A phononic response of the thin film through a lattice distortion stabilizes the charge on the Au cluster. Researchers in the Department were able to characterize the system in detail using scanning tunneling microscopy (STM), which revealed the distribution of electrons in the various occupied and unoccupied orbitals as well as the orbital energies.

Figure 6.10 displays images of a flat $\text{Au}_{18}^{4-}$ cluster as an example. The top three panels show STM images taken at different voltages between tip and sample, indicating that the imaging process is dominated by the electronic rather than geometric structure of the Au cluster. The “flowers” reflect the nodal structure of the electron density distributions, comprised of superimposed 6s orbitals of the constituent Au atoms. The resulting electronic states are quantized (due to the finite size of the system) and only partially occupied. The energies of the electronic states are clearly resolved in the scanning tunneling spectra (STS) shown in the lower panel. The spectra were measured for two tip positions marked by
Fig. 6.10. Set of STM images of flat Au$_{18}^+$ cluster at three different tunneling voltages (upper panels) along with scanning tunneling spectra (lower panel) measured from −2.0 eV to +2.0 eV at the positions marked by the colored dots in the image taken at ∼−0.4 eV (leftmost upper panel). The current images (middle panel) have been obtained at voltages corresponding to the observed maxima of the scanning tunneling spectra.

the dots in the leftmost image of the upper panel. When the tip is placed in a position where the electron density vanishes, the STS peak disappears. The five so-called current images (middle panel) have been taken at voltages corresponding to the respective peak positions (or electronic energies). Note that the 18th Au atom (i.e., the rightmost one in the honeycomb-like structure shown in the center upper panel) makes the geometric structure of the Au$_{18}^+$ cluster asymmetric, which is clearly reflected in the asymmetry of the electron densities. If this extra Au atom were absent, the electron densities would be symmetric. Hence the measured electronic structure disclosed details of the geometric structure.

Apart from the choice of a suitable oxide/metal system, members of the Department have also been able to control the system’s properties by making use of the so-called strong metal support interaction (SMSI), in which an oxide film is grown over supported metal particles, a particularly feasible feat when reducible oxides are used as supports. The third case study that we will recount relied on the SMSI of platinum (Pt) nanoparticles with a reducible support provided by a Fe$_3$O$_4$ film grown on a Pt single crystal. After heating to 850 K, the capacity of the system to adsorb carbon monoxide (CO) is drastically reduced, which is typical for the SMSI effect. A close look at the surface images obtained by STM revealed
Fig. 6.11. Acts in forming the active tri-layer phase starting from FeO(111)/Pt(111) and its reaction with CO to form CO$_2$ based on density functional theory calculations. At center is an STM image of tri-layer FeO$_2$/Pt(111) formed at 20 mbar of O$_2$ at 450 K; the inset shows an atomic-resolution image.

well-structured and facetted nanoparticles. However, images with atomic resolution showed a corrugation that did not stem from platinum but rather from a well-known, well-ordered double-layer film of ferrous oxide (FeO). One may thus reduce the complexity of the model system to a bilayer FeO film on a Pt single crystal, whose structure has been studied in detail and characterized at the atomic level. The 10% mismatch between the FeO lattice constant and that of Pt gives rise to a characteristic Moiré pattern in the STM image. The bi-layer film is nonreactive under ultra-high vacuum conditions. However, the situation changed dramatically with respect to CO oxidation at ambient conditions (1 atm) in a reactor affording a careful control of the relative amounts of oxygen (one part, 20 mbar), carbon monoxide (two parts, 40 mbar) and helium as a buffer gas. Ramping up the temperature linearly at a rate of 1 K per minute from 300 K to 455 K, the CO oxidation ignited at 430 K.

The intriguing finding was that the catalytic activity of the FeO/Pt system in question was more than an order of magnitude greater than that of clean platinum (at 450 K). Usually SMSI diminishes catalytic activity; whereas, here researchers
in the Department observed a strong *enhancement*. Further detailed experimental and theoretical (density functional theory-based) investigations revealed a scenario that made sense of this enhancement. The scenario is presented in Fig. 6.11. In Act 1, oxygen interacts with the bi-layer FeO film on Pt by pulling up an iron atom above the adsorbed-oxygen layer. This lowers the energy required to remove an electron at the interface to allow for an electron transfer to oxygen. This results in the formation of a transient $O_2^{2-}$ molecule (Act 2), which dissociates and, at a higher oxygen coverage, gives rise to a local 0-Fe-O tri-layer (Acts 3 and 4). The central panel of Fig. 6.11 displays an STM image of such a tri-layer formed in situ at an elevated $O_2$ pressure in the microscope. It owes its appearance mainly to the Moiré structure of the FeO bi-layer and covers about 80–90% of the surface. When exposed to CO (Act 5), the tri-layer oxidizes it to $CO_2$ (Act 6), leaving behind an oxygen vacancy in the film, which fills in again if the oxygen pressure is sufficiently high. Thus, the tri-layer is restored. If, however, the gas phase is oxygen-poor, the tri-layer is consumed and the reaction stops. Further investigations in the Department have confirmed that the iron oxide film de-wets the Pt single crystal surface under oxygen-poor reaction conditions by forming small iron oxide particles, which leaves the Pt crystal surface bare. The bare Pt surface then determines the reactivity of the system. Heating of the de-wetted surface in vacuum leads to the formation of the FeO bi-layer again which, at higher oxygen pressure, transforms into the tri-layer.

Freund and coworkers found as a corollary that a properly designed oxide film on a metal support can promote electron transfer to an adsorbed molecule. One such combination of materials is a bi-layer of MgO on Ag, which leads to the formation of a stable $O_2^-$ molecular ion even under ultra-high vacuum conditions. A key experimental advance that made establishing this scenario possible was the development of an ultra-high vacuum electron spin resonance (ESR) spectrometer capable of determining magnetic properties of para- and ferro-magnetic species on surfaces, including their alignment and orientation. Hence they were able to conclude that the electron transfer to oxygen is the key step in initiating the oxidation reaction. This is in accord with Mott & Cabrera’s theory of oxidation mentioned above and the long-neglected theories of catalytic activity proposed by Georg-Maria Schwab and Feodor Feodorovich Volkenshtein in the 1950s and 1960s. It has been the availability of 21st century techniques and apparatus to study surface interactions on an atomic level that brought us back to the future.

Advancing such innovative, enabling instrumentation has been among the Department’s core activities. Other instruments developed by the Department include: a photoemission electron microscope (PEEM) with ultimate resolution attained by implementing corrections for both chromatic and spherical aberrations; a micro calorimeter whose sensitivity is sufficient to measure temperature-dependent heats of adsorption on nano-particles with aggregate sizes down to about a hundred atoms; and a photon STM, which adds chemical sensitivity through local excitation of a fluorescence signal by electrons from the tip.
The Director of the Department of Chemical Physics is Hans Joachim Freund, born in 1951 in Solingen. He studied Physics and Chemistry at the University of Cologne. As a graduate student in Georg Hohlneicher’s group, he set up, in 1973, an X-ray photoelectron spectrometer (XPS) to study multielectron excitations of gaseous and adsorbed species. Prior to his appointment as Director at the FHI in 1996, he held Professorships at the Universities of Erlangen-Nürnberg (1983–1987) and Bochum (1987–1996), where he launched his research on model systems in catalysis.

The following researchers previously or currently affiliated with the Department of Chemical Physics for periods of several years had a noticeable impact on the Department’s work:

- Katharina Al-Shamery (PhD in Chemistry 1989, Universität Göttingen, adviser Prof. M. Quack; FHI 1996–1999; at present Professor at Carl von Ossietzky-Universität, Oldenburg, Germany)

- Marcus Bäumer (PhD in Chemistry 1994, Ruhr-Universität Bochum, adviser Klaus Rademann; FHI 1996–2002; at present Professor at Universität Bremen, Germany)

- Aidan Doyle (PhD in Chemistry 2000, University of Limerick, FHI 2002–2004; at present Associate Professor at Manchester Metropolitan University, UK)

- Javier Giorgi (PhD in Chemistry 1999, University of Toronto; FHI 2000–2002; at present Associate Professor at University of Ottawa, Canada)

- Markus Heyde (PhD in Chemistry 2001, Humboldt Universität zu Berlin, adviser Klaus Rademann; at FHI since 2003)

- Thorsten Klüner (PhD in Theoretical Chemistry 1997; Ruhr-Universität Bochum; adviser Hans-Joachim Freund; FHI 1994–2004; at present Professor at Carl von Ossietzky-Universität, Oldenburg, Germany)

- Christiane Koch (PhD in Theoretical Physics 2002, Humboldt Universität zu Berlin; adviser Hans-Joachim Freund; FHI 1998–2003; at present Professor Universität Kassel, Theoretische Physik III, Kassel)

- Helmut Kuhlenbeck (PhD in Physics 1988, Universität Osnabrück, adviser Manfred Neumann; at FHI since 1996)

- Jörg Libuda (PhD in Physical Chemistry 1996; Ruhr-Universität Bochum; adviser Hans-Joachim Freund; FHI 1993–2005; at present Professor at Universität Erlangen-Nürnberg, Germany)

- Randall Meyer (PhD in Chemistry 2001, University of Texas at Austin, FHI 2001–2004; at present Assistant Professor at University of Illinois at Chicago, USA)

- Niklas Nilius (PhD in Physics 2001, Humboldt Universität zu Berlin; adviser Hans-Joachim Freund; at FHI since 2003)

- Zhihui Qin (PhD in Physics 2006; Institute of Physics, Chinese Academy of Sciences; FHI 2006–2009; at present Associate Professor at Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, China)

- Thomas Risse (PhD in Chemistry 1996, Ruhr-Universität Bochum; adviser Hans-Joachim Freund; FHI 1997–2010; at present Professor at Freie Universität, Berlin, Germany)
Department of Molecular Physics

Macroscopic reaction rates as observed, e.g., in the experiments of Michael Polanyi and others during the 1920s and 30s, 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 find out whether individual polar molecules – as opposed to polar molecules in the bulk – carry an electric dipole moment. A beam of polar molecules was to be sent through an inhomogeneous electric field and its deflection monitored. Kallmann & 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 & 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.”

Kallmann & 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. 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. Perhaps no other experiment is so often cited for elegant conceptual simplicity. Among the descendants of the Stern-Gerlach experiment and its key concept of sorting quantum states via space quantization are the prototypes for nuclear magnetic resonance, optical pumping, the laser and atomic clocks, as well as incisive discoveries such as the Lamb shift and the anomalous increment in the magnetic moment of the electron, which launched quantum electrodynamics.

Despite their import, impact and lineage, neutral molecular beams and the gas-phase chemistry and physics that come along with them, had been absent at the institute from about 1933 until 2002, when Gerard Meijer was appointed to establish a department for the “pursuit of molecular physics and spectroscopy.” The Department of Molecular Physics that ensued launched a research program organized around translationally cold neutral molecules and molecular beam spectroscopy of clusters and biomolecules, both neutral and ionized. The former topic in particular, which involves deceleration and trapping of molecules by means of electric and magnetic fields, can be regarded as an extrapolation of what Polanyi, Kallmann, Reiche and others had sought to do in their time.

In multipole focusers as well as in the deflection elements used in typical molecular beam experiments, the field gradient is perpendicular to the beam axis and exerts no force parallel to the beam axis. The forward (longitudinal) velocity distribution of a supersonic molecular beam is centered at a rather high velocity, ranging typically between 300 and 2000 m/s, depending on the molecular mass and the source conditions. Even at the low end of this velocity range, the kinetic energy of the molecules is on the order of 100 K, when expressed as energy divided by Boltzmann’s constant. This is much larger than the depth of any potential energy well that can be realized for typical polar molecules using an electrostatic field, which amounts to only about 1 K. Therefore, a direct longitudinal confinement of the beam molecules by an electrostatic field is impossible.

However, the molecules’ longitudinal and transversal velocity spreads are about the same, corresponding to a kinetic energy of about 1 K. Therefore, a potential well – with a gradient parallel to the molecular beam axis – could longitudinally confine the molecules, provided the potential moved along with the molecules in the beam at their most probable velocity. The confinement would be just as effective as the usual transversal confinement by a multipole focuser mounted parallel to the beam. Thus, a multipole focuser mounted perpendicular to the beam would produce the requisite longitudinal confinement, forcing the molecules on the beam...
axis to oscillate, both in position and velocity, around the center of the perpendicular multipole. Although the most probable velocity of the beam molecules would not be affected, the pack of molecules would remain flocked together while moving in the forward direction – it would be longitudinally focused (bunched). Moreover, if the velocity of this moving potential energy well were variable, a fraction of the beam molecules could be brought to any desired final velocity. So for instance, in order to decelerate the beam molecules, the potential well would have to be gradually slowed down such that the molecules in the beam would spend more time on the leading slope of the longitudinal potential well, thereby feeling a force opposing their motion. And vice versa, in order to accelerate the molecules, the potential well would have to be gradually sped up, thus pushing the molecules forward on the trailing slope of the potential well. The hypothetical apparatus just described functions almost exactly like a real-life Stark decelerator (or accelerator). However, rather than moving the electrodes that generate the longitudinal confinement, the elements of a static electrode array are energized or grounded synchronously with the movement of the molecules, thereby generating a traveling potential energy well. Depending on the timing sequence used to energize or ground the electrodes, the molecules can be either transported along the beam axis at a constant velocity or gradually decelerated or accelerated to any desired final velocity.

Stark manipulation of molecular beams has been considered and tried before. Electric field deceleration of neutral molecules was first attempted in 1959 at MIT by John King, who strived to produce a slow ammonia beam intended for a maser with an ultra-narrow linewidth. In the 1960s, at the University of Chicago, Lennard Wharton constructed an eleven meter long molecular beam machine for the acceleration of ground-state LiF molecules from 0.2 to 2.0 eV, with the goal of studying reactive scattering at hyperthermal collision energies. Both of these experiments were unsuccessful and were abandoned after the graduation of the PhD students involved. The first successful experimental demonstration of Stark deceleration took place in 1999 in Meijer’s laboratory at the University of Nijmegen, where a beam of metastable CO molecules was slowed down from 225 m/s to 98 m/s. It was also Meijer who coined the term “Stark decelerator” or “Stark accelerator,” for Johannes Stark, who prior to his embroilment in “German Physics,” discovered the eponymous effect, by which an electric field characteristically shifts the energy levels of atoms and molecules.

Interest in Stark manipulation of molecular beams had been rekindled in the 1990s by the growth of “cold molecules” as a research topic in atomic, molecular and optical physics. Indeed, Stark deceleration has largely shaped the field of cold molecule research, as it became almost instantly the “workhorse” of the field. Moreover, the quantum-state selected molecular beam that exits a Stark decelerator has a tunable velocity, which is ideally suited for many applications. For instance, decelerated beams can be used in high-resolution spectroscopic studies to extend the available observation time and, by virtue of the uncertainty principle, to improve the attainable energy resolution. Decelerated beams also enable the study of (in)elastic collisions and reactive scattering down to zero collision...
energy and the study of the threshold behavior involved. Last but not least, a Stark decelerator enables trapping of neutral polar molecules.

Traps are key to further research in the field of cold molecules, in which the production and study of quantum degenerate gases of polar molecules is a particularly prominent objective. Trapping can also be used to prolong observation times to such an extent that radiative lifetimes of metastable molecular states can be accurately measured or the effects of the black-body radiation on molecules investigated. As John Fenn put it, “[b]orn in leaks, the original sin of vacuum technology, molecular beams are collimated wisps of molecules traversing the chambered void that is their theatre ... On stage for only milliseconds between their entrances and exits, they have captivated an ever growing audience by the variety and range of their repertoire.” That the time the molecules are on stage is normally limited to milliseconds follows from the typical speed of the molecules (hundreds of meters per second) and the length of the vacuum chamber (a meter).

This time limitation can in part be overcome with a storage ring, a type of electrostatic trap in which low-field seeking beam molecules travel inside a one-meter vacuum chamber for over a mile, thus stretching the duration of their performance not by extending the theatre but by making the best of it. In a storage ring the molecules are kept in orbit by an array of electrostatic focusing elements. The most straightforward way of obtaining a storage ring for neutral molecules is to bend a single hexapole focuser onto itself to form a torus. Such a toroidal ring, however, does not confine the molecules longitudinally; an injected packet of molecules would spread and eventually fill the entire ring uniformly. However, this problem can be overcome by breaking the symmetry of the ring, e.g., by cutting it into segments separated by small gaps. The molecular beam packets can then be kept together (bunched) by changing the electric fields synchronously with their passage through the gaps, in analogy with the operation of a synchrotron for charged particles. The circling packets of molecules can then repeatedly interact, at well defined times and positions, with electromagnetic fields and/or with other atoms or molecules. When used as a low-energy collider to measure collision cross sections, the number of encounters per unit time scales as the square of the number of packets in the ring – which depends on the number of the ring’s segments. Moreover, more segments enable storage of higher-density packets. Therefore, it’s advantageous to cut the ring into as many segments as practically possible. A photograph of a molecular synchrotron consisting of 40 straight hexapoles, each 37 mm long, is shown in Fig. 6.12. Adjacent hexapoles, whose axes make an angle of $9^\circ$ with respect to one another, are separated by gaps 2 mm wide. The resulting polygonal structure has a diameter of 0.5 m.

In one series of experiments performed in the Department, packets of Stark-decelerated deuterated ammonia ($^{14}$ND$_3$) molecules with a forward velocity of about 125 m/s were tangentially injected into the synchrotron. At its entry, a packet is several millimeters long and consists of about a million molecules. All these molecules are in the upper inversion doublet component of a single rotational level, the ground-state level of para-ammonia, hosted by the vibrational and
electronic ground state. Once the molecular packet was inside the synchrotron, the hexapole fields were switched on, keeping the molecules both in orbit and transversely focused. By temporarily switching to a higher-voltage configuration whenever the packet passed through a gap, the molecules with a forward velocity spread of 1 m/s, corresponding to a temperature of 0.5 mK, were kept bunched while revolving.

Figure 6.12 shows the density of the ammonia molecules as a function of time after injection into the synchrotron. A total of 13 packets were injected at a rate of 10 Hz, after which the loading was suspended. The revolving packets then trailed each other by a distance of 3 hexapoles, with the first and the last injected packets 4 hexapoles apart. The molecules were laser-ionized and the ion signal due to the 13 packets was recorded for a selected number of laps. Even after 1025 laps, i.e. after the molecules traveled for more than a mile and passed a gap or hexapole 41,000 times, their signal could still be clearly discerned; the temporal width of 21 μs corresponds to a packet length of 2.6 mm. The density of the ammonia molecules in the synchrotron was seen to decrease exponentially with time at a rate of about 0.31 per second, which is caused, about equally, by collisions with background gas and excitation to an untrappable high-field seeking state by the blackbody radiation present in the room-temperature chamber. These measurements epitomize the level of control of molecular beams that can currently be achieved and set the stage for novel experiments that are yet to come.

Another research area currently pursued at the Department is spectroscopy of molecules, clusters, and biomolecules in the gas phase, one example being the infrared spectroscopy of gold clusters.
Conventional absorption spectroscopy is fairly difficult to apply, as the fragile clusters are highly dilute, i.e. in the form of molecular beams or confined in traps, where the attainable line-integrated absorber density is not sufficient for observing an absorption signal. An alternate route is to record the effect that the light exerts on the sample, in which case a sufficiently large fluence (number of photons/cm²) may yield an observable signal, especially if the sample is photo-ionized by the incident radiation. The resulting ions or ionic fragments can then be mass-selectively detected with a unit efficiency. This so-called ‘action spectroscopy’ provides high sensitivity and is cluster-size selective. The crux of ‘action spectroscopy’ in the IR is a widely tunable laser of plentiful fluence, which is needed to induce the typically multiphoton processes involved.

During the last fifteen years, Meijer and coworkers have pioneered the application of infrared (IR) Free Electron Lasers (FELs) to obtain vibrational spectra of gas-phase species. The IR-FELs have provided access to weak modes in the far-infrared part of the spectrum corresponding to, e.g. metal-metal vibrations. Additionally, the spectroscopy in the gas phase has made it possible to extract the low-frequency modes which, in the case of deposited or embedded clusters, are often obscured by absorption in the substrate.

The absorption of far-IR photons can be detected by the ‘messenger method,’ which is based on forced evaporation of a weakly-bound ligand from the cluster complex upon the absorption of a small number of IR photons. The ‘messenger method’ assumes that only the metal cluster acts as a chromophore while the detached atomic or molecular ligand merely delivers the message about the absorption event without perturbing the structural properties of the cluster. This assumption is fulfilled for most transition metal clusters complexed with rare gas atoms. In combination with density functional theory calculations, the experimental IR (multi) photon dissociation, IR-(M)PD, spectra often enable an unambiguous determination of the clusters’ structure.

Experimental information on the structure of charged gold clusters has been obtained from ion mobility measurements, trapped ion electron diffraction, and anion photoelectron spectroscopy. Significant structural differences between singly charged cationic and anionic gold clusters have been thereby identified and it could be concluded that the size at which the initially planar clusters morph into 3D structures strongly depends on their charge state. In combination with information available from vibrational spectroscopy of neutral gold clusters, researchers at the Department of Molecular Physics were able to obtain a complete picture of the charge state dependence of the structures. The charge-state dependence is exemplified in Fig. 6.13(a) for a gold cluster containing seven atoms. In this case, all three charge states (cation, neutral, anion) have distinct structures, although the rearrangement that takes place between the neutral species and the anion is only minor. At an increased electron density, the average coordination of the gold atoms decreases, resulting in the formation of increasingly open structures. For larger anionic gold clusters, such as Au_{19} and Au_{20}, tetrahedral structures have
Fig. 6.13. (a) The structures of gold clusters containing seven Au atoms vary for the different charge states. (b) Comparison of experimental and calculated IR spectra of Au$_{19}$ and Au$_{20}$ clusters.

been found and the IR spectra shown in Fig. 6.13(b) point unambiguously to these geometries for the corresponding neutral clusters as well.

The Director of the Department of Molecular Physics is Gerard Meijer, born in 1962 in Zeddam, the Netherlands. He was brought forth into a world which abounded in quadrupolar and hexapolar focusers and molecular beam deflectors, at least from his personal perspective: he was a student at the University of Nijmegen where Toni Dymanus along with Jörg Reuss founded the first school of atomic and molecular physics in the Netherlands to use neutral beams and quantum-state selection. From that time on, Meijer’s interests comprised manipulation of molecules and their probing via spectroscopy. Prior to his appointment as Director at the Fritz Haber Institute in 2002, Meijer held a Professorship at the University of Nijmegen (1995–1999) and the Directorship of the FOM Institute for Plasma Physics in Nieuwegein, “FOM-Rijnhuizen” (2000–2003).

The following research groups have been based at and supported by the Department of Molecular Physics:

- Vibrational Spectroscopy of Gas Phase Ions, led by Knut Asmis (PhD in Physics 1996, Freie Universität Berlin, adviser Ludger Wöste; at FHI since 2003; previously group leader at the Freie Universität Berlin)
- Vacuum UltraViolet Photoionization Studies, led by Uwe Becker (PhD in Physics 1977, Technische Universität Berlin, adviser Hans Bucker; at FHI since 1989; previously Professor at Universität Würzburg)
- Micro-Structured Devices to Manipulate Molecules, led by Horst Conrad (PhD in Physical Chemistry 1976, Ludwig-Maximilians-Universität München, adviser Gerhard Ertl; at FHI since 1981)
Current Era

- Spectroscopy and Chemistry of Metal Clusters and Cluster Complexes, led by André Fielicke (PhD in Chemistry 2001, Humboldt Universität, adviser Klaus Rademann; at FHI since 2003)
- Interactions of Molecules with Fields, led by Bretislav Friedrich (PhD in Chemical Physics 1981, Czech Academy of Sciences, adviser Zdeněk Herman; at FHI since 2003; previously Senior Research Fellow and Lecturer at Harvard University)
- Infrared Excitation of Gas-Phase Molecules and Clusters, led by Gert von Helden (PhD in Chemistry 1994, University of California at Santa Barbara, adviser Mike Bowers; at FHI since 2003; previously Research Scientist at FOM Rijnhuizen)
- Electronic Structure of Surfaces and Interfaces, led by Karsten Horn (PhD in Physical Chemistry 1976, University of London, adviser John Pritchard; at FHI since 1976)
- Manipulating the Motion of Large Molecules, led by Jochen Küpper (PhD in Chemistry 2000, Universität Düsseldorf, adviser Karl Kleinermanns; at FHI since 2003; previously Post-Doc at FOM Rijnhuizen)
- Cold and Controlled Collisions, led by Bas van de Meerakker (PhD in Physics 2006, University of Nijmegen, adviser Gerard Meijer; at FHI since 2003)
- Atom and Molecule Optics, led by Wieland Schöllkopf (PhD in Physics 1998, University of Göttingen, adviser Peter Toennies; at FHI since 2003; since 2008, scientific head of the FHI free electron laser project; previously a Feodor Lynen Fellow at Harvard University)

Department of Physical Chemistry

In the centennial year of the Institute, the Department of Physical Chemistry was still in transition, following the appointment in 2008 of Martin Wolf as successor to Gerhard Ertl. Since his arrival, the Department has occupied a temporary laboratory space, which is to be replaced by a new building (to be completed in 2013) that will provide a dedicated infrastructure necessary for laser and scanning tunneling microscopy experiments.

Researchers in the Department of Physical Chemistry investigate the dynamics of elementary processes at surfaces and interfaces, and in solids, with the objective of developing a microscopic understanding of the dynamics of electronic excitations, energy transfer processes and photoinduced surface reactions, as well as processes occurring at a single-molecule level. These elementary processes take place on ultrashort time scales (typically on the order of pico- to femtoseconds) and on atomic length scales (typically on the order of Ångströms). To attain the requisite temporal and spatial resolution, Martin Wolf and his coworkers have implemented an array of ultrafast laser spectroscopy and scanning probe microscopy techniques.
To date the Department’s research has focused on:

- Ultrafast Dynamics in Solids and at Interfaces
- Molecular Processes at Surfaces
- Complex Dynamics

A core activity of the Department is the study of the dynamics of elementary processes at surfaces, interfaces and in solids by ultrafast, time-resolved laser spectroscopy. Wolf and coworkers have employed a broad spectrum of time-resolved techniques to study the dynamics of electron transfer, solvation processes and vibrational excitations at adsorbate-covered surfaces, photo-induced surface reactions as well as the dynamics of electronic excitations, scattering processes and low-energy excitations in solids. The mechanisms of optically-induced phase transitions in highly-correlated materials have received particular attention. On the other hand, molecular processes at surfaces have been studied on a single-molecule level. Scanning probe microscopy (in part combined with optical excitation) has allowed imaging, manipulation and spectroscopy, as well as initiation and probing, of chemical processes on well-characterized surfaces. Further activities of the department have entailed the study of complex systems and nonlinear dynamics, in part related to nanobiology and to electrochemistry, as well as theoretical studies of reactive soft matter, individual molecular machines and of their networks, complemented by studies of nonequilibrium pattern formation in electrochemical systems and of general aspects of chemical kinetics. As part of the research on ultrafast dynamics in solids, time-resolved studies of correlated materials were launched recently and will be highlighted here to illustrate one of the new lines of research taking shape under Martin Wolf.

Inherent to any multi-electron system, electronic correlation effects are key to chemical bond formation and optical excitation of molecules, as well as the electronic and magnetic properties of solids. A simple, but fairly accurate predictive model of the electronic structure of solids assumes that the electrons move independently of one another in an effective periodic potential defined by the ions of the crystal lattice and the mean interaction of the electrons among themselves. This model, combined with the Pauli principle, leads directly to the electronic band structure of solids, which allows us to understand, among other things, the origins of metallic, semiconducting and insulating behavior. However, the independent-electron approximation neglects effects resulting from correlations and interactions among the electrons, i.e. the effects the quantum state of one electron, e.g. its spin, bear on the dynamics of the other electrons in a solid. These electronic many-body effects are at the heart of such striking solid-state phenomena as superconductivity and ferromagnetism. In the case of ferromagnetism, the interplay between the electrostatic and exchange interaction (enshrined in the Pauli principle) results, in certain materials at subcritical temperatures, \( T < T_c \), in an ordering of all the electron spins along a single direction. Raising the ferromagnet’s temperature leads to the excitation of spin waves,
which diminishes the magnetic order and, above the critical temperature $T > T_c$, induces a phase transition to a magnetically disordered state. In superconductors, an attractive interaction between two electrons (typically with opposite spins and velocities) leads to the formation of Cooper pairs, which condense into a distinct ground state whose electrical resistivity vanishes. For high-$T_c$ superconductors, the exact nature of the electron-pairing interaction has not yet been understood and thus represents one of the outstanding problems in solid state physics.

The independent electron approximation, in its simplest form, also neglects the dynamic interaction of the electrons with the ion lattice and so leaves out any lattice distortions that may arise in response to the quantum state of the electrons. This is a serious shortcoming of the model in certain situations, as the interactions of electrons with the collective excitations (phonons) of the lattice are responsible for a wealth of intriguing solid-state phenomena. One prominent example is the formation of charge density waves (CDW), which, at low temperature, give rise to an insulating phase characterized by the formation of an electronic band gap at the Fermi level that precludes electron transport; as a result, the electric conductivity vanishes at low $T$. The driving force behind this phenomenon is the minimization of the total energy of both the electrons and the lattice ions through a periodic lattice distortion. This periodic distortion leads, in turn, to a reduction of the electronic energy and the opening of the band gap, a mechanism which is often referred to as the “Peierls instability.” Above a critical temperature, $T > T_c$, the CDW system undergoes a phase transition to a metallic state in which the lattice distortion is lifted. Thus CDW materials, like superconductors, exemplify solids where correlation effects or electron-phonon interactions result in a temperature-induced phase transitions – sudden and pronounced changes of their physical properties, such as magnetization or electric conductivity, at a characteristic critical temperature.

Under typical experimental conditions, CDW systems undergo quite slow temperature changes and thus tend to be close to thermodynamic equilibrium. Researches in the Department, however, are exploring what new insights into the dynamics of these systems might be obtained by knocking them rapidly out of equilibrium – on a timescale much shorter than the time required for the system to re-equilibrate. Such a sudden perturbation could be realized by ultrashort laser excitation, which couples differently to the electronic, spin and lattice degrees of freedom. Since relaxation processes in solids typically occur on femtosecond time scales, laser pulses with a comparable pulse duration have to be used for the excitation (note that in 100 fs, light covers the distance equal to the diameter of a human hair). The light pulses used for such experiments span, respectively, the frequency and pulse duration range from THz to X-ray and from picoseconds to attoseconds. Together with ultrashort electron pulses for diffraction experiments, such schemes have been making their way into the Department’s laboratories as well.

One effective means to investigate ultrafast processes has been the pump-probe technique, shown schematically in Fig. 6.14: A 'pump' laser pulse excites the
sample, for instance, heating up the electrons or driving the electron spins out of their equilibrium orientation. In order to analyze the time evolution of the resulting nonequilibrium state, a second, ‘probe’ laser pulse hits the sample after a variable time delay, $\Delta t$. This pulse monitors the transient changes of the system’s properties. Varying the time delay $\Delta t$ makes it possible to map the evolution of the system step by step. Depending on the experimental conditions and the properties to be monitored, the materials’ response is detected by a probe pulse via a variety of methods, including optical reflection, absorption or transmission, non-linear optical frequency generation, spatially resolved light scattering, or angle-resolved photoelectron spectroscopy, to name only those employed in the Department.

The use of the pump-probe technique to study the dynamics of correlated materials is illustrated below for the case of two systems: In the first example, Wolf and coworkers excited the electron spins in antiferromagnetic NiO using an ultrashort magnetic field pulse at a Teraherz frequency resulting in a precessional motion of the spins spanning exactly six periods. In the second example, Department members induced an insulator-to-metal transition in TbTe$_3$ with an intense femtosecond laser pulse and observed the ensuing transient changes in the electronic band structure.

The goal of the first experiment was to control the magnetic state of a solid on an ultrafast timescale. The magnetization was varied by applying a torque induced by a time-dependent external magnetic field, whose frequency, set to be in resonance with the spin system, ensured an efficient energy transfer to the solid. Such a resonant excitation induces a precession of the spins around an equilibrium axis, similar to that of a gyroscope acted upon by a mechanical torque. In contrast to ferromagnets, antiferromagnetic materials exhibit high resonance frequencies, which implies a faster energy transfer to the spins. At temperatures below $T_c = 623$ K NiO is an antiferromagnet with an exchange-interaction driven antiparallel ordering of spins of nearest-neighbor Ni$^{2+}$ ions. Figure 6.15 shows experimental data illustrating the control of the electron spin dynamics in an NiO single crystal by an ultrashort magnetic field pulse. The spin dynamics was probed via the Faraday effect, which resulted in a rotation of the polarization plane of the probe pulse and was proportional to the transient magnetization. The magnetic field pulse was derived from an intense THz pulse (with
Fig. 6.15. Ultrafast spin precession in NiO: (a) Crystal structure of NiO with antiparallel electron spin ordering between the Ni$^{2+}$-lattice planes. The green arrow shows the direction of the incident THz beam. (b) Magnetic field $B(t)$ and (c) Spectrum of the intense THz pump pulse. (d) Time evolution of the induced magnetization at the precession frequency of 1 THz. (e) Control of spin precession by double pulse excitation. The precession was “switched off” after 6.5 cycles by the second THz pulse which had arrived after a time delay $\Delta t = 6.5$ ps.

a duration of about 1 picosecond), which carried a magnetic field of about 0.15 T and an electric field of 0.5 MV/cm at the peak intensity. Its broad frequency spectrum ranged from 0.5 to 2.5 THz and thus covered the spin resonance of NiO at 1 THz.

Figure 6.15(d) shows the time evolution of the magnetization probed by the Kerr effect. The magnetization exhibits pronounced oscillations whose period immediately after the arrival of the pump pulse is 1 ps. This corresponds to an induced precessional motion at the resonance frequency of 1 THz, which decays within about 30 ps. Measurements carried out as a function of the fluence of the pump pulse demonstrate that the spins were actually excited by the magnetic field of
the THz pulse rather than its electric field, which is not absorbed by NiO due to a large band gap. This result refuted a common assumption that the effects of magnetic fields on matter are negligible at frequencies above 1 GHz and that the light–matter interaction is dominated by the electric field.

Intense THz magnetic field pulses allowed not only the induction of spin precession but also its extinction on demand. This was achieved by exciting the sample by a pair of THz pump pulses which were delayed with respect to one another: the second, delayed pulse induced a precessional motion that was out of phase with the precession due to the first pulse, and thereby “stopped” the spin precession. This is shown in Figure 6.15(e) for a pump pulse pair delayed by 6.5 precession cycles. Similar sequences of pulses (of much lower frequencies) have been used in nuclear spin resonance to investigate molecular structure. The extension to the THz domain (THz-ESR) would require, however, magnetic field strengths about 100 times stronger than currently available in the Department.

The second example is concerned with the dynamics of photoinduced phase transitions in a CDW material, probed by observing changes in the materials’ electronic band structure. A textbook example of solids exhibiting CDW behavior are tri-tellurides, RTe₃, with R = lanthanide. At low temperature, these are characterized by the opening of an electronic band gap along a particular crystal direction, which endows these materials with highly anisotropic electric transport properties. The band gap opening is driven by a periodic lattice distortion in the crystal and gives rise to a “Peierls instability.” Above a critical temperature, the lattice distortion is lifted and the band gap closes again, restoring the metallic phase. By substituting different lanthanides, members of the Department have been able to control the width of the band gap and thus the critical temperature (T_c ≈ 340 K for TbTe₃).

As the opening of a band gap is primarily an electronic phenomenon, it could occur, in principle, as fast as an electronic excitation, which, owing to the small mass and energies of electrons in solids, takes place on a femtosecond time scale. However, if the changes of the electronic band structure were governed by a lattice distortion (i.e., by the motion of the lattice ions), the time scale of the CDW phase transition would be dictated by the much slower rate of the ionic motion (or frequency of the CDW mode), typically several hundred femtoseconds. Thus techniques capable of time–resolving the dynamics of the photoinduced phase transition have the ability to reveal whether the transition is driven by a (slow) lattice distortion or by an (ultrafast) rearrangement of the electrons. Wolf and coworkers have investigated the time dependence of the dynamics and the mechanism of the CDW transition on the requisite, ultrafast time scales. In their experiments, they made use of a modified pump–probe scheme based on photoemission spectroscopy, see Fig. 6.16. An infrared pump pulse excited the electronic structure of TbTe₃ with an excitation density sufficient to induce an insulator–to–metal transition. The concomitant changes of the electronic structure were detected by angle–resolved photoelectron spectroscopy, which probed directly the electronic band structure, E(k), by measuring the electron energy E and momentum k in the
Fig. 6.16. Probing the transient electronic structure of TbTe₃ in the course of its ultrafast insulator-to-metal transition induced by femtosecond-laser excitation: (a) Time- and angle-resolved photoemission spectroscopy. A TbTe₃ sample was excited by an IR pulse ($hν_{\text{Pump}} = 1.5$ eV, about 50 fs duration) and probed after a time delay $Δt$ with a UV pulse ($hν_{\text{Pump}} = 6$ eV, about 90 fs duration). The photoelectron intensity and kinetic energy $E_{\text{kin}}$ were measured as a function of the emission angles ($α$, $θ$). (b) Insulator-to-metal transition: Above the critical temperature $T_c$ (or 100 fs after laser excitation) the band gap of the CDW phase closes. (c) “Snapshots” of the electronic band structure $E(k)$ in TbTe₃ for different time delays $Δt$. After laser excitation, the gap has closed and the band dispersion near the Fermi level, $E_F$, changed after a time delay of 100 fs. Such a delayed collapse of the band gap is characteristic of the “Peierls type” mechanism (see text).

crystal planes, see Fig. 6.16(a). With such an ‘IR-pump’ – ‘photoemission probe’ scheme, a movie of the electronic band structure $E(k)$ could be recorded, with each frame showing the transient population and the changed electronic band structure $E(k)$ at a given time.

Figure 6.16(c) shows five “snapshots” of the temporal evolution of the electronic band structure of TbTe₃ following upon femtosecond-laser excitation of the sample. Remarkably, the electronic structure remained nearly intact immediately after the laser excitation pulse hit ($Δt = 0$), and it took about 100 fs for a substantial modification of the band dispersion around the Fermi energy ($E_F$) to occur. The observed modification to a nearly free-electron-like dispersion is characteristic for a metallic (conducting) behavior and hence for a closing of the system’s CDW gap. That the delayed collapse of the gap only occurred after a time delay of 100 fs proved that the electronic structure change was associated with the nuclear
rather than electronic motion, thus conforming to the “Peierls type” mechanism. Furthermore, a detailed analysis of the transient changes of the electronic structure revealed oscillations arising from a vibrational mode in TbTe₃ (identified as the amplitude mode of the charge density wave), which could be attributed to the periodic lattice distortion of the CDW phase. The frequency of this mode, of about 2.5 THz, is consistent with the observed time delay of $\Delta t = 100$ fs required for the closing of the CDW gap.

The technique of time-, energy- and momentum-resolved photoemission spectroscopy has provided direct insights into the dynamics of the electronic structure of solids. In particular, the influence of electron-phonon coupling and other collective excitations on the (single-particle) band structure of solids could be observed directly through time-domain measurements. In future work, Wolf and coworkers will extend this technique by implementing new generation schemes for ultrashort VUV pulses, selective excitation of low energy modes and spin-resolved detection to obtain a complete picture of the electron dynamics in solids throughout the Brillouin zone.

The Director of the Department of Physical Chemistry is Martin Wolf, born in 1961 in Schwabach. He studied Physics at the Freie Universität Berlin and completed his PhD thesis at the FHI on surface photochemistry under Gerhard Ertl in 1991. In 1991–92 he was a Feodor Lynen Fellow at the University of Texas at Austin. Back at the FHI in 1992 as a staff scientist, he launched his research on ultrafast spectroscopy. Prior to his appointment in 2008 as a Director at the FHI, he held a Professorship in Physics at the Freie Universität Berlin (2000–2010).

The following research groups are currently supported by the Department of Physical Chemistry:

- Spatiotemporal Selforganization and Electrochemistry, led by Markus Eiswirth (PhD in Chemistry 1987, Ludwig-Maximilians-Universität München, adviser Gerhard Ertl; at FHI since 1990, previously Postdoctoral Fellow at Stanford University)

- Structural and Electronic Surface Dynamics, Max Planck Research Group led by Ralph Ernstorfer (PhD in Physics 2004, Freie Universität Berlin, adviser Frank Willig; at FHI since 2010; previously Postdoctoral Associate at the Max Planck Institut for Quantum Optics, Garching)

- Surface Femtochemistry and Ultrafast Carrier Dynamics, led by Christian Frischkorn (PhD in Physics 1997, Universität Göttingen, adviser Udo Buck; at FHI since 2008; previously Group Leader at the Freie Universität Berlin)

- Nanoscale Science, led by Leonhard Grill (PhD in Physics 200, Laboratorio TASC Trieste and University of Graz, adviser Silvio Modesti; at FHI since 2008; previously Research Group Leader at the Freie Universität Berlin)

- Time-resolved Second Harmonic Spectroscopy, led by Alexey Melnikov (PhD in Physics 1998, Moscow State University, adviser Oleg Aktsipetrov; at FHI since 2010; previously Group Leader at the Freie Universität Berlin)
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- Complex Systems, led by Alexander Mikhailov (PhD in Physics 1976, Moscow State University, adviser Moisej Kaganov; at FHI since 1995; previously Leading Research Associate at the N.N. Semenenov Institut for Chemical Physics, Russian Academy of Sciences)

- THz Physics, led by Tobias Kampfrath (PhD in Physics 2006, Freie Universität Berlin, adviser Martin Wolf; at FHI since 2010; previously Postdoctoral Fellow at FOM Institute for Atomic and Molecular Physics, Amsterdam)

- Dynamics of Highly Correlated Materials, led by Patrick Kirchmann (PhD in Physics 2009, Freie Universität Berlin, adviser Martin Wolf; at FHI since 2011; previously Postdoctoral Fellow at Stanford University)

- Raman Spectroscopy, led by Bruno Pettinger (PhD in Physics 1972, FHI and Technische Universität München, adviser Heinz Gerischer, at FHI since 1970)

- Electron Dynamics, led by Julia Stähler (PhD in Physics 2007, Freie Universität Berlin, adviser Martin Wolf; at FHI since 2009; previously Postdoctoral Fellow at the University of Oxford)