



Surface reaction dynamics

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The study of surface chemical reaction dynamics is crucial to many important areas of research such as heterogeneous catalysis, photocatalysis, material corrosion and etching, to name just a few. Many fundamental questions, for example mechanisms of important catalytic reactions, rely on the study of surface reaction dynamics. Prof. Gerhard Ertl's

achievements in this area exemplify the importance of this field. During the last few decades, the field of surface reaction dynamics has become one of the most active areas in fundamental physical chemistry research. Surface reaction dynamics studies also have great potential for advancing our understanding of reactions on the surfaces of nanoparticles, which is badly needed. New frontiers have been developed during the past decades. New advanced surface experimental techniques have been developed to probe surface structures and chemical reaction dynamics at a much more detailed level. More detailed dynamics on very different

surfaces can be understood from these new experiments. On the other hand, theoretical efforts in surface chemical reaction dynamics have also made significant advances, providing detailed mechanistic understanding of physical and chemical processes at different interfaces. It is quite hopeful that through detailed experimental and theoretical studies, studies of surface dynamics can reach a much higher level.

This themed issue includes nine review papers on various topics in surface reaction dynamics; three of the nine papers are tutorial reviews, written by leading experts in the field. In the first

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Xueming Yang

Xueming Yang obtained his PhD degree (1986) at the University of California, Santa Barbara. After postdoctoral work at Princeton and Berkeley, he was appointed as an associate research fellow in 1995 and became a tenured research fellow at the Institute for Atomic and Molecular Sciences in Taipei in 2000. In 2004, he moved to the Dalian Institute of Chemical Physics, Chinese Academy of Sciences. He became a fellow of American Physical

Society in 2006, and a member of the Chinese Academy of Science in 2011. His speciality is developing advanced experimental methods to investigate both gas-phase chemical dynamics and surface reaction dynamics.



Alec M. Wodtke

Alec M. Wodtke received his BA degree (1981) from the University of Utah in Chemistry. He obtained his PhD degree (1986) in Physical Chemistry from UC Berkeley. From 1988–2010, he was on the faculty of the Department of Chemistry & Biochemistry at the University of California, Santa Barbara. In 2010, he was awarded the prestigious Humboldt Professorship, which he assumed at the Georg-August University (Göttingen), also simultaneously

being appointed as a director at the Max Planck Institute for Biophysical Chemistry. He is known for his work in the field of experimental chemical dynamics, especially concerning vibrationally excited molecules on surfaces.

paper, Diesing and Hasselbrink (DOI: 10.1039/c5cs00932d) have reviewed recent progress in the study of surface metal heterostructures, such as metal–insulator–metal, metal–semiconductor and metal–semiconductor oxide–semiconductor heterostructures, which have been used to gain insights into the understanding of energy and charge transfer processes in surface chemistry on these surface structures, particularly on the topic of surface chemical reaction induced non-adiabatic processes that lead to the creation of electron-pairs and the dynamics of related energy and charge redistribution.

In the second paper, Wodtke (DOI: 10.1039/c6cs00078a) has focused this review on the topic of electronically nonadiabatic interactions between molecules and metal surfaces. Such nonadiabatic interactions are well known, particularly in the interaction between diatomic molecules and metal surfaces that molecular vibration can be strongly coupled to the electrons of the metal. However, how the coupling of nuclear motion to electrons can influence chemical reaction probabilities is still not well understood. This review has provided detailed accounts on this issue and discussed how the electronically non-adiabatic influence of chemical reactions can be clearly demonstrated.

In the third paper by Morris and co-workers (DOI: 10.1039/c5cs00375j), recent advances in the heterogeneous chemistry of the most important atmospheric oxidants, O₃, NO₃, and OH, have been reviewed. These oxidants play a central role in atmospheric chemistry, aerosols and the oxidation of materials. The paper provided a comprehensive review on the recent experimental and computational studies on the detailed reaction mechanisms and kinetics for gas-phase oxidants' interactions with organic surfaces, using new research methods crossing the boundary between surface science and atmospheric chemistry. It is encouraging to see that such research will provide a more accurate and complete description of atmospheric chemistry.

In the chapter by Yang and coworkers (DOI: 10.1039/c5cs00448a), they have provided a comprehensive review on the recent studies of elementary reaction

processes of photocatalysis of important molecules such as water and methanol on single crystal TiO₂ surfaces. The review is focused on studies of the rutile TiO₂(110) surface, but some results of other TiO₂ surfaces are also provided. These studies have provided fundamental insights into the elementary chemical processes important to photocatalysis on TiO₂, which will stimulate further investigation into this important area. At the end of the review, a new dynamics-based photocatalysis model based on recent experimental studies has also been discussed, pointing out the need for more definitive surface chemistry studies in photocatalysis.

In the fifth paper by Kroes and Díaz (DOI: 10.1039/c5cs00336a), they have reviewed the state-of-the-art dynamics calculations on the reactive scattering of H₂ from metal surfaces, which is an important model system of elementary reactions in heterogeneous catalysis, using both quantum and classical dynamics methods. These theoretical studies are performed within the Born–Oppenheimer static surface model. Most calculations are based on potential energy surfaces or forces computed with density functional theory (DFT) within the generalized gradient approximation to the exchange–correlation energy. The paper also describes the accurate methods that have become available for molecule–surface interaction in global PESSs. It is now possible using these newly developed tools to study the dynamics of the H₂ + metal surface reactions with chemical accuracy, providing deep insights into the fundamental mechanism of this model surface chemical reaction.

In the paper by Guo and coworkers (DOI: 10.1039/c5cs00360a), they have focused on the topic of dissociative chemisorption processes that are the initial and rate-limiting step in many heterogeneous processes. In this review, they have shown overwhelming experimental evidence that dissociative chemisorption is non-statistical in nature, and excitations in different vibrational modes have a huge effect on reactivity for chemisorption. Quantum dynamics methods can now be used to investigate this process. The review provides an overview on recent

progress made in this area, especially in constructing high-dimensional potential energy surfaces for polyatomic molecules on transition metal surfaces and in quantum dynamical studies of dissociative chemisorption on these potential energy surfaces. Mode and bond selectivity in dissociative chemisorption are emphasized in the paper and are discussed using the recently proposed sudden vector projection model.

Faust and Nathanson (DOI: 10.1039/c6cs00079g), in their tutorial review, have described experimental aspects of two techniques for investigating the dynamics of the interaction of gas phase molecules with liquid surfaces under vacuum conditions, liquid microjets and coated wheels. A historical survey of the two techniques is provided in this review. In addition, the strengths and shortcomings of each technique are also discussed for scattering and evaporation experiments. Finally, recent microjet studies on the energy transfer between O₂ and liquid hydrocarbons, HCl dissociation in salty water, and super-Maxwellian helium evaporation have been presented.

In the review by Hase and coworkers (DOI: 10.1039/c5cs00482a), two aspects in the simulations of collisions of protonated peptide ions, peptide-H⁺, with organic surfaces have been presented. The first aspect is a detailed description of the classical trajectory chemical dynamics simulation methodology, such as MM, QM + MM, and QM/MM, to investigate the peptide-H⁺ + surface collision. In another aspect, a few examples are provided from the theoretical simulations on energy transfer, surface-induced dissociation, soft-landing, and reactive-landing for peptide-H⁺ + surface collisions. These simulations are in good agreement with experiment, thus providing atomistic interpretations of the peptide-H⁺ + surface collision dynamics.

In the final paper in this themed issue, Chadwick and Beck (DOI: 10.1039/c5cs00476d) present a tutorial review of their quantum state resolved experiments designed to investigate gas–surface reaction dynamics. The experimental techniques used for state specific reactant preparation and for the detection of surface bound reaction products developed

in their laboratory are also described in detail. The review also provided excellent examples of the studies of methane reactions on Ni and Pt surfaces, which show clear evidence of vibrational mode specificity and bond selectivity, as well as steric effects in chemisorption reactions. These state-of-the-art experimental investigations provide important benchmarks for developing a detailed microscopic understanding of chemical reactivity at the gas–surface interface.

From the nine reviews in this themed issue, which only represent a small part of the research carried out in the field, we can see that surface reaction dynamics studies have gone far beyond the boundary of traditional surface chemistry, which is more related to heterogeneous catalysis.

Not only can we now study gas phase interactions with metal surfaces at the quantum state specific level, studies on the dynamics of molecular interactions on liquid surfaces, aerosols and organic surfaces can also be carried out in great detail using various techniques. This shows that surface reaction dynamics has a more broad impact in the study of chemistry in different areas.

Another important trend in surface reaction dynamics is the study of nonadiabatic surface dynamics in both thermal and photoinduced chemical reactions on surfaces, and the experimental results show that nonadiabatic surface processes are important in catalysis and photocatalysis. We have also seen more powerful and accurate theoretical tools have been

developed to understand surface chemical reactions at the atomic and molecular level. These developments have pushed the study of surface reaction dynamics to a new level. However, there are also great challenges in this field. Firstly, even though we have made significant progress in the study of surface reaction dynamics under well-controlled conditions, studies of surface dynamics under more complicated conditions are still lacking. Secondly, theoretical surface dynamics require more accurate and powerful tools to study surface processes with chemical accuracy (~ 1 kcal mol⁻¹). We hope we can directly meet these challenges in the study of surface reaction dynamics through the development of new experimental and theoretical methods.