

Probing Chemical Dynamics at Surfaces

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An account is given of recent progress concerning chemical reaction dynamics at surfaces. The goal is to elucidate the reaction dynamics at the molecular level, both as time and distance is concerned. The methods of study include molecular beam scattering, scanning tunnelling microscopy, and (femtosecond) laser spectroscopy. Systems studied include elementary interactions of NO, CO, and O₂ at single crystal metal surfaces.

Keywords Chemical reaction dynamics, surface science, molecular beam scattering, scanning tunnelling microscopy, laser spectroscopy, metals, single crystal

The progress in synthetic organic chemistry has been spectacular in recent years, as exemplified in the present proceedings. Molecules of ever increasing complexity can be made. Likewise in catalysis, progress has been great; more complex materials are being used for catalytic purposes and novel catalysts are synthesised. In many cases progress is dictated by experience, intuition and trial and error. However, the understanding of the mechanism of a catalytic reaction is not available for many applications and cannot be obtained by the synthesis of novel catalysts. In particular, for applications in for instance the automotive industry, the demands on the catalysts is increasing to such an extent, that true 'atomic engineering' is desired to fully control the catalytic process. It is safe to say that the semiconductor industry manages to achieve such control at the nanoscopic level in a more refined fashion than the catalytic chemists.

There are several routes to a detailed microscopic

understanding of surface reactions: first of all, modelling of catalytic reactions at the molecular level is necessary.^{1,2} In this case the force field or potential energy surface governs the motion of the reactants, either through the Newtonian dynamics or even through the quantum mechanics of molecular motion on this force field. Thus information is obtained on a molecular distance and time scale. The theorists are capable of making 'real time movies' of how reactants move through a transition state to a final product. These movies are conceptually very useful. They show chemists how to envision the progress of a chemical reaction and develop an intuition about the transition states or bottlenecks of chemical reactions.

It is essential to test these modelling results experimentally. This should not be done at the level of overall rates, because very different microscopic dynamics can fortuitously lead to the same overall 'macroscopic' kinetics. Experiments should test theories directly at the molecular level. In addition, such experiments should indicate to theorists what the important elements of their theories should be, and what kind of simplifications are allowed. In this way, experiments also lead to new concepts concerning reaction dynamics.

What is the ideal experiment? This would be a movie camera that makes snapshots of chemical reactions while they pass through the transition state and do this with resolving power at the molecular level. This means a length resolution on the order of a fraction of a nanometer and a time resolution of tens of femtoseconds. The latter time is the vibrational period of a simple di-

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atomic molecule like O_2 or NO . To reach this goal ultra-fast spectroscopic tools are required that can distinguish individual atoms or molecules. Such tools are available.

To study chemical reactions in detail at the molecular level often implies that surface analytical tools are required, that operate in ultra high vacuum (UHV).³ This is a high price to pay, since most chemical reactions of practical interest are not carried out in vacuum, but rather at high pressures. Here the field of semiconductor manufacturing is in a better position, because here increasingly so called dry processing is used which is carried out in vacuum. Analysis of a process concerning semiconductor manufacturing is often easier by the tools of modern surface science, because the process concerned is carried out in vacuum.

To return to our ideal catalytic experiment: it has to be carried out using the tools of surface science and modern time resolved spectroscopy. Here the distance and time scales needed indeed can be reached. Scanning tunnelling microscopy (STM) allows surface studies with a resolution of fractions of nanometers. This technique is well documented in the surface science literature, see for instance recent issues of the Journals 'Progress in Surface Science' or 'Surface Science Reports'. However, the time resolution of the method is limited to microseconds at the very best. Time resolution of a few femtoseconds in surface science experiments has been obtained recently, see reference.^{4,5} In this case the lateral resolution is determined by the wavelength of the light used and is at most micrometers. Up to now, no attempt to really combine the methods has been successful. In this report I will briefly give an example of a femtosecond study of a surface reaction.

There is an other method, that gives information on dynamics at the molecular level. This is by using scattering experiments. By colliding molecular beams of reactants with a surface information about the dynamics of the molecule-surface interaction can be obtained from the scattering pattern of the molecules. This gives a direct insight into the force field at the molecular level. Scattering experiments are used by physicists to study matter at all sizes: from small dust part particles with micron size to elementary particles.⁶

It is outside the scope of this article to explain the methodology of molecular beam scattering. Briefly, a collimated stream of molecules with the same velocity is aimed at a surface in UHV. The density of the beam is

very low, equivalent to pressures around 1 mPa. After formation of the beam in a so-called supersonic free jet, the molecules do not collide with each other. The translational energy of the molecules is set by the temperature of the orifice through which the gas at high pressures (typically 1×10^5 Pa) expands supersonically into vacuum. The energy can also be adjusted by mixing molecules with light carrier gases, such as H_2 or He .⁷ The molecular beam passes through several collimating apertures, which prevent gas other than the beam to flow from high pressure regions to the UHV chamber containing the sample surface. Around the surface detectors capable of detecting individual molecules can be rotated to monitor the reflection pattern. A schematic of a molecular beam apparatus is shown in Fig. 1(left).

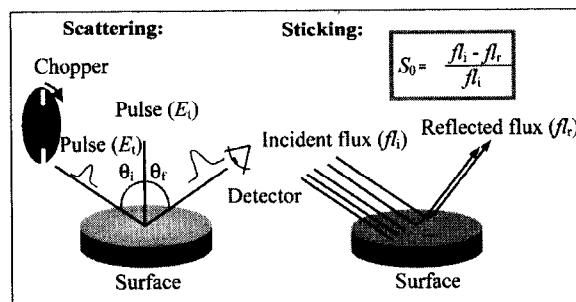


Fig. 1 Schematic diagrams of a beam surface scattering experiment (left) and a measurement of sticking coefficients using molecular beams (right).

The physical picture that arises from the analysis of the scattering patterns is shown in Fig. 2. Fig. 2A represents the situation for a molecule that hits a smooth and inert surface. Because the surface is smooth the component of the momentum along the surface p_{\parallel} is conserved as for light reflecting from a mirror. Because the molecule has a mass in the same order of magnitude as the mass of the surface atoms, the molecule can transfer perpendicular momentum p_{\perp} to the surface, or vice versa. This implies that the molecule can heat (or cool) the surface. This situation can be represented by the scattering of an ellipsoid (the molecule) from a set of flat cubes, each of which has a mass corresponding to that of a surface atom. The scattering pattern from such a surface can be computed easily when quantities like the mass ratio, the translational energy of the molecule and the surface temperature are known. The width of the resulting angular distribution $\Delta\theta$ is rather narrow when the energy of the molecule is higher than thermal. Although

this picture clearly is an oversimplification of reality it nevertheless describes the interaction between thermal

noble gas atoms and closed packed metal surfaces quite well.^{8,9}

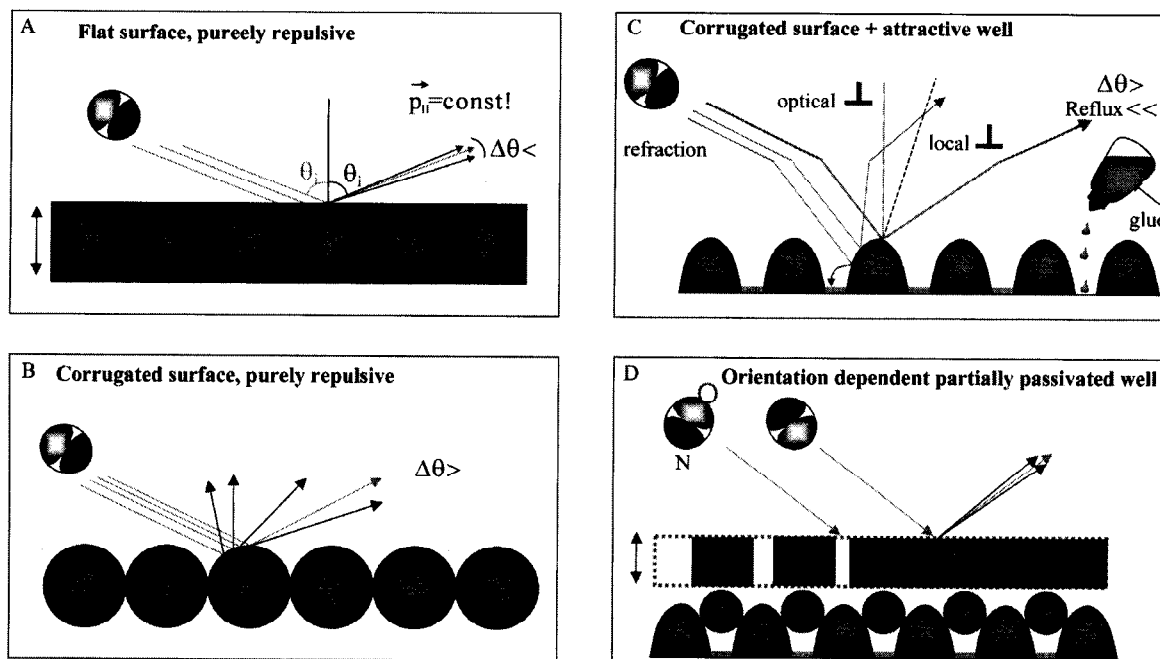


Fig. 2 Schematic diagrams of prototypes of gas-surface interactions as can be probed by molecular beams. Side views of the surface atoms or cubes are presented. A) Molecular scattering in which parallel momentum is conserved and the surface is represented by hard cubes. B) Molecular scattering from individual surface atoms. C) Molecular scattering in the presence of a strong chemisorption well. D) Molecular scattering for a partially passivated surface, containing specific sites, where chemisorption is possible. Note that in this case the interaction is also strongly orientation dependent.

Another limiting case occurs when the surface can be thought of as individual atoms, represented by little balls in Fig. 2B. In this case the velocity parallel to the surface is not conserved, and the scattering can be seen as the reflection of light from a rippled mirror, just as can be seen in case of a sunset over a quiet sea. The width of the resulting angular distribution $\Delta\theta$ is in this case broader when the energy of the molecule is higher than thermal. This situation is encountered for the scattering of fast ions from surfaces, but can all ready be seen when O_2 molecules at energies of 100 kJ/mol impinge on a Ag(111) surface.^{10,11}

In both of these cases no attractive force between molecule and surface was taken into consideration. If one does, the situation of Fig. 2C is obtained. Here 'glue' representing a attractive, chemical force is added, causing the molecules to chemisorb at the surface. The attractive force is of longer range than the re-

pulsive force and deflects the molecule towards the surface, where it collides with respect to an effective local normal. In order to chemisorb all translational energy of the molecule has to be absorbed by the surface. Since the surface is extended and has many degrees of freedom, this is often possible.

Molecular beams are particularly useful to study such absorption processes, as is depicted in Fig. 1 (right). When molecules are reflected from the surface they lead to a pressure rise in the UHV chamber surrounding the crystal.^{12,13} When the molecules are adsorbed (or pumped) by the crystal this pressure rise is absent. By measuring the pressure rise in the UHV chamber when a beam of molecules impinges on the surface the sticking coefficient S_0 of the surface can be measured for various conditions of the incident beam. This sticking coefficient is a quantity that, on the one hand can be computed using molecular dynamics simula-

tions, and on the other hand is often the rate determining step in a catalytic reaction in real life. As an example, the rate determining step of ammonia synthesis from N_2 on an Fe-catalyst is the dissociative sticking coefficient of N_2 on Fe.^{14,15}

An intriguing recent example of this kind of measurements and its connection to theory is the scattering of NO or CO from clean and H-covered Ru(0001).^{16,17} At the clean surface the angular distribution of scattered particles is very broad, as shown in Fig. 3. This points to a picture of a collision of the molecules at an atom-like surface, Fig. 2B. In addition, the sticking coefficient is almost unity. So most molecules are stuck in the

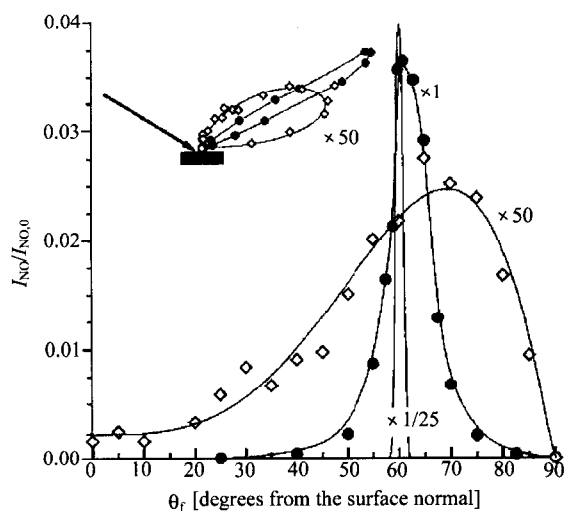


Fig. 3 Angular distributions measured for scattering of NO with a translational energy of about 160 kJ/mol from clean (open diamonds) and H-covered (full circles) Ru(0001). The sharp distribution around the specular angle of 60° indicates the angular width of the primary beam. Note the remarkable decrease of the angular width in case of H-coverage. H turns the surface into a molecular mirror (From reference 16).

attractive chemical force, that seems to be uniform over the surface; like Fig. 2C with few ‘bumps’ and lots of glue. It is well known that Ru binds CO or NO very strongly. The metal atoms are lacking their neighbours at the surface and have electrons available to form chemical bonds with reactive species from the gas phase. Recent calculations from our group confirm this picture.¹⁸ It becomes more interesting when the Ru surface is covered by hydrogen atoms. The scattering pattern changes dramatically, as shown in Fig. 3. The reflected molecules

appear in a very narrow cone around the specular direction; the hydrogen atoms have passivated the Ru surface, and turned it into a molecular mirror. One could perhaps rationalise this, by invoking that the H-atoms have formed chemical bonds with the available Ru electrons, in analogy to the case of Silicon surfaces. These Si surfaces in vacuum have directed molecular orbitals available (dangling bonds) to form a chemical bond and once chemical bonds formed, the surfaces are completely inert. This is also the case for diamond surfaces, the hardest of all. On metals, however, the electrons are delocalised and such a picture is harder to imagine. Nevertheless, to our great surprise H-covered Ru does still bind NO and CO in an activated process.^{13,16-18} This means that our surface is adsorbing molecules in one part of the unit cell, while elsewhere in the same unit cell the surface is like a mirror. Thus the character of the force field changes over distances of less than a tenth of a nanometer! The physical picture of the interaction is one of a mirror with very localised holes in it, as shown in Fig. 2D.

Density functional theory enables one to study the origin of these phenomena. It turns out that H makes the Ru surface repulsive, with the exemption of a single spot, on top of a Ru atom.¹⁸ If CO approaches this site it feels the repulsion by the three hydrogen atoms surrounding the Ru-atom. However, it is possible to ‘push these aside’ to form a chemical bond with the Ru atom. In order to form it the Ru atoms moves up out of the surface plane by about 0.06 nanometer. This is an activated process, that leads to a weak chemical bond when the surface is allowed to relax; *i. e.*, to adapt its geometry to form the strongest chemical bond. The orientation of the CO is very important in this respect. The above is only possible when the molecule approaches the surface with the C-end towards the surface. When the O-end is in front, no chemical bond is formed whatsoever. Experimentally, this can be studied for NO molecules. Using the Stark effect and hexapole lens focusing a state selected beam of NO molecules can be prepared that can be oriented in front of the sample surface.¹⁹ Such experiments show that there is a very strong orientation dependence of the interaction. This is very reasonable, because it is known that NO and CO always bind through their N- or C-end. Such experiments with oriented beams also indicate that in many cases molecules reorient themselves before they form a chemical bond. In other

words, NO oriented sideways with the O-end down can reorient itself on a femtosecond timescale, so that it can form a bond with the reactive N-end.²⁰ This phenomenon is also known as 'steering'.^{21,22} The experiments and their analysis shows that the bonding of the NO molecule is very orientation dependent. In Fig. 2D this is indicated by the fact that for the O-end down molecules no binding sites or holes exist.

From the examples given above it is clear that it is possible to obtain a detailed picture of the atomic scale potential energy surface and the interaction dynamics from the analysis of molecular beam scattering experiments. The examples refer to the direct formation of bonds, or to a direct scattering or reflection event. In some cases molecular beam experiments provide more information about the reaction dynamics, albeit in a more indirect fashion. An example of this is the dissociative chemisorption of O₂ on Ag surfaces.^{11,23} This process by itself is exothermic, but the dissociative sticking coefficient is on the order of 10⁻⁶ for thermal energy oxygen. Detailed analysis in our group has shown that the first step in dissociative chemisorption is molecular chemisorption of O₂ in a state with a strongly decreased molecular bond strength, a state often referred to by O₂⁻.²⁴⁻²⁶ There is an activation barrier to be overcome with a height of more than 30 kJ/mol. Accelerating the O₂ in the molecular beam to this energy allows this barrier to be overcome without any problem on Ag(110).²⁷⁻³⁵ Subsequently, the O₂⁻ bond needs to be broken and Ag—O bonds formed. The Ag—O at the surface forms so-called —Ag—O—Ag—O—Ag— added rows. Here molecular beam studies indicated a curious phenomenon: the sticking coefficient for dissociative chemisorption drops by two orders of magnitude when covering the surface with a few percent of atomic oxygen.²⁸ A second observation was made by STM: the Ag-atoms needed in the added Ag—O rows were obtained from step edges, pits and imperfections at the surface.^{36,37} The surface is incapable of giving up Ag-atoms from the flat terraces. Putting all of this information together yielded the following 'ruin game' model, depicted in Fig. 4.³⁸ O₂ molecules impinge on a silver surface and form molecularly chemisorbed O₂⁻ when the translational energy is high enough to overcome the activation barrier. These O₂⁻ species diffuse over the surface and have a probability to desorb as O₂ from the terraces. This probability is

dramatically enhanced if the O₂⁻ meets an oxidic Ag—O added row. Only when the O₂⁻ manages to reach a step edge, it dissociates, 'picks up' Ag and inserts into the added row. It is clear that when a high density of added rows is present at the surface the probability of forming O-atoms at a step edge from a chemisorbed O₂⁻ is greatly reduced. The model described above could be easily formulated analytically using statistical theory, and the experimentally observed coverage dependence of the dissociative sticking coefficient could be reproduced very nicely. This shows that again molecular beams studies can give strong clues to the nature of the chemical dynamics at the molecular level.

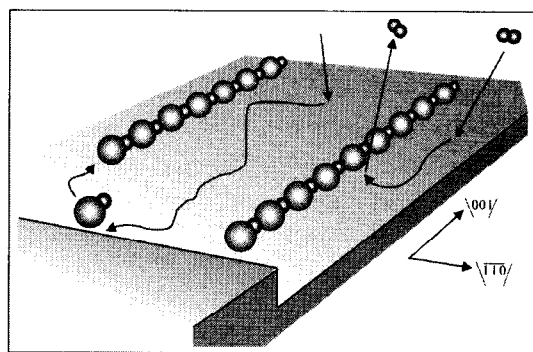


Fig. 4 Ruin game model for dissociative chemisorption of O₂ on Ag(110) (From reference 38).

The ultimate experiment would involve a direct observation of a molecule while forming a chemical bond. Molecular beams will never achieve this goal, because the observation of the scattered particle is made long after the scattering event, not during the scattering event. Recently, the use of ultra-fast laser spectroscopy has come to a help here. Often such experiments are set up as a pump-probe events.³⁹ A fast laser pulse energises a molecular systems that is adsorbed and in equilibrium at a surface. A good example is the co-adsorption of CO and O-atoms at a Ru(0001) surface.⁴⁰ For this system, there is a high barrier towards CO₂ formation, and the reactants can co-exist at the surface. A fast laser pulse heats the surface, both the electronic and the phonon (lattice vibration) system. This provides sufficient energy that the reaction can proceed. A competing channel is to desorb the CO. By monitoring the CO₂ desorption, or by measuring the infrared absorption spectrum of the CO on a femtosecond timescale will allow one eventually to monitor how bonds are broken and bonds are formed in

real time. It is clear that a very broad field of research is only now opening up here and that there is a lot of promise for the future.

Hopefully, this report has demonstrated that is possible to obtain detailed information on the dynamics of chemical reactions at surfaces at the molecular level. The insight obtained is detailed and deep. The price to pay for it is, that only model reactions under very suitable conditions can be studied. It is hoped that such studies will contribute to better understanding of catalytic reactions at surfaces and that true 'atomic engineering' of catalysts based upon understanding at the molecular level will become possible.

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