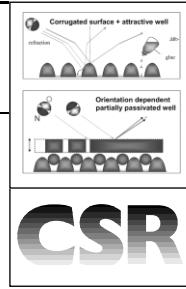


Molecular beams and chemical dynamics at surfaces

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Received 25th July 2002

First published as an Advance Article on the web 23rd January 2003

The use of molecular beams to study chemical dynamics at surfaces is outlined. The techniques is briefly introduced and its applications are given in a few areas. Scattering experiments give detailed information about the first steps toward a chemical reaction at a surface. Beams with enhanced population of specific quantum states make an even more detailed analysis possible. Adsorption at surfaces can be studied very well using beam methods, especially in the case of activated processes. Beams can be used to grow novel structures. Beams allow the study of chemical reactions at surfaces, and in particular those where product are directly ejected into the gas phase, or where reactions take place upon impact. Finally the study of liquid surfaces is briefly introduced.

1 Molecular beams, an introduction

A molecular beam is a tool for research in chemical dynamics. It is an old tool, that was introduced by Dunoyer in 1911 and expanded ever since, also in surface science.¹ Molecular beams allow the study of reaction dynamics under a variety of conditions, in the gas-phase, in clusters—mimicking liquid, and at solid surfaces. A recent book summarizes the state of the art in all those fields.² In this review I will confine myself entirely to the application of molecular beams in surface science and reaction dynamics at surfaces.

A molecular beam is a well collimated stream of gas, in which the constituent atoms or molecules do not collide with each other. In this way the stream of gas can be aimed at a specific target. There are two important aspects to molecular beams. At first they allow the study of a system, that is far away from equilibrium. This is due to the fact, that the translational and internal energy of the molecules in the beam can be independently tuned. This property makes molecular beams very useful in the study of processes, that are dominated by activation barriers. It can for certain systems be trivial to increase the reaction rate by many orders of magnitude using molecular beams. Secondly, molecular beams allow collision experiments under single collision conditions. In such experiments reactants are aimed at each other or at a surface. If a product is formed it is certain that this is due to a single reactive encounter between the reactants. In addition, scattering experiments can be performed. From the deflection of the molecules in the collision, information about the interaction and more specifically the interaction potential can be obtained.

The fact that molecular beams are streams of low density gas means that they need to propagate through a medium that does not disturb them over the length scale of the experiment. The mean free path for the propagating beam has to be on the order of meters, which means, that the beams propagate in a vacuum. In the case of a surface science experiment there is the additional constraint that the surface studied should not be contaminated by the residual gas in the vacuum through which the beam propagates. This is usually a much more stringent constraint, which means that the interaction between molecular beams and surface has to take place in ultra high vacuum (UHV), at pressures around 10^{-8} Pa, a pressure that is very far from the usual operation pressures in the chemical industry. Here reactions at surfaces are carried out all the time at the surfaces of catalysts at ambient pressures or higher.

In many cases progress in catalysis is dictated by experience, intuition and trial and error. For applications in for instance the automotive and energy producing industries, the demands on the catalysts are increasing to such an extent, that true 'atomic engineering' is desired to fully control the catalytic process. To obtain the required detailed microscopic understanding of surface reactions, modelling of catalytic reactions at the molecular level is necessary. At this level 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 in this force field. Thus information is obtained on a molecular distance and time scale. 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 one should envision the progress of a chemical reaction and develop an intuition about the transition states or bottlenecks of chemical reactions.³

It is essential to test these models experimentally. This should not be done at the level of overall rates, because very different

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nanoscopic 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 takes snapshots of chemical reactions while passing through the transition state and does 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 diatomic molecule like O₂ or NO. To reach this goal ultra-fast spectroscopic tools are required that can distinguish individual atoms or molecules. Such tools are available in 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.⁴ In this case the lateral resolution is determined by the wavelength of the light used and is at most micrometers.

Molecular beams constitute a complementary method, that gives information on dynamics at the molecular level. 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 particles with micron size to elementary particles. In all those cases the scattering experiment always can serve as a direct test of theories at the level of the particle size. Although the progress in theory is impressive, it should be tested all the time at the level where the theory is developed. Molecular beams are a very important means of reaching this goal in chemical dynamics.

This article gives a very brief overview of the use of molecular beams in surface science with a focus on chemical dynamics. In all cases only very few papers can be mentioned and those will only serve as an entry into the literature through references cited in the papers. The choice of the work cited here obviously has to be personal and biased.

2 Experimental procedures

It is outside the scope of this article to explain the methodology of molecular beam scattering. Essentially, a molecular beam is produced by letting gas expand through a small orifice into a region of lower pressure. There are two regimes of operation pressure. When the mean free path of the expanding gas is large with respect of the size of the orifice one is in the Knudsen or molecular flow regime. There are no collisions between the molecules as they leave the orifice into the vacuum chamber, and the molecules are fully equilibrated to the walls of the gas line and its orifice. The energy in the molecules corresponds to the temperature of those walls. When the mean free path of the expanding gas is small with respect to the size of the orifice one is in the supersonic flow regime. In this case there are many collisions between the molecules as they exit the orifice. The molecules will now adjust their velocities during the expansion. The velocity distribution becomes sharper than the usual Maxwell–Boltzmann distribution of an effusive source, and the

speed increases somewhat. The mean speed remains proportional to the orifice or nozzle temperature and can be adjusted this way. Due to the collisions during the expansion of the beam into vacuum the internal degrees of freedom of the molecules, in particular rotation, are cooled very efficiently and the energy is transferred to translation. A very powerful way to vary the energy of the beam is to use the combination of a light carrier gas and a small percentage of a heavy seed gas. In the expansion the seed gas will approximately acquire the velocity of the light carrier gas and its energy will increase by the mass ratio. The principles of molecular beam production and operation are well documented.⁵ A typical supersonic nozzle diameter is about 0.1 millimetre and operation pressures are atmospheric.

A molecular beam introduces by definition gas into a vacuum chamber and consequently raises its pressure. A beam produced by a Knudsen source can be used under many conditions, because the amount of gas can be controlled at will. Thus Knudsen sources are used to dose gases on surfaces in a UHV chamber. For supersonic jet sources this is not possible. To obtain a good expansion a minimum gas flow is required and such a gas flow would completely destroy the ultra high vacuum around the sample surface. Therefore, the supersonic molecular beam needs collimation and differential pumping. This is sketched in Fig. 1. Here it is seen that the molecular beam passes

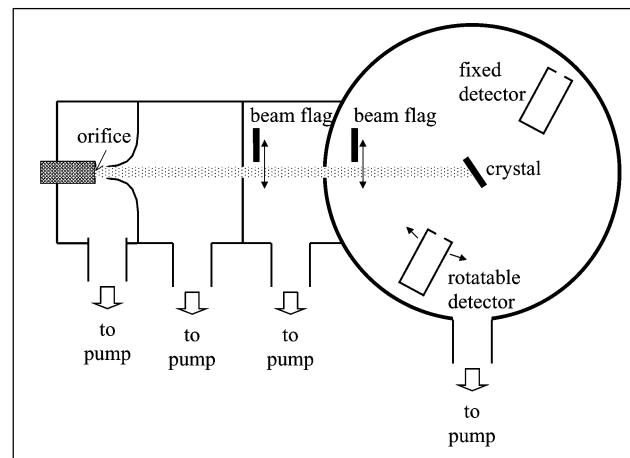


Fig. 1 Schematic diagram of a molecular beam machine. A gas at elevated pressure emanates from an orifice. The gas stream is collimated in three differential pumping stages to reduce the gas load on the target chamber. Only the part of the gas stream that reaches the target though all collimators is indicated as shaded. In the UHV target chamber a crystal is positioned in the beam path. The pressure and the target chamber and particles reflected or desorbed from the sample surface are detected by particle detectors. Inert beam flags can be moved into the beam to determine the beam intensity and the sticking coefficient.

through several collimating apertures, which prevent gas other than the beam flowing directly to the crystal to reach the UHV chamber containing the sample surface. Gas hitting a collimator is scattered back into a differential pumping region and ends up in a pump. The intensity of a molecular beam depends strongly on the design of the system, but intensities of $10^{15} \text{ mol cm}^{-2} \text{ s}^{-1}$ can be achieved routinely. This corresponds to roughly one atomic layer s^{-1} .

The molecules in the beam will be partly reflected from the surface, and partly absorbed onto it. The reflection pattern (which is determined by the interaction of the molecules with the surface) is monitored by detectors capable of detecting individual molecules. Detectors that can be rotated around the surface are usually mass spectrometers with electron impact ionisation, and these are used in most cases. However, photo-ionisation of scattered molecules can often also be used to obtain state-resolved detection of heavier molecules. This generally requires lasers as light sources. The degree of adsorption (the sticking probability) can be measured by

monitoring the residual gas pressure in the chamber while beaming at the crystal under study, and comparing with the case of an inert beam flag onto which no adsorption occurs.⁶ In case of a large sticking probability the pressure will be low, since most molecules will remain on the surface.

3 Scattering studies

He diffraction

One of the first molecular beam scattering experiments ever carried out was the study in Stern's lab in Hamburg on He scattering from LiF.¹ The experiment demonstrated the diffraction of He from the LiF surface, and thus demonstrated the wave nature of a particle beam, and showed that molecular beams can be used to study surface structure due to the wavelength of a thermal He beam which is on the order of a tenth of a nanometer. An advantage over other diffraction techniques, such as electron or X-ray diffraction, is the very strong surface sensitivity of He diffraction, because the thermal atoms cannot penetrate the surface. This has led to a large number of publications of the determination of surface structures by He diffraction, which continues to today. However, determination of surface structures is not the topic of the current review, and the reader is referred to textbooks.^{7,8}

He diffraction or thermal energy atom scattering (TEAS) is not only useful to determine surface structures, but also to determine interaction dynamics at surfaces. A very recent example of this method, introduced by Poelsema and Comsa is given in a recent paper from my group, where the formation of small CO clusters on a Ru(0001) surface covered by hydrogen atoms is studied by TEAS.⁹

Heavy particle scattering, simple models

An important simplification in the analysis of He scattering is the large mass mismatch between He and most other atoms that are the constituents of solid surfaces. Therefore, energy transfer between the He atom and the surface is very much limited and elastic He diffraction or inelastic He scattering can be modelled rather easily and quantum mechanically. The situation is very different when heavier atoms or molecules are scattered from a

surface. In this case energy exchange between projectile and surface will be facile, and in most cases only classical mechanics can be used to model the interaction. Some of the physical pictures that arise from the analysis of molecular beam scattering patterns are 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 ($p_{||}$) is conserved as for light reflecting from a mirror. In the case of He scattering from close packed metal surfaces this picture may be appropriate. Molecules like CO, NO or O₂, which have masses of the same order of magnitude as the mass of the surface atoms, can transfer (or gain) perpendicular momentum (p_{\perp}) to (from) the surface. 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 if 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 if the energy of the molecule is higher than thermal ($\Delta\theta \approx 20^\circ$). 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.¹⁰

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 the case of a sunset over a quiet sea. In this case, the width of the resulting angular distribution is broader if the energy of the molecule is higher than thermal ($\Delta\theta \geq 40^\circ$). This situation is typically encountered for the scattering of fast ions from surfaces, but can already be observed for O₂ impinging on a Ag(111) surface molecules at energies of about 100 kJ mol⁻¹.¹¹

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

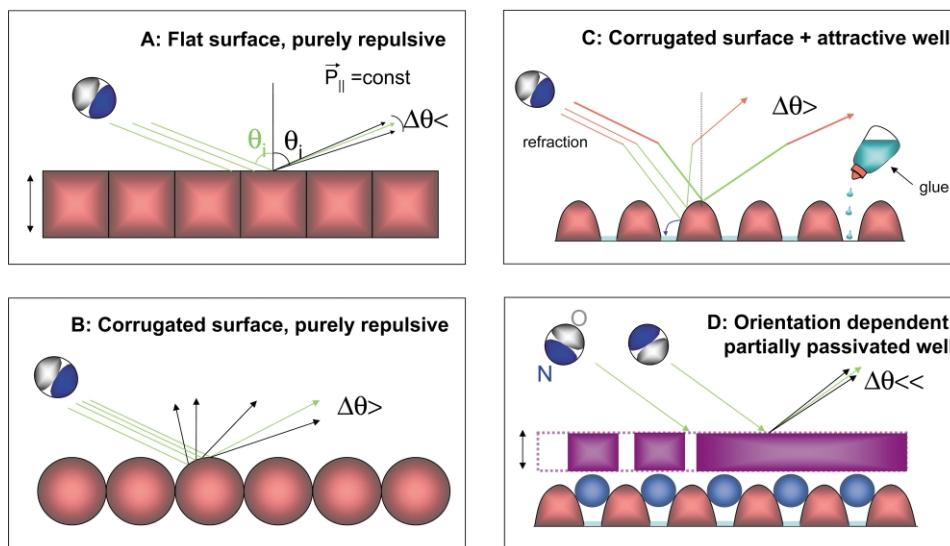


Fig. 2 Schematic diagrams of prototypes of gas–surface interactions as can be probed by molecular beams, presented as side views of the surface atoms or cubes. (A) Molecular scattering in which parallel momentum is conserved and the surface is represented by hard cubes. (B) Molecular scattering from 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. From ref. 3.

the surface is extended and has many degrees of freedom, this is often possible. In the case where the molecule does not get adsorbed a very broad angular distribution will be the result of the molecule surface collisions, see *e.g.* NO scattering from Ru(0001).¹² The data is reproduced as Fig. 3, ($\Delta\theta \approx 40^\circ$).

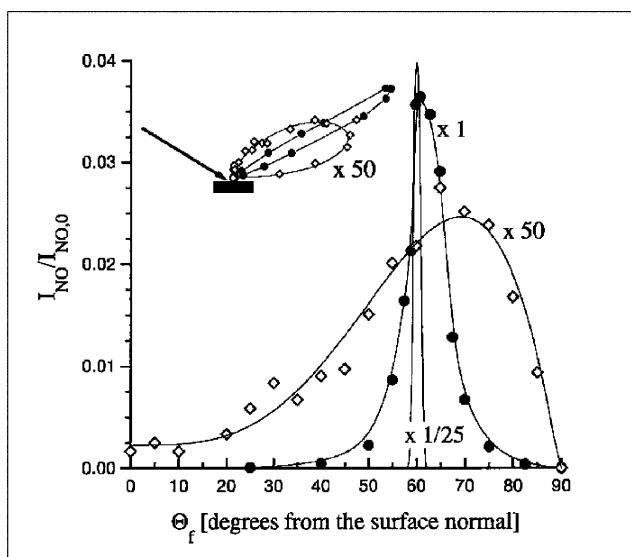


Fig. 3 Angular distributions measured for scattering of NO with a translational energy of about 160 kJ mol⁻¹ from clean (open diamonds) and H-covered (filled circles) Ru(0001). The sharp distribution around the specular angle of 60° indicates the angular width of the primary beam. Note the remarkable decrease of the angular width in case of H-coverage. Hydrogen turns the surface into a molecular mirror. From ref. 12.

The scattering of NO from a Ru surface becomes more interesting if the surface is pre-covered by hydrogen atoms. The scattering pattern changes dramatically, as also shown in Fig. 3. The reflected molecules appear in a very narrow cone ($\Delta\theta < 10^\circ$), 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 under vacuum have molecular orbitals available (dangling bonds directed away from the surface) that can actively form chemical bonds. Once chemical bonds are formed, the surface becomes completely inert. On metals, however, such a picture is harder to imagine since the electrons are delocalised. Nevertheless, to our great surprise H-covered Ru does still bind NO and CO in an activated process.¹³ 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 dramatically over distances of less than a tenth of a nanometer! The physical picture of the interaction that emerges is one of a mirror with very localised—chemically active—holes in it, as shown in Fig. 2D.

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 direct scattering or reflection events. Given the large number of degrees of freedom involved the amount of information obtained remains limited. More specific and detailed experiments are needed to unravel the intricacies of the molecule-surface interaction.

Molecular scattering, preparation and resolution of the internal states

The higher specificity of experiments can be obtained by preparation of the molecules in the molecular beams in specific

quantum states, by the detection of scattered molecules in specific quantum states, or both. The experiments in the latter cases are of enormous complexity. Both state preparation and detection usually require laser based optical methods. In the field of interaction of hydrogen with solid surfaces several experiments have been done in this area. An interesting example, including its theoretical analysis is described by Watts *et al.*¹⁴ State preparation of the molecular beam is done using stimulated Raman pumping. Detection of the scattered molecules is accomplished by resonance enhanced multi photon ionisation (REMPI). H₂ molecules are prepared in the $v = 1, J = 1$ state, with v being the vibrational and J the rotational quantum number. The molecules are detected in two rotational states of $v = 1$ and two for $v = 0$. It is found that the survival of the vibrationally excited molecules in their collision with the surface is high at low incident energies (5 kJ mol⁻¹). A theoretical analysis using wave packet calculations confirms the survival probability found, but cannot reproduce the redistribution of the energy among the available degrees of freedom in the case of de-excitation of a $v = 1$ molecule. In spite of these discrepancies it is truly remarkable how much the understanding of such interactions has advanced.

Also for heavier molecules experiments with quantum state specificity have been carried out. Geuzebroek *et al.* studied rotational excitation of state selected and oriented NO molecules with an Ag(111) and determined the orientation dependent rotational excitation by REMPI.^{15,16} It was found that rotational excitation is much stronger for the O-end of the NO molecule than for the N-end, through which the chemical bond to the surface is made.

The groups of Auerbach and Wodtke have managed to prepare molecular beams of NO in highly excited vibrational states.¹⁷ In this case a pumping and dumping scheme was used exciting the molecule to an intermediate electronic state, from which it is de-excited to a vibrationally excited ground state molecule. An example is shown in Fig. 4. Here the kinetic

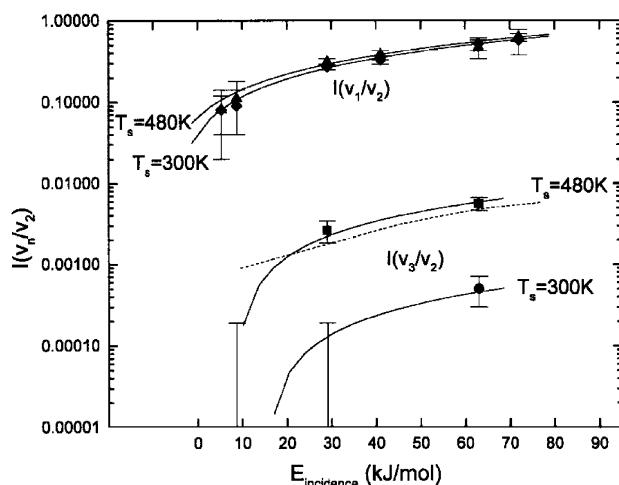


Fig. 4 Incidence kinetic energy dependence of the excitation and de-excitation probability for NO ($v = 2$) scattering from Au(111) for two surface temperatures. De-excitation ($v = 2 \rightarrow 1$): triangles and diamonds. Excitation ($v = 2 \rightarrow 3$): squares and circles. Lines are explained in the original reference. From ref. 17.

energy and surface temperature dependence of the excitation and de-excitation rate of NO ($v = 2$) is shown. Both rates increase with increasing energy. But de-excitation shows no dependence on surface temperature, whereas the excitation shows a very strong one. Analysis of the data shows that the surface is the main sink or source of vibrational energy. Mechanisms involving energy transfer to and from the surface electrons have been invoked. However, according to Huang *et al.* no electron mediated process put forward to date is capable of explaining simultaneously the vibrational excitation and de-

excitation observed in Fig. 4. Clearly, coupling to the electron–hole pair continuum of the surface is a process important for chemical dynamics at surfaces. This process is far from being fully understood. It points to the fact that electronically non-adiabatic processes have to be included explicitly in the description of chemical reactions at surfaces.¹⁸ In most cases the electronic degree of freedom is ‘hidden’ in the effective lower adiabatic potential energy surface describing the interaction.

3 Adsorption studies

The scattering studies in the preceding section demonstrate to what level of detail the gas–surface interaction can be studied. These experiments are very sensitive to the entrance valley of the potential energy surface. They show the first route towards dissociation of molecules at surfaces, the first step in a chemical reaction. But by definition those scattering studies do not exhibit any chemical reactivity. For that case the molecules need to reside at the surface, with the exception of the Eley–Rideal reactions, to be discussed later. So adsorption at the surface is the first step in a surface chemical reaction. Two types of adsorption are being discerned: trapping and sticking. For trapping the molecule adsorbs at the surface and comes into thermal equilibrium with it, but subsequently desorbs on a timescale that is short with respect to the experimental time scales (microseconds or more) but long with respect to typical equilibration times with the surface (a few picoseconds at most). Trapping will occur in rather weakly bound states and is often associated with physisorption. In sticking the molecule resides for a time that is long with respect to the experimental timescale of typically seconds to minutes. Sticking will occur for more strongly bound molecular states usually associated with chemisorption. Since the residence time of an adsorbate depends exponentially on surface temperature, the surface temperature is a key parameter in adsorption studies.

Trapping and desorption

Trapping at the surface followed by desorption can be detected in two different ways. At first the intensity of the desorbing signal as a function of angle Θ_f with the surface normal can be measured. In such an experiment the incident beam preferably comes in at a large angle (Θ_i) with the surface normal, so that the velocity has a considerable component along the surface. If the intensity of the desorbing molecules shows a dependence of $\cos^n(\Theta_f)$ one sees that there is no parallel component to the exit velocity. Thus the initial parallel momentum has been fully accommodated to the surface. If the exponent $n \approx 1$ the desorption is not activated. If $n > 1$ the desorption is activated. A second way to detect desorbed molecules is by time-of-flight (TOF) techniques. If the molecules are fully accommodated to the surface the TOF spectrum will correspond to a Maxwell–Boltzmann distribution. If desorption is activated the TOF distribution will correspond to a higher temperature, representing the barrier height. This has been well documented in a review by Comsa and David.¹⁹ The information that can be obtained from desorption studies in general has recently been reviewed by Hodgson.²⁰

Trapping into a weakly bound state can be the precursor to a subsequent surface reaction. Such a sequence of events leading to dissociative adsorption at surfaces has been studied carefully in the authors group for the system O_2 adsorption on Ag over the years. Many of the results can be summarized in Fig. 5. Panel a of this figure summarises the states that have been seen at the surface in many experiments by a number of groups, see *e.g.* ref. 11. At first there is physisorbed O_2 , there is molecularly chemisorbed O_2^- , and there are oxygen atoms. Scattering

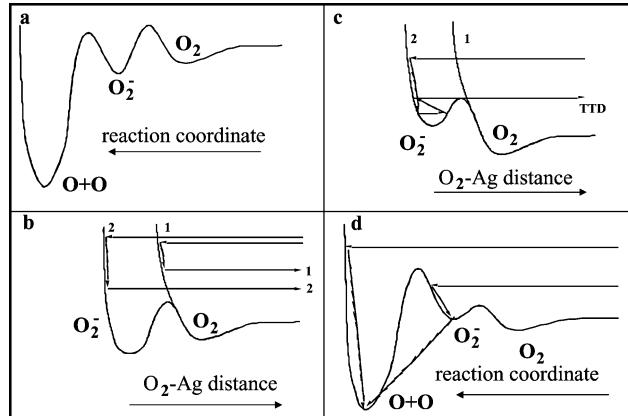


Fig. 5 Schematic potential energy diagrams for the interaction between O_2 and Ag(111). Four panels are shown. In **a** the three states into which O_2 can adsorb at the surfaces are depicted as a function of a reaction coordinate. In **b** the two potentials leading to direct inelastic scattering are shown. In **c** a trajectory representing a one dimensional representation of transient trapping–desorption in the O_2 -state is shown. In **d** two pathways leading to dissociative chemisorption are shown. From ref. 11.

experiments demonstrated that the O_2 and O_2^- states exhibit different scattering dynamics, as indicated in Fig. 5b, where path 1 refers to scattering along the physisorption potential and path 2 to scattering along the molecular chemisorption potential. It was initially thought that dissociation would occur as soon as the molecule entered into the molecular chemisorption potential, but this turned out to be not the case. In fact, as shown in Fig. 5c, scattering along path 2 could give rise to trapping into an activated intermediate state, from which desorption with excess energy could be observed. This was called transient trapping–desorption, trapping taking place in a transient state, rather than a stable state. The ultimate sticking will be discussed in the next section. The role of trapping into precursor states has been studied by many groups and recently by Mullins' group for O_2 adsorption on transition metal surfaces.²¹

Sticking

Molecular beams can be used to study absorption as well as scattering processes. When molecules are reflected from the surface, this leads to a pressure rise in the ultra-high vacuum chamber surrounding the crystal.⁶ When the molecules are adsorbed (or pumped) by the crystal on the time scale of the experiment 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 at zero coverage S_0 of the surface can be measured for various conditions of the incident beam. This sticking coefficient is a quantity that can also be computed, for instance using molecular dynamics simulations.¹⁰ The value of the sticking coefficient is of particular importance if the sticking of the molecule to the surface represents the rate determining step in an industrially or otherwise relevant catalytic process. For instance, the rate determining step of ammonia synthesis from N_2 on an Fe-catalyst is the dissociative sticking coefficient of N_2 on Fe.²² The experiments show an enhancement of the sticking coefficient with energy of at least four orders of magnitude. Later, similar experiments have been carried out for Ru(0001) surfaces. The results by Diekhöner *et al.* are shown in Fig. 6a, together with results from two other groups.²³ At first the remarkable increase of the dissociative sticking coefficient of N_2 at Ru(0001) is seen. Although the sticking does not go up to unity for high translational energies, the increase is enormous. In the experiments it was found that thermal vibrational excitation of the molecular beams gave rise to a considerable increase of the sticking coefficient. It might be tempting to

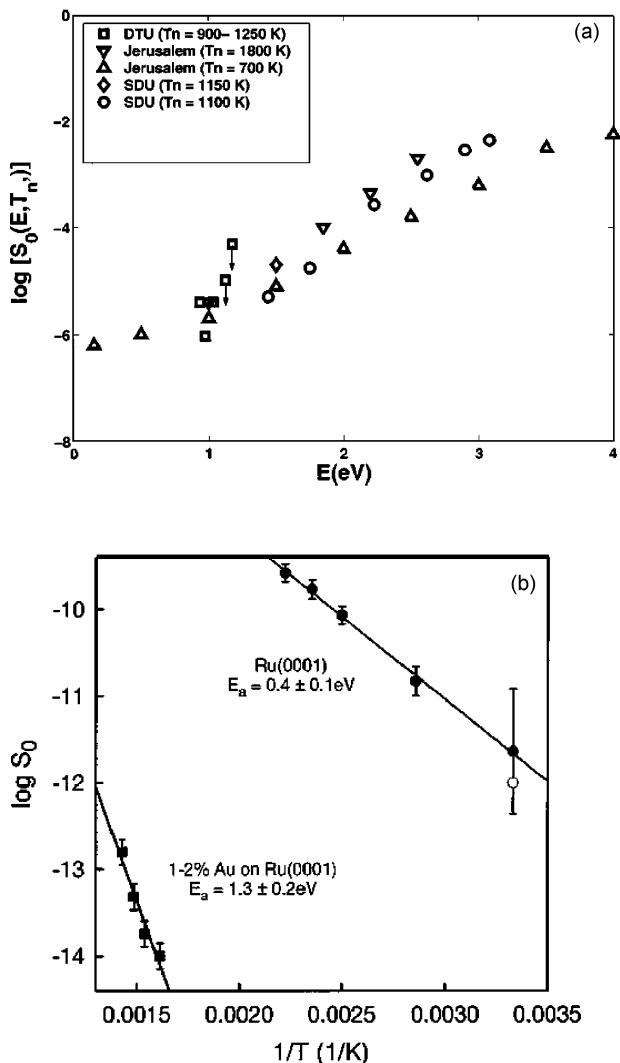


Fig. 6 (a) The logarithm of the sticking coefficient S_0 for dissociative chemisorption of N_2 on Ru(0001) as a function of the translational energy in eV and for several nozzle temperatures. Data from three different experimental groups are shown. See ref. 23 for details. (b) Arrhenius plot of measured thermal sticking coefficients for dissociative chemisorption of N_2 on Ru(0001) as a function of the inverse temperature. Circles represent data measured at the clean Ru(0001) surface, squares represent data for the Ru(0001) surface for which the steps have been covered by gold. From ref. 24.

interpret the very low sticking coefficient as being due to a very small fraction of sufficiently energetic molecules in the gas mixture of a chemical reactor. However, this is only part of the story. The sticking coefficient that is relevant for industrial processes may not be the one that is measured by a molecular beam and a perfect single crystal. This was dramatically demonstrated by Dahl and co-workers.²⁴ These authors measured the thermal sticking coefficient at Ru(0001) as a function of reactor (surface and gas) temperature. The results are reproduced in Fig. 6b. An apparent activation energy of about 0.4 eV is found, which is not recognised in the energy dependence of the sticking curve of Fig. 6a. Subsequently Dahl *et al.* evaporated a small amount of gold in their surface. It is known that the Au will reside at steps and defects of the Ru surface. The effect is dramatic: the sticking coefficient drops several orders of magnitude in addition. Now the apparent activation energy is about 1.3 eV which is indeed where the molecular beam data show an onset in the increase of the sticking coefficient. The authors conclude from their experiments and theoretical study using density functional theory that dissociative sticking at the perfect terraces of Ru(0001) is a translationally highly activated process. Under thermal condi-

tions, dissociation at steps and defects will dominate the dissociative adsorption process. Dissociation may be seen as thermal adsorption on a physisorption precursor followed by diffusion to and dissociation at a step.

For oxygen dissociation at Ag(111) similar processes may be operative. But there is one big difference. There are activated precursor states involved. The first step is activated adsorption into a O_2^- -like precursor, followed by dissociation at surface imperfections, as was also proposed for the Ag(110) surface.²⁵ In addition, at Ag(111) a direct dissociation at high energies is also possible.¹¹ These two processes are indicated by arrows in Fig. 5d.

The data for N_2 adsorption on Ru(0001) shown in Fig. 6a clearly demonstrated that the nozzle temperature influences the sticking coefficient. This is attributed to vibrational excitation of the molecules in the beam source, which is not quenched in the expansion. A direct measurement of the effect of vibrational excitation of CH_4 when sticking at Ni(100) has been made recently by Juurlink *et al.*²⁶ The vibrational excitation of the ν_3 mode in the beam has been produced by laser excitation. A very dramatic increase of the methane dissociation of more than an order of magnitude has been observed.

Calorimetry

Molecular beams have also facilitated an entirely novel way to determine adsorption energies at surfaces. In most cases the adsorption energies, that have served as an input to figures like 5 are determined from thermal desorption experiments. However, in many cases a number of assumptions enter into the analysis of those experiments, rendering a good determination of the adsorption energy as a function of coverage impossible. King and co-workers have invented a novel way of measuring heats of adsorptions for molecules at surfaces using microcalorimetry.²⁷ In these experiments a molecular beam delivers a small amount of molecules at a surface. The sticking probability is determined *in situ* by the King and Wells method.⁶ Therefore, the amount of adsorbed molecules can be determined accurately. The heat of adsorption can be determined from the temperature rise of the crystal, which is measured by infrared emission. The experiment is only possible for very low heat capacity surfaces, which in practise is realised using single crystals that are only several tens of nanometers thick. In later experiments, also in Campbell's group, pyroelectric detection schemes have been used.²⁸

4 Growth studies

Molecular beams are an excellent tool to deposit well defined layers. This is because only the desired spot at the surface is irradiated by the beam, and the crystal support *etc.* are not in touch with the beam. In addition, the gas load on the vacuum chamber by the beam will be very small, because the collimated beam only hits the target. If the sticking coefficient is unity, there will not be any pressure rise in the chamber.⁶ The best known application of molecular beams to grow high quality layers is in molecular beam epitaxy (MBE).²⁹ Here effusive beams of metal atoms, semiconductor atoms, or precursor molecules containing atoms to be deposited, are well collimated and aimed at a surface in UHV to grow the layer concerned. Perhaps unfortunately, there is almost no connection between the fields of molecular beam epitaxy and chemical dynamics studied by molecular beams.

Another area where molecular beams, again often effusive but collimated, are used is the growth of ice films. Like in MBE, in most studies there is little interest in chemical dynamics at the

ice surface and more in the structure of the film instead. In Kay's group a lot of work has been carried out on the growth of water ice films on substrates. It has been demonstrated how amorphous and crystalline water ice can be grown and what the kinetic and thermodynamic properties of the films are. Quite recently it also turned out to be possible to grow ice films with different porosities by changing the angle of incidence of the molecular beam with respect to the substrate.³⁰ A very recent paper by Haq *et al.*³¹ summarizes how water bilayers can be grown on a metal surface and how those interact with HCl.

5 Reaction studies

Langmuir–Hinschelwood reactions

The often claimed ultimate goal of studies using molecular beams at surfaces is to elucidate chemical reaction dynamics at surfaces. Most heterogeneous chemical reactions are supposed to take place *via* the Langmuir–Hinschelwood mechanism. In this mechanism the reaction sequence is the following: (1) adsorption of the reactants from the gas phase; (2) dissociation of (some of) the reactants; (3) diffusion of the reactants to an appropriate site at the surface, where the reaction can take place; (4) desorption of the products. Molecular beams are very well suited to study the first steps, and also the last, because the detectors used to monitor scattered molecules can also be used to detect desorbing molecules. The actual reaction is not well visible to molecular beams. Surface spectroscopies are needed to provide additional information on the reaction dynamics. Femtosecond lasers may offer such opportunities.³² But because the adsorption and desorption can be studied very precisely molecular beams can give very valuable information about the reaction dynamics. Reactions studied are usually rather simple and include oxidation of NO, CO and methanol on metal surfaces, see *e.g.*,³³ and the partial oxidation of methane leading to synthesis gas.³⁴ An impressive new machine has been built to study chemical reactions at complex surfaces as reviewed by Libuda and Freund.³⁵

Abstraction reactions

If a reaction proceeds along the Langmuir–Hinschelwood mechanism the reactive event itself is invisible to the molecular beam methodology. However, if the reaction is a consequence of the direct collision of the reactants, to be discussed in the next section, or leads to the instantaneous ejection of products, molecular beam machines can be very useful. This has been the case for reactions of halogens with semiconductor surfaces, but here I will focus the attention on recent work on the oxidation of Al(111). Despite its technological significance and its potential benchmark character the interaction of O₂ with Al(111) is not very well understood. Despite the enormous exothermicity, the dissociative adsorption of O₂ occurs with very small probability. Perhaps even more remarkable is the fact that the O-atoms after dissociation are found to be widely separated. At first this was considered to be due to transient mobility. In the dissociation the atoms are repelled with so much energy that they are far separated. However, this turned out to be very unlikely. The only solution to this paradox was, that in the dissociative adsorption of O₂ one of the O-atoms is directly ejected into the gas phase. In a molecular beams machine Komrowski *et al.* were able to directly identify the departing O-atoms, which carry a distinct signature of this unusual dissociation process.³⁶ The understanding of this seemingly simple reaction is far from complete. Perhaps electronically non-adiabatic transitions need to be considered explicitly.¹⁸

Eley–Rideal reactions

Other types of reaction that can be characterized very well by molecular beams are those that occur upon direct impact of a reactant from the gas phase onto an adsorbed reactant. These are called Eley–Rideal reactions, and most evidence for their occurrence is based upon kinetic analysis of surface reactions and the reaction order. However, kinetic data cannot be uniquely inverted into dynamical mechanisms and a direct identification could only be achieved by molecular beams. In an Eley–Rideal reaction the translational energy of one of the reactants is directly used and partially retained in the final velocity of the product. In addition, all energy gained by acceleration in a chemisorption potential well must be used in the reaction. It will be clear that accommodation to the surface will turn the Eley–Rideal mechanism into a Langmuir–Hinschelwood mechanism. In fact, the transition from one to the other is not extremely sharp, as pointed out first by Harris and Kasemo, who showed that a so-called (translationally) hot precursor could be intermediate between the two mechanisms of Eley–Rideal and Langmuir–Hinschelwood.³⁷ A lot of seminal work in this field has been carried out by Rettner and Auerbach. Data obtained for the reaction of a beam of H atoms impinging on Cl atoms adsorbed on Au(111) to yield HCl is reproduced in Fig. 7a. It can be seen that the ejected HCl emerges such from the surface that the initial momentum of the hydrogen is retained. Clearly, the hydrogen did not accommodate in the deep potential well before the surface, and did not lose its translational energy. More evidence for the occurrence of an Eley–Rideal reaction can be obtained from the vibrational state distribution. If the exothermicity of the reaction is mostly available to the product, it has to be vibrationally excited. This is shown in Fig. 7b. Clearly $v = 1$ is most populated, implying that the HCl is formed with excess internal energy. The work by Rettner shows, that both the indirect and the direct reaction mechanism are active. For the HCl formed in the Eley–Rideal reaction, about half of the available energy is actually carried away by the molecule. The other half has to be transferred to the surface by direct momentum transfer or quenching of internal energy in the molecule. Other systems for which Eley–Rideal reactions have been demonstrated are the reactions between incident H-atoms with adsorbed H-atoms to yield H₂. Also the isotopic substitutions have been studied for a number of substrates.³⁸

Collision induced reactions

In the Eley–Rideal reaction the incident particle uses its kinetic energy to initiate a reaction in which it participates. In collision induced reactions the incident particle does not need to participate. The earliest examples refer to studies concerning desorption and dissociation of physisorbed molecules, such as methane. In later experiments chemisorbed molecules are also included. As an example I mention the work by Åkerlund *et al.*³⁹ These authors dissociate and desorb O₂ chemisorbed on Ag(110) and Pt(111) by energetic Xe atoms. It turns out that the Xe needs about twice the energy than is minimally needed to induce the desired reaction. The similarity of the energy dependence of desorption and dissociation induced the authors to invoke the same energised state of the system, created by Xe impact, that can drive both processes. This state can perhaps also be created by other processes, like photon or ion impact.

Liquid surfaces

Although the reactivity of liquid surfaces is extremely interesting, molecular beam studies have very rarely been carried out for liquid surfaces. The obvious reason is the vapour pressure of

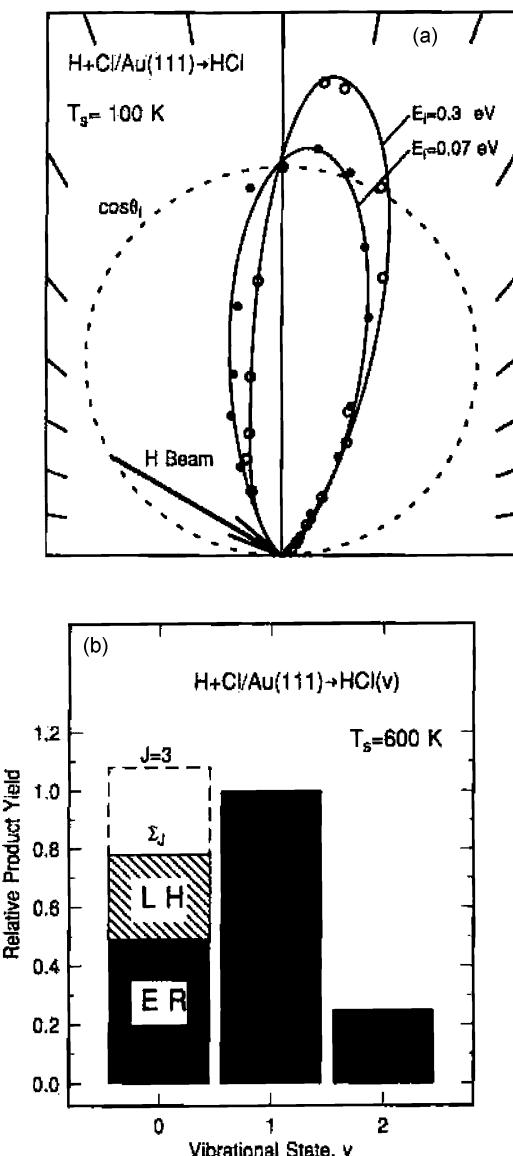


Fig. 7 (a) Polar representation of the angle dependence of the HCl product ejection from an Au(111) surface at which adsorbed Cl atoms react with incoming H atoms in a direct, Eley-Rideal reaction. From ref. 41. (b) Vibrational state distributions for the HCl product. The solid bars indicate the contribution from the Eley-Rideal mechanism, the shaded region for $v = 0$ is due to the Langmuir-Hinselwood mechanism and the dashed line indicates the contribution from $J = 3$. From ref. 41.

most liquids that precludes the facile inclusion of a liquid surface into a molecular beam machine. The group of Nathanson has carried out a number of very important pioneering studies in this field. The problem of the vapour pressure of the liquid was solved by a very carefully designed system of differential pumping stages around the liquid surface. In this way contamination of the beam sources and detectors by for instance H_2SO_4 could be avoided. In addition, there is the problem of the contamination of the liquid surface itself. This was solved by the adhesion of a thin film of liquid to a disk, rotating through a liquid-containing reservoir at the lower part. This very special experimental arrangement makes the scattering of molecular beams from liquid surfaces possible. An example is given in Fig. 8. This schematically shows the possible pathways of DCl in its interaction with liquid glycerol.⁴⁰ All channels known from the scattering from solid surfaces can be detected: inelastic scattering, trapping followed by desorption, but also long time bulk solvation and desorption following immediate exchange. The incoming acid molecules readily dissipate their excess energy at the glycerol surface and thermalise, even at kinetic energies up to 100 kJ mol^{-1} . It is

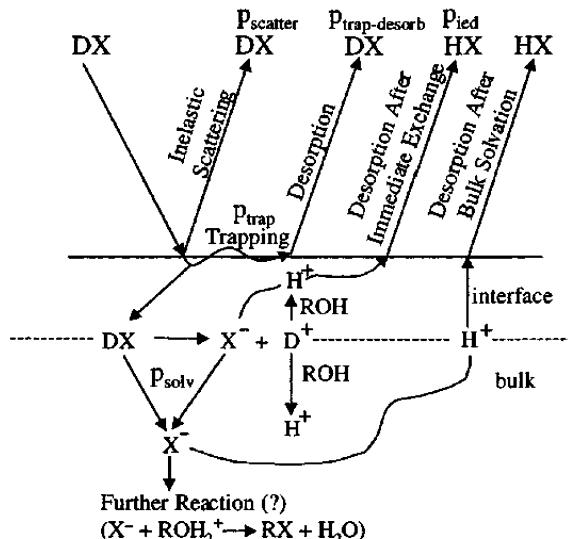


Fig. 8 Observed pathways for an acidic hydrogen halide molecule (DX) colliding with and into liquid glycerol (ROH). The various outcomes of a DX surface collision are indicated. DX dissociation and HX recombination may occur both in the interfacial and bulk regions of the liquid. From ref. 40.

fascinating to see how all knowledge acquired for molecular beam scattering from solid surfaces can be put to work for interactions at liquid surfaces.

6 Conclusions

Molecular beams are very useful tools for the study of the dynamics of gas–surface interactions. Although most of the work has been done for simple systems, such as diatomic molecules in their ground state interacting with close packed metal surfaces, more complex problems have also been tackled. Molecular beams with molecules prepared in one or a few quantum states allow the finer details of the quantum mechanics of the interaction to be studied and have introduced state-to-state chemistry, well known from gas phase chemical physics, into surface science. In addition, much more complex surfaces, such as liquid surfaces have also been studied. Molecular beams are an excellent tool to study direct reactions at surfaces, where either direct impact from the gas phase or direct ejection of products into the gas phase can be studied. Molecular beams are also instrumental in detailed adsorption studies, and in the preparation of novel thin films.

7 Acknowledgements

This article was prepared while the author enjoyed the hospitality of the Université de Paris Sud, where he acted as Professeur Invité. Jean-Pierre Gauyacq is thanked for his careful reading of the manuscript.

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