Surface Reaction Dynamics

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Surface reactions differ from chemical reactions in general only by the fact that they occur at an interface between two media. It is often implicitly understood that one of the media is a solid and the other a gas or a liquid. The number of scientifically and technically important surface reactions is enormous and we can here mention only a few phenomena, where surface reactions are key ingredients like catalytic reactions, as in ammonia synthesis, oil cracking, methanol production and catalytic combustion. In material science, surface reactions affect corrosion, steel hardening and hydrogen embrittlement. In electrochemistry, there are electrode reactions in, e.g., fuel cells and hydrogen production by photoysis. In biology and medicine, surface reactions are important for bioadhesion, biomembranes and biocompatible materials.

While it used to be a domain exclusively for chemists, the study of surface reactions is now an occupation also for a rapidly increasing number of physicists 1). This occurs as an outgrowth of condensed matter physics, where surface physics now is one of the most active subfields, but also with an input from molecular physics. The traditional type of surface physics has concentrated on the solid state properties of well defined surfaces and absorbed layers. Such studies were dominant during the 1960s and 1970s and have produced both an enormous improvement in our understanding of these systems and developed a great number of surface-sensitive tools and theoretical methods. These tools and methods are of key importance also for the class of phenomena that we shall discuss here. For example, by combining low-energy-electron diffraction (LEED), photoemission spectroscopies in the ultraviolet and X-ray (UPS, XPS) and electron energy loss spectroscopy (EELS) and also with high resolution (HREELS) and infrared spectroscopies (IR) with relevant theoretical approaches, a detailed picture of the atomic positions and electron structure of many adsorption and coadsorption systems has been obtained. This background knowledge about static systems is of the highest importance, when an attempt is made to describe the reaction dynamics of similar systems.

Before we discuss specific surface reactions some general features of chemical reactions are considered. First we make a distinction between reaction kinetics and reaction dynamics. The former deals primarily with rates of chemical reactions, and the microscopic details; most of the physics of a reaction is embedded in the rate constants. It is usually understood that the reaction takes place between ensembles of reactants, which are characterized by a thermal distribution of translational and internal energy. Consider the reaction

$$AB + C \rightarrow A + BC$$

illustrated in Fig. 1. If, as is indicated there is an activation barrier, $E_a$, only reactants with an energy higher than this barrier may react. Even when the energy is "above" the barrier, the reaction probability (cross section) may in general be a function of, e.g., energy (internal and/or translational) and of reactant orientations. In reaction kinetics such details of the reaction are summarized in the famous Arrhenius formula for the reaction rate,

$$R = \nu(T) \exp(-E_a/kT),$$

where $T$ is the temperature and $\nu$ the so called prefactor.

In reaction dynamics, on the other hand, one tries to map out the reaction path and the dependence of the reaction cross section on internal and translational energies of the reactants and on reactant orientations. The distribution of reaction energy into the quantum states of the reaction products gives important information in this mapping. Experimental studies of reaction dynamics therefore require molecular-beam type experiments, where the state of excitation and directions of the incoming and scattered beams can be controlled and determined.

In the energy transfer processes that can occur, when two molecules (say AB and C) collide, three types of scattering can be distinguished:

- Elastic, $AB + C \rightarrow AB + C$, where translational energy is going over to translational energy of another motion, with no loss of energy,
- Inelastic, $A^*B + C \rightarrow AB^* + C$, where in addition there may be energy transferred between translational and internal modes (such as vibrational, rotational and electronic ones) and between the internal modes, and
- Reactive, $AB + C \rightarrow A + BC$, where in addition to the above possibilities there is a transfer between translational and internal energy and chemical energy. The reactive event differs from the two other types, in that chemical bonds are broken and formed.

For the specific case of molecules or atoms impinging on a surface, the experiment and the possible results of such events can be as illustrated in Fig. 2. The numbers in Fig. 2a indicate the aforementioned possibilities of (1) elastic scattering, (2) inelastic scattering, where the energy and momentum losses are sufficiently small to allow the atom/molecule to escape back to the gas phase and (3) trapping at the surface, due to too large energy and/or momentum loss for case 2 to occur. Case 3 is the simplest type of reactive scattering. Both the purely inelastic and the trapping events are accompanied by an energy redistribution, where the elementary excitations of the solid and of the atom/molecule are involved. Fig. 2b is an attempt to illustrate this in diagrammatic form. The incoming beam is assumed to be monochromatic with energy $E_i$ in vacuum. Molecules, which upon interaction with the surface lose less energy than $E_i$ may escape out into the vacuum with an energy loss distribution as indicated in the upper right diagram of Fig. 2b. The lost energy must then remain in the solid, as indicated in the left diagram. The maximum energy that can be released to the solid, $E_{\text{max}}$ is the
The effects.

The most striking new feature of this molecule-solid scattering event, as compared to gas-phase reactions, is the participation of the excitations of the solid.

The interaction between a beam of molecules and a solid is a non-equilibrium situation, where both the excitations of the solid and of the scattered species in general will result in a distribution deviating from the thermal. The observation of the solid excitations, such as electron-hole pairs, phonons and other collective excitations, is very much hampered by the fact that these excitations lie inside the solid. For sufficiently energetic excitations, however, the electron-hole pairs can cause emission of electrons and radiation, which can be detected as exoelectrons and surface chemiluminescence, respectively. The molecular excitations resulting from the collision with the surface can be detected in various ways. The translational state can be measured directly with a time-of-flight technique or inferred from measured angular distributions. The rotational, vibrational and electronic excitations can also to some extent be deduced from time-of-flight measurements. Still more detailed information can be obtained by analyzing the outgoing molecular beam with laser spectroscopy, e.g., laser-induced fluorescence.

One can conclude from this that the desired experiment measures the energy-loss spectrum and the internal excitation or de-excitation that results from the scattering of monochromatic, state-characterized atomic or molecular beams. The theory should take into account the additional features present in molecule-surface reactive scattering (as compared to gas-phase scattering) such as:

(a) the quasi-continuous electronic excitation spectrum, which in metals goes all the way from an excitation energy of zero, but in semi-conductors and insulators starts at the non-zero energy-gap energy,
(b) the continuous phonon excitation spectrum, which for single-phonon excitation, ranges from zero frequency to a cut-off at the Debye frequency, whereas for multi-phonon excitations can go on with no upper limit.
(c) the greater ease to satisfy momentum-conservation requirements, thanks to the inhomogeneity at the surface and the ability of the substrate electrons and phonons to take up energy and momentum, and
(d) the possibility of perfect orientation of a reactant or collision partner, which is adsorbed on the surface.

After these more general considerations we discuss a number of recent experiments and calculations that give some insight into the microscopic details of surface-reaction dynamics. From Ar and Xe scattering (Panel 1) we learn that an atom can gain and lose energy, when scattered against a surface. Argon, xenon and neon are inert gases and therefore have a weak interaction with the surface. Still they couple sufficiently strongly to show these effects of inelastic scattering, indicating an exchange of energy with the excitations of the substrate. The Ar case demonstrates pick up of translational energy from the substrate, and the Xe case shows two distinctly different scattering channels, a direct one, where the Xe atoms return into the vacuum after a single round trip in the physisorption well and a hopping-desorption channel, where the Xe atoms have been trapped in the surface region for some time before desorbing into vacuum.

In similar experiments with inelastic Ne scattering on Ni, the energy loss has been identified with a specific event, namely a low-energy transfer (≥15 meV) due to Rayleigh-type surface phonons.

The potential-energy surface describing the interaction of the inert-gas atom with a solid is simply the potential curve of Fig. 3a, slightly corrugated along the surface. This physiosorption curve is characterized by the long-range, attractive van der Waal forces and the short range, kinetic-energy repulsion between the atom and
host electrons. The program to determine these potentials from elastic scattering of atoms from surfaces is in rapid development. For inert-gas atoms the well depth is typically \( \geq 0.1 \text{ eV} \).

For a reactive molecule the potential-energy curve can have the shape as in Fig. 3b. In this case the horizontal axis should be interpreted as the reaction coordinate, i.e., the coordinate of the curve that connects the local minima and saddle points of the potential-energy surface. The curve shows three minima: a physisorption well for the molecule (1), a molecularly adsorbed state (2), and a dissociatively adsorbed state (3). The schematic curve of Fig. 3b has been extracted from the theoretical model results for \( \text{H}_2 \) on a close-packed surface Mg (0001). According to these data the following scenario can be drawn for hydrogen molecules impinging on that surface: An \( \text{H}_2 \) molecule with low kinetic energy is very likely to bounce off the surface. A repulsive potential-energy barrier without any sizable corrugation makes its passage difficult outside the first layer of magnesium atoms. The situation is thus pretty close to that of a He or other inert atom. Sufficiently hot molecules can pass the barrier, however, and penetrate a few Ångströms closer to the surface. A majority of them then become trapped at the surface, as efficient mechanisms slow the molecule down. A trapped molecule may perform (damped) oscillations in and out from the surface. At the same time, the adsorbed molecule can slide almost freely along the surface. Eventually it can dissociate into two hydrogen atoms, adsorbed on the surface but almost free to migrate along the surface.

The external barrier for \( \text{H}_2 \) on Mg is indirectly confirmed by the measured very low sticking probability, less than \( 10^{-6} \). Such a low sticking probability is not typical for molecules on metals, however. Most of the reactive molecule/metal system investigated experimentally so far have shown sticking coefficients of the order of unity, e.g., \( \text{O}_2 \) on Ni, W, Ti, Fe, ... , and CO on Ni, W, Cu, ... , \( \text{H}_2 \) on Ni, Nb, ... , which indicates that (i) the activation barriers (if any) of most molecule-metal systems are much smaller than in the \( \text{H}_2/\text{Mg} \) case and (ii) the energy transfer between these molecules and the metal substrate is efficient enough to give a high sticking coefficient.

Experimental observations of dynamic effects have also been made for \( \text{H}_2 \), \( \text{D}_2 \), and \( \text{N}_2 \) molecules desorbing from metal surfaces (see Panel 2). With hydrogen the average translational energy of the desorbing molecules is considerably larger than that predicted by a Maxwellian distribution with the sample temperature as the relevant temperature. In a similar experiment with \( \text{N}_2 \) molecules desorbing from an iron surface, a higher fraction of vibrationally excited molecules than predicted from the sample temperature has been observed. Both these examples illustrate incomplete energy relaxation along the reaction coordinate and demonstrate clearly that adsorption-desorption-reaction phenomena at surfaces cannot in general be treated by quasi-equilibrium approaches. The hot desorption effect where \( \text{CO}_2 \) molecules of very high kinetic energy are produced in the surface reaction \( \text{CO} + \text{O} \rightarrow \text{CO}_2 \), also supports this conclusion.

When a molecule, rather than an atom, is scattered off a surface there can in addition to changes in translational energy be changes in the state of internal excitation of the molecule. Certain conclusions about such changes can be drawn from measured angular and velocity distributions, but direct measurements are of course preferred. During the past year a number of reports (see Panel 3) have demonstrated the conversion of translational energy into rotational energy in \( \text{CO}_2 \) scattering on surfaces. Attempts to fit the population of rotational states to an equilibrium distribution have been only partly successful, and in the most thorough investigation, strong deviations from Boltzmann distributions have been observed. Since the scattering is mainly direct inelastic scattering, there is actually no reason to expect equilibration to the surface temperature at all.

The technique used in these experiments to map out the population of rotational states is laser-induced fluorescence (LIF). Panel 3 shows the experimental arrangement for laser-induced-fluorescence (LIF) analysis of surface-scattered molecules. The scattered beam is crossed with a tunable laser beam, and the total fluorescence yield is measured as a function of the laser-light frequency. From these data, the populations of the rotational states e.g., can be calculated.

During the past year, three experiments of the type illustrated in Fig. 3 have been reported. When a rotationally cold beam of NO was scattered against an NO-covered Pt(111) surface, the rotational distribution was Boltzmann-like at a temperature very close to that of the substrate. This was attributed to trapping and complete accommodation of NO, followed by desorption. Scattering of a thermal (300 K) beam against an Ag(111) surface at 475-720 K also showed a Boltzmann rotational state distribution, but with only partial accommodation, i.e., the scattered rotational temperature was lower than the surface temperature.
Panel 4 — "Hot Precursors" in Surface Reactions

The rate of energy exchange between an impinging molecule and a solid surface is slow enough to let the translational and internal energies of the molecule for some time be quite different from those of an adsorbed, equilibrated molecule. For a chemisorption system the net heat of adsorption may be of the order of 1 eV, which could give the molecule a high excess energy on the surface, possibly corresponding to a temperature of the order of 10^4 K.

The reaction kinetics resulting from such hot precursors differs in general considerably from that governed by thermal fluctuations in an equilibrium system. For example, in the latter case activation barriers may enter explicitly into reaction rates, while with hot precursors the reaction may take place at energies "above" the activation barrier, without any need for energy supply from a heat bath.

As an explicit example the kinetics for the water reaction on Pt (H2 + 1/2 O2 → H2O) has been worked out in the hot precursor model[1]. An important conclusion from this work is that the traditional classification of surface catalytic reactions (see Fig. 4) becomes questionable.

Panel 5 — Surface Chemiluminescence and Electroluminescence

For all chemisorption systems, a substantial rearrangement of the substrate and adsorbate valence electrons takes place during adsorption. Because the time of interaction is short this rearrangement may result in electronic transitions in the broadened affinity level of the Cl atom is filled by a second electron from Na.

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REFERENCES