Surface Reaction Dynamics

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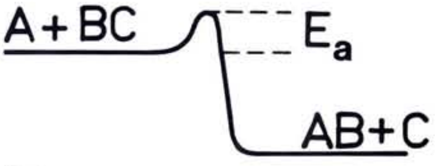


Fig. 1

Surface reactions differ from chemical reactions in general only by the fact that they occur at an interface between two media. It is often implicity 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 photolysis. 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 (IRS) 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 ν 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 give 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.

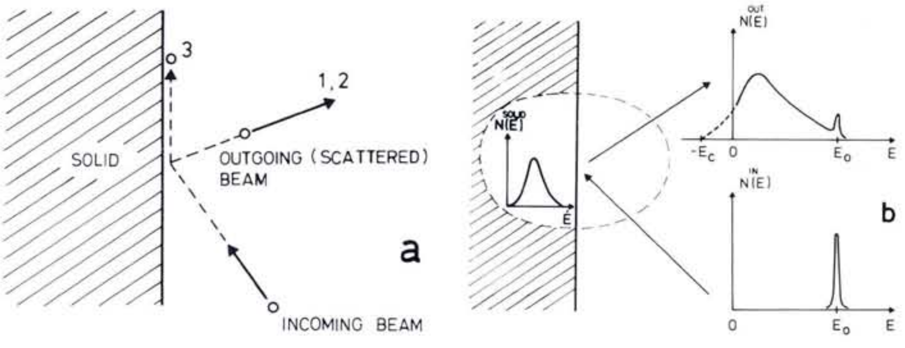
In the energy transfer processes that can occur, when two molecules (say AB and C) collide, three types of scattering can be distinguished:

- *elastic*, $AB + C \rightarrow AB + C$, where translational energy is going over to translational energy of another motion, with no loss of energy,
- *inelastic*, $AB^* + C \rightarrow AB^+ + C$, where in addition there may be energy transfered 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 specifc 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_o in vacuum. Molecules, which upon interaction with the surface lose less energy than E_o 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_{max} is the

Fig. 2



sum of the incoming energy E_0 and the adsorption (reaction) energy E_c. This oversimplified picture correctly sets the energy limits of the problem but neglects the complications that arise when conversion between translational and internal (rotational, vibrational, electronic) energies of scattered molecules are considered.

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 about the Debye frequency, whereas for multi-phonon excitations can go on with no upper limit.

Both these phenomena can give lifetime effects for molecular excitations and motions at surfaces. The theory should, in particular, calculate the shape of the excitation spectra for the phonon and the electron-hole-pair mechanisms, and from this deduce the shape of the energy-loss spectrum and the absolute and relative sizes of the effects.

Panel 1 - Inelastic Noble Gas Scattering

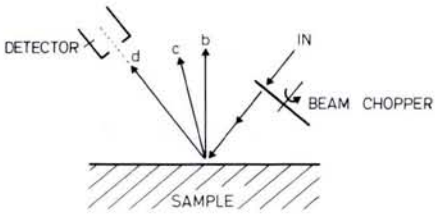


Fig. 1.1

Experimental geometry (Fig. 1.1): A collimated and fairly monochromatic beam of atoms is formed by a set of differential-pumping stages separated by apertures. The beam is then chopped in the main chamber, to give a pulsed beam of molecules, and the flight time between chopper and detector is measured. Knowing the velocity of the incident beam, the velocity increase or decrease due to interaction with the sample can be measured (provided the trapping time at the sample is negligible).

Ar scattered off a polycrystalline W surface: Fig. 1.2 shows the number of Ar atoms vs the time of flight for an Ar beam of average temperature 300 K[2]. It clearly demonstrates that the mean velocity of the scattered beam increases with increasing energy, i.e., the Ar atoms pick up translational energy in the scattering.

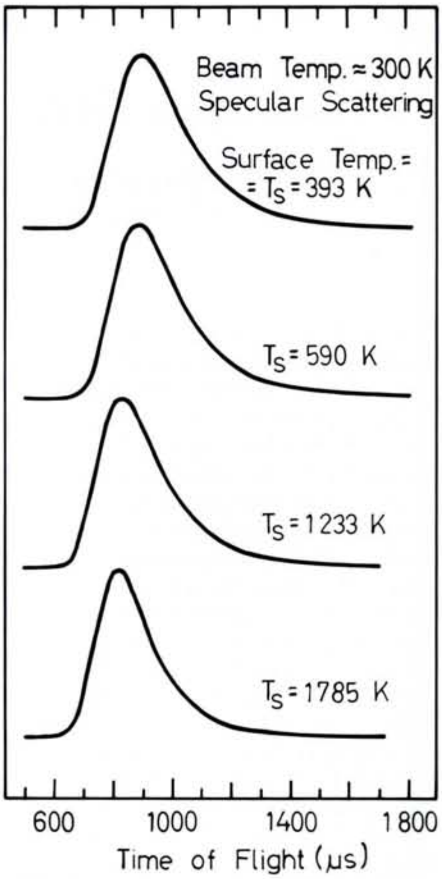


Fig. 1.2 — Redrawn from Ref. 2.

The surface also introduces some other new features, such as

(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

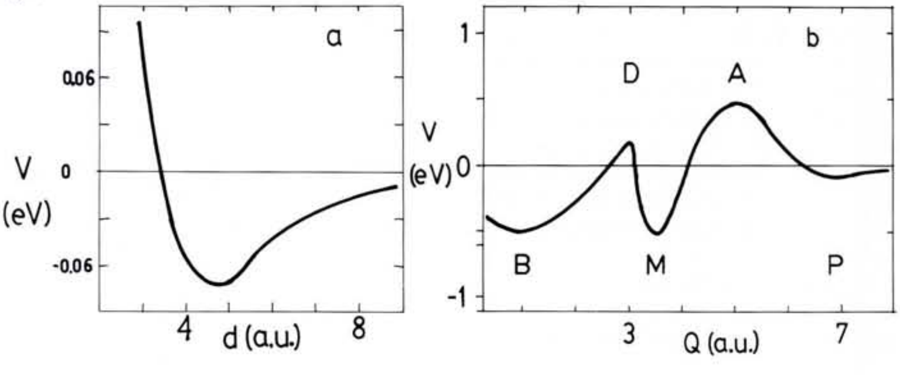
(d) the possibility of perfect orientation of a reactant or collision partner, which is adsorbed on the surface.

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[4].

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 physisorption curve is characterized by the long-range, attractive van der Waal forces and the short range, kinetic-energy repulsion between the atom and

Fig. 3



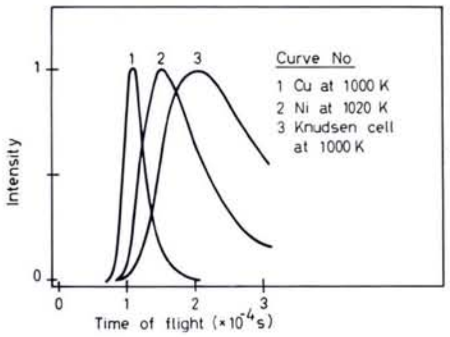
host electrons. The program to determine these potentials from elastic scattering of atoms from surfaces is in rapid development. For inert-gas atoms the well depth is typically ≥ 0.1 eV.

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 moleculary (associatively) chemisorbed state (2), and a dissociatively adsorbed state (3). The schematic curve of Fig. 3b has been extracted from the theoretical model results for 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 H_2 molecule with low kinetic energy is very likely to bounce off the surface. A repulsive potential-energy barrier without any sizable corrugation meets it several Ångströms 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 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., O_2 on Ni, W, Ti, Fe,..., and CO on Ni, W, Cu,..., 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 H_2/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 H_2, D_2 and 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 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 CO_2 molecules of very high kinetic energy are produced in the surface reaction $CO + O \rightarrow CO_2^{gas}$, also supports this conclusion.

Panel 2 — Desorption of Non-equilibrated Molecules



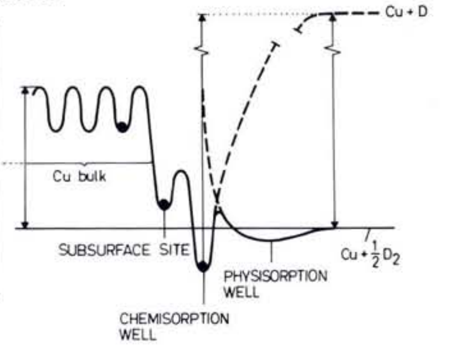


Fig. 2.1 — Redrawn from Comsa G., Proc. Int. School on Mat. Sci. and Tech. Erice, July 1981 (Springer Verlag) 1982.
Fig. 2.2 — Redrawn from Comsa G. and David A., Surface Sci, 116 (1982).

In a series of papers Comsa and co-workers[7] nave described the velocity distributions of H_2 and D_2 molecules that desorb from several metals (Pd, Cu, Ni), after having reached the surface regions as diffusing atoms from the interior of the sample. The velocity distributions have in all cases shown up significant or striking differences from the Maxwellian distributions.

The hydrogen (deuterium) atoms are introduced into the sample by exposing its back side to a high pressure of H_2 (D_2). The sample is mounted vacuum tight so that it separates the high pressure region from the ultrahigh-vacuum system. Hydrogen atoms which diffuse through the sample recombine on and desorb from the (cleaned) surface facing the vacuum system. The velocity distribution (at different angles) is measured by a time-of-flight arrangement.

Results for Cu and Ni at 1000 K are shown in Fig. 2.1 together with the distribution obtained from a Knudsen cell at 1000 K, simulating a Maxwellian distribution. The measured velocity distributions obviously deviate strongly from a thermal distribution characterized by the sample temperature.

Fig. 2.2 shows (for the Cu case) the model proposed by Comsa and co-workers to explain these observations. According to the model the high kinetic energy of the desorbing molecules is **not** achieved through an activation barrier for adsorption but instead from the high potential energy felt by an atom that penetrates the outermost layer of metal atoms. Rather than losing this excess energy and being trapped in the chemisorption well, the H atoms recombine to form hot H_2 molecules. This could be one example of the "hot precursor" motion discussed in Panel 4. In chemistry language this state of high potential energy would be called the "transition state" or the "activated complex"

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 NO 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 — Transfer of Energy from Translational to Rotational Modes

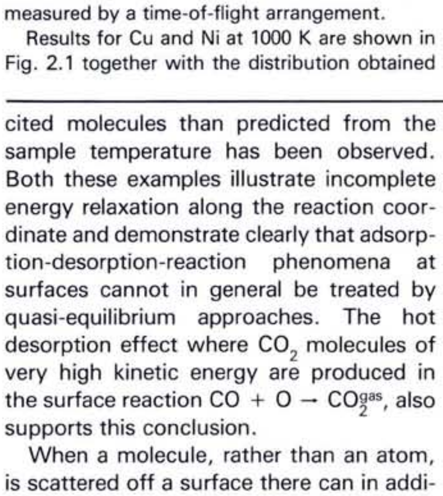


Fig. 3

Fig. 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[8]), 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[9]), 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 adorbed, equilibrated molecule. For a chemisorption system the net heat of adsorption may be of the order of 1-5eV, which could give the molecule a high excess energy on the surface, possibly corresponding to a temperature of the order of 10^4K.

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 ($H_2 + \frac{1}{2} O_2 \rightarrow H_2O$) has been worked out in the hot precursor model[11]). An important conclusion from this work is that the traditional classification of surface catalytic reactions (see Fig. 4) becomes questionable.

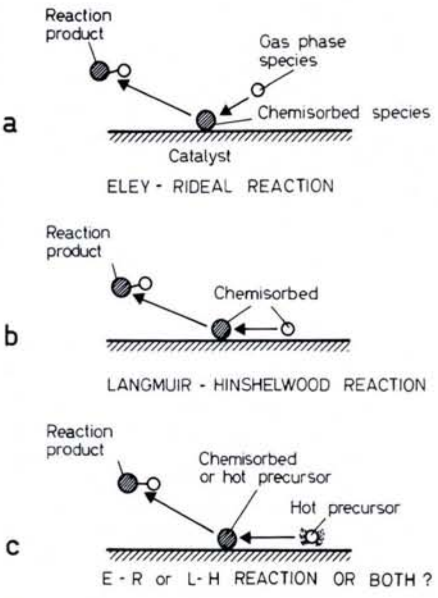


Fig. 4

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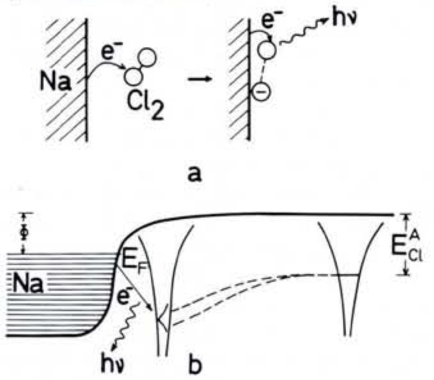
which previously has proved to be very successful in similar gas-phase studies. Such measurements combined with velocity-distribution measurements (perhaps by measuring Doppler shifts) are expected to give enormous improvements in our understanding of molecular scattering dynamics at surfaces.

In the introduction it was underlined that the interaction of atoms and molecules with a surface often involves situations with incomplete energy exchange, resulting in non-equilibrium conditions. Several of the previous examples have demonstrated this. A molecule impinging on a surface, with which it interacts strongly, cannot be viewed as a mere golf ball landing in a sand trap (Panel 4). It rather possesses for some while a high energy as a "hot precursor" on the surface and will therefore react with other species on the surface in a manner that is very different from a situation, where it were chemisorbed at the bottom of the chemisorption well. This view makes the traditional classification of surface catalytic reactions as either of the Langmuir-Hinshelwood or Eley-Rideal types quite ambiguous.

Panel 5 — Surface Chemiluminescence and Exoelectron Emission

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 involving rather large energies. The experimental observations of photon emission (surface chemiluminescence) and electron emission during adsorption are direct evidence for such non-adiabatic electronic processes. The photon and electron emission has been observed for a number of system (O_2 + metals, and halogens + alkali metals)[12]). The Na + halogen system has been given a theoretical treatment in terms of a simple one-electron, two-level picture[13]). The experimental situation is illustrated in Fig. 5, where a Cl_2 molecule is shown to approach a Na surface. By a process analogous to that used to discuss the corresponding gas-phase reaction, the Cl_2 molecule captures an electron from the Na metal. The so formed Cl_2^- molecule dissociates into a Cl^- and Cl atom. Light or electron emission occurs when the shifted and broadened affinity level of the Cl atom is filled by a second electron from Na.

Fig. 5 — Redrawn from Ref. 10.



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