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Next-Generation Fusion Devices**

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Low Energy Molecule-Surface Interaction Processes of Relevance to Next-Generation Fusion Devices

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Abstract

The mechanisms which may lead to molecular release or scattering from surfaces exposed to low energy (0.1 - 100 eV) particle irradiation or photon and electron irradiation are summarized. The charge and electronic state, angular, translational and internal energies of the departing molecules are, where possible, described and the physical origin of the characteristics of each distribution explained. On the basis of our current understanding of these surface processes, we argue for the use of medium- to high-Z metal surfaces in plasma facing components of the gas-blanket type divertor recently proposed for ITER. By operating such surfaces at sufficiently elevated temperatures, the release of highly vibrationally excited hydrogen molecules via Eley-Rideal-like surface recombination reactions could be suppressed.

[Key words] surfaces, scattering, molecules, desorption

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1. Introduction

Next-generation fusion reactors such as the International Thermonuclear Experimental Reactor (ITER) make use of so-called divertors to scrape off and exhaust plasma edge impurities which would otherwise have a detrimental effect on device operation. It has been estimated that power densities in the divertor of the ITER reactor will be of the order of 35 MWm^{-2} [1]. Although remarkable progress has been made in the development of divertor plate materials and cooling concepts [2], it would seem necessary to reduce peak heat loads to $<10 \text{ MWm}^{-2}$. The strategy is to operate the divertor under conditions of high density and rely on gas phase atomic and molecular processes to spread the heat load over the entire divertor structure [1]. Plasma temperatures at the divertor plate surfaces of around 1 eV and neutral particle densities up to 10^{15} cm^{-3} are then envisaged [1].

Existing divertor modelling codes do not yet take account of certain atomic, molecular and particle-surface processes which may be important, or even dominant, at such low temperatures and high neutral particle densities [3,4]. We mention as examples processes involving vibrationally excited molecules and molecular ions, exothermic ion-molecule reactions and molecule formation or dissociation processes on surfaces [4]. Little is known about several of these processes, particularly the particle-surface processes, on divertor relevant materials at the low collision energies of current interest for ITER. In an attempt to partially redress this deficit, we briefly review and attempt to assess the likely relative importance of those *particle-surface processes* spanning the translational energy regime 0.1 - 100 eV which may lead to the release of molecular species from surfaces, and therefore be of relevance to the currently proposed divertor concept. In so doing, we will in general unashamedly avoid the use of terms such as physical and chemical sputtering, radiation enhanced sublimation and evaporation and disruption erosion. These processes and their implementation in modelling codes have been reviewed, eg. in [5] and the deficits noted. In this paper we prefer to base our discussion on microscopic physical processes, with the rational that some of the processes show little respect for the boundaries which appear to separate some of the commonly used categories.

We will draw the bulk of our information from surface science investigations performed under well controlled conditions. Such detailed (often ultra high vacuum) experiments are particularly suited to identifying, isolating and understanding individual processes, a discussion of which forms the bulk of this paper. Clearly though, the question arises as to the *relevance* of knowledge gained from such ‘ideal’ experiments to the conditions which might exist at the surface of a divertor plate of a fusion device. It would seem reasonable to suppose that *mechanisms* will be ‘portable’ and relevant to ‘real’ surfaces. The crucial question is to identify the dominant mechanisms and their rates on ‘real’ surfaces. In this respect it is important to note that it is possible to calculate reaction rates in the harsh environment of an industrial catalytic reactor (high temperature and pressure) using data from measurements of the behaviour of the reactants on well-defined single crystal surfaces under UHV conditions [6]. The reason is simply that on an atomic scale, real surfaces at ‘elevated temperatures’ can be thought of as ‘assembled’ from a small number of the most thermodynamically favourable well ordered surface configurations separated by steps and defects whose catalytic activity can also be characterised in single-crystal experiments. If the same can be said of divertor surfaces (on the atomic scale), then the potential exists to use surface science data obtained under an appropriate mix of ‘ideal’ conditions to simulate the behaviour of ‘real’ divertor surfaces.

2. Mechanisms Leading to Molecule Release from Surfaces

Most of the detailed information available on the interaction of neutral and ionised species with surfaces in the low energy regime comes from studies at the extremes of the energy regime of interest in this review (0.1 - 100 eV). At low translational energies (below ~1 eV), quantum state specific supersonic neutral beam experiments have provided a very detailed picture of the dynamics of the interaction of H, D, H₂, D₂ and some heavier molecules such as NO with well characterised surfaces. Above ~100 eV, experiments with both ionised and neutral molecular beams have provided detailed insights into charge transfer processes and molecular dissociation, again at well characterised crystal surfaces under UHV conditions. Very little information is

available which bridges the energy gap between the practical upper limit of supersonic beam experiments and the practical lower limit of most ion beam based experiments. However, the situation is rapidly changing, motivated in part by the needs of the fusion community and the technological interest in techniques for low damage, low temperature epitaxial thin film growth and in the dry processing of microelectronic devices.

A plethora of processes can lead to the release of molecular species from surfaces. These are illustrated schematically in Fig. 1 and described in more detail in the following sub-sections. Particles can be thermally desorbed. Particles may simply be scattered, or they may leave as a consequence of the exothermicity of a chemical reaction, in response to momentum transfer by energetic particle irradiation, and via a variety of direct and substrate mediated electronic processes induced by incident electrons and photons. Molecular species may, in principle, be rotationally, vibrationally and translationally 'hot' (or cold!), reflecting the detailed dynamics of the ejection, reflection or desorption process.

Particles may also depart from the surface in an electronically excited or ionized state. The creation of such a state may (as in the case of certain electron and photon induced desorption mechanisms) be intimately related to the ejection process itself. However, the probability of survival of such a state, at least for particle ejection from *metal* surfaces, can be qualitatively understood by reference to Fig. 2. If, in the near surface region, the ionisation level of the particle lies energetically above the Fermi level of the metal, the probability that the particle leaves the surface as an ion may be quite high. Similarly, if the affinity level of the particle lies close to or below the Fermi level over the range of particle-surface separations where the electron tunneling probability is high, the probability of negative ion emission could also be high. However, for hydrogenic species near metal surfaces with work functions of ≈ 5 eV (i.e., for all but alkali or alkali-covered metals), simple image potential considerations lead us to expect the ionisation level to lie well below, and the affinity level well above, the Fermi level. In this case the probability P_s of survival of a non-equilibrium product is given roughly by a formula of the type derived (originally in terms of velocities) by Hagstrum [7], viz.

$$P_s \propto \exp(-\tau_n/\tau_e)$$

where τ_e represents the electron transfer time of ~ 1 fs at metal surfaces and τ_n the timescale for the departure of the particle from the surface. Even for 100 eV low mass particles, the exponential dependence on the ratio τ_n/τ_e leads to the establishment of near-equilibrium [8] level populations and consequently, to very low ionized or electronically excited particle fractions. However, for contaminated and graphite surfaces (where τ_e may be much larger) and alkali metal surfaces (where the assumptions underlying the derivation of the above equation are no longer valid), high negative ion fractions have been reported (e.g. up to 10 % H⁻ from a graphite surface [9]).

To provide an overview, we have attempted in the following sub-sections to illustrate each of the processes shown in Fig. 1 with suitable examples from the literature. We have restricted ourselves to a discussion of the angular, translational energy and internal energy distributions. The charge and electronic state distributions are not explicitly addressed, but they will of course be influenced by the above-mentioned general considerations. It has not been our intention to provide a complete review of all published work. Instead, our central aim has been to introduce and explain the general concepts and to illustrate as clearly as possible the physical processes which are believed to be operative. It is our hope that through an understanding of those processes, it may be possible to actually avoid certain ‘troublesome’ processes via an appropriate choice of the plasma facing material or surface operating temperature.

2.1 Thermal Desorption of Molecularly Adsorbed Species

Despite being in thermodynamic equilibrium with a surface, a molecularly adsorbed species may nevertheless thermally desorb (Fig. 1a). The surface binding energy of individual molecules may be overcome by the transfer of sufficient energy from the phonons of the substrate to the molecule-surface vibrational co-ordinate. It might be

expected that the dynamical parameters of such desorbing molecules would reflect the temperature of the surface, i.e. that the angular distribution would be cosine, the velocity distribution Maxwellian and the rotational and vibrational population distributions would follow the Boltzmann law. That this is in general unlikely to be the case was argued quite early by Comsa [10]. A glance at a two dimensional representation (Fig. 3) of a possible potential energy surface (PES) for a diatomic molecule interacting with a surface makes the reason for such doubts immediately clear. The existence of a region of *elevated potential energy*, such as an *adsorption barrier* in the final section of the *desorption path* (region a of Fig. 3), can clearly lead to the transformation of a thermally activated desorption process into an apparently exothermic process. The translational energies of desorbing molecules reflect the detailed dynamics of 'rolling off' this barrier. Any curvature in the exit path for the desorption process, as present in Fig. 3, could clearly lead to vibrational excitation of the desorbing species which would then, for the same reason, bear little or no relation to the temperature of the surface. The same general comments apply to molecules which are formed via the recombination of surface adsorbed species (region c on the PES of Fig. 3) and equilibrate totally or partially in the molecular adsorption region of the PES (region b on the PES of Fig. 3) before desorption occurs.

2.2 Prompt Molecular Desorption Following Surface Recombination (L-H) Reactions

If the region b on the PES of Fig. 3 is absent (i.e. a stable molecularly chemisorbed species does not exist), recombination reactions of surface equilibrated, adsorbed species (so-called Langmuir-Hinshelwood reactions, Fig. 1b) may lead to the prompt desorption of molecules from the surface. Again the comments of the previous subsection apply. A now classic example of non-cosine angular distributions and non-equilibrated velocity distributions following such a thermally induced surface recombination reaction was investigated by Comsa and David [11] for the recombinative desorption of H₂ and D₂ from Cu(100) and Cu(111) surfaces (Fig. 4a,b).

The dynamics of the desorption process has in this case been investigated in considerable detail by Küchenhoff et al. [12] using the model potential energy surface of Fig. 5. This study was prompted by the above results and by the non-Boltzmann vibrational population distributions (Table 1) observed for the recombinative desorption of H₂ and D₂ from Cu(110) and Cu(111) by Kubiak et al. [13]. In the latter experiments the vibrational population of the $v = 1$ state was found to exceed that expected from a Boltzmann distribution at the surface temperature by up to two orders of magnitude. That the barrier for *adsorption*, at least for the Cu(111) surface, is indeed late* and the exit path for the *desorption* process indeed curved has recently been verified by *ab initio* calculations of the potential energy surface within the local density functional generalised gradient approximation by Hammer et al. [14].

Enhanced vibrational populations have also been observed for the desorption of D₂ from Pd(100) by Zacharias [15]. Both the latter experiment and that of Kubiak et al. [13] for H₂ and D₂ desorption from Cu(110) and Cu(111) found non-Boltzmann rotational state distributions characterised by mean energies considerably less than kT_{surface} .

* A 'late barrier' is one which is located at a small molecule-surface separation but a large atom-atom separation in the molecule. The intra-molecular bond is therefore broken 'late' in the interaction of the molecule with the surface.

2.3 Prompt Molecular Desorption Following Gas-Surface Recombination (E-R) Reactions

The direct reaction of a particle from the gas phase with a surface-adsorbed species can lead to the abstraction of the adsorbed species from the surface (so-called Eley-Rideal reactions, Fig. 1c). The observation by Hall et al. [16] and Eenshuistra et al. [17] of highly vibrationally excited hydrogen molecules emanating from a metal box containing hydrogen in the presence of a heated filament (up to $v=9$ in [16]) lead to the inference that this process was occurring. The first well controlled experiments involving the formation of hydrogen molecules via this process were reported by Rettner [18]. Using atomic deuterium beams with translational energies of 0.07 eV and 0.36 eV incident on an atomic hydrogen covered Cu(111) surface, Rettner obtained the angular distributions of released HD shown in Fig. 6 [19]. The beams were incident at 60° to the surface normal. The dependence of the shape of the angular distribution on incident beam translational energy is clear evidence for a direct process in which the incident particle has not yet equilibrated completely, if at all, with the surface. The mean translational energy of the HD product was 1.1 ± 0.2 eV, independent of the emission angle within 20° of the surface normal [19]. The dependence of the mean rotational energy on vibrational state is reproduced in Fig. 7 and the vibrational state distribution is shown in Fig. 8 [19]. These results reveal that hardly any energy has been transferred to the crystal lattice in the interaction. The degree of rotational excitation was found to decrease with increasing vibrational excitation, reflecting the partition of a fixed total energy (incident translational energy E_T^i plus reaction exothermicity of $\Delta E_{ex} \sim 2.3$ eV [20]) among the product degrees of freedom viz.

$$E_T^i + \Delta E_{ex} = E_T^f + E_V^f + E_R^f.$$

The reaction exothermicity is given by the difference between the energy gained by formation of the H_2 (or HD or D_2) bond, E_{H-H} , and the energetic cost of breaking the H- (or D-) surface bond, E_{H-S} , viz.

$$\Delta E_{ex} = E_{H-H} - E_{H-S}.$$

The energy in the product vibrational degree of freedom is therefore restricted to the range

$$E_v^f < E_T^i + E_{H-H} - E_{H-S}$$

by energy conservation considerations. The only conceivable explanation for the observation of $H_2(v=9)$ in the experiment of Hall *et al.* [16] is, therefore, that the adsorbed atomic hydrogen was in a weakly bound sub-surface site, was only very weakly bound to the surface [21], or the adsorbate-surface bond was highly vibrationally excited. Recent experiments by Fukutani *et al.* [22] have demonstrated the possibility to distinguish surface and sub-surface hydrogen and determine both the absolute amount of hydrogen present and its depth distribution with monolayer resolution. It should therefore be possible using techniques such as those to at least check for the presence, and measure the concentration and location of any sub-surface hydrogen in proposed divertor materials at their anticipated operating temperature.

For energetic hydrogen impact (E_T^i large), the nature of the binding site or degree of adsorbate vibrational excitation is of little importance in determining the energetics of the product vibrational excitation, as the above inequality shows.

The cross section for the reaction was found by Rettner and Auerbach [19] to be $\sim 3.8 \pm 0.5 \times 10^{-16} \text{ cm}^2/\text{adsorbed atom}$ for incident D-atom energies of 0.07 - 0.36 eV. This is roughly four times the geometrical cross-section of HD, suggesting that the incident atom may (contrary to the simplified picture depicted in Fig. 1c) first hit the surface before reacting with the adsorbate. In this experiment, *all the desorbed particles, independent of the vibrational quantum state, appear to arise from E-R reactions.* Note that this latter conclusion is *not at variance* with the measurements of the

vibrational populations of H_2 effusing from the heated filament sources of Hall et al. [16] and Eenshuistra et al. [17] reported earlier, as in those experiments the effusing flux will contain both non-equilibrated *desorbed* H_2 created on the inner walls of the container and hot *gas phase* H_2 from within the box.

In the experiments of Rettner [18,19] discussed above, the lack of a significant contribution to the desorption flux of hydrogen arising from L-H reactions is not difficult to rationalise, despite the high surface concentration of adsorbed hydrogen. If the surface temperature were high enough for L-H reactions to occur (≈ 300 K [19]), they would quickly deplete the concentration of adsorbed hydrogen, making the probability for a direct interaction between a gas phase hydrogen atom and an adsorbed hydrogen atom very small. Of course, at a very high incident hydrogen flux, it may be possible to reach a regime where the L-H recombination time is comparable to or longer than the average time between successive impacts from the gas phase on a given adsorption site, leading to the co-existence of both desorption channels.

Valuable theoretical insights into the E-R reaction mechanism have been provided by Jackson and Persson [20] and Kratzer and Brenig [21]. A two-dimensional cut of the model PES used by the latter authors for the reaction of gas phase H with H adsorbed on a tungsten surface is reproduced in Fig. 9. The gas phase hydrogen atom approaches from the upper right hand corner of the PES and the H_2 molecule leaves through the narrow, vertical exit channel on the left. The atom from the gas phase is *accelerated* before hitting the adsorbed atom. The observed high vibrational excitation was found by Kratzer and Brenig [21] to be a consequence of this acceleration and the high curvature of the PES compared to the PES for the L-H reaction (Fig. 5). The influence of the kinetic energy of the impinging H-atom on the probability of populating a given vibrational state is reproduced in Fig. 10 [21]. We observe there an increasing population of the higher vibrational states with increasing kinetic energy over the range 0.05 eV to 0.3 eV. The authors also report [21] a decrease in the number of reactive collisions with increasing incident atom kinetic energy or increasing attraction of the impinging atom to the surface and attribute this observation to the increasing difficulty at shorter interaction times for the system to find its way into the

narrow exit channel in Fig. 9. It remains to be clarified whether these trends would persist for non-normal incidence, and yet higher impact energies of relevance to future divertor designs (up to ~ 100 eV).

Several experiments at higher incident particle energies have been performed. An attempt by Jiang et al. [23] to observe product ions from E-R type reactions between incident 10 eV N^+ ions and CO adsorbed on Ni(100) and Cu(100) was unsuccessful. However, one of the first clear demonstrations of the E-R mechanism was provided by the observation by Kuipers et al. [24] of the protonation of 1 - 9 eV $N(C_2H_4)_3N$ incident on a hydrogen-covered Pt(111) surface. The product ion yield was found to increase with the kinetic energy of the incident molecule, a result believed to reflect the translational energy dependence of the initial ionisation step of the incident molecule rather than the efficiency of the abstraction reaction itself [24]. More recently, Yang et al. [25] have observed recombination reactions between incident 30 - 250 eV Cs^+ ions and surface species (Si and O) for scattering from a Si(111) surface in the presence of adsorbed H_2O . They invoke a substantial influence of momentum transfer between the incident molecule and the surface atom in forming the product molecule.

It is unclear whether the formation of hydrocarbon molecules following the exposure of graphite and carbon containing materials to hydrogen [26] proceeds via the L-H or E-R mechanisms, an intermediate case [27], or a combination of these.

2.4 Desorption and Sputtering Induced by Incident Atomic and Molecular Species

Incident atomic and molecular species can simply displace adsorbed species, with part of the adsorption energy of the incident particle being carried away by the displaced desorbing species [28]. Energetic atomic and molecular impact can lead, via direct momentum transfer, to the initiation of chemical reactions on surfaces (chemistry with a hammer [29]) with the possible liberation of a molecular product. Pre-existing

molecules may also be desorbed from surfaces [30] following either the direct impact of incident energetic particles (chemistry with a sickle) or momentum transfer from secondary particles which have been set in motion by the initial energetic particle impact. Diebold et al. [31] have measured cross sections in the range of 10^{-15} cm² for desorption of neutral CO from a Ni(111) surface exposed to rare-gas ion (He⁺, Ne⁺, Ar⁺ and Kr⁺) bombardment at impact energies from 10-500 eV.

At yet higher incident particle energies (which are not the subject of this review), an extensive literature exists (see eg. [32] and refs. therein). However, the validity of the binary collision approximation, which forms the basis of commonly used computer programmes to simulate *physical sputtering* at higher energies (such as TRIM [33] and MARLOWE [34]), becomes questionable at low energies. The need for molecular dynamics simulations in the low energy regime has been noted already by Reiter [5]. However, such simulations require reliable potentials, not just for perfect surfaces, but also for step and kink atoms and defect inundated surface morphologies. A limited number of molecular dynamics simulations do exist for the near threshold physical sputtering regime. Amirav and Cardillo [35] have shown that P₂ and P₄ molecules are efficiently sputtered from the surface of InP(100) by 16 eV Xe atoms. Molecular dynamics simulations have also shown that 6 - 30 eV argon atoms can induce efficient sputtering of materials such as nickel [36].

Low energy neutral and ionised particle impact can lead to electronic excitation [37,38], which introduces the possibility of a variety of ejection mechanisms which are discussed in more detail in the next section (2.5). These 'electronic' mechanisms may in principle act alone, or in addition to the role of direct momentum transfer by collisions. Diebold and Varga have investigated the influence of the charge state of low energy incident beams on secondary ion production in the CO/Ni(111) system and on ionized cluster emission from LiF [39,40]. Except for the above-mentioned work, very little additional information is in fact available, either from experiments or computer simulations, on low energy (< 100 eV) atomic and molecular impact induced ejection of *molecular species* from surfaces.

2.5 Desorption Induced by Electron and Photon Irradiation

In principle, both substrate atoms and adsorbates may be desorbed from surfaces by electron and photon irradiation (Fig. 1d). The desorption may occur via a direct process, in which the initially bound configuration of the particle-surface system is directly excited by the incident electron or photon, or via a substrate-mediated process, where the first step involves the creation of a localised or non-localised electronic excitation of the substrate. These processes are illustrated schematically in Fig. 11.

In the so-called Menzel-Gomer-Redhead (MGR) mechanism [41], a direct transition from a bonding to an antibonding electronic configuration is induced (Fig. 11a). Provided the upper state lifetime is comparable to or longer than the time required for the particle to escape from the immediate vicinity of the surface, desorption occurs. This mechanism is generally inefficient on metal surfaces, as the upper state lifetime is typically of the order of femtoseconds while the nuclear motion occurs on the timescale of molecular vibrations, namely 10-100 fs.

In the Antoniewicz mechanism [42], a direct transition from the ground state to a bound upper state is induced by the incident radiation. If the topography of the upper state is such that the particle is accelerated *toward* the surface, the system may find itself in an unbound vibrational state upon relaxation (Fig. 11b). The probability of desorption from metals may be significantly higher than that for the MGR mechanism as the Antoniewicz mechanism can take advantage of the strongly repulsive inner wall of the lower state to 'compensate' for a short propagation time on the upper state.

In the mechanism suggested by Knotek and Feibelman [43], a core hole is generated on a near surface atom by the incident electron or photon (Fig. 11c). Relaxation of this initial excitation via Auger decay could leave a surface species in a singly or doubly ionised state (for intra- and interatomic Auger decay respectively) which may be antibonding with respect to the surrounding atoms. If this excitation is not quenched on the time-scale for nuclear motion, the species may be ejected from the surface.

The adsorption of an incident electron or photon can also result in the production of electron-hole pairs in the conduction band of the solid. The resulting energetic electrons (sometimes referred to as ‘hot’ electrons [44]) may scatter through higher lying negative-ion-like resonance’s of the adsorbate-substrate system (Fig. 11d). This *indirect* process [44] looks formally just like the Antoniewicz mechanism (Fig. 11b), as the addition of an image potential-like contribution

$$V_{im} = -1/4z,$$

(to describe the presence on the adsorbed particle of an additional electron) to the initial state potential curve, leads to an upper to lower state relative topography just like that assumed by the Antoniewicz mechanism. The efficiency of the desorption mechanism again depends critically on the residence time of the electron in the upper state. Under very high fluence conditions, achievable in the laboratory for example via the use of intense femtosecond laser pulses, a sufficiently high density of ‘hot’ electrons may be produced to enable several such electron scattering events to occur [45]. Transitions to the upper state provide the ‘kicks’ necessary for the adsorbate to climb the vibrational ladder and permit desorption to occur.

Evidence that multiple electronic transitions indeed play a role at high laser fluences is given in Fig. 12, which shows the expected [45] non-linear fluence dependence of the desorption yield of NO from a Pd(111) surface exposed to 200 fs pulses of 620 nm laser light at a repetition rate of 10 Hz [46]. The authors estimate a peak electronic temperature of ≈ 3000 K is reached on the time-scale of the laser pulse. This decays after about 1 ps via diffusion and coupling to the lattice, which reaches a peak temperature of ≈ 650 K, before the common electronic and lattice temperature equilibrates with the bulk on a timescale of ~ 10 ps. However, even ‘off-normal’ events in the divertor of a fusion device, which are estimated [47] to deliver 2-10 MJ/m² in 0.1-3 ms to plasma facing surfaces, fall a factor of at least 10^6 short of the energy densities delivered by the above-mentioned fs laser pulses. This deficit effectively rules out any role for multiple electronic transition type desorption mechanisms in contributing to the desorption flux in the initial instants of an ‘off normal’ event.

2.6 Scattering

The scattering of low energy neutral and ionised molecular species from surfaces (Fig. 1e) may be accompanied by charge transfer, fragmentation, rotational and vibrational excitation and deexcitation, and abstraction and desorption of surface species. At the very lowest energies of interest here (~ 0.1 eV), only molecular rotations and substrate phonons may be excited, provided the incident molecule is neutral and in its vibrational ground state. As the kinetic energy is increased, the details of any attractive part of the interaction are expected to become less important and the collision will become more impulsive in nature. At the same time, vibrational excitation, electron-hole pair excitation and finally ionisation and dissociative scattering become energetically permissible. These and a host of other phenomena which lie outside the scope of this article have been reviewed recently by Amirav [48], Ceyer [49], Gerber [50], Rettner and Auerbach [51] and others [52-55].

Angular distributions of scattered molecules depend sensitively on the incident beam translational energy, incidence angle and charge state. For neutral N_2 scattering from a W(110) surface at 800 K, the width (FWHM) of the angular distribution decreases from $32 \pm 2^\circ$ at an incident beam energy of 0.09 eV to $19 \pm 1^\circ$ at 1 eV [51] (Fig. 13). The scattering potential is, however, essentially 'flat' and the incident molecule experiences quasi-specular reflection, often shifted toward grazing exit angles reflecting a preferential loss of energy from the surface normal component of the particle motion [48]. As the incident particle kinetic energy or surface normal energy is increased yet further, the scattering potential becomes more corrugated, resulting again in broader angular distributions [56,57]. This effect is seen in Fig. 14 for the scattering of O_2 from Ag(111) [56]. The dependence on incident beam energy of the angular distributions of CO^+ scattered from Pt(100) is shown in Fig. 15 [58]. The authors suggest that the acceleration of the beam toward the surface in the attractive part of the molecule surface interaction potential leads to a strong enhancement in the loss of surface normal energy via the excitation of phonons.

During scattering, a fraction of the incident beam kinetic energy may be transferred to the rotational and vibrational degrees of freedom of the molecule and the vibrational degrees of freedom of the substrate. Rotational state distributions for NO following scattering from Ag(111) at a surface temperature of 750 K are shown as a function of the energy of the incident beam in Fig. 16 [51]. The effect of the incidence energy on the vibrational populations is shown in Fig. 17 [51]. Van den Hoek et al. [59] have performed molecular dynamics simulations of the partition of energy between these degrees of freedom for O₂ scattering from a Ag(111) surface over a range of incidence energies between 1 eV and 3 keV (Fig. 18). However generalisations to other systems are difficult, as the results obtained will depend on the precise details of the interaction potential and the geometric arrangement of the surface atoms.

An extensive theoretical analysis by Gross et al. [60] has shown that vibrational excitation can arise purely from scattering on the electronically adiabatic ground state PES in the so-called entrance channel of the PES (region a of Fig. 3), particularly if the entrance channel exhibits curvature (as in Fig. 3) and the vibrational frequency of the molecule changes upon the molecule approaching the surface. If the system were to access for a short time an electronic configuration different from that in the entrance channel (such as the molecular chemisorption region 'b' of the PES in Fig. 3) or electronically non-adiabatic processes occur, vibrational excitation may also result [61,62]. The mechanism of vibrational excitation in the former case, where a transient change in the electronic configuration occurs, is similar to that which leads to vibrational excitation in the Antoniewicz mechanism of desorption discussed earlier (section 2.5 and Fig. 11b). Without the support of multi-dimensional calculations on reliable potential energy surfaces, it does not at present seem possible to distinguish the various possible origins of vibrational excitation observed in experiments.

At incident neutral molecule translational energies exceeding the molecule dissociation energy, the dissociative scattering channel will compete with the sticking, chemisorption and non-dissociative scattering channels. Experiments on molecular dissociation induced by 'impulsive' collisions with chemically inert solid surfaces have

been performed, e.g. by Gerber and Amirav [63]. Classical trajectory studies on *planar*, rigid surfaces by the same authors showed that energy transfer to the rotational degree of freedom is very efficient [63]. The angular momentum J acquired by the molecule upon impact leads to a reduction in the depth of the unperturbed intramolecular potential $V_0(r)$, viz.

$$V_J(r) = V_0(r) + J^2/2\mu r^2$$

where μ is the reduced mass of the molecule and r the internuclear separation. Dissociation may occur at low J with the assistance of vibrational excitation, which although less efficient [63], may suffice to overcome the centrifugal barrier. At sufficiently high J , the molecular potential $V_J(r)$ becomes purely repulsive and dissociation proceeds unhindered. This result was also shown to hold for *corrugated* surfaces by van den Hoek and Kleyn [59] in the afore-mentioned classical simulation of O_2 scattering from Ag(111). In a further classical trajectory study by the same group, this time for 70 eV O_2 scattering from Pt(111), Kirchner et al. [64] showed that early in the interaction, approximately twice as much energy was transferred from the translational to the rotational as to the vibrational degree of freedom, independent of the final outcome of the scattering event. Later in the trajectory, those molecules which finally dissociate were found to possess much more vibrational than rotational energy, while those which do not dissociate have roughly the same amount of energy in vibration and rotation.

As the collision energy is increased, the surface appears more corrugated. For 70-200 eV H_2 scattering from Ag(111) at not too large angles of incidence to the surface normal, the dissociation probability was found by van Slooten et al. [65] to exhibit $E_i\theta_s^2$ scaling, where E_i denotes the incident beam energy and θ_s the total scattering angle of the dissociatively scattered H-atoms. This could be understood by assuming that most collisions were governed by the interaction of an incident dumbbell or ellipsoid shaped molecule with a *single* surface atom [66].

If the incidence angle is increased sufficiently toward grazing, shadowing effects eventually become important at all energies. The lateral corrugation of the interaction potential may still be large, but the trajectory of the molecule comes to be dominated by the surface normal directed forces experienced by the molecule in passing over the ‘peaks’ of the corrugated molecule-surface interaction potential. The classical trajectory calculations of Van den Hoek et al. [59] show that for grazing incidence of 1 eV - 3 keV O₂ on Ag(111) and constant surface normal energy of 11.7 eV, both the total energy loss and the dissociated fraction goes through a maximum at several 10’s of eV incident beam energy before becoming independent of energy beyond several 100 eV. These conclusions will of course lose their validity if the surface is atomically rough on length scales smaller than the trajectory length of the molecule in the surface interaction region.

If the incident molecule is positively ionised, and charge transfer to non-bonding states of the neutral molecule is energetically possible, dissociative scattering may occur. On the other hand, charge capture to bound states may be accompanied by vibrational excitation. A concrete example is provided by the H₂⁺ molecule. Upon approach to a metal surface, both the bound singlet X¹Σ_g⁺ and unbound triplet b³Σ_u⁺ states of H₂ are probably populated by charge transfer [67] (Fig. 19). Adiabaticity arguments suggest that charge transfer will occur as the molecule approaches the surface. The branching ratio for these two charge transfer channels is unknown in the energy range of interest here. However, at beam energies of several keV and glancing incidence (surface normal energies of the order of 1 eV), detailed measurements of H₂⁺ and D₂⁺ scattering from Cu(111) seem to suggest that between 30% and 80% of the beam may be non-dissociatively scattered [68]. Positive and negative product ion fractions for 400 eV H₂⁺ and H₃⁺ irradiation of graphite at surface normal energies of around 50 eV have been reported by Tsumori et al. [9] and positive and neutral product fractions for 0.2-1 keV H₃⁺ irradiation of Ni(111) at normal energies of 2-10 eV by Willerding et al. [69].

Incident neutral molecules or initially ionised molecules which neutralise to a bound state can still dissociatively scatter, even under conditions where the purely collisional mechanisms discussed earlier are not important. Fast neutral H₂ (keV energies) in its

ground electronic state is efficiently dissociated in grazing collisions with metal surfaces [70,71]. It has been proposed [71] that the dissociative scattering dynamics of fast molecules is influenced by additional (higher lying) potential surfaces of quite different topography to that of the adiabatic ground state, via processes analogous to those discussed already for desorption in section 2.5. If we convert the experimentally measured total translational energy losses to losses per unit time in the interaction region [71], we discover that keV energy molecules dissipate energy at rates in the 0.1-1 eV/fs regime. Most of the energy appears to be transferred to the metal conduction electrons via an efficient electron-hole pair excitation mechanism [72]. The resulting 'hot' electrons are therefore continuously available to populate higher lying electronic states of the molecule-metal system. Classical simulations of this process have successfully reproduced the essential features of the measured orientation distributions of the internuclear coordinate of a large number of dissociatively scattered diatomic and polyatomic molecules [73]. Most of the molecules studied to date appear to dissociate via potential surface hopping induced vibrational excitation in the entrance channel region of the ground state PES [73]. The same mechanism predicts a high vibrational excitation of non-dissociatively scattered molecules, a prediction which awaits experimental verification.

3. Conclusion

The microscopic mechanisms responsible for the formation of molecules on surfaces and of their departure from surfaces as a result of low energy particle-surface interactions (including photon-surface interactions) are quite well understood from several decades of surface science investigations. This is particularly so for metal surfaces. Although the rotational, vibrational and electronic state populations of departing molecules exhibit complex system-specificities and surface structure dependencies, two generalisations do seem possible *for metal surfaces* at least:

- the fast (10's of fs) electronic relaxation times characteristic of conduction band electrons in metals imply that at the low ejection velocities of interest here, the product state distributions will generally be dominated by dynamical processes involving the *lowest lying adiabatic electronic state* of the system, and
- product angular, translational, vibrational and rotational distributions are unlikely to be thermal distributions characterised by the temperature of the surface.

The recommendation which emerges from our current understanding of particle-surface processes in the 0.1-100 eV impact energy regime is to use *medium to high-Z metals* for the surfaces of divertor structures exposed to the low energy particle irradiation characteristic of the proposed ITER divertor operation mode. With this choice, penetration and 'physical sputtering' of surface material will be minimized. At sufficiently elevated surface temperatures, surface damage will be self-annealing on the microscopic scale relevant to the processes discussed in this paper. This will lead to the properties of the surface being more consistent and predictable. By operating devices at a sufficiently high surface temperature, thermal desorption of adsorbed H₂ or diffusion of any adsorbed atomic hydrogen, followed by L-H surface recombination reactions, will occur. This will lead to a low concentration of surface and sub-surface hydrogen and a relatively low vibrational excitation of the desorbing H₂. In contrast, a 'low' surface temperature would permit, in the absence of efficient particle induced desorption, a high concentration of surface hydrogen to become established, increasing the probability of Eley-Rideal reactions and the probability that the desorbing H₂ is highly vibrationally excited.

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Figure Captions

Fig. 1. Schematic illustration of processes which may in principle lead to the emission of molecular hydrogen (H_2 , H_2^+ or H_3^+) from surfaces: a) thermal desorption of molecularly adsorbed species; b) prompt desorption following surface recombination of adsorbed species (Langmuir-Hinshelwood reaction); c) prompt desorption following the direct reaction of a species from the gas phase with a surface adsorbed species (Eley-Rideal reaction); d) direct (right) or substrate mediated (left) desorption induced by incident heavy particles, electrons and photons; e) direct scattering of molecules incident from the gas phase, possibly accompanied by fragmentation (e.g. $H_3^+ + e^-$ (metal) $\rightarrow H_2 + H$).

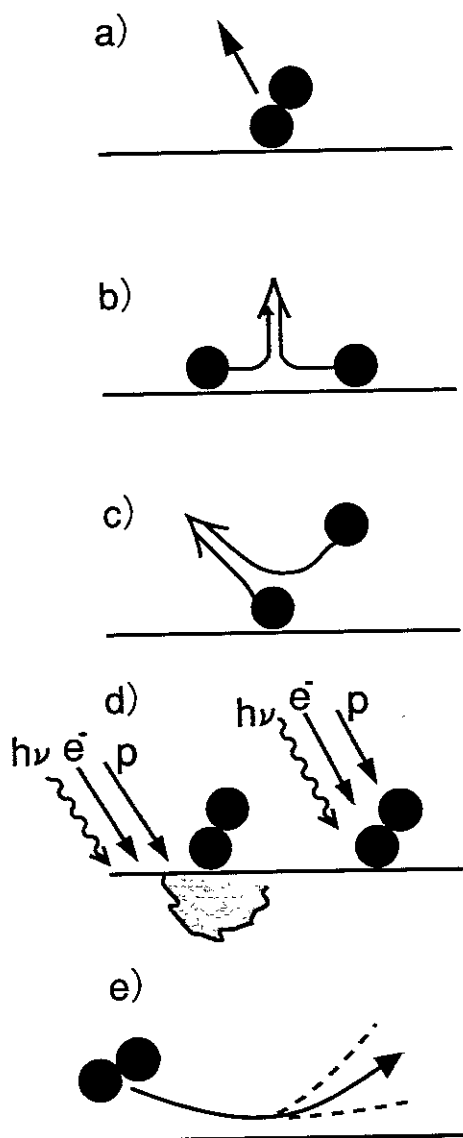


Fig. 2. Schematic illustration of the shift and broadening experienced by atomic or molecular ionisation and affinity levels in the vicinity of a metal surface (ϵ_F is the Fermi level of the metal, I and A the ionisation and affinity levels of the atom or molecule; for simplicity of representation, the ad-particle potential is shown as a single Coulomb-like well).

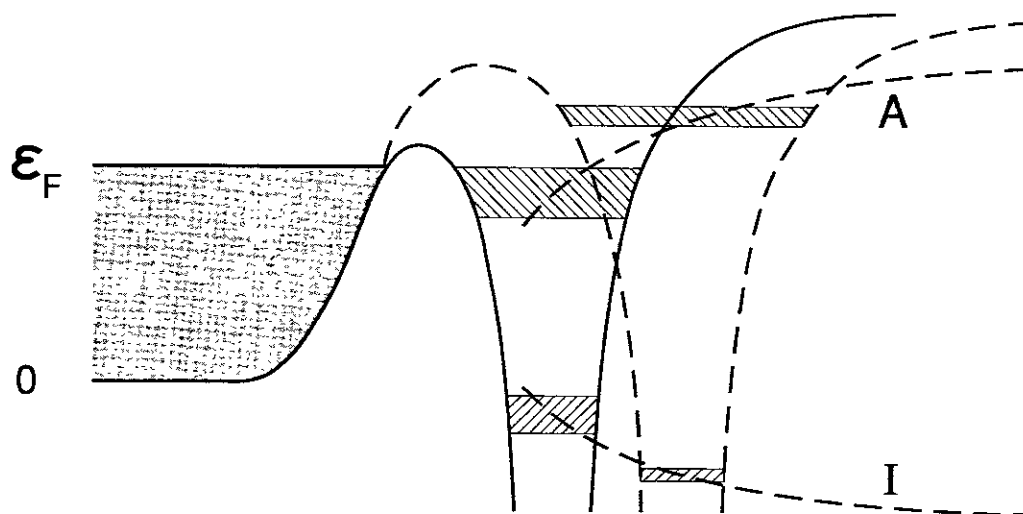


Fig. 3. Contour plot of the potential energy surface (PES) for a diatomic molecule interacting with a surface as a function of the separation x of the atoms in the molecule and the distance z of the molecule centre of mass from the surface. Region a of the PES represents the gas phase molecule in the initial (final) stage of adsorption (desorption). Region b represents a molecularly chemisorbed species. Region c represents the dissociative chemisorption of the molecule on the surface. We emphasise that the shape of such potential energy surfaces depend on the chemical nature of the constituents of the molecule, the location of the molecule with respect to the nearby surface atoms, the chemical nature and geometrical arrangement of the surface atoms and the molecular orientation with respect to the surface.

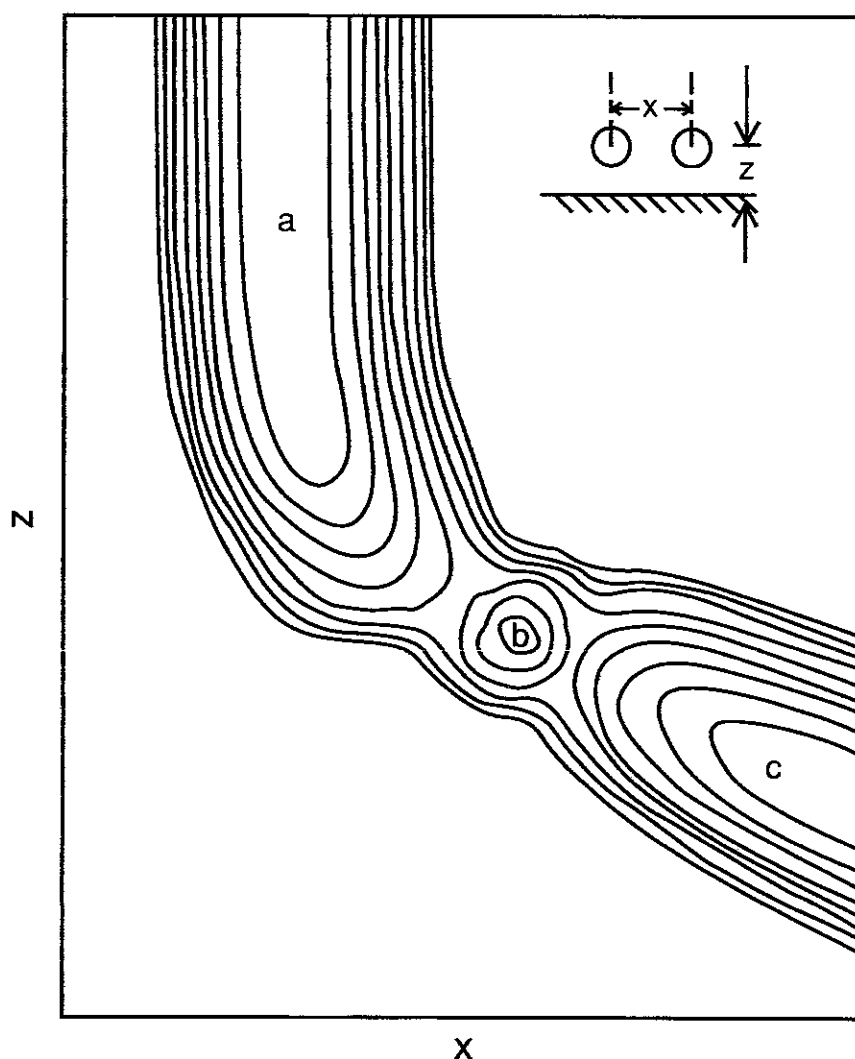


Fig. 4. a) Normalised flux of D_2 molecules desorbing from Cu(100) (\times) and b) mean energy of D_2 molecules desorbing from Cu(100) (\times) and Cu(111) (\circ) as a function of the polar angle of desorption ϑ (adapted from fig. 3 of [11], with permission).

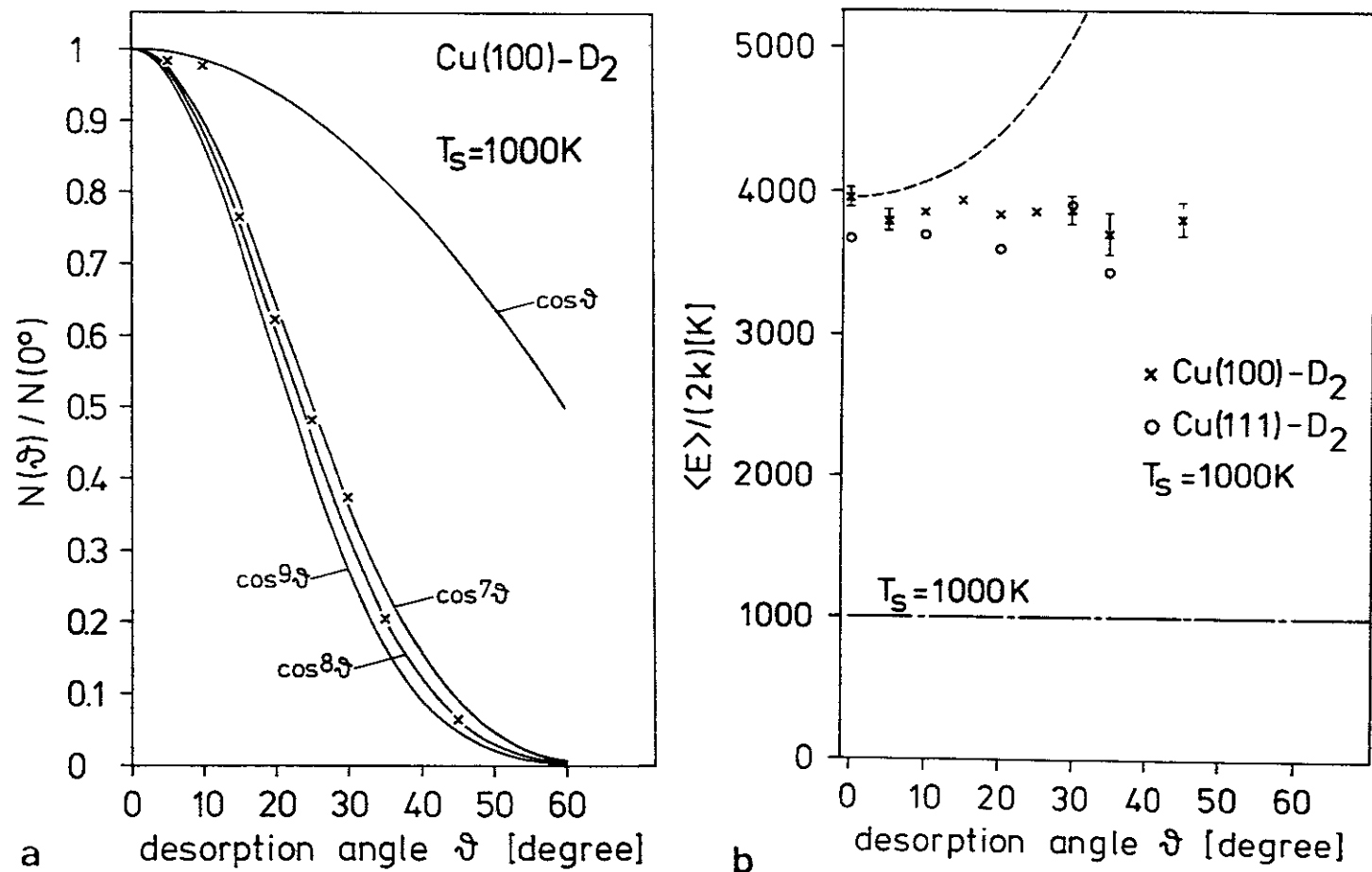


Fig. 5. Model PES for H_2 interacting with Cu as a function of the co-ordinates x and z (see caption to fig. 3). The separation of two contour lines is 0.1 eV (fig. 1a of [12], with permission).

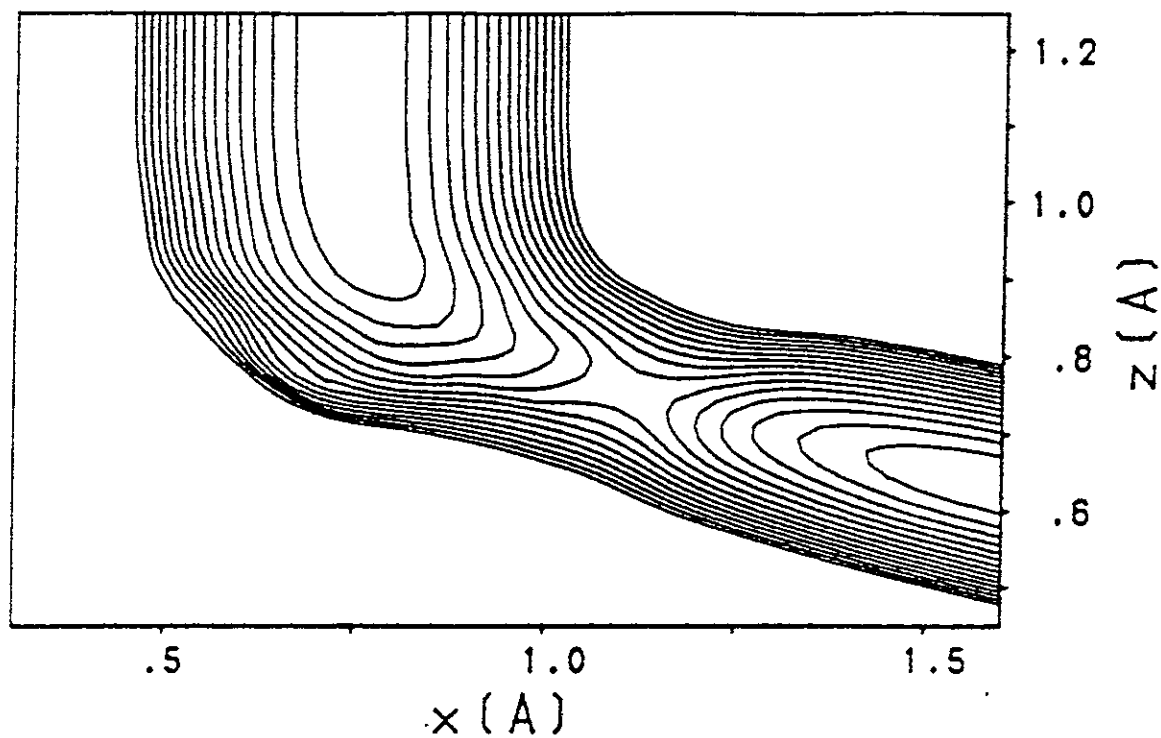


Fig. 6. Angular distribution of HD molecules desorbed from a H-covered Cu(111) surface at 100 K exposed to D-atom beams of kinetic energies of 0.07 eV (■) and 0.37 eV (●) incident at 60° to the surface normal. The solid curves are drawn to guide the eye (fig. 2 of [19], with permission).

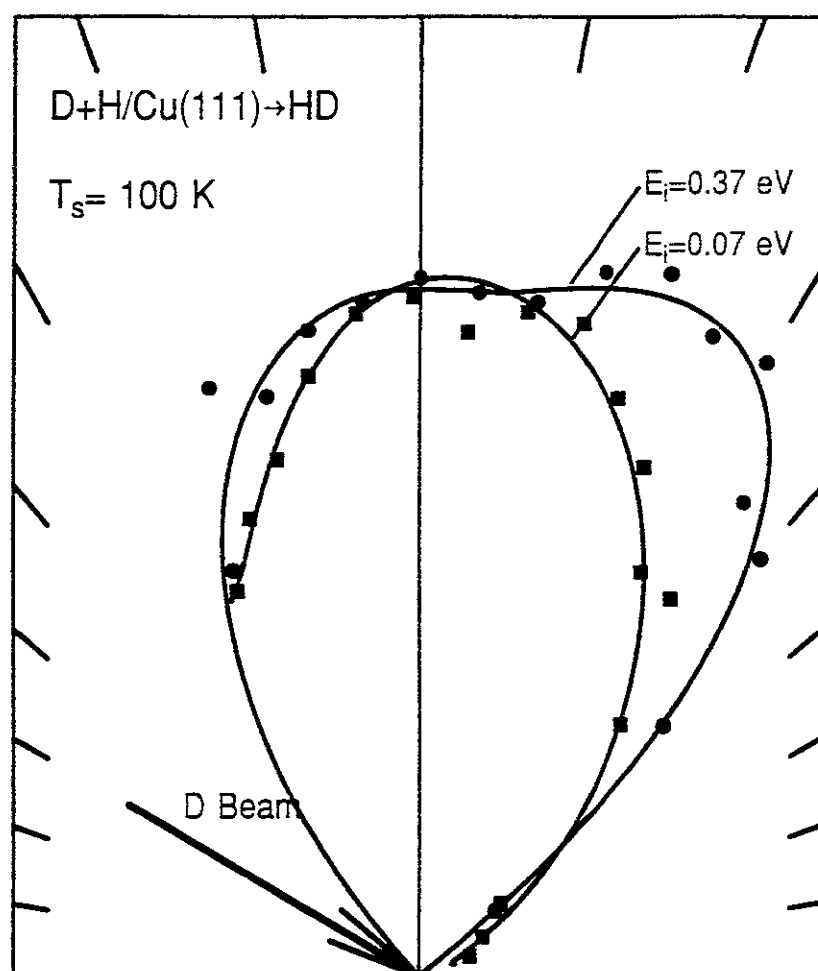


Fig. 7. Vibrational state dependence of the mean rotational energy of HD molecules produced via the reaction of incident D-atoms with a H-covered Cu(111) surface at 100 K. The mean translational energy was measured to be 1.1 ± 0.2 eV (fig. 8a of [19], with permission).

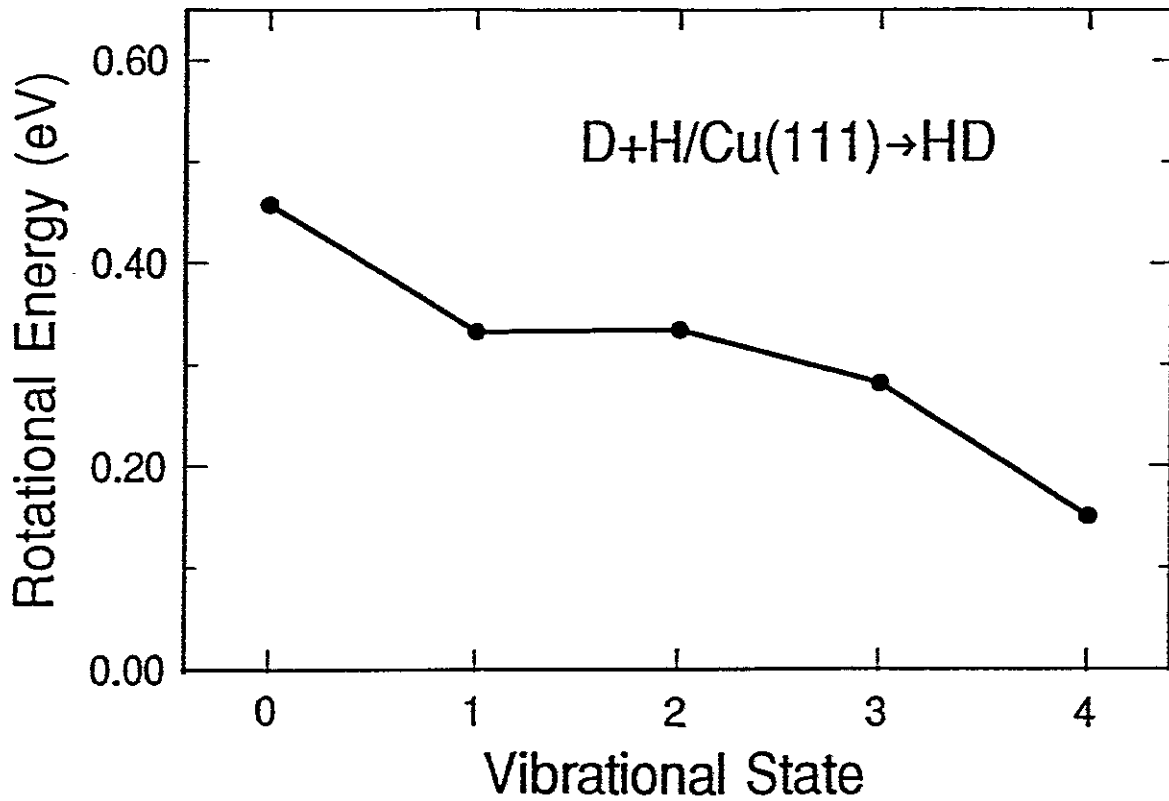


Fig. 8. Vibrational state (flux) distributions of HD molecules produced via the reaction of incident D-atoms with a H-covered Cu(111) surface at 100 K. The mean translational energy was measured to be 1.1 ± 0.2 eV (adapted from fig. 7a of [19], with permission).

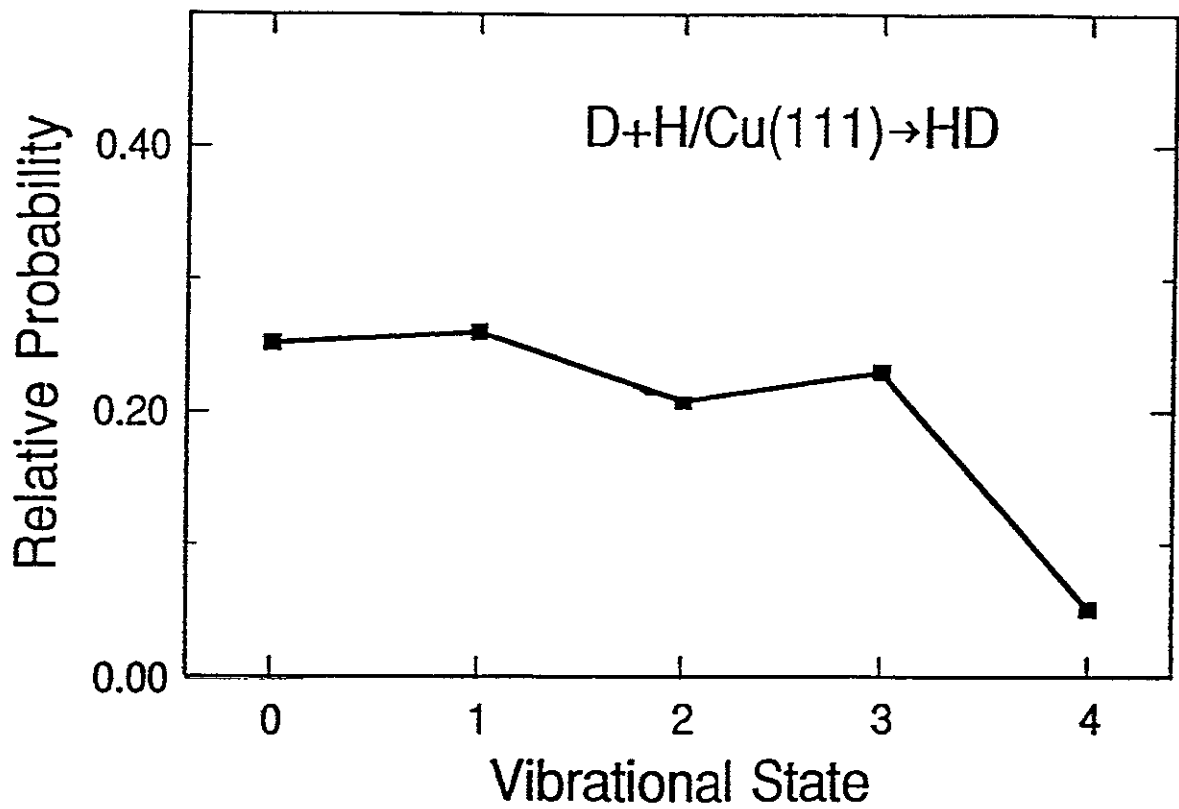


Fig. 9. Model PES for the Eley-Rideal reaction of a gas phase H-atom (incident along the surface normal) with an H-atom adsorbed on a tungsten surface. Contour lines are drawn in steps of 0.5 eV as a function of the distance z between the centre of mass of the molecule and the surface and the separation x of the two H-atoms (fig. 1 of [21], with permission).

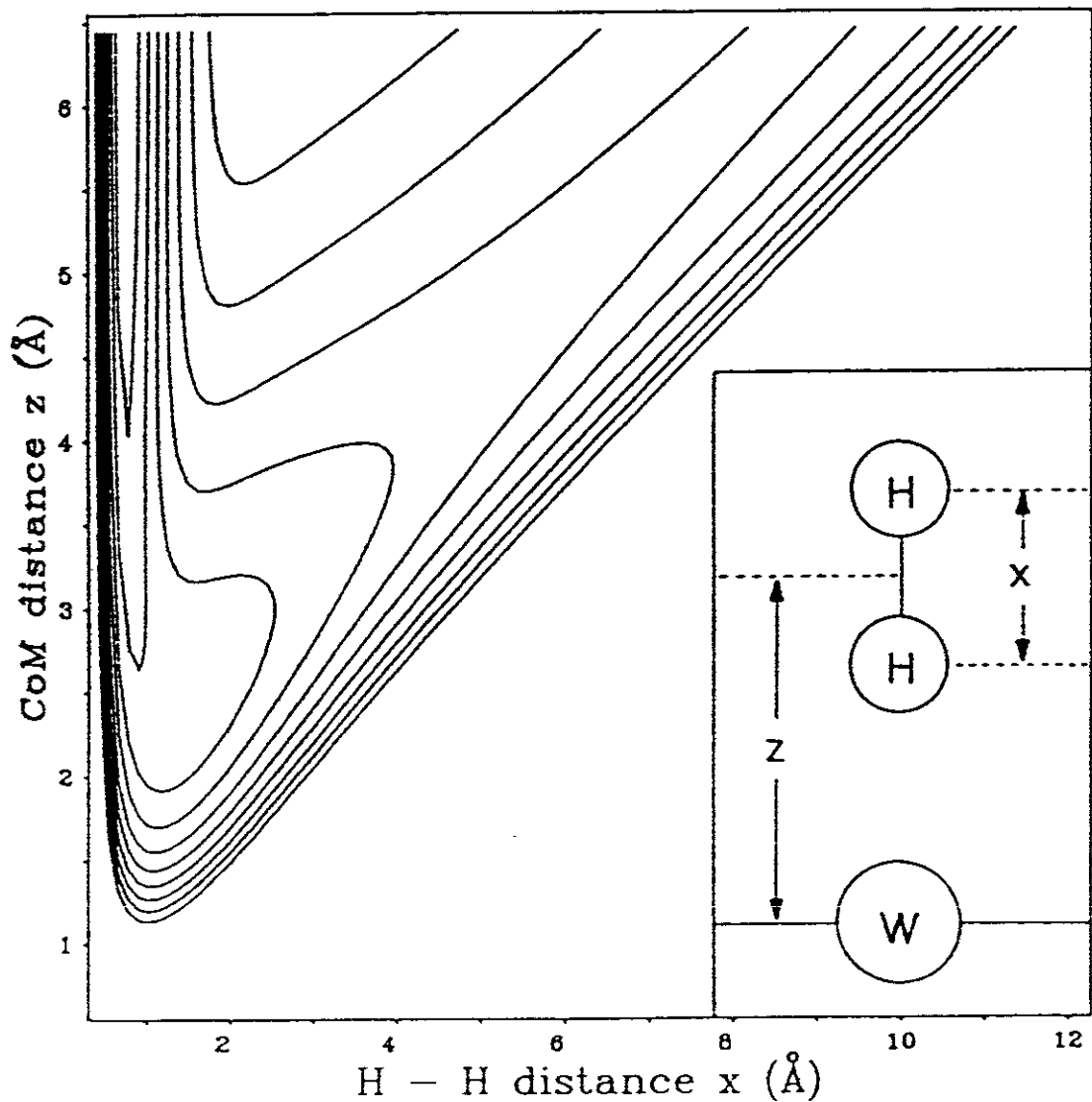


Fig. 10. Probability of occupation of the $v = 0$ (o), $v = 1$ (\diamond), $v = 2$ (Δ), $v = 3$ (+), $v = 4$ (\times) and $v = 5$ (\bullet) vibrational states of H_2 desorbed from a tungsten surface via the Eley-Rideal reaction mechanism as a function of the kinetic energy of the normally incident H-atom for the PES shown in Fig. 9 (fig. 2 of [21], with permission).

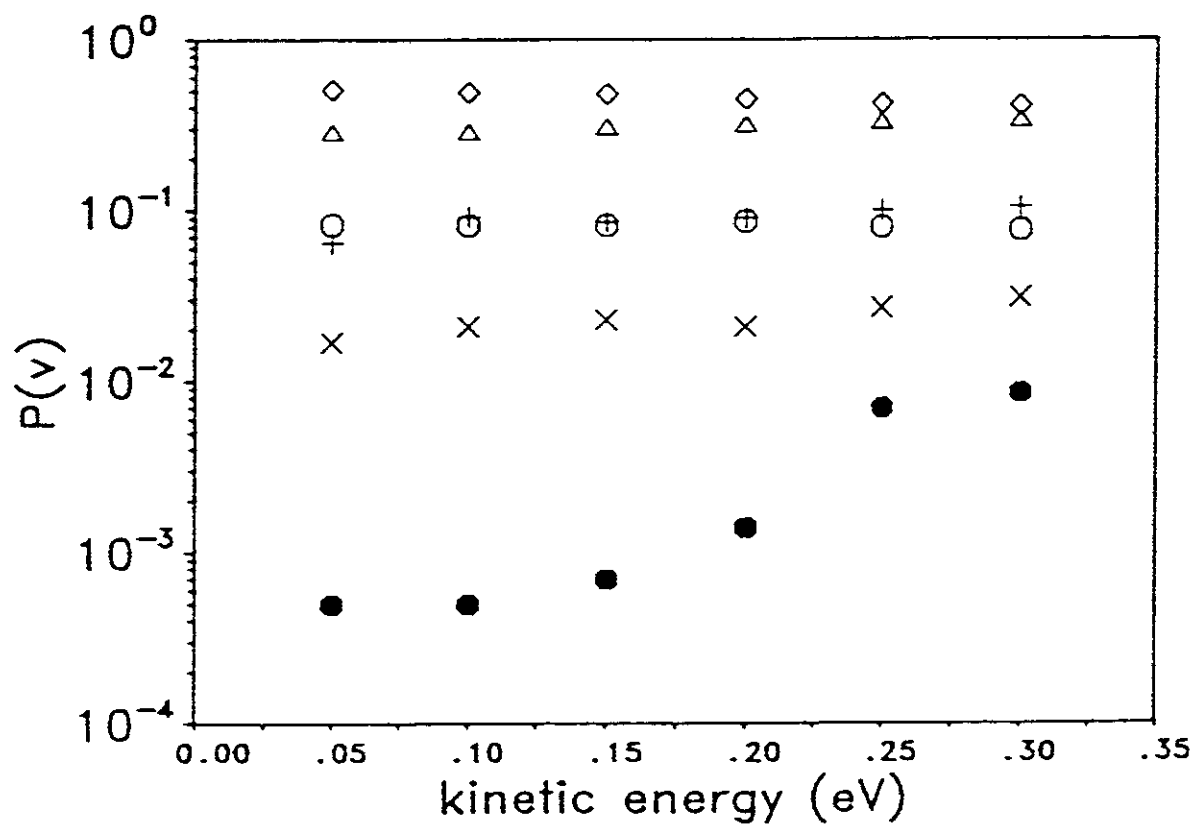


Fig. 11. Schematic illustration of processes which may lead to desorption of molecular species from surfaces following electron or photon irradiation: a) direct excitation to an unbound state (Menzel-Gomer-Redhead mechanism [41]); b) direct excitation to a bound state followed by acceleration toward the surface and subsequent deexcitation (Antoniewicz mechanism [42]); c) excitation of a core hole by the incident electron or photon, followed by Auger decay of the initial excitation, leaving the resulting ionised species in a non-bonding configuration allowing desorption to occur (Knotek-Feibelman mechanism [43]); d) electron-hole pair creation by adsorption of the incident radiation leads to ‘hot’ electrons which if scattered through negative-ion like resonance’s of the adsorbate may lead to vibrational excitation and desorption via one [44] or more [45] excitation-deexcitation cycles of the type illustrated by the potential curves in b).

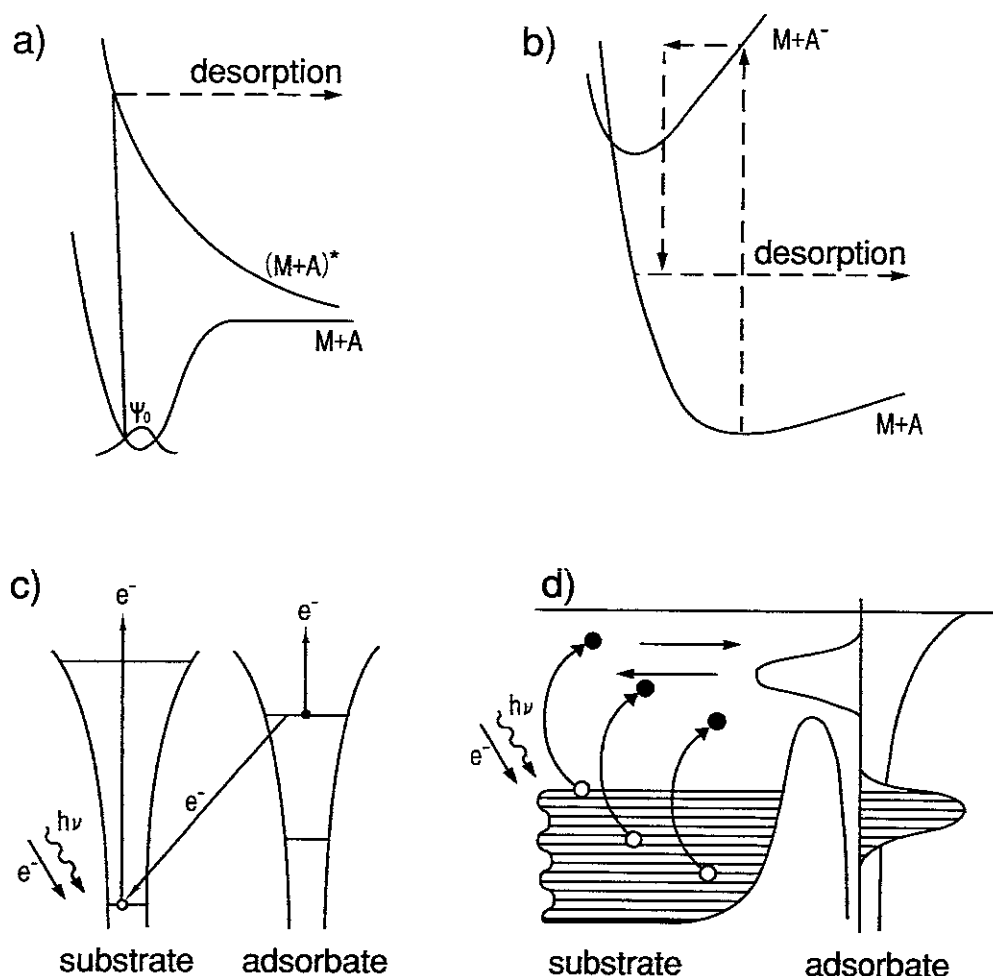


Fig. 12. Dependence on laser fluence of the yield of NO desorbed from a Pd(111) surface by 200 fs, 620 nm laser irradiation at a repetition rate of 10 Hz (fig. 1 of [46], with permission).

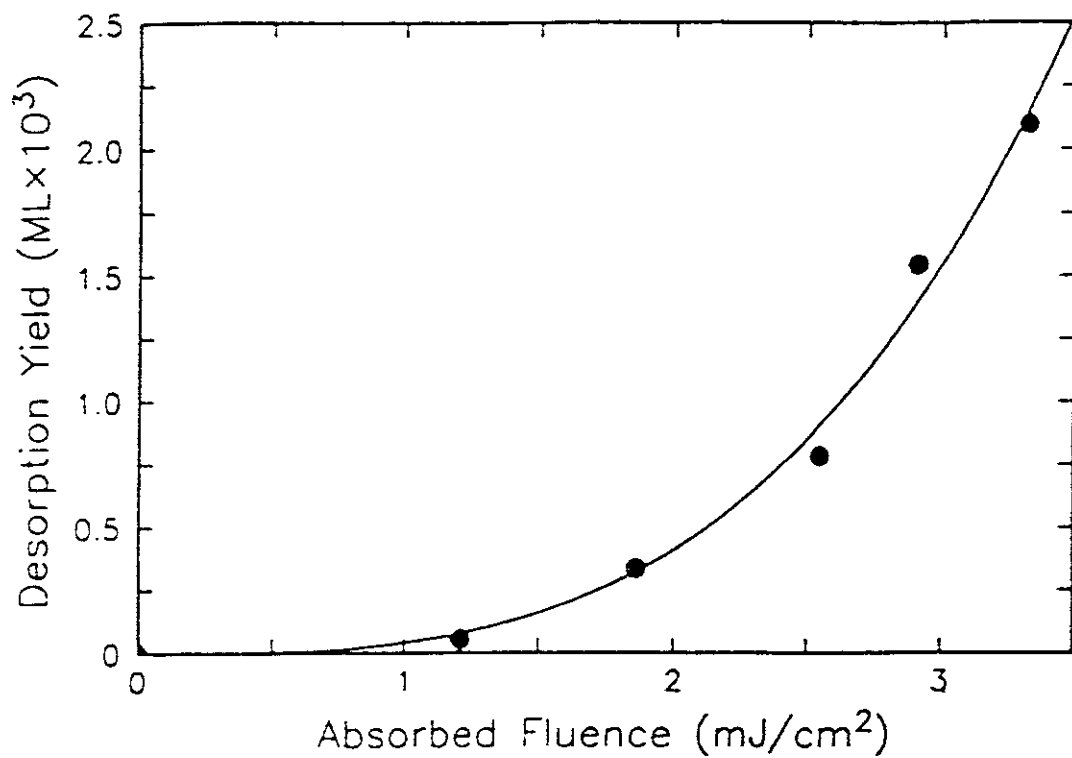


Fig. 13. Angular distributions of N_2 scattered from a W(110) surface at a temperature of 800 K. The beam was incident at 45° to the surface normal with translational energy a) 0.09 eV and b) 1 eV. In b) the angular distribution for He is also shown (adapted from fig. 4 of [51], with permission).

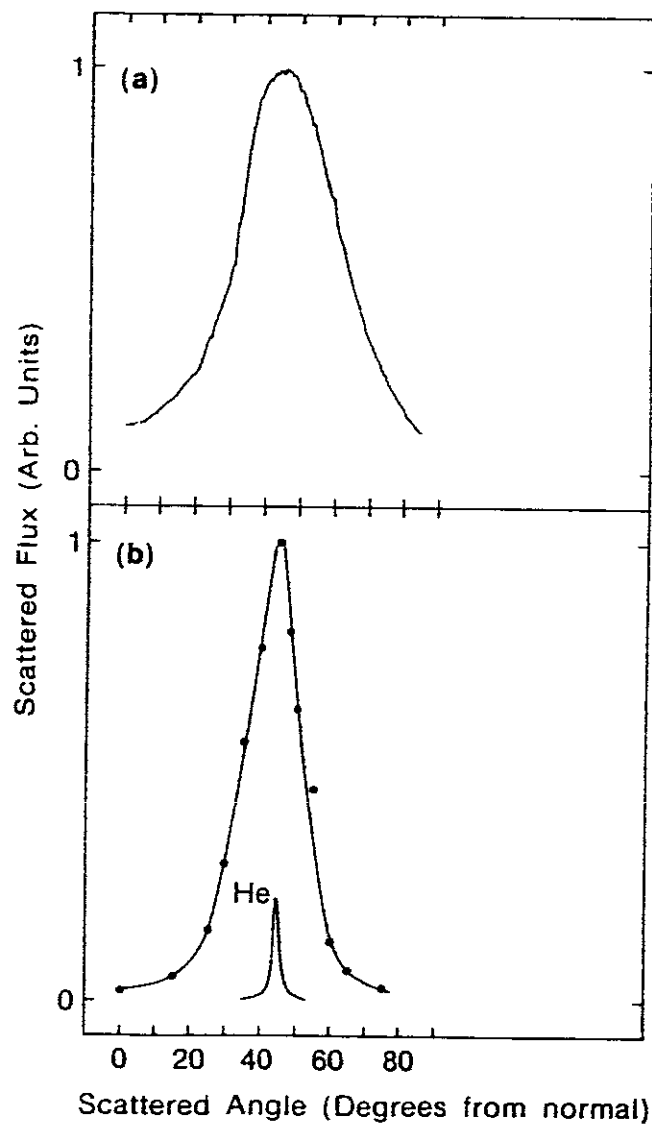


Fig. 14. Topographical representation of the intensity of scattered O_2 as a function of departure angle θ_f (see inset) and flight time between the crystal and the detector for incident beam energies $E_i = 1.56, 1.16$ and 0.91 eV and incidence angles θ_i (see inset) of $38^\circ, 43^\circ$ and 52° . $E_n = E_i \cos^2 \theta_i$ is the normal energy of the incident beam to the surface in each case. Contour lines are drawn at 30%, 50%, 70% and 90% of the peak maximum (fig. 1 of [56], with permission).

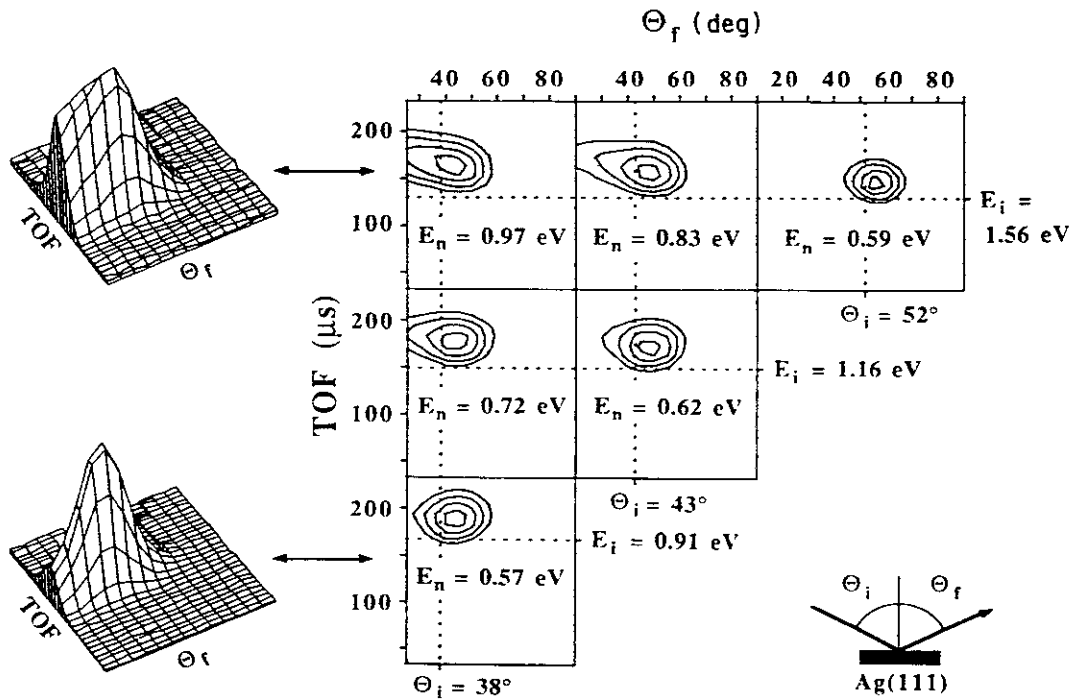


Fig. 15. Angular distributions of CO^+ scattered from a Pt(100) surface. The beam was incident at 60° to the surface normal with translational energies of 30, 50, 70 and 100 eV (fig. 14 of [58], with permission).

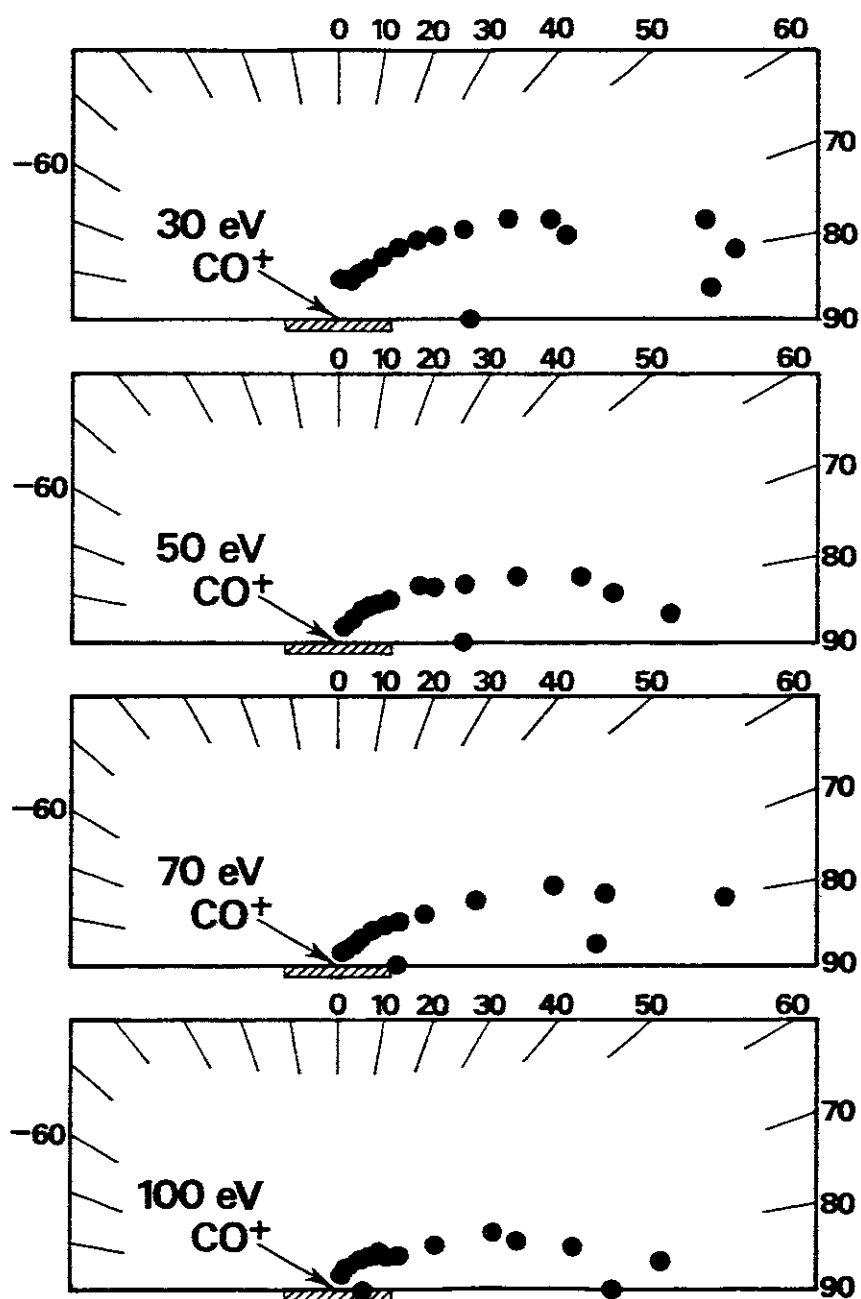


Fig. 16. Rotational state distributions for NO scattered from a Ag(111) surface at 750 K. The beam was incident at 15° to the surface normal with translational energies of 0.85 eV (upper curve) and 0.09 eV (lower curve) (fig. 2 of [51], with permission).

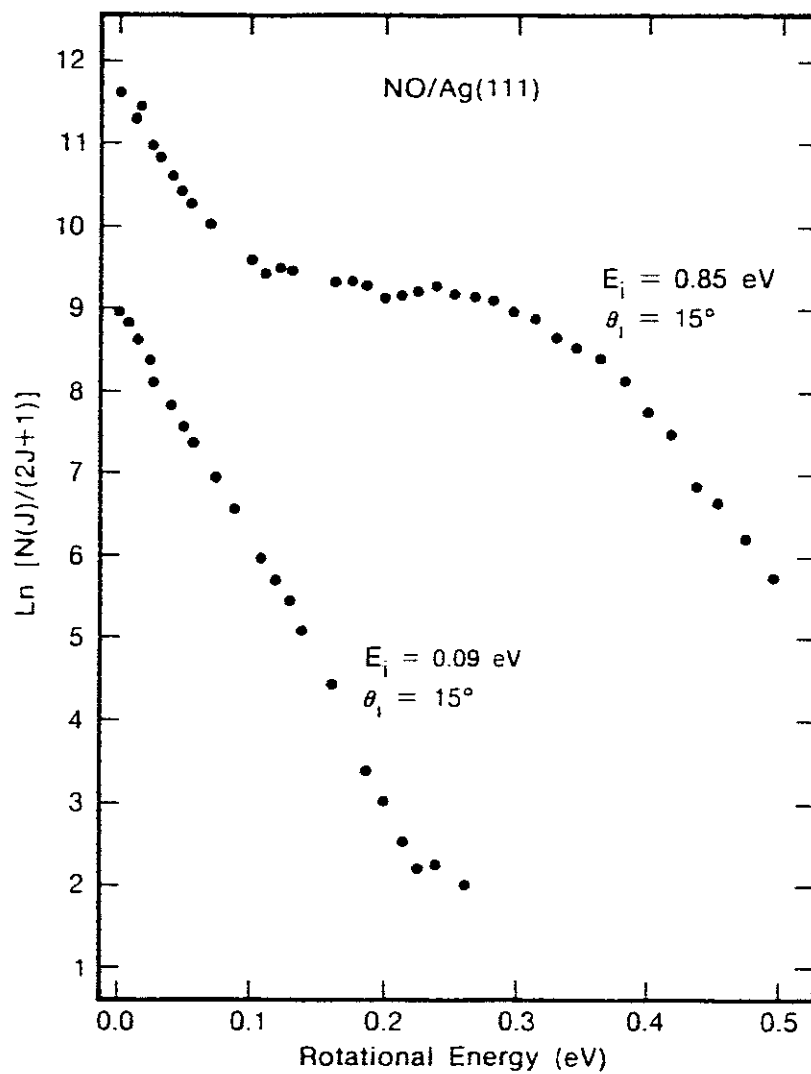


Fig. 17. Dependence on surface normal energy E_n of the population ratio $\text{NO}(v=1)/\text{NO}(v=0)$ for NO scattered from a Ag(111) surface at 760 K and incidence angles θ_i to the surface normal of 15° , 30° and 45° (fig. 3 of [51], with permission).

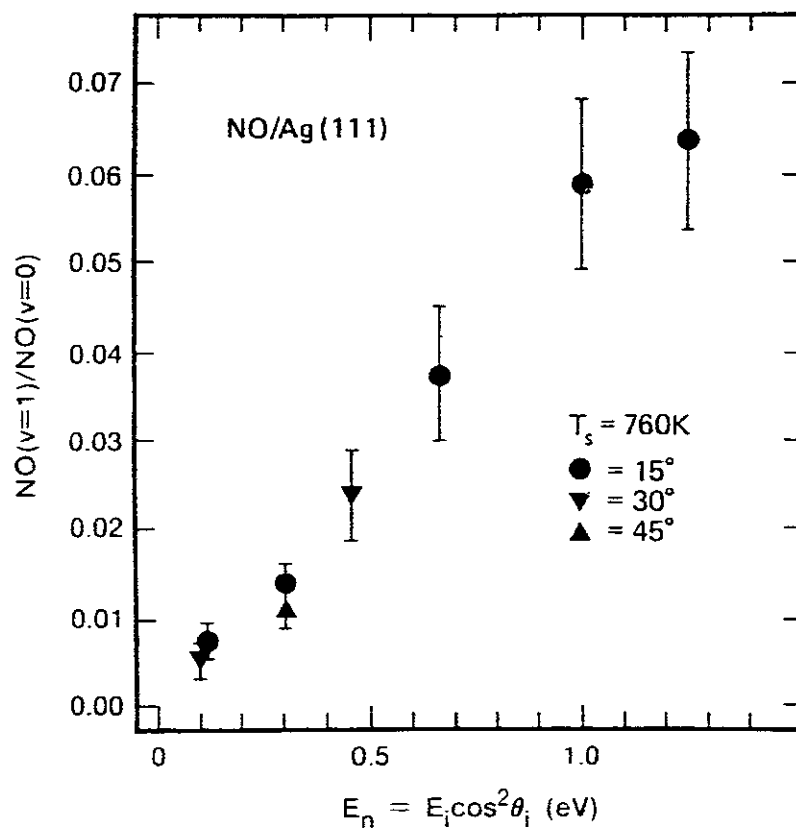


Fig. 18. Molecular dynamics calculation of the total energy loss ΔE_{tot} (for non-dissociated molecules), energy loss to the solid ΔE_{solid} and energy loss to internal degrees of freedom ΔE_{int} as a function of total incident molecule energy for O_2 scattering from $\text{Ag}(111)$ for a surface normal energy $E_n = 11.7$ eV (adapted from fig. 9 of [59], with permission).

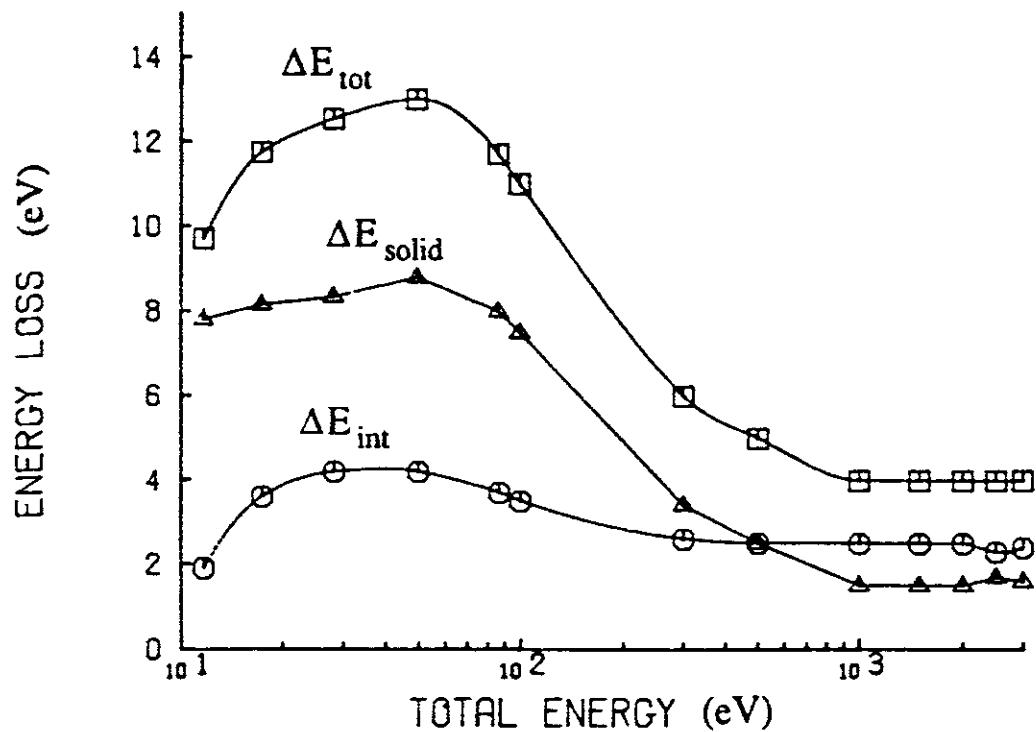
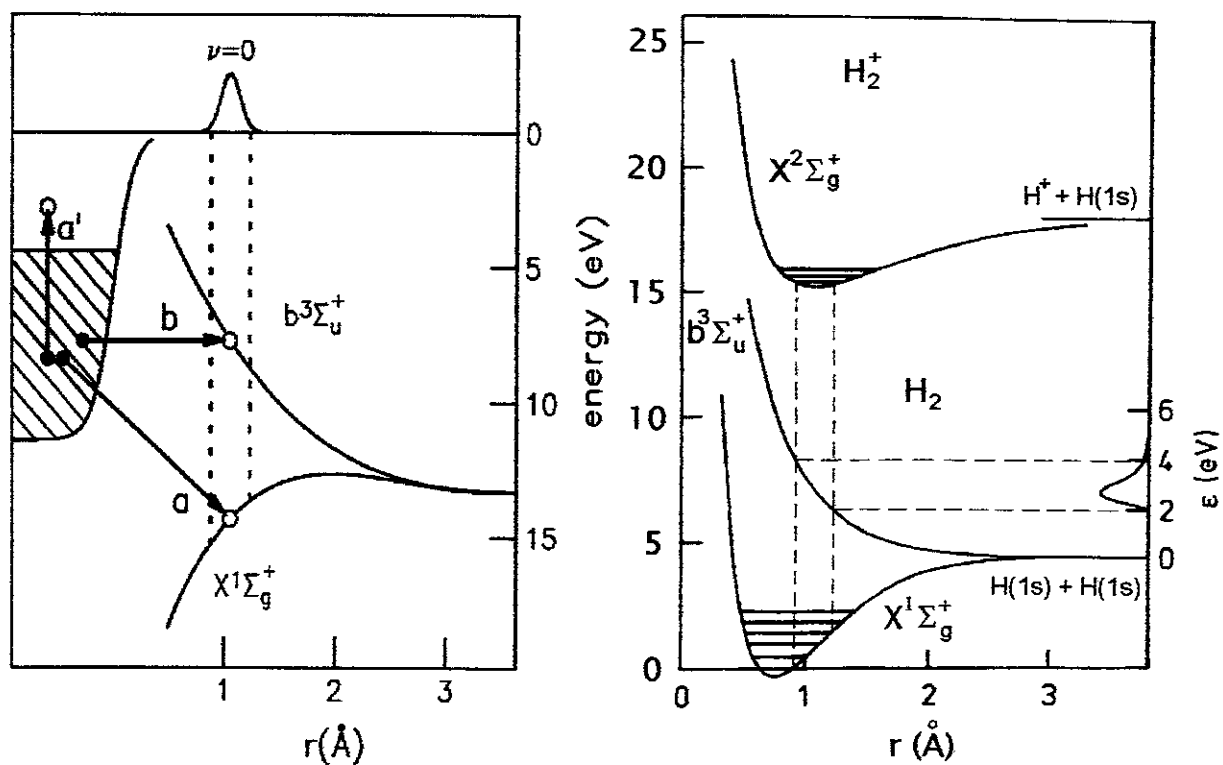


Fig. 19. Charge transfer (left) from the surface of a solid (here Al) to an incident ionised molecule (here H_2^+) can lead to (right) dissociative scattering or non-dissociative scattering, accompanied by vibrational excitation.



Tables

Table 1. Comparison of the calculated [12] vibrational populations of the $v = 1$ and 2 levels of H_2 and D_2 following desorption by the Langmuir-Hinshelwood reaction mechanism with those expected from a Boltzmann distribution the surface temperature and with those observed in the experiments of Kubiak et al. [13].

State	Molecule	Theory	Boltzmann	Cu(111)	Cu(110)
P($v = 1$)	H_2	0.04	0.0009	0.08 ± 0.03	0.05 ± 0.01
P($v = 1$)	D_2	0.19	0.0060	0.35 ± 0.20	0.24 ± 0.20
P($v = 2$)	H_2	1×10^{-4}	8×10^{-7}	< 0.01	< 0.01
P($v = 2$)	D_2	3.3×10^{-3}	3.6×10^{-5}	< 0.04	< 0.04

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