Dissociation in molecule-surface collisions

REVIEW ARTICLE

Dissociation in molecule–surface collisions

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Abstract. Dissociation at surfaces is a very important process, both scientifically and technologically. Dissociative chemisorption of molecules impinging at surfaces with thermal energies forms the basis of many processes, like catalysis. In thermal collisions it is evident that the kinetic energy of the impinging molecules is insufficient to break the molecular bond. Electronic processes occurring in the close proximity of the surface must drive the dissociation. At high translational energies ($E > 10$ eV) both collision-induced dissociation, due to direct momentum transfer, and electronic dissociation are energetically allowed for fast molecules. In the case of negative ion formation, e.g. the formation of O_2^- in O_2 surface scattering, most of the dissociation observed can be attributed to mechanical dissociation. The dissociation has been shown to scale mainly with the normal energy and shows a strong orientation dependence. In case of the formation of positive hydrogen ions in molecule–surface collisions Van Slooten *et al* have found that the degree of dissociation scales with the total energy times the total scattering angle squared. This points to the importance of dissociation induced by a collision with a single substrate atom. At high translational energies both collision-induced dissociation, due to direct momentum transfer, and electronic dissociation are energetically allowed.

1. Introduction

In a very recent and beautiful paper Bruen, Wintterlin, Behm and Ertl (1992) demonstrated the dramatic event of molecular dissociation at a surface. When thermal O_2 impinges on an Al surface, the molecular bond is broken so violently that the resulting atoms are found widely separated at the surface. The driving force for the dissociation is the formation of very strong bonds with the Al surface, leading to an exothermic process. From the experiment it is clear that most of the available energy is disposed of in repulsion between the O atoms in the molecule. The observations on this process have been made with scanning tunnelling microscopy (STM), a static probe, long after the dissociation event. The STM sees an average distance between the O atoms. From STM observations, information about the dynamics of the dissociation event cannot be taken directly. For instance, STM does not indicate whether the O_2 molecule spontaneously dissociates when it approaches the surface, or equilibrates in a precursor and dissociates at a later time. In this report I will discuss some experiments in which the dynamics of dissociation of molecules at surfaces has been studied using beam scattering experiments. In section 2 some supersonic beam experiments are discussed (thermal $< E < 2$ eV) that provide information on dissociative chemisorption. As an introduction to the discussion in section 3, results on rotational excitation of oriented NO will be presented. In section 3 results on the

scattering of higher-energy beams are presented $(80 < E < 3000$ eV). In 3.1 and 3.2 O_2 and NO scattering from Ag and Pt(111) are discussed. It will be shown that here the surface can be considered flat. In section 3.3 H_2 scattering from Ag(111) is discussed. Here collisions with individual surface atoms are dominant. This report is concluded in section 4.

2. Molecular beam scattering

2.1. Dissociative chemisorption

Molecular beam experiments are very useful in studying dissociation dynamics. Studies on the dissociative chemisorption of H_2 on Cu surfaces suggest that in that case the dissociation proceeds instantaneously, see e.g. Hayden (1991), Holloway (1991), and Kleyn (1992). Dissociative chemisorption is activated for H_2 on Cu and the corresponding energetic barrier can be overcome by both translational and vibrational energy, as evidenced in several theoretical studies, see e.g. Harris *et al* (1988), Holloway (1991). This is demonstrated in figure 1, where the sticking coefficient for dissociative chemisorption of D_2 is plotted as a function of the normal energy $E_n = E_i \cos^2(\Theta_i)$ (Rettner *et al* 1992a). Here E_i is the incident beam energy and Θ_i the angle of incidence measured from the surface normal. For an uncorrugated surface for which parallel momentum is conserved, E_n is the quantity of relevance, rather than E_i. It is clear that the sticking coefficient increases by many orders of magnitude and approaches unity for high energy. E_n can be obtained for different nozzle temperatures by mixing the D_2 molecules in carrier gases such as H_2 or Ne. The higher the nozzle temperature the larger the vibrational excitation of the D_2 molecules in the primary beam. Several curves for different nozzle source temperatures in figure 1 demonstrate the role of vibrational excitation. Clearly this vibrational excitation strongly enhances dissociative chemisorption. The effect of vibrational excitation has been demonstrated experimentally by Hayden and Lamont (1989, 1991) and Rendulic and co-workers (Anger *et al* 1989, Berger *et al* 1992). The importance of vibrational excitation to dissociative chemisorption has been demonstrated earlier theoretically by e.g. Harris *et al* (1988) and by Holloway and co-workers, see Holloway (1991). The seemingly enormous importance of vibrational excitation as manifested for example in figure 1 is in part due to the fact that the vibrational quanta of hydrogenic molecules are very large. From the theoretical studies it emerges that the 'cheapest' way to achieve dissociative chemisorption is to put all the energy in translation, rather than in translation and vibration, see Holloway (1991). The reverse process, anomalous vibrational excitation in recombinative desorption of H_2 from metal surfaces, has been observed by Kubiak *et al* (1985), Zacharias and David (1985) and Schröter *et al* (1989).

Very recently Rettner *et al* (1992b) and Hodgson *et al* (1992) demonstrated that for conditions where the activation barrier for dissociative chemisorption of hydrogen can be overcome, for instance by imparting sufficient translational energy to the molecule, direct vibrational excitation is also observed. This vibrational excitation is taken as evidence that the molecule starts to access the dissociative part of the potential energy surface, but does not entirely dissociate, returning intact into the gas phase. In such experiments the region of the potential energy surface close to the barrier to dissociation is sampled directly. In this case, a very close correlation between adsorption and scattering is observed. This is very relevant, because scattering
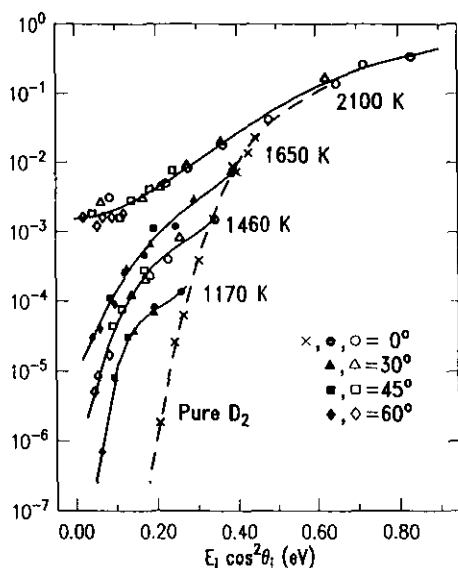
Figure 1. Probability of dissociative chemisorption (sticking) of D_2 on Cu(111) plotted as a function of the normal energy $E_n = E_i \cos^2(\Theta_i)$. θ_i is indicated in the figure. Data are shown for seeded beams with four different nozzle temperatures as indicated and a solid line is drawn to guide the eye through each set of data points recorded at the same nozzle temperature. The crosses (followed by the dashed curve) represent data for pure D_2 expanded from a nozzle at temperatures from 875 to 2100 K. From Rettner *et al* (1992a).

experiments allow characterization of both the initial and the final state, yielding more information on the interaction dynamics than when only the initial state of the molecule is varied and sticking is observed. Such a close correlation has also been seen in other scattering experiments with supersonic molecular beams—see for example the work on scattering and physisorption of H_2 on Cu (Andersson *et al* 1989), scattering and dissociative chemisorption of CO on Cu (Hayden and Godfrey 1990) or the orientation dependence of scattering and molecular chemisorption of NO on Pt(111) (Kuipers *et al* 1980, Tenner *et al* 1991a).

However, not in all cases is the dynamics of (dissociative) chemisorption so clearly reflected in scattering experiments. A potential energy surface describing the interaction between H_2 and Mg has been calculated by Nørskov *et al* (1981). It shows that there exists an intermediate H_2^--like state and that dissociative chemisorption may not occur directly, like for H_2 on Cu(111), but that equilibration in this H_2^- state may be required. Such an intermediate also exists for O_2 chemisorption on Pt(111) and Ag(111). The interaction between O_2 and Pt(111) is characterized by three stable binding configurations: O_2 physisorption, O_2 molecular chemisorption (in which the molecule is adsorbed as a negative ion-like species) and dissociative chemisorption (Luntz *et al* 1988). Luntz *et al* (1988, 1989) have shown that in this case the dissociation of thermal molecules involves equilibration in the physisorption precursor.

At higher translational energies dissociative chemisorption without equilibration in the physisorption precursor is observed. One could suspect that in this case direct

dissociation occurs, just like in the case of activated dissociative chemisorption of H_2 on Cu(111) mentioned above. However, Rettner and Mullins (1991) have shown that for O_2 dissociation on Pt(111). like for N_2 on Fe(111), dissociation does not proceed instantaneously. Instead, equilibration in the O_2^--like state is demonstrated in a titration experiment. Surprisingly, although dissociative chemisorption is an *exothermic process it cannot proceed directly and the deep potential well of the O* atoms at the surface is defended by strong barriers that do not give way to energetic molecules, but rather only every once in a while to accommodated molecular ions at the surface. *Scattering of O_2 from Pt(111) closely resembles scattering of Ar by the same crystal* although in the former case about 25% of the molecules dissociatively chemisorb (Wiskerke *et al* 1992). Apparently the directly scattered molecules only see 'inert' sites of the unit cell. Conversely, all molecules hitting an 'active' site do chemisorb and are not seen in direct inelastic scattering. Therefore, direct inelastic scattering of O_2 from Pt(111) may resemble scattering of Ar from the same crystal. Chemisorption of O_2 on Ag(111) is another example of such a system. In this case the probability for dissociative chemisorption is very low at all experimentally accessible energies (Spruit and Kleyn 1989, Raukema *et al* 1992).

In conclusion to this short overview of dissociative chemisorption in low-energy (thermal–2 eV) molecule–surface collisions, I might note that in some cases dissociation occurs instantaneously, in a single collision so to speak. In many cases, however, dissociation does not happen in a single collision event; it is an activated process in which one or more precursors are involved. In all cases the nature of the dissociation is electronic or chemical by nature, see for example Kleyn *et al* (1982), Gadzuk and Nørskov (1984), Gadzuk (1985), Gadzuk and Holloway (1985) and Kleyn (1990). Since the translational energies in these collisions are well below the dissociation energy of the gas phase molecule, mechanical or collision-induced dissociation yielding free atoms in the gas phase cannot occur in these collisions.

2.2. *Orientation dependent rotational excitation*

Before discussing experiments in which enough energy is available for direct molecular dissociation, I will briefly introduce some observations made concerning interactions of oriented molecules and surfaces. For direct dissociative chemisorption the vibrational degree of freedom is more directly coupled to the dissociation process than the rotational degree of freedom. For the impulsive processes to be discussed in the following sections, the molecular orientation appears to be very relevant, which for example can be seen in studies of collisions of oriented (hyper-)thermal NO molecules and surfaces (Tenner *et al* 1990a,b, Geuzebroek *et al* 1991). These studies on orientation-dependent rotational excitation are very relevant in the present context. The most important results of these studies are reproduced in figure 2. Shown is the *rotational excitation of NO impinging at an Ag(111) surface at* $\Theta_i = 45°$ *and* $E_i = 0.34$ eV (Geuzebroek *et al* 1991). The panels of the figure depict results for three different final angles and two orientation distributions of the primary beam. The beam *can be prepared such that either the N end of the molecule or the O end is preferably* oriented towards the surface. The data are shown for the peak in the angular distribution at $\Theta_i = 52°$(b), towards the normal at $\Theta_i = 35°$ (a) and towards the surface at $\Theta_i = 70°$. Here Θ_f is measured from the surface normal. Most rotational state distributions shown can be characterized by an effective temperature. However, it has been demonstrated that this temperature is not indicative of thermalization of the molecules at the surface, but is the result of direct inelastic scattering. The clearly

bimodal and non-thermal distribution measured at $\Theta_i = 70°$ for the O end towards the surface is a signature of direct rotational excitation in the collision. Rotational excitation of NO at Ag(111) has been the topic of many studies and a good summary for our present discussion can be found in figure 3, where the rotational excitation of NO at a flat structureless Ag surface is plotted as a function of the initial orientation of the molecular axis. In this figure, which has been produced in a classical trajectory study by Tenner *et al* (1991b) using a potential originally proposed by Voges and Schinke (1983), it is evident that the rotational excitation is a strong function of the molecular orientation and is very different for both ends of the molecule, when the molecular axis is inclined by about 45° or 135°. The O end leads to much higher rotational excitation than the N end, which is also observed in the data of figure 2. The (local) maxima observed in the rotational excitation function (figure 3) lead to enhanced intensities for the corresponding J-states. These maxima are the so-called rotational rainbows, see e.g. Schinke and Bowman (1983) and Kleyn and Horn (1991).
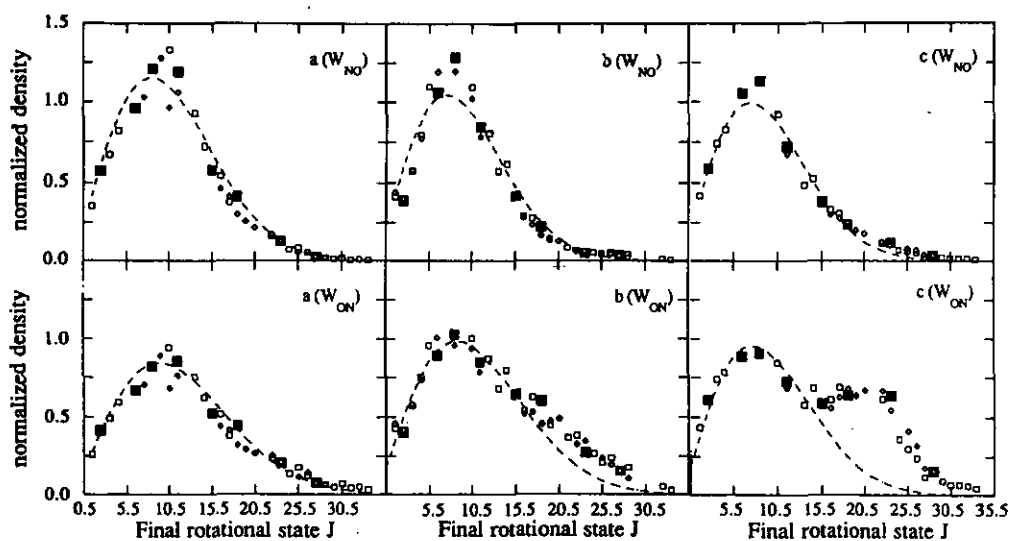

Figure 2. Final rotational state distribution for two orientational distributions W of the NO beam (top and bottom panels). The W_{ON} beam has a larger probability for the O end of the molecule to hit the surface and the W_{NO} beam for the N end. The NO molecules are impinging at an Ag(111) surface at $\Theta_i = 45°$ and $E_i = 0.34$ eV. The data are shown for the peak in the angular distribution at $\Theta_i = 52°$ (b), towards .he normal at $\Theta_i = 35°$ (a), and towards the surface at $\Theta_i = 70°$ (c). Further details cai. be found in Geuzebroek *et al* (1991).

It is instructive to study the energy dependence of the rotational excitation. This has been done by Voges and Schinke (1983), who showed that the O-end peak and position of the rotational rainbow linearly depends on the incoming energy. The corresponding rainbow peaks therefore shift to higher values. At some value the rotational energy transfer will get so high that the molecular dissociation energy can be exceeded. Thus extrapolating: initial rotational excitation, strongly depending on the initial molecular orientation, will determine the final degree of dissociation. This
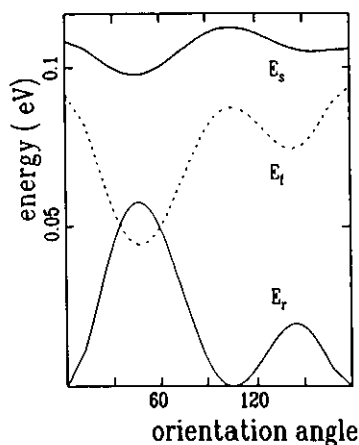
Figure 3. Rotational excitation E_r, energy transfer to the 'solid' E_s and final translational energy E_f for NO molecules normally impinging with $E_i = 0.2$ eV on an initially stationary surface 'cube' of mass 240. The results are plotted as a function of the orientation of the molecular axis. Small orientation angles correspond to an NO molecule with its O end towards the surface. From Tenner *et al* (1991b).

indeed has been observed as will be discussed in the section on the dissociation mechanism of fast O_2.

3. Fast beam scattering

It would be very interesting to approach this dissociation limit of the molecule by ever increasing the translational energy. However, this is very difficult experimentally and has only been done for heavy molecules, such as I_2 by Amirav (1990) and co-workers. For most other systems a jump in energy needs to be made, going from nozzle beam technology to ion beam technology. Many scattering studies of low-energy ion beams have been performed, also for systems in which dissociative chemisorption does occur, see e.g. Kasi *et al* (1990), Akazawa and Murata (1988, 1989a, 1989b, 1990) and Okada and Murata (1992). Although ion beams are used, the situation might be similar to that of scattering of a fast neutral, because often complete neutralization (>99.9%) occurs in the ion–surface collision. However, this similarity is not always present; this will be discussed later. In some cases grazing incidence is used to keep the normal energy E_n low.

3.1. Scattering of O_2 molecules

Reijnen *et al* (1989b) have performed scattering experiments in which a 100–3000 eV O_2^+ beam is reflected from an Ag(111) surface at specular scattering for $\Theta_i = 85°$. Time-of-flight (TOF) analysis has been applied to the scattered neutrals and negative ions. The probability for forming O_2^+ is very low and positive ions are not detectable at grazing angles. A result of such a scattering experiment in which an 270 eV O_2^+ beam is reflected from an Ag(111) surface is shown in figure 4. Shown is a TOF spectrum of the scattered neutrals and negative ions. The large structure at 32 μs is due to O atoms and O_2 molecules, the latter forming the 'hat' on top of the much broader TOF distribution of the O atoms. In this case a separation between O atom and O_2 molecule yield can be easily made. The shape of the spectrum of the neutrals is attributed to the fact that two processes occur in the neutralization of O_2^+. The atoms are formed in dissociative neutralization yielding a broad TOF distribution; ground state O_2 molecules are formed by an Auger process,

not affecting the TOF distribution (Snowdon *et al* 1986). Also O_2^- ions are clearly observed at most experimental energies. From the yield of O_2^- with respect to O_2 Reijnen *et al* conclude that the probability for charge transfer is at least a few per cent. From the analysis of the data it has been concluded that the probability to form O_2^- close to the classical turning point along the trajectory is higher, but that most of the O_2^- reneutralizes in the exit channel or autodetaches when vibrationally hot. By contrast to the reasonably efficient O_2^- formation, O^- ions are almost absent in the spectrum at low energies (< 2000 eV), although O atoms are abundantly made by dissociative neutralization. Apparently the molecules can pick up another electron whereas the atoms cannot, as judged from the absence of O^- ions at low energies. Reijnen *et al* (1989b) have attributed the O^- ions observed at high energies to collision-induced dissociation of O_2^-, which will be discussed later.
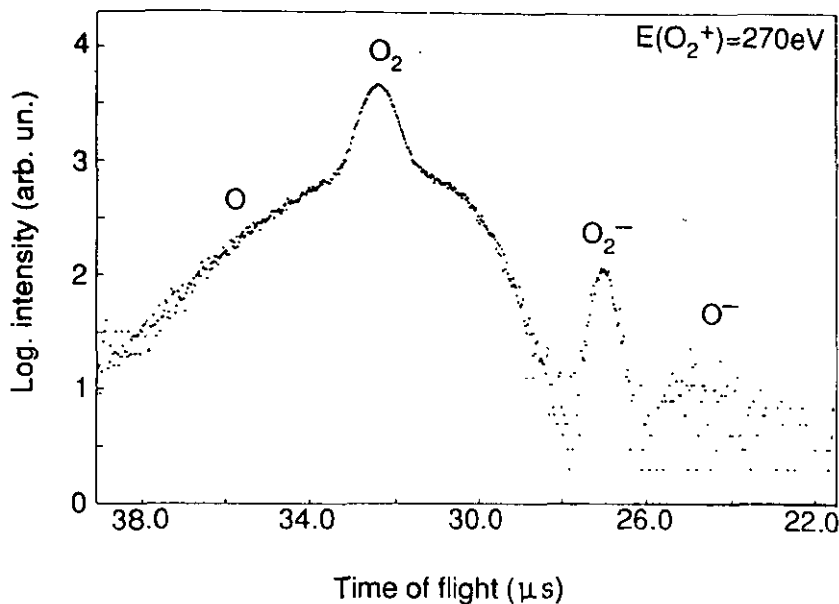

Figure 4. TOF distributions for neutrals and negative ions resulting from specular scattering of O_2^+ at $E_i = 270$ eV and $\Theta_i = 85°$. The negative ions are separated from the neutrals by post-acceleration. The intensity at the detector is plotted on a $\log_{10}$ scale in arbitrary units as a function of the target–detector flight time in μs. From Reijnen *et al* (1989b).

From the TOF spectrum of figure 4 it is evident that neutralization of positive ions leads to a large degree of dissociation, whereas the amount of dissociation for the negative ions is small. Increasing E_i leads to a sudden appearance of dissociation of O_2^-, i.e. O^- formation. The corresponding threshold is clearly shown in figure 5 (Reijnen *et al* 1989b). The x-axis shows $E_n = E_i \cos^2(\Theta_i)$, the cosine factor being 0.0076 for $\Theta_i = 85°$. The threshold is consistent with the onset of collision-induced or mechanical dissociation in trajectory calculations, also shown in the figure. In this context collision-induced dissociation is used when the dissociation is driven by direct momentum transfer to the atoms in the molecule in their collision with the surface, and not by a change in the intermolecular potential due to an electronic effect. It

can be seen that collision-induced dissociation occurs when E_n is about four times the dissociation energy of O_2^- and E_i is about 500 times this value. Clearly E_n is the important factor in the dissociation and not E_i. This can be seen very nicely in a plot of the average internal excitation of the O_2 molecule and the excitation of the solid as a function of E_i, while keeping E_n constant (Van den Hoek and Kleyn 1989a). From these calculations it is clear that experiments at grazing angles of incidence can mimic experiments with low total energy but more normal angles of incidence very well. This is experimentally very convenient. It makes a bridge possible between the nozzle beam experiments of section 2 and the ion beam experiments of section 3.
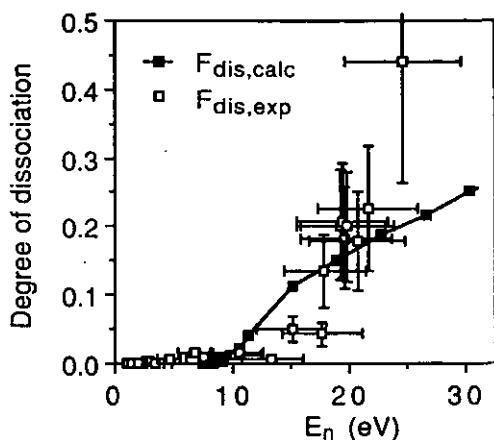

Figure 5. Degree of dissociation $F_{dis,exp}$ for the TOF experiment and $F_{dis,calc}$ for the classical trajectory calculations as a function of $E_n = E_i \cos^2 \Theta_i$. The line through the computed points was drawn to guide the eye. From Reijnen *et al* (1989b).

From the good agreement between theory and experiment it was concluded that collision-induced dissociation is the primary mechanism in the dissociation of O_2^-. To avoid any interference from charge transfer to O atoms formed by dissociative neutralization, it is preferable to perform experiments using neutral beams. These beams can be produced by resonant neutralization of an ion beam. Such experiments have been performed for negative ion formation when scattering O_2 or NO from Ag(111) and Pt(111) by Reijnen *et al* (1989a, 1991b). Typical results are shown in figures 6 and 7. In these figures the negative ion yield resulting from an 93 eV incident neutral O_2 beam scattered from Ag(111) and of an 80 eV beam from Pt(111) is plotted as a function of the final scattering angle Θ and the final energy E_i. Two features are seen. At first, a clear peak at specular for Ag(111) and somewhat beyond specular for Pt(111) and in both cases at about 90% of the primary beam energy. This peak is attributed to O_2^-. Secondly a broader feature at about half the primary beam energy and much broader in angle, which is attributed to O^-. At higher impact energies O formation leads to a clear peak. The results for incident positive ions are very similar (Pan *et al* 1986, 1989; Reijnen and Kleyn 1989a). This similarity demonstrates that dissociative neutralization yielding initially O atoms does not lead to additional negative ion formation, and that all negative ions formed are due to O_2
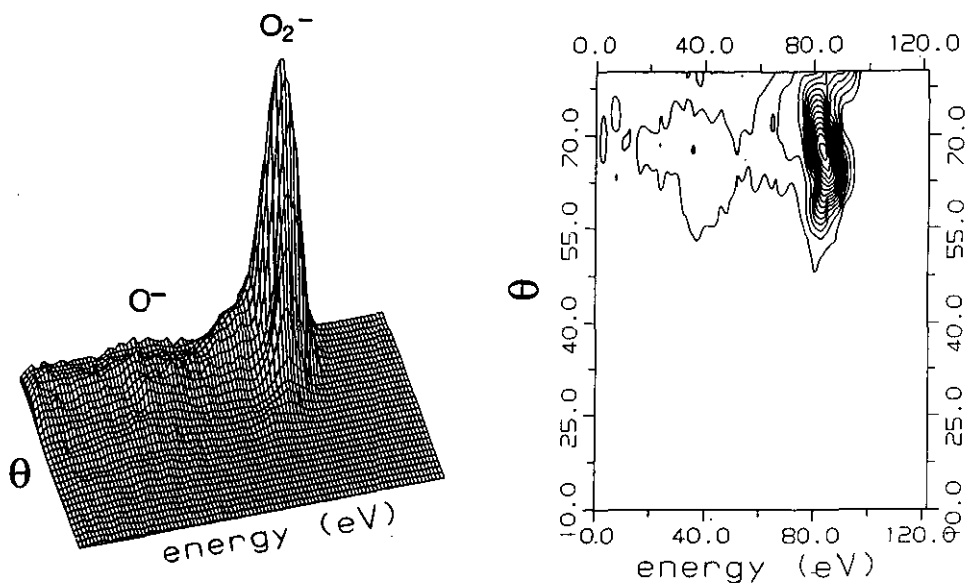
Figure 6. Three-dimensional distribution $I(E', \Theta)$ and corresponding contour diagram for the negatively charged products of 93 eV O_2–Ag(111) scattering for $\Theta_i = 70°$. No correction for the energy-dependent transmission of the energy analyser is applied. From Reijnen *et al* (1991b).

molecules either in the beam or formed by Auger neutralization in the close proximity of the surface.

The dissociation of O_2^- for the case of O_2/Ag(111) has been attributed to collision-induced dissociation. Calculations using pairwise additive potentials derived from HFS–LCAO pair potentials in fact overestimate the degree of dissociation (Van den Hoek *et al* 1988, 1989a). However, in those calculations the charge transfer is entirely neglected and this may lead to corrections to the degree of dissociation. One would expect that similar calculations for O_2/Pt(111) would give rise to a smaller degree of dissociation, because the potential for the bigger Pt atom would appear less steep on a semilogarithmic plot leading to an effectively smaller corrugation of the molecule–surface potential and a smaller anisotropy of the potential with respect to molecular orientation. Both effects lead to less dissociation. This is what one would get for a 'universal' potential like the Ziegler–Biersack–Littmark potential (Ziegler *et al* 1985). However, the measured degree of dissociation observed in case of Pt(111) is much higher. At first this was attributed by Reijnen *et al* (1991b) to electronic dissociation. Close to the surface the O_2^- potential turns entirely repulsive and leads to enhanced dissociation when compared to O_2/Ag(111). This would be reasonable in view of the probabilities for dissociative chemisorption. The latter is orders of magnitude higher for O_2/Pt(111) than for O_2/Ag(111). However, such an explanation that the O_2 feels a strong repulsive force when close to the surface is at odds with the observations by Rettner and Mullins (1991) that O_2 does not dissociate at impact at Pt(111), as mentioned earlier.

This controversy is at least partially solved by a HFS–LCAO calculation of the O–Pt pair potential by Kirchner *et al* (1992). It turns out that due to relativistic contraction
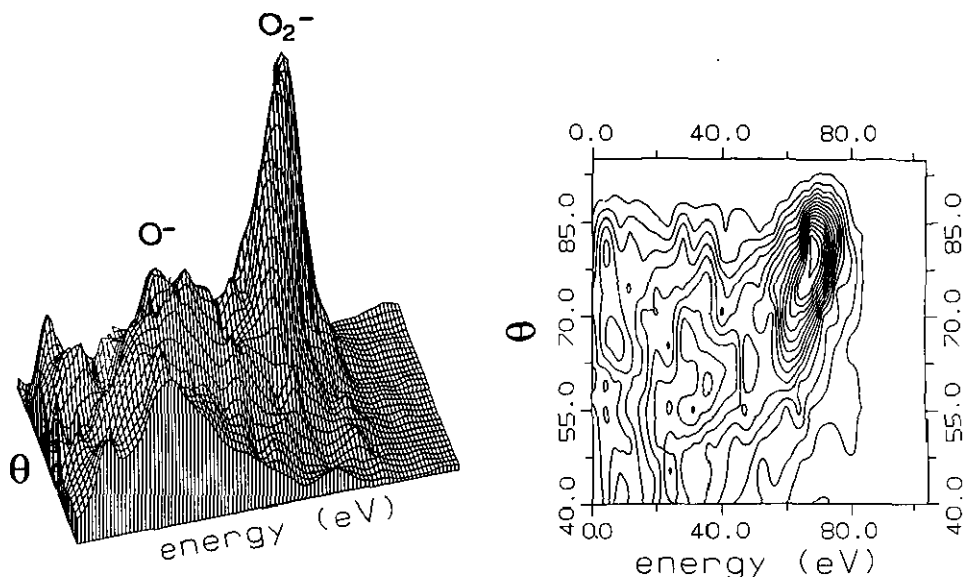
Figure 7. Three-dimensional distribution $I(E', \Theta)$ and corresponding contour diagram for the negatively charged products of 80 eV O_2–Pt(111) scattering for $\Theta_i = 70°$. No correction for the energy-dependent transmission of the energy analyser is applied. From Reijnen *et al* (1991b).

of the wave functions of the platinum core electrons, the valence orbitals also shrink. This makes Pt atoms effectively smaller and the potential would appear steeper and having a shorter range. This increases the corrugation of the molecule–surface potential and the anisotropy of the potential with respect to molecular orientation. Especially in grazing incidence the latter effect increases the degree of dissociation. At more normal angles of incidence, the increase in corrugation also leads to enhanced dissociation.

The calculations by Kirchner *et al* (1992) showed that the strategy of constructing a potential developed by Van den Hoek *et al* (1989b) does not always work. Van den Hoek *et al* have fitted for several systems a Born–Mayer potential to the HFS–LCAO pair potential above say 10 eV, which leads to a useful extrapolation at lower energies. This was evident in both experiments on O_2 scattering in the 50–200 eV range as for hyperthermal scattering (1–2 eV) (Van den Hoek *et al* 1989b). For O_2–Pt this extrapolation did not give the right repulsion at lower energies and the presence of a well has to be included in the fit. To what extent these effects are specific to the O–Pt system is not clear at present.

3.2. Dissociation mechanism for O_2 scattering

The classical trajectory calculations also give an idea about the dissociation mechanism. Calculations by Van den Hoek *et al* (1988) showed that the impact points for dissociative and non-dissociative scattering O_2/Ag(111) are almost identical. Therefore, the effect of the impact parameter is only slight, except possibly at acute grazing angles of incidence (Zonnevylle *et al* 1989). By contrast the orientation dependence of the degree of dissociation is large. This has been shown by Van

den Hoek and Kleyn (1989a), who present the average orientation of molecules undergoing dissociation. It is clear from their work that for grazing incidence, molecules with their internuclear axis along the surface normal have a much higher dissociation probability than when the axis is parallel to the surface plane. This orientation dependence has also been seen in the analysis of rotational excitation of oriented NO molecules scattered from an Ag(111) surface, as discussed above and demonstrated in figure 3. From this similarity one is led to the conclusion that the initial excitation in a collision leading to dissociation is also rotational excitation. This can be nicely seen in figure 8, where the probability of rotational and vibrational excitation is plotted for several incident energies at normal incidence (Van den Hoek 1989b). At low incidence energies it is mainly rotational excitation that occurs and a beautiful rotational rainbow is seen (Kleyn and Horn 1991). At higher energies the amount of rotational excitation decreases and vibrational excitation sets in. Even a vibrational rainbow is seen. The decrease of the rotational excitation is due to 'chattering': i.e. the molecule hits the surface with both ends and most of the rotational excitation introduced in the collision with the first end of the molecule is removed when the second end of the molecule hits the surface (Polanyi and Wolf 1982, 1985). In this second collision, efficient rotational to vibrational energy transfer can occur. This model has been proposed by Gerber and Elber in a series of papers (Gerber *et al* 1983, 1986). The prevalence of rotational excitation in molecule–surface conditions has also been found in an analytical model by Bitensky and Parilis (1984, 1985).

The transfer of rotational energy to vibrational energy can be seen nicely for a set of classical trajectories for O_2 scattering from Pt(111) at $E_i = 70$ eV and $\Theta_i = 70°$. In figure 9 the rotational and vibrational state distributions are shown at three positions along the trajectory (Kirchner *et al* 1992). The first position is when the molecule has lost 5% of its initial translational energy and starts climbing the repulsive wall. The second position is when the O atom nearer to the surface reverses its normal velocity. The third position is when the other O atom reverses its velocity. Until position 2 is reached the molecule gains about twice as much rotational excitation as vibrational excitation: the first hit leads mainly to rotational excitation. In scattering from a very corrugated surface at approximately $\Theta_i = 45°$ the orientation dependence of the dissociation probability disappears, due to the equal importance of the parallel and normal momentum in the excitation process. This can be seen in the work by Van den Hoek and Kleyn (1989b).

3.3. Fast hydrogen scattering

The discussion in this section so far has been centred on O_2 and NO molecules. However, the interaction between hydrogen and surfaces in high-energy collisions also deserves some special attention. Hydrogen–metal interactions are model systems, which are rather easily accessible for theoretical studies of the potential energy surface and have been studied extensively at low energies, see section 2. Quantum effects are important for hydrogen, which gives the system an additional richness compared to systems like O_2, the nuclear motion of which can be described mainly by classical mechanics, see Holloway (1991). (Nevertheless, the presence of an isotope effect in dissociative chemisorption of O_2 on Ag(111) points to the importance of tunnelling even for 'heavy' molecules (Reijnen *et al* 1991a).) Another source of interest in hydrogen surface interactions arises from fusion research. Intense beams of D atoms (1 MeV, many amperes equivalent) are needed for heating and current drive in
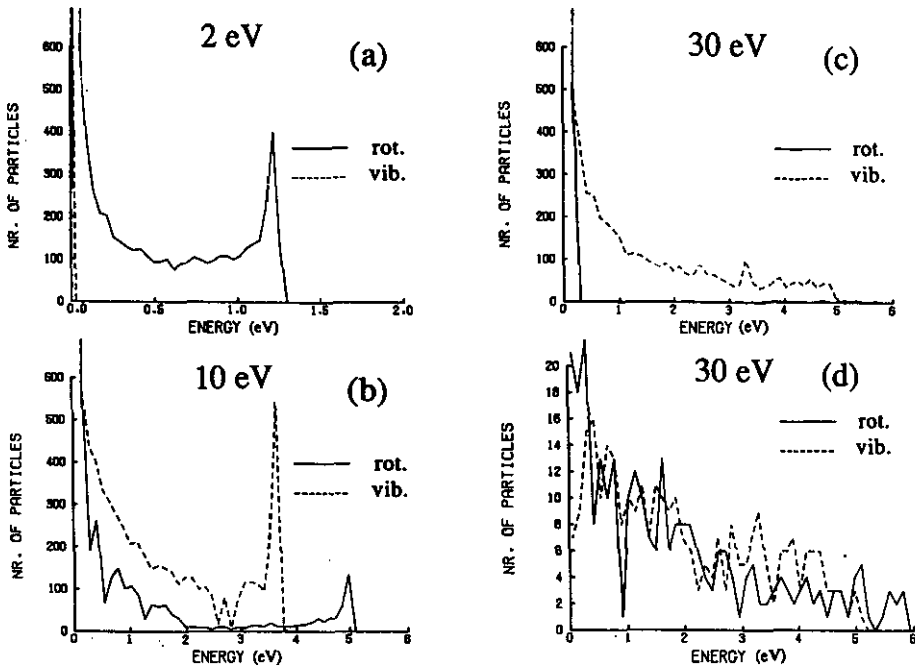
Figure 8. Distributions of rotational and vibrational excitation of O_2 molecules scattered from Ag(111). The distributions have been obtained from classical trajectory calculations. In panels (a)–(c) the molecules have been scattered from a flat rigid surface for different energies at normal incidence as given in the figure. In panel (d) the molecules have been scattered from the corrugated Ag(111) surface at normal incidence and $E_i = 30$ eV. From Van den Hoek and Kleyn (1989a).

next-generation tokamaks like ITER the International Experimental Reactor being developed by Europe, Japan, Russia and the USA. These beams are produced by neutralization of D^- ion beams and this has triggered a large interest in the construction of hydrogen negative ion beams (Kleyn 1990b, Bacal and Skinner 1990). These beams in turn can be made by negative surface ionization (Van Os *et al* 1987, Heeren *et al* 1991, 1992). At FOM these processes have been studied extensively and it has triggered studies on the interaction of energetic neutral H_2 with solid surfaces. Most recently, Van Slooten *et al* (1991, 1992a) have studied scattering of H_2 from Ag(111).

In the experiments only charged products could be detected. Both H_n^+ and H^- ions have been detected, roughly in equal amounts. A crude measurement indicates that less than 1% of the scattered particles are charged. Energy spectra of scattered positive ions are shown in figure 10. Results are shown at two incident energies, several find scattering angles and for both incident neutral molecules and molecular ions. Two peaks can be seen in the spectra for incident neutrals. These are attributed to H^+ and H_2^+. The amount of H_2^+ is far less in the case of incident molecular ions than for incident neutrals. The positions of the peaks are approximately the same for incident ions and neutrals. The proton peak is clearly shifted to the left of the binary collision value minus the dissociation energy of the molecule or molecular ion, which is approximately half the beam energy. The latter value is found for H^-
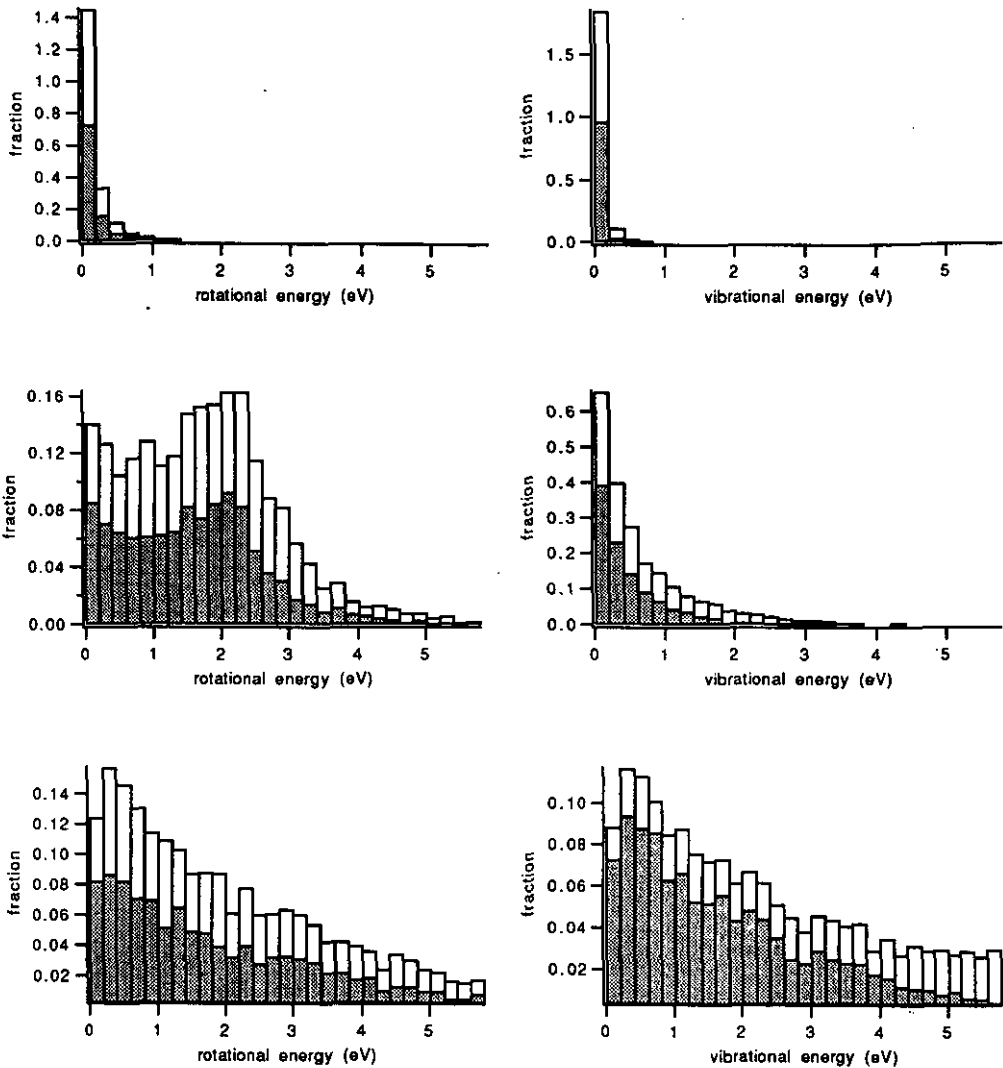
Figure 9. Distribution between rotational (left hand side) and vibrational energies (right hand side) as calculated for O_2 scattered from Pt(111) at $E_i = 70$ eV and $\Theta_i = 70°$. The shaded areas represent the finally non-dissociating molecules and the unshaded areas the dissociating molecules. The unshaded distribution is plotted on top of the shaded one. The distributions are evaluated along the trajectory at three positions as discuss.·d in the text. From Kirchner *et al* (1992).

formation, which indicates the negative ion formation is a resonant process. Clearly positive ion formation is a non-resonant process irrespective of the charge state of the incident particles. This points to resonant neutralization followed by re-ionization for incident positive ions and collisional ionization of ground state molecules for incident neutrals (Aono and Souda 1987, Souda *et al* 1987, Tsukada *et al* 1985). The angular distributions shown by Van Slooten *et al* (1992a) in their paper show that the angular distributions for the protons peak approximately around the specular angle, whereas the molecules are preferably found along the surface at very small grazing exit angles.
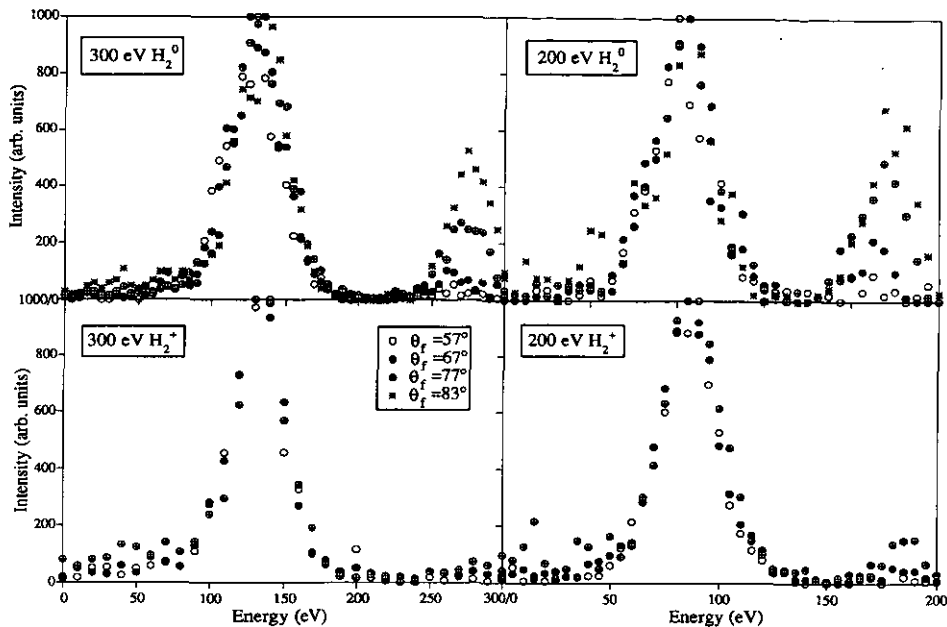
Figure 10. Intensity distributions for different outgoing angles as a function of final energy for product positive ions in the scattering of hydrogen from Ag(111) along the [11$\bar{2}$] direction for $\Theta_i = 80°$: (a), 300 eV H_2^0, (b) 300 eV H_2^+, (c) 200 eV H_2^0, (d) 200 eV H_2^+. The peak in the middle of the spectrum is attributed to H^+, the one to the right of the spectrum to H_2^+. No correction for the energy-dependent transmission of the energy analyser has been applied. From Van Slooten *et al* (1992a).

This can also be seen in figure 10. It is interesting to contrast the behaviour with rotational excitation of NO scattering in figure 2, where the largest excitation of the molecules is found for grazing exit angles.

The degree of dissociation is much higher for incident positive ions. Van Slooten *et al* attribute this to the predominance of dissociative neutralization of H_2^+, followed by reionization of the H atoms formed. This channel is absent for incident neutrals. It is studied extensively in Osnabrück, see e.g. Willerding *et al* (1984), Imke *et al* (1986, Tappe *et al* (1991), Rechtien *et al* (1991), Rechtien (1992). Recent studies by Rechtien *et al* question the occurrence of dissociative neutralization in the case of fast H_2^+ scattering from Cu(111), because very similar results are obtained for fast H_2 scattering. This is a very intriguing result. These authors also show an orientation dependence in the dissociation dynamics. They correlate this dependence with potential energy surfaces for H_2 dissociation as used by Harris *et al* (1988). The predominance of non-dissociative Auger neutralization is questioned for fast H_2^+ scattering at Ag(111) by Schins *et al* (1992). Also Van Slooten *et al* (1992a,b) infer that resonant dissociative neutralization is dominant at Ag(111).

That the formation of molecular ions in collisions of H_2 and Ag(111) occurs at all may be considered to be in striking contrast with experiments in which the reverse process occurs, an incident molecular ion yielding neutral products, such as those shown in figure 4 (Reijnen *et al* 1989b, Willerding *et al* (1984). Here dissociation is predominant, but it is due to resonant neutralization, a channel which is absent

for the scattering of neutrals. Nevertheless, survival of positive molecular ions in surface scattering has been seen by Eckstein *et al* (1975) and later by e.g. Heiland and Taglauer (1982) and Balashova *et al* (1982) at ion energies which are at least an order of magnitude larger than the molecular dissociation energy. These surviving molecules have been attributed to very special trajectories in which each atom of the molecular ion is scattered from a different surface atom, but the relative velocity after scattering is sufficiently small to prevent dissociation. This has been demonstrated theoretically by Bitensky and Parilis (1984, 1985) and Jakas and Harrison (1985).

The molecular survival in the present experiments by Van Slooten *et al* (1991, 1992a) is observed under different conditions— E_i being much smaller— than in the earlier work by Eckstein *et al* , Heiland and Taglauer, and Balashova *et al* . Given this difference the collision dynamics might be different. Therefore, the scattered intensity I and the degree of dissociation have been studied as a function of the azimuthal orientation of the crystal ϕ, Θ_i, Θ_f and E_i. It was found that the intensity strongly depends on ϕ but that the degree of dissociation $F_{dis} = I(H^+)/I(H^+ + H_2^+)$ does not depend on ϕ. F_{dis} does show a strong dependence on Θ_i, Θ_f and E_i. At first a correlation of the observed F_{dis} with E_i or E_n was tried, but no correlation was observed at all. However, it was found that F_{dis} scaled very well with $E_i\Theta^2$, where Θ is the total laboratory scattering angle ($\Theta = 180° - \Theta_i - \Theta_f$). This is shown in figure 11. Note that the same scaling is found both for H_2 and D_2.
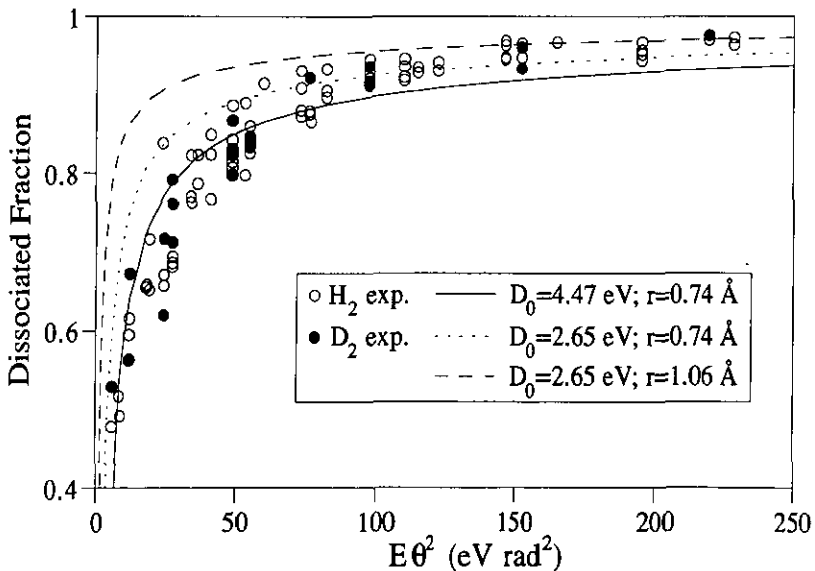

Figure 11. Dissociated fraction $F_{dis} = H^+/(H^+ + H_2^+)$ as a function of the product of beam energy and total scattering angle squared $(E\Theta^2)$ for H_2 and D_2 scattering from Ag(111). In the figure the calculated curves are also drawn: (——) bond length H_2, $D_0 = 4.47$ eV; (······) bond length H_2, $D_0 = 2.65$ eV; (- - - -) bond length H_2, $D_0 = 2.65$ eV. From Van Slooten *et al* (1992a).

Collision-induced dissociation in molecule–surface scattering is expected to differ from collision-induced dissociation in molecule–atom scattering in the gas plane.

In the surface case the breaking of the bond is normally viewed as being due to the cooperative contribution of the surface atoms while in the gas phase the dissociation has to proceed via just one collision. A typical surface case is found for the $O_2/Ag(111)$ system as discussed above. From the range of the interaction potential it is clear that for $O_2/Ag(111)$ scattering the dissociation process involves the interaction with many surface atoms. Some feeling for the potential range governing the interaction with the molecule is given by the potential for Ag–O (Van den Hoek and Kleyn 1989a). This potential reaches a value of 50 eV at an interatomic distance of 1.01 Å; a value of 500 V is reached at 0.56 Å. The distances for the corresponding Ag–H potential are considerably smaller: 0.63 Å for 50 eV and 0.28 Å for 500 eV (Van Slooten *et al* 1992b). This smaller range, the observed scaling of F_{dis} with total scattering angle, and the absence of crystal orientation dependence are reminiscent of gas phase collisions. Thus, in the case of H_2 scattering it is likely that the dissociation process can be described by independent H_2–Ag atom collisions. In a first paper Van Slooten *et al* (1991) used a gas phase model based on atom–molecule collisions. In this model, developed in Mahan's group, the collision between a fast molecule BC and a stationary atom A is treated as a collision involving three hard spheres (Cheng *et al* 1970). One of the atoms in the molecule, B, hits the atom, A, and recoils, while in the collision C is not affected. This so-called spectator model has often been applied to inelastic scattering processes (Andersen *et al* 1980, Budenholzer *et al* 1985, Sigmund 1978, 1981). In the high-velocity limit, where the collision is vibrationally and rotationally sudden, Mahan and co-workers showed for the angle region studied here that the energy transferred to the internal modes of BC can be written as $E_{int} = mE\Theta^2$ where m is defined as $m = m_A m_C/(m_B(m_A + m_B + m_C))$. This factor is very close to one for both H_2 and D_2 colliding with Ag. The scaling with $E\Theta^2$ is indeed the one Van Slooten *et al* found experimentally for F_{dis}. The threshold for dissociation, which is smooth in figure 11, would appear as a step function in such a model and modifications of the model are needed. After a simple amendment Van Slooten *et al* (1991) have extended the model to treat BC as a rigid rotor, so that the A–B atom collision is rotationally sudden. With only one fitting parameter, there was good agreement with the data. Next, Van Slooten *et al* (1992a) derived an expression for the dissociated fraction in terms of the rotational excitation of a hard ellipsoid. Korsch and Schinke (1981) studied the rotationally inelastic scattering of a hard ellipsoid within the infinite-order sudden approximation. For small ellipsoid eccentricity they derived a formula for the classical total differential cross section which has served as a starting point for Van Slooten *et al* (1992a). These authors finally obtained:

$$F_{dis} = \left\{ \sqrt{1 - \sqrt{\frac{\mu D_0}{M}} \frac{r}{(A-B)} \frac{1}{\sqrt{E\Theta^2}}} \right.$$
$$\left. \left[1 + \frac{1}{6}\epsilon^2 \left(2 + \sqrt{\frac{\mu D_0}{M}} \frac{r}{(A-B)} \frac{1}{\sqrt{E\Theta^2}} \right) \right] \right\} \left(1 + \frac{1}{3}\epsilon^2 \right)^{-1} \tag{1}$$

where ϵ denotes the ellipsoid eccentricity defined as $\epsilon = (A^2 - B^2)^{1/2}/A$ (A and B being the main axes of the ellipse); r denotes the bond length and μ the reduced mass of the molecule. D_0 is the dissociation energy. For a collinear collision the turning point is reached where the atom–atom potential equals D_0; for a perpendicular collision it is reached at $D_0/2$ (Korsch and Schinke 1981). These distances are

directly extracted from the potential and lead to a value of 0.68 for ϵ (Korsch and Schinke 1981). Van Slooten *et al* point out that equation (1) following from the model just described contains no fitting parameters; in contrast to the model used earlier by Van Slooten *et al* (1991). In figure 11 the solid line represents the calculated curve according to equation (1). The agreement between theory and experiment is surprisingly good. In the calculation the dissociation energy of H_2 ($D_0 = 4.47$ eV) is used. This is an upper limit because the beam is not in the ground state. However, the calculated curve for slightly excited H_2 almost coincides with the curve drawn in figure 11. Similarly good agreement is obtained when taking the dissociation energy of H_2^+ ($D - 0 = 2.65$ eV), but keeping the molecular bond length fixed to that of H_2. Thus for low values of $E\Theta^2$ the dissociation can be described solely as the consequence of rotational excitation. However, for high values of $E\Theta^2$ the calculated curve underestimates F_{dis}. This might be due to vibrational excitation, which is ignored in the model but certainly plays a role at high values of $E\Theta^2$.

The scaling with $E\Theta^2$ has also been found in a model calculation by Bitensky and Parilis (1984) assuming a string model. It is doubtful that a string model is appropriate here; the similar scaling found must be due to a mathematical correspondence between a string model and scattering from a single atom. Very recently, classical trajectory calculations using an extrapolated HFS/LCAO Ag–H pair potential have been carried out by Van Slooten *et al* (1992b) to investigate whether the H_2 molecules do indeed collide only with a single surface atom, or whether the nature of the collision is such that it can be described using only a single collision. It appears that for $\Theta_i < 75°$ collisions with a single surface atoms are indeed predominant. In the collision initially rotational excitation occurs and a figure very close to figure 9 has been found for H_2 scattering at Ag(111). In addition, the scaling with $E\Theta^2$ has also been found in the classical trajectory studies.

In this context it is interesting to mention a recent study by Beauregard and Mayne (1992). These authors have studied dissociative scattering of HD from W(001) using classical trajectory calculations. Unlike Van Slooten *et al* , Beauregard and Mayne used a (LEPS) potential energy surface that includes dissociative chemisorption. In their calculations lower translational energies were studied. Therefore, the transition as a function of initial energy from dissociative chemisorption discussed in section 2 to collision-induced dissociation discussed in section 3 can be nicely seen. In fact, it turns out that there is an intermediate process: dissociative trapping. In this case the HD bond is broken, but there is insufficient energy to remove both fragments from the surface, leading to one scattered atom and one chemisorbed atom. In the energy domain of the work by Van Slooten *et al* dissociative trapping does not occur, because the beam energy is too high.

Summarizing the studies of Van Slooten *et al* : in the experiments using inciden$\cdot$ H_2^+ the observed dissociation of the product ions is mainly caused by dissociative neutralization into a repulsive ($b^3\sigma_u^+$) state. The dissociation of the product ions in neutral H_2 scattering from Ag(111) can be described in terms of the rotational excitation following from the collision between the incidents species and a single Ag atom. The ionization step and the dissociation step in the experiments seem to be decoupled. The analysis based upon simple analytical scattering models has been confirmed by classical trajectory studies.

4. Conclusion

Concluding this overview of dissociation in molecule–surface interactions it is appropriate to state first that it is far from complete and is centred around some recent experiments, most of which have been carried out in the authors group at the FOM–Institute of Atomic and Molecular Physics. In our studies two mechanisms for dissociation have been encountered. One is an electronic transition, often via the formation of a (transient) negative ion—this mechanism is responsible for dissociative chemisorption at very low translational energies of the molecules.   The other dissociation mechanism is impulsive collisions leading to collision-induced dissociation. This mechanism is operative at energies above 10 eV. In this case rotational excitation is often the first step towards dissociation.   The repulsive interaction leading to rotational excitation is that of an anisotropic molecule and an essentially flat surface in the case of O_2 and NO scattering, and is that of an anisotropic molecule and essentially individual surface atoms in the case of H_2 scattering.

Acknowledgments

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