Harpooning in Surface Scattering: O_2^- Formation in Collisions of O_2^+ from Ag(111)

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Harpooning transitions or long-range electron jumps have been observed in collisions of O_2^+ at 100–300 eV from Ag(111) leading to negative molecular O_2^- ions. It is demonstrated that the ions are formed in nonviolent collisions and with reasonable probability. The origin and relevance of these harpooning transitions are discussed.

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Harpooning reactions are well-known chemical reactions in the gas phase.[1] The reactions proceed via an ionic intermediate, e.g., $K+Br_2 \rightarrow K^+ + Br_2^- \rightarrow KBr + Br$. The ionic intermediate can be formed at a crossing of the potential energy surfaces for the neutral (covalent) and ionic states. This crossing occurs at large separation of the reactants, because of the long-range Coulomb attraction of the ionic state. This explains the term "harpooning": The electron (harpoon) jump at the potential curve crossing brings the (Coulombic) rope from one reactant to the other and they can attract each other at large distances, which results in the chemical reaction. The formation of ion pairs has been observed as soon as there is enough energy to form the pair in an (endothermic) harpooning reaction. From studies of ion-pair formation much information has been obtained about the understanding of harpooning reactions.[2]

Can harpooning occur at surfaces? Theoretical work has indicated that this is indeed the case.[3] What is needed is a curve crossing. This should be induced by the electrostatic image force, which is proportional to $1/4z$ where z is the distance between the reactant and the surface. In the gas phase the curve crossings are induced by the Coulomb force directly, which leads to stronger lowering of the ion-pair state. Therefore the harpooning transition at surfaces is less probable, and the lowering of the ionic state is much less and may not cross the neutral state, i.e., the Fermi level. This is confirmed by the studies of H^- and O^- formation in scattering or sputtering experiments.[4,5] Large negative-ion yields are only observed when the work function of the surface is lowered to about 2.5 eV.[4] So far the formation of negative molecular ions has not been reported; their importance has been inferred from chemiluminescence studies of halogen-sodium reactions.[6]

Recent studies on vibrational excitation of NO in collisions with a Ag(111) surface have invoked the importance of an ionic intermediate to get effective vibrational excitation.[7] In addition, ionic intermediates have been invoked to explain the energy and angle dependence of the sticking of N_2 on W(110).[8] In general, harpooning transitions will be very important for the transfer of energy in gas-surface interactions.[3]

Therefore direct experimental studies of harpooning at surfaces are important, and should be aimed to observe these reactions at clean metal surfaces. The reaction itself, however, is invisible, because it will lead to sticking of the reaction products at the surface. To study the dynamics of harpooning one should perform experiments in which the important step of the reaction, i.e., the negative-ion formation, occurs and in which the collision energy is sufficiently high to prevent subsequent sticking. O_2 on Ag is a good candidate to study these processes. It is known that molecularly chemisorbed O_2 is negatively charged. For Ag(110) a peroxolike (O_2^{2-}) species is invoked from vibrational spectroscopy, and for Ag(111) photoelectron-spectroscopy data indicate a superoxolike (O_2^-) state.[9,10] Calculations confirm the negative-ion nature of the chemisorbed state, although the bonding to the surface has an important covalent character.[11] Consequently the neutral state of the system can be expected to intersect the potential of the ionic $Ag^+ + O_2^-$ at a reasonably large molecule-surface distance. Therefore we have studied O_2 scattering from Ag. Because it is very difficult to make O_2 beams in the electronvolt range, we use an O_2^+ beam, assuming that it neutralizes (in part) into the ground state of O_2 when approaching the surface. Energetic beams are necessary because the process of negative-ion formation is endothermic by a few electronvolts. In this paper we will demonstrate the first observation of harpooning transitions at surfaces, by showing that O_2^+ grazingly incident at Ag(111) is efficiently converted into O_2^-.

The experimental setup is a modified version of the one used by Tenner *et al.*[12] to study alkali-metal ion scattering.[12] The positive ions are produced by an electron-impact ionization (Nier) type O_2^+ gun. This delivers a typical beam intensity of 1×10^{-9} A at the crystal. The beam consists of approximately 95% or more of O_2^+ ions, as determined in a test setup with a Wien filter. The electron energy is 40 eV; therefore the O_2^+ ions will be vibrationally hot. Also metastable ions will be present in the beam. The crystal is mounted in a two-axis goniometer. The scattered ions are detected with a 90° cylindrical electrostatic-energy analyzer, which can be rotated around the crystal in and out of the scattering plane. The Ag(111) sample gives a sharp low-energy electron-diffraction pattern and has been shown to be atomically clean by low-energy ion scattering.

The results for scattering of a beam of O_2^+ with an energy of 300 eV from Ag(111) leading to negative ions is shown in Fig. 1. The angle of incidence θ_i measured from the surface normal is 70°. The figure shows the angular and energy spectrum of the negative ions. Two peaks are visible at 130 and 275 eV for the specular direction. These clearly can be identified with O^- and O_2^-, assuming that for scattered O^- each of the atoms carries half of the translational energy of the corresponding O_2^-. The energy corresponds approximately to two subsequent collisions with Ag atoms. In Fig. 2 a similar spectrum for $\theta_i = 70°$ and an energy of 100 eV is shown. It is clear that the yield of O^- is much lower. By varying incident energy and θ_i we find that the O^- yield seems to scale with the normal component of the impact velocity, and can exceed the O_2^- yield. Scanning the azimuth of the crystal over 360° gives a very nice symmetrical pattern corresponding to the hexagonal structure of the Ag(111) unit cell.

Energy spectra for scattered positive ions are quite different. The counting rates are an order of magnitude lower for positive ions than for negative ones, and only O^+ is observed. The positive-ion yield increases with decreasing θ_i, in contrast to the negative-ion yield. The O^+ peak appears always at lower energies than the corresponding O^- peak. This is indicative that for positive-ion formation close encounters are needed.[13]

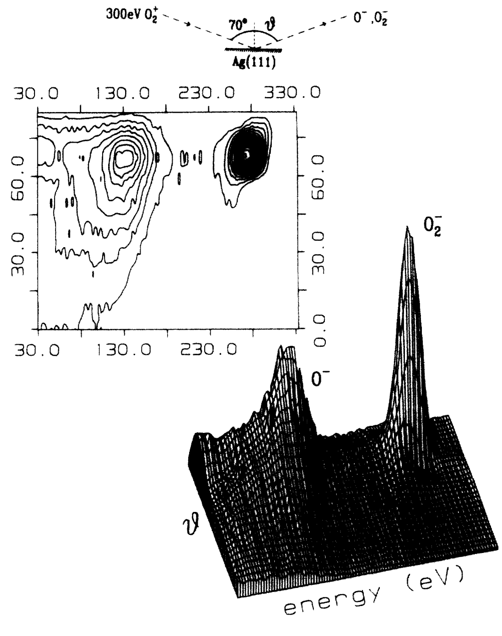

FIG. 1. Intensity distribution for negative ions formed in glancing collisions ($\theta_i = 70°$) of 300-eV O_2^+ ions with Ag(111) along the $(11\bar{2})$ azimuth. The measured intensity is plotted three dimensionally and in contour representation as a function of the final energy and polar scattering angle. The axes are identical for both representations. No correction for the energy-dependent transmission of the energy analyzer has been made. Inset: Scattering geometry and the definition of the angles.

The large negative- to positive-ion ratio indicates that the probability for negative-ion formation dominates and that negative ions are not formed at defect sites. A crude estimate shows that the total scattered negative-ion yield is of the order of a few percent of the primary beam. The scattered neutrals could not be detected in our apparatus. Another estimate of the total conversion efficiency has been obtained by our covering the crystal with K from an alkali dispenser. The resulting energy and angular distribution for the negative ions is shown in Fig. 3. Beam energy is 300 eV and $\theta_i = 70°$. The K coverage is estimated to be about 0.2 and not yet saturated.[14] In Fig. 3 the O^- peak energy corresponds to collisions with K. The O_2^- energy spectrum shows two humps, one corresponding to collisions with K and one with Ag, indicating that the surface is partially covered. The peak intensity in Fig. 3 is about a factor of 10 larger than for the clean surface. Since alkali-metal-covered surfaces are well known for their large negative-ion yield, on the order of 50%, this intensity for the covered surface confirms our estimate of a conversion efficiency of a few percent.

Three important events take place during the collision: (1) the neutralization of the positive ion, (2) the (hard) collision with the surface, and (3) the attachment of a second electron. It seems likely that the first event occurs before the other two. For the first step resonant neutralization followed by Auger deexcitation and Auger neutralization are the most likely processes in view of the

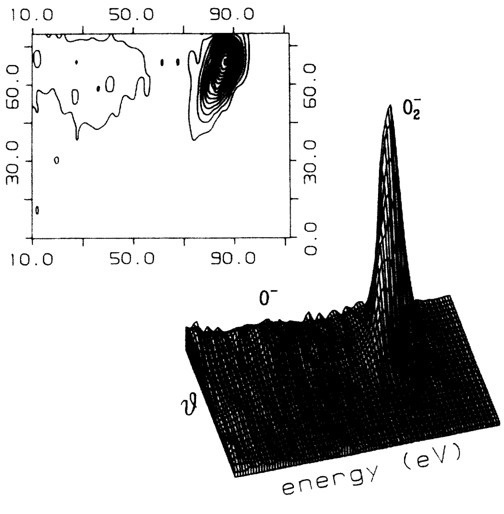

FIG. 2. Intensity distribution for negative ions formed in glancing collisions ($\theta_i = 70°$) of 100-eV O_2^+ ions with Ag(111) along the $(11\bar{2})$ azimuth.

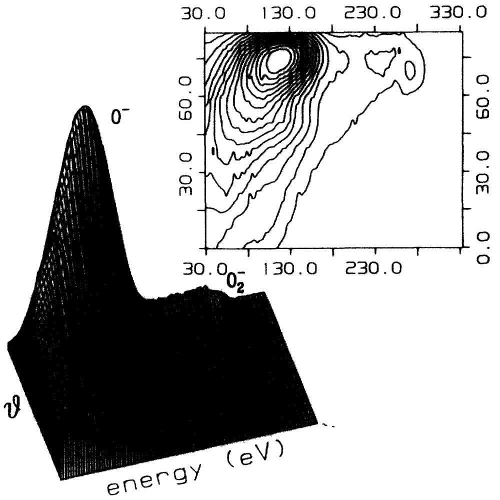

FIG. 3. Intensity distribution for negative ions formed in glancing collisions ($\theta_i = 70°$) of 300-eV O_2^+ ions with a partially K-covered Ag(111) surface along the (1$\bar{1}$0) azimuth.

low beam energy.[15] Bae and Peterson demonstrated that the resonant neutralization of O_2^+ on Cs, a target with a low ionization potential, can lead to dissociative states, i.e., to O atoms.[16] Very recent data, however, suggest that neutralization occurs into Rydberg states of O_2 followed by predissociation.[17] In case of a hard collision with a surface, there may be no time for predissociation and Auger deexcitation can occur instead. This would lead to neutralization into molecules, which in turn leads to O_2^- as observed for the most "gentle" collisions in Fig. 2. A change of the work function by our covering the surface with K could lead to a different neutralization and negative-ionization pattern, leading to O^- formation as seen in Fig. 3. That a change of the surface could lead to a different neutralization process is confirmed by the absence of O_2 molecules in the neutralization of O_2^+ on Ni(111) studied by Heiland and coworkers.[18] From calculations by Hochmann *et al.*, however, it appears that Auger neutralization into the ground state of O_2 cannot, in general, be excluded.[19] The change between Figs. 1 and 3 could also be due to the fact that the K-covered surface is rougher, as can be derived from LEED observations,[14] leading to collision-induced dissociation.

A subsequent event is the hard collision. The probability for impulsive energy transfer in this collision, leading to dissociation, is small for specular scattering. Consequently, the scattered O_2^- is only observed in the specular direction. The angular and energy distribution for the atomic ions is much broader than for the molecular ions. This is due to two effects. At first hard impulsive collisions will lead to dissociation and cause a spread in both the angular and energy distributions. In addition, initial neutralization into a dissociative state of O_2 will give the O atoms a relative energy of around 4 eV leading to broadening as identified earlier.[18]

The most important step is the attachment of another electron to the molecular ion or atomic ions. This occurs with a reasonable probability and in grazing collisions, with a distance of closest approach larger than 1 Å. This is the most remarkable observation of the experiments reported here. It is well known that the negative-ion yield is large when $\Phi - A_e - \Delta E$ is small, where Φ is the work function (4.8 eV), A_e the electron affinity and ΔE a level shift.[4] The A_e of ground state O_2 is around zero and the A_e of atomic O is 1.46 eV. Expansion of the O_2 bond will lead to an enhancement of the A_e with at most 2 eV. ΔE is due to the $-1/4z$ image force attraction, which is usually on the order of 1 eV. This is insufficient to allow resonant negative-ion formation. Apparently the affinity level of O_2 is shifted much further down, by chemical forces other than the image force, which indeed has been confirmed by quantum-chemical calculations.[11]

Having demonstrated that harpooning transitions occur for the O_2/Ag(111) system, we now turn to the relevance to chemisorption for this system. It is very likely that for a slow O_2 molecule approaching the surface the harpooning transition can happen on the way towards the surface, leading to chemisorption as O_2^-. A potential diagram suggested by Campbell indicates that the binding energy of O_2^- to Ag(111) is only 0.3 eV.[20] The low sticking probability of O_2, on the order of 10^{-6}, indicates that the negative-ion state is not accessible for thermal molecules, because of a barrier. Clearly the high translational and possibly also vibrational energy of the initial O_2^+ is sufficient to overcome this barrier, since the O_2^- relative yield is much larger than 10^{-6}. It also indicates that indeed the harpooning transition is responsible for the chemisorption of molecular oxygen on Ag surfaces. From this we conclude that the importance of harpooning transitions in energy-transfer processes at surfaces has been established experimentally and will add another dimension to these processes which traditionally are being thought of as collisions of hard spheres.

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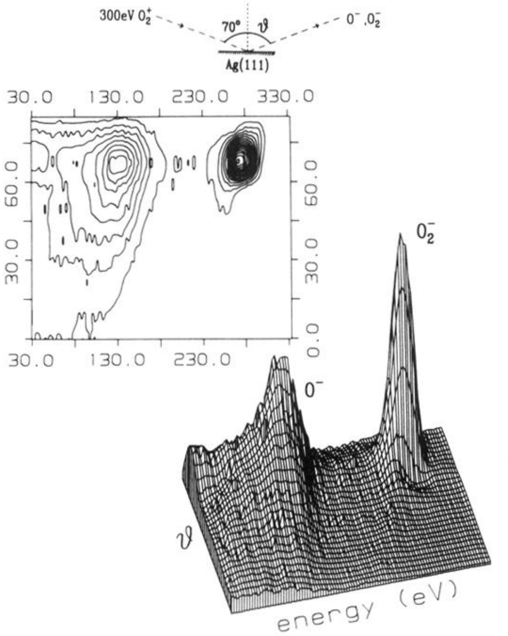

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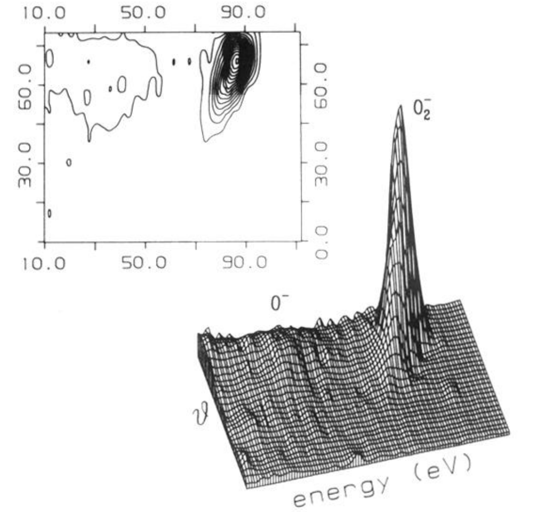

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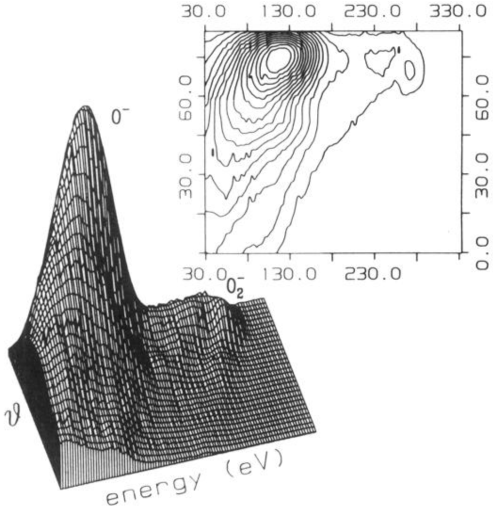

FIG. 3. Intensity distribution for negative ions formed in glancing collisions ($\theta_i = 70°$) of 300-eV O_2^+ ions with a partially K-covered Ag(111) surface along the $(1\bar{1}0)$ azimuth.