

Dissociative sticking of O₂ on Al(111)

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The dissociative sticking probability, S_0 , of O₂ on Al(111) has been measured as a function of incident translational and vibrational energy. S_0 rises from $\approx 10^{-2}$ for energies ≈ 30 meV to near unity in the range 0.6–2.0 eV, demonstrating an activated dissociation event. Vibrational excitation enhances the sticking. Surface temperature has no effect on S_0 . A peculiar dependence on polar angle is observed. The results are used to discuss possible mechanisms for the recent observation [H. Brune *et al.* Phys. Rev. Lett. **68**, 624 (1992)] of widely separated O atoms after O₂ dissociation on Al(111). [S0163-1829(97)02123-1]

Dissociation of diatomic molecules on solid surfaces (dissociative sticking) is of broad scientific and practical importance. A major reason is the intrinsic scientific interest to understand bond breaking and bond formation at solid surfaces, and the origin of activation barriers for these events.^{1–3} Dissociation of molecules and subsequent formation of adsorbate-substrate bonds are, furthermore, key events in a large number of technologies, e.g., in surface processing of semiconductors, heterogeneous catalysis, metal oxidation, chemical-vapor deposition, and diamond film growth.

The prototype system for dissociative sticking over the past 20 years is H₂ on Cu surfaces.^{1,4–6} The two main reasons are the simplicity of the H₂ molecule and the existence of a large activation barrier for H₂ dissociation. Major experimental and theoretical challenges have been to understand the nature of the barrier, how it originates from the electron structure of the combined H₂-Cu and H-Cu systems, and how it can be overcome by adding translational, vibrational or rotational energy or by orienting the H₂ molecule relative to the surface.^{1,4–6}

The detailed understanding produced by the H₂/Cu system forms an important conceptual framework when dissociative sticking of less simple diatomic molecules is addressed. O₂ dissociation on metals is, from a combined scientific and technological viewpoint, probably the most important of the latter. A major reason is the central importance of O₂ in the oxidation of metal and semiconductor surfaces, in heterogeneous catalytic oxidation, e.g., in car exhaust catalysis, and generally in catalytic oxidation of inorganic and organic molecules.

The system explored in this report—O₂ dissociative sticking on Al(111)—is likely to become an equally prominent model system as H₂/Cu. This expectation is based on the following: (i) Oxidation of aluminum is already one of the most important model systems for metal oxidation. (ii) It is since long known⁷ that the dissociative sticking probability of thermal (300 K) O₂ molecules on Al surfaces is very low, $\leq 10^{-2}$. The reason is not known. An activation barrier for dissociation might be anticipated but has not been shown experimentally and preliminary theoretical work does not indicate a barrier.⁸ (iii) The Al(111) surface is relatively simple from a theoretical point of view, compared to e.g., the transition metals. (iv) In a recent, scanning tunneling microscope

(STM) study of the final positions [on the Al(111) surface] of the dissociation fragments (O atoms), the remarkable observation was made that the O atoms were always separated by more than 80 Å at low coverage, although the thermal mobility was negligible.^{9,10} This intriguing observation alone motivates a thorough scrutiny of the dissociation dynamics of O₂ on Al(111). Recent theoretical attempts¹¹ do not support the original tentative interpretation.^{9,10} This result also draws attention to the possible nonadiabaticity of the O₂ sticking dynamics, including nonadiabatic charge transfer (with associated quantum events, like exoelectron^{12–15} and photon emission^{15–17} and ballistic motion of the dissociation fragments.¹⁸)

In light of (i)–(iv) above, it is surprising that no detailed energy-resolved sticking coefficient data exist for O₂ on Al(111), especially since such information has played a key role in the understanding of the H₂/Cu system. In the present work, we report such data. Specifically, we observe a strong energy dependence of the sticking coefficient, demonstrating an activated process. Both translational and vibrational energy of O₂ are effective in overcoming the barrier. There is no indication of a precursor-mediated sticking. A peculiar dependence on incident angle is observed. Using these data we speculate about the possible role of charge-transfer-induced dissociation of O₂ on Al and about the mechanism for the above-mentioned large separation of the O fragments.

The experiments were performed in a fairly conventional molecular-beam scattering apparatus similar to the one described in Ref. 19. The sticking measurements were made in a ultrahigh vacuum using the method of King and Wells (KW),²⁰ measuring the reflected fraction of O₂ molecules (for $10^{-2} < S_0 < 1$), and with Auger electron spectroscopy (AES) for $10^{-3} < S_0 < 0.46$. The latter was employed when the S/N ratio in the KW method was unfavorable due to the combination of a small S_0 and a weak mass 32 signal when Xe was used as a seeding gas. The Auger signal was calibrated with the KW method in the overlapping S_0 regime. Surface cleanliness was controlled by AES and achieved by successive cycles of sputtering and annealing until no oxygen or other impurities were seen in AES. Between each sticking measurement one cleaning sequence of sputtering and annealing was sufficient. Low O₂ doses were used to avoid loading the sample with oxygen. The beam energy of O₂ molecules was controlled by the nozzle temperature, and

by seeding in He and antiseeding in Xe, respectively. Partial population of vibrationally excited states was obtained by nozzle heating. The beam energy was calculated from the known total heat capacities of the involved gases and by assuming negligible vibrational cooling, while the rotational cooling was taken from Ref. 21. The energy spread of the beam was estimated using the procedure described in.²¹ In all experiments the calculated thermal excitation of the O₂ singlet state ¹Δ_g was negligible, <10⁻³.

The main results are shown in Figs. 1–3. In Fig. 1(a) the sticking coefficient at normal incidence is displayed as a function of translational energy E_t . S_0 rises steeply in the energy range 0.024–2 eV from the lowest measured value, $(1.4 \pm 0.5) \times 10^{-2}$ at 24 meV, to an almost constant value of $S_0 \approx 0.90 \pm 0.04$ in the energy range 0.6–2.0 eV. For comparison, the S_0 value of Brune *et al.* for the ambient gas was 5×10^{-3} ($2 \text{ kT} \approx 50 \text{ meV}$)¹⁰ while our measured value, at the same energy of the O₂ beam, is 5×10^{-2} . No clear threshold for $S_0(E_t)$ is observed. It approaches zero value smoothly, as seen in Fig. 1(b). The inflection point of the experimental $S_0(E_t)$ curve occurs at $\approx 200 \text{ meV}$.

The role of the vibrational energy of O₂ was explored by preparing the beam with a significant fraction (up to 20%) of vibrationally excited molecules (absolute fractions are given in the figure caption of Fig. 1). These experimental points are represented by filled symbols in Figs. 1(a) and 1(b). The enhanced sticking, observed at low E_t [Fig. 1(b)], is likely to be caused by vibrationally assisted sticking but before drawing this conclusion, we must take into account the broadening of the translational energy distribution due to antiseeding in Xe. The latter is unknown, therefore an analysis was made of how large the translational-energy spread is actually required to explain the experimental data without invoking vibrational energy promotion of the sticking. We find that $\Delta E/E$ must be larger than 0.75 at $E_t = 100 \text{ meV}$. We regard this as unrealistically large and conclude qualitatively that there is a positive vibrational promotion of the sticking. A plot of S_0 versus E_t [Fig. 1(c)], where the contribution from the vibrationally excited molecules only ($v \geq 1$) has been extracted [see Fig. caption of Fig. 1(c)], strongly suggests that the vibrational energy is much more effective than translational energy (at normal incidence) in promoting sticking.

Figure 2 shows how S_0 depends on the polar angle at two different translational energies. For both energies, S_0 initially falls slowly as the incidence becomes more oblique, and then rises to a maximum at $\approx 25^\circ$ for both energies. Note that this is an absolute maximum for $E_t = 112 \text{ meV}$. After the maximum, S_0 falls faster towards zero than what the normal energy scaling (NES) curve²² in Fig. 2 predicts. These measurements were performed with an azimuthal angle corresponding to a direction $\approx 7^\circ$ away from the [112] direction.

An issue of prime interest—not the least for theoretical modeling—is if the sticking event occurs in a “direct” channel, or via an intermediate (chemisorbed or physisorbed) precursor state. In the latter case S_0 should generally have a significant temperature dependence due to thermally activated dissociation or desorption from the precursor state. Figure 3 shows the T dependence of S_0 for three different E_t . The weak or nonexistent T dependence is a strong indication of a direct sticking channel without a precursor state.

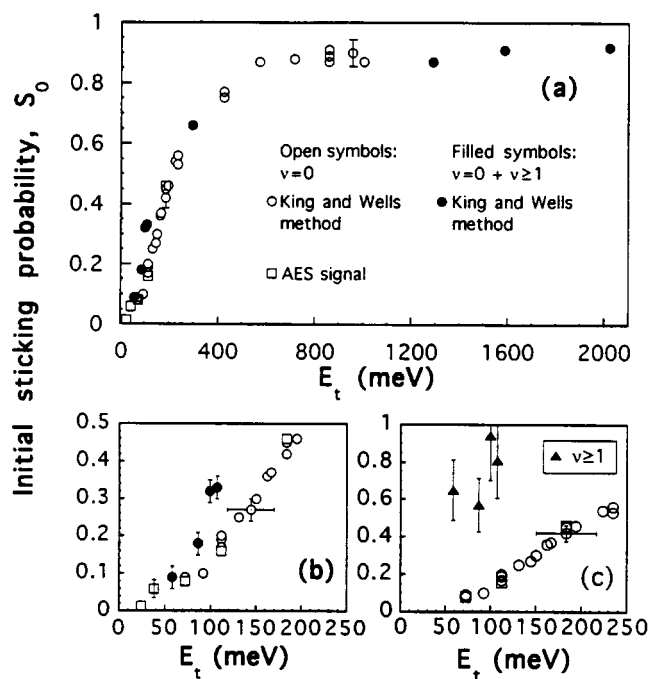


FIG. 1. (a) The initial sticking probability, S_0 , of O₂ on Al(111), at normal incidence, as a function of translational energy E_t . Open and closed symbols represent experiments with ground-state and mixed ground-state and vibrationally excited O₂ molecules, respectively. The excited-state populations of the latter are as follows (going from low to high E_t): (●) $\nu=1$: 7.5%, 14.7%, 17.5%, 18.9%, 11%, 7.6%, 13.1%, and 17.4%, $\nu=2$: 0.6%, 2.6%, 4.0%, 4.8%, 1.5%, 0.6%, 2.0%, 3.9%, respectively. (b) Enlargement of the low-energy region in Fig. 1(a). (c) Calculated S_0 vs. E_t for vibrationally excited molecules (▲). These data points were calculated by a simple deconvolution procedure. A “true” $S_0(E_t)$, for a vibrationally cold, pure O₂ beam was first obtained by deconvoluting the beam-energy spread from the experimental $S_0(E_t)$ curve using the data in (a), (b). These $S_0(E_t)$ values were then subtracted from the corresponding S_0 values for the antiseeded beam, having a fraction of vibrationally excited molecules. The S_0 values obtained in this way represent an upper limit of the true S_0 for vibrationally excited molecules, due to an unknown and therefore uncorrected small contribution to $S_0(E_t)$ from the translational energy broadening in the antiseeded beam. The horizontal error bars indicate the calculated beam-energy spread²¹ for a pure O₂ beam, while the vertical error bars are statistical errors from 3–5 measurements. In all panels, circles (open and filled) correspond to experiments performed with the KW method, while the open squares were deduced from the AES signals.

It also indicates that phonons play a minor role in activating the dissociation. (Energy transfer from the molecule to the phonon bath is of course still a viable channel for energy dissipation²³).

The results in Figs. 1–3 demonstrate an activated dissociative sticking with theoretically challenging features. The implication is that the dissociation occurs on a multidimensional potential-energy surface (PES) (or on more than one PES; see below). It is thus not correct to discuss the activated dissociation in terms of a single-activation barrier. A range of “activation barriers” exist, whose magnitudes depend on e.g., the orientation of the O₂ molecule, the point of impact on the surface unit cell, and internal excitations of the mol-

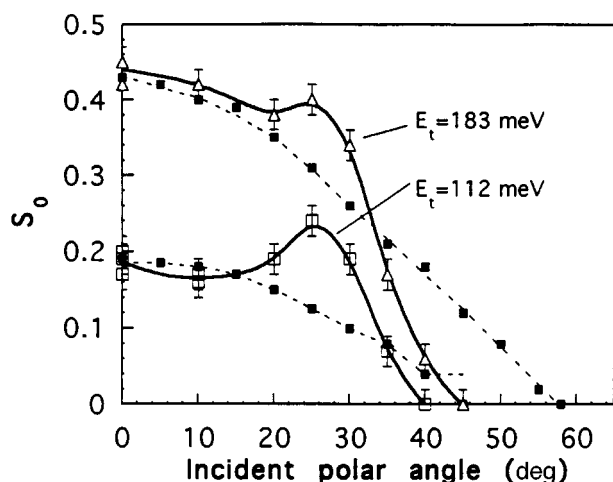


FIG. 2. S_0 as a function of incident polar angle at two different beam energies: $E_t=112$ meV, and $E_t=183$ meV, respectively. The filled squares show the result of the NES assumption constructed from Fig. 1(a).

ecule. The angular dependence (Fig. 2) shows that there is no simple NES. The vibrationally assisted sticking [Fig. 1(c)] might suggest a complex trajectory before the transition state or the “seam”²⁴ is passed through, into the dissociating trajectories (but an alternative and simpler interpretation is mentioned below). Phonons seem to play a secondary role for the dissociation event.

In our brief speculative discussion we comment (i) on the possible role of charge transfer²⁵ and (ii) on the interpretation of the experiment by Brune *et al.*⁹ Electron transfer is important in the dissociation of electronegative molecules like O_2 and Cl_2 on alkali metals.^{12-18,26} The initial event is an electron transfer from the Fermi level to the antibonding, lowest unoccupied molecular orbital (LUMO) of the diatomic, creating a transient negative ion, inducing nuclear separation (dissociation), paving the way for further electron transfer. In this picture the roles of translational and vibrational energy are: Increased translational energy means that the O_2 molecule, for a given orientation and impact trajectory, comes closer to the surface before the classical turning point is reached, with an associated larger downshift (due to the image interaction) of the energy of the LUMO, and there-

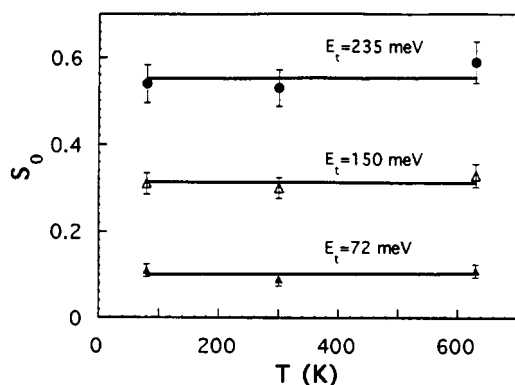


FIG. 3. Temperature dependence of S_0 at three different E_t . Lines are drawn to guide the eye.

fore an increased overlap with the filled metal states. The resulting larger charge transfer to the molecule at higher normal incident energy promotes separation of the two nuclei. As more normal translational energy is added, more trajectories reach the dissociation “seam,” i.e., S_0 increases. Increased sticking due to vibrational energy excitation proceeds via a different mechanism; the larger average internuclear distance of a vibrationally excited molecule increases the overlap (the Franck-Condon factor) between the neutral and the negative-ion states, at a given distance from the surface.

This picture applies quite well to Cl_2 on alkali metals and reasonably well to O_2 on alkalis.^{12-18,26} The much lower electron affinity of O_2 compared to Cl_2 , and the larger work function of Al(111) compared to alkalis make the $O_2/Al(111)$ system more complicated, since all important events occur so close to the surface, that the image picture breaks down and orbital hybridization becomes important. Due to the latter, the $^1\Delta_g$ state may also have to be considered, in addition to the negative-ion state(s) of O_2 . In spite of these complications, the picture above provides a useful conceptual framework of how translational and vibrational energy can promote the sticking, even for $O_2/Al(111)$.

Finally, we (employ the present and earlier results^{27,28}) to speculate about possible mechanisms for the surprising observation by Brune *et al.*⁹ that dissociated O atoms on Al(111) are separated >80 Å at low coverage. An important fact for this discussion is that dissociative sticking at the low-incident energies in the experiment, is a rare event; only $\approx 1\%$ of the molecules hitting the surface dissociate (in contrast e.g., to Cl_2 sticking on K which occurs with unity probability¹⁴). Thus we can try to understand the large O-atom separation in terms of rare events. This is not possible when $S_0 \approx 1$, e.g., at the higher energies in Fig. 1.

There are three partly overlapping ideas in circulation about the mechanism(s). (i) the original work⁹ suggested that the two O atoms separate along the surface, and that the excess energy gained in the process of replacing the O-O bond with two O-Al bonds is dissipated sufficiently slowly (low “friction”) that the two hot atoms can separate >80 Å. Recent theoretical attempts to rationalize this idea have failed,¹¹ the energy dissipation appears effective. (ii) In the second idea,¹⁸ the trajectories of the two fragment atoms are very different; one of them is directed towards the surface and immobilized near the point of impact, while the second atom performs a “ballistic” motion. The dissociation can, e.g., be driven by the charge transfer discussed above, creating an intermediate repulsive state (e.g., $O-O^-$). The ballistic motion may be by a hot atom or by a temporary negative ion. A neutral atom will by far have the lowest friction as discussed in,¹¹ moving essentially as a van der Waals interaction specie along the surface. The crucial question is if its lifetime as a neutral is long enough. (iii) The third idea is just a limiting case of (ii), where the ballistic trajectory escapes from the surface into vacuum. In the latter case, no close neighbors would be seen at low coverage, since only a single atom is deposited by each dissociating O_2 . (AlO instead of O emission would give the same result). The exothermicity of the O_2/Al system is sufficiently large to allow such events energetically.²⁹

The major problem with (ii) or (iii) is not to accept the basic idea (it has been demonstrated theoretically and experimentally^{13,14,18,27,28}) but to understand how *every* sticking event can lead to large O-O separation or O emission. One intuitively expects a range of separations from very close ones to very large ones, depending on the exact incident trajectories. The key, as noted above, may be the very low absolute value of the sticking coefficient of a room temperature gas, $S_0 \approx 10^{-2}$. It allows for an interpretation where only very special initial trajectories of favorably oriented O₂ molecules dissociate, with final nuclear trajectories that create the large O-atom separation. For example, if only mol-

ecules oriented nearly perpendicularly to the surface dissociate (at small E_t) then a ballistic motion according to (ii) or (iii) above might result.¹⁸ As we show in this report at higher-incident energies (larger S_0), the phase space for dissociation increases and a larger variety of dissociating trajectories are expected. It would therefore be extremely interesting to repeat the Brune *et al.* experiment for a range of incident energies.

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