Rebonding Effects in Separation and Surface-Diffusion Barrier Energies of an Adatom Pair

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For Al adatom pairs on Al(100), first-principles calculations imply a small separation energy of 0.07 eV, resulting from Al-surface rebonding as adatom-adatom bonds break. Calculated barriers for Al-pair and single-Al diffusion are 0.66 and 0.80 eV. The pair barrier is lower because pairs reside farther above surfaces, where potential corrugation is weaker, and because an Al surmounting a barrier gains energy from its partner, whose bond to the surface strengthens.

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This Letter presents an interpretation of two surprising results derived from field-ion microscope (FIM) observations of Pt, Re, W, and Ir adatoms on W surfaces[1-4]: first, that E_s, the energy required to separate a pair of adatoms while they both remain adsorbed, is generally less than $\frac{1}{6}$ the cohesive energy per bond of a comparable bulk solid,[1-3,5,6] and second, that the activation energy for surface pair diffusion often equals or is less than that for single-atom diffusion.[4] To understand these phenomena, I have applied a recently developed first-principles, self-consistent, scattering theory of adsorption energies[7] that uses the local-density-functional[8] description of electron exchange and correlation, and treats the total energy versus nuclear positions of a spatially compact group of atoms adsorbed on an otherwise perfect, infinitely extended metal crystal. I show that small values of E_s result from compensation between the cost of breaking an interadatom bond and the gain attendant on the simultaneous strengthening of adatom-surface bonds. The lowering of the pair-diffusion activation barrier relative to that for an isolated adatom results from two effects: (1) An adatom surmounting a diffusion barrier accepts energy gained by a neighboring adatom as the latter's bond to the surface rehybridizes and strengthens, and (2) an adatom pair resides farther above a surface, where the potential is less corrugated, because the formation of the interadatom bond weakens the adatom-surface bond.

To minimize computational effort, I consider Al self-adsorption on a two-layer, rigid Al(100) substrate. Reduction in labor results from the weakness of the Al pseudopotential[9] and the consequent slow spatial variation of the electron pseudodensity, and because simple-metal atoms require a smaller orbital basis than transition-metal atoms. Despite its simpler nature, the Al/Al(100) system is predicted to manifest both interesting effects, a low E_s, 0.07 eV, and a pair-diffusion barrier of 0.66 eV relative to 0.80 eV for single atoms. Thus little is lost in avoiding the complexity of the transition-metal species actually studied in the FIM.

The cohesive energy of Al is 3.34 eV/atom. Since Al is fcc, there are six bonds per Al atom, and one is tempted to identify (3.34 eV)/6 = 556 meV as the energy gained in forming an Al—Al bond. Thus one might estimate $E_s \approx 0.5$ eV for two Al adatoms on an Al surface. FIM observations of transition-metal systems argue otherwise. For example, E_s is found to be only 82 meV for a pair of Ir atoms adsorbed on W(110) while the cohesive energy per bond of Ir is 1160 meV[5]; indeed all measured adatom-adatom separation energies[1-3,5] are small relative to the energy per bond of the comparable bulk solid. I attribute this fact to the rehybridization effects that underly Pauling's bond-order–bond-length correlation.[10] Consider an Al-adatom dimer on Al(100). Each atom of the dimer has *five* nearest neighbors. The bond-order–bond-length concept implies that the ad-Al bonds to the surface will therefore be weaker and longer than those of a single Al adatom which has only four nearest neighbors. Thus energy gained in the adatom-adatom interaction is compensated by the cost of weakening of the Al-surface bonds. This compensation, as documented below, explains the smallness of the calculated Al-Al separation energy compared to 556 meV.

Rebonding also helps explain the relatively low activation energies for adatom-pair diffusion observed in FIM studies.[4] Until now it has been widely assumed that it is just the distance dependence of the interadatom potential that determines whether single-adatom or pair diffusion has the lower barrier.[4,11] The idea is that if the preferred value of the adatom-pair bond length is close to the distance between single-adatom adsorption sites then a hop of the first atom of the pair costs the energy expended in stretching the interadatom bond plus that needed to surmount the single-atom diffusion barrier. In this case the pair-diffusion barrier exceeds that for a single adatom. Alternatively, if the preferred interadatom separation is close to the distance between a single-atom adsorption site and the site of a single-atom diffusion barrier, then the interadatom bond is compressed at equilibrium in the substrate potential, and the energy required for one of the adatoms to surmount a barrier is reduced by the energy released in relieving the compression. The former case is thought to be exemplified in diffusion of Ir on W(211) and the latter in diffusion of Re or W on the same surface.[4]

This discussion ignores the fact that the strength of the adatom-substrate interaction depends on the presence or absence of a second adatom. Consider the extreme example of a C and an O adsorbed on some substrate. If the C-O separation is large, the C is triply bonded to the surface. If it is small, the adatoms will form a CO molecule whose axis is along a surface normal, with the C weakly and singly bonded to the surface and the O not bonded to it at all. Because the C-surface interaction is weak in this situation, the C atom will sit far from the surface where the corrugation of the potential is slight. Thus the CO-diffusion barrier is much lower than that for an isolated C, even though the energy to stretch the CO bond is large. Similar reasoning applies to the less extreme example of two Al adatoms on Al(100). At equilibrium the adatom-adatom interaction results in a weaker and longer adatom-surface bond. Accordingly, the ad-Al pair resides in the less corrugated potential that exists higher above the outer atomic plane of the substrate. In addition, if in pair diffusion one atom surmounts a barrier first and the other later, then energy transfer between the two atoms can aid the process. Specifically, the atom not surmounting the barrier strengthens its bond to the surface as its partner moves away. On the assumption that the energy it gains in rebonding is transferred to the diffusing atom, the activation barrier for diffusion is diminished.

The method I use to explore these ideas[7] is founded on the phenomenon of screening of the adatom-induced one-electron potential, $V(\mathbf{r})$. Since $V(\mathbf{r})=0$ at distances substantially larger than a screening length from a spatially compact cluster of adatoms, the Schrödinger equation can be cast as a scattering problem: Bloch waves incident on the compact region containing the support of the adatom-induced potential generate "outgoing" Bloch waves. The advantage of scattering theory is that its equations only involve the compact region of space where $V(\mathbf{r})\neq 0$. Thus, on adoption of the "matrix Green's function" scattering method,[7] which corresponds to working in a localized-orbital basis from the outset, the set of equations that determine wave-function coefficients is *finite*. I use the following localized basis: At each Al site I center an s, p_x, p_y, and p_z function. Each radial function is of the form r^l times a linear combination of Gaussians (cf. Table I) chosen to give a good fit to the exact isolated Al-atom pseudowave function of the same symmetry,[9] from the nucleus to a distance of 0.65 times the bulk-Al nearest-neighbor separation. In addition, to provide variational freedom for Smoluchowski smoothing of the substrate electron charge[12] and formation of the surface dipole, I situate "floating" p_x, p_y, and p_z orbitals atop each surface Al and also atop each ad-Al at a distance of 3.0 bohrs along a surface normal.[13] The floating orbitals are of the form $r_i \exp(-\alpha r^2)$, $i=1$, 2, and 3, with $\alpha=0.15$ bohr^{-2}. The calculations use the Perdew-Zunger parametrization[14] of the Ceperley-Alder[15] local exchange-correlation potential, and the norm-conserving pseudopotentials of Bachelet, Hamann, and Schlüter.[9] Methods for calculating various matrix elements, for dealing accurately with large electrostatic energies, and for calculating forces on nuclei are discussed in detail in Ref. 7.

TABLE I. Coefficients c and attenuation constants α (in bohr^{-2}) for $l=0$ and 1 radial functions of Al, $R_l(r) = r^l \sum_\alpha c_\alpha \exp(-\alpha r^2)$.

α	c_α
	$l=0$
0.11	0.423 181 58
0.29	0.400 650 17
0.63	−0.670 543 45
	$l=1$
0.15	0.263 648 87
0.29	0.022 511 07

Since one wishes to evaluate separation and activation barrier energies, which correspond to extremal points of the adatom energy hypersurface, it is useful to compute the energy gradient directly for each trial adatom geometry by use of the Hellmann-Feynman theorem[16] plus Pulay corrections for basis incompleteness.[17] I follow the calculated gradient to the neighborhood of an extremal energy, then, linearly extrapolating, bring it to a value sufficiently close to zero. Extremal energies quoted below correspond to geometries in which each adatom is subject to a force of less than 0.05 eV/bohr in magnitude.

In what follows, atom coordinates are given as (u,v,h). The lateral components u and v are in units of 5.42 bohrs, the Al(100) surface lattice spacing, while h, the height above the substrate surface, is in units of 3.83 bohrs, the separation of the two Al(100) planes. The origin for (u,v,h) is taken to be at an Al-substrate nucleus. Thus $(0.5,0.5,h)$ represents a fourfold hollow position at a height of $h\times 3.83$ bohrs above the surface, $(0.0,0.5,h)$ a bridge position, etc.

In the computation of the surface diffusion barrier for one ad-Al and E_s for an ad-Al pair in neighboring fourfold hollows, a relatively small cluster of substrate atoms contains all the basis orbitals that significantly overlap the adatom-induced one-electron potential. They are located at $(n,m,0)$ with $n=-2,\ldots,2$ for $m=0$ and 1, at $n=-1,0,1$ for $m=-1$ and 2, and at $(n+0.5,m+0.5,-1)$ with $n=-2,-1,0,1$, for $m=-1,0,1$.[18] The energy minimum for a single ad-Al is found at $(0.5,0.5,0.861)$. The energy at this site is -4.39 eV relative to what one would find for $(0.5,0.5,\infty)$ using the same orbitals for the Al at ∞ as were used for $h=0.861$. These orbitals, however, are inadequate to describe an Al atom in free space, because long-ranged Gaussians have been deliberately excluded to avoid problems associated with linear dependence. In addition, spin effects that are important for an isolated Al have been averaged over. The correction of the energy of the isolated Al for these facts results in a calculated absolute binding energy of 3.03 eV for a single Al adatom. Evidently this value is much closer to the cohesive energy of bulk Al, 3.34 eV/atom, than to the 2.23 eV one would obtain from bond counting. This result indicates that ad-Al—surface-Al bonds are stronger than Al—Al bonds in bulk Al, in accord with the fact that at equilibrium the ad-Al—surface-Al bond is 0.36 bohr shorter than the bulk bond length of 5.42 bohrs. (Henceforth, all energies quoted include the correction of 1.36 eV/ad-Al to the energy of the isolated Al atom.)

A saddle point is found on the energy surface for a single ad-Al at the bridge site (0.0,0.5,1.11), corresponding to a binding energy of 2.23 eV. This implies that the barrier to diffusion of an isolated ad-Al is 0.80 eV. The corrugation of the Al-surface potential requires the migrating atom to increase its height above the surface by 0.95 bohr to surmount the barrier. In searching for the equilibrium configuration of the two ad-Al's in neighboring fourfold hollows, I allow the atoms to move off symmetry axes because of their attractive interaction. The energy minimum, found for adatoms at (±0.483, 0.5,0.940), corresponds to a total binding energy of 6.13 eV, and thus to $E_s = 0.07$ eV for the ad-Al pair separation energy. Notice that this small value of E_s is accompanied by substantial changes in the binding site of each adatom. In particular, the height of each ad-Al increases by 0.3 bohr while the displacement away from the fourfold symmetry axis is 0.09 bohr. As I discuss further below, the latter displacement reflects the fact that the Al-Al interaction is at least partially a direct one. The former indicates the weakening of the adatom-substrate bonds. To help interpret the smallness of E_s, I compute the binding energy of a single ad-Al at the site (0.5,0.5,0.940), i.e., in a fourfold hollow, but at the increased height above the surface associated with Al-dimer binding. I find this energy to be 2.98 eV. Thus to separate a dimer without allowing the individual Al's to relax toward the substrate costs 0.18 eV. The reason that this value is only 32% of the 556-meV Al cohesion per bond is that the valence electrons that were involved in the dimer bond relocate and participate in Al-surface bonds. Thus only a fraction of an Al—Al bond energy is expended in the separation of an Al pair. The evidence for the strengthening of the Al-surface bonds upon dimer separation is the reduction in the ad-Al height: Each separated ad-Al regains 54 meV as it relaxes 0.3 bohr toward the surface. This relaxation energy compensates further for the energy required to break the dimer bond, reducing the 0.18 eV needed to separate the Al pair at the height of 3.6 bohrs to the quoted separation energy, $E_s = 0.07$ eV.

In the computation of the diffusion barrier for an Al dimer, the set of orbitals that overlap the adatom-induced potential is larger than used so far. It contains Al orbitals centered at $(n,m,0)$ with $n = -2,\ldots,2$ for $m = -1, 0, 1$ and $n = -1, 0, 1$ for $m = -2$ and 2, and at $(n+0.5, m+0.5, -1)$ with $n,m = 2,\ldots,1$. The energy-vs-height curve for a single Al for the larger orbital cluster is lower by about 0.01 eV than for the smaller cluster, while the force is unchanged to three places. To minimize error, barrier heights quoted here are differences of energies calculated for the same cluster.

For a hop of one Al of a dimer perpendicular to the dimer axis, I find a saddle point when the Al's are located near (−0.438, −0.129, 1.138) and (0.463, 0.474, 0.901). The corresponding adsorption energy is only 5.48 eV, implying a barrier height of 0.66 eV. To understand how rebonding effects have lowered this barrier relative to that for single-Al migration, first recall that the migrating Al of the dimer started from a height of 3.60 bohrs above the surface, where in the absence of its partner it would have been 0.054 eV less tightly bound than an isolated Al at equilibrium 3.30 bohrs above the surface. Second, when it is at the saddle site, its partner has relaxed back to a height of 3.45 bohrs, regaining 0.042 eV via rehybridization of its bond to the surface. The sum of these two energies evidently accounts for most of the barrier lowering.

Of course, migration from first- and second-neighbor hollow sites is only the first step in dimer migration. One must also consider the barrier to the reverse process, in which the dimer atoms are restored to first-neighbor hollows. To obtain the height of this barrier, one needs the energy minimum for a pair of Al's located in second-neighbor hollows. The calculations show that this minimum occurs when the Al's are located near (±0.5, ±0.5, 0.867) and equals 5.94 eV. Interestingly, this means that the ad-Al interaction is now repulsive. The barrier to restoring a configuration with ad-Al's in first-neighbor hollows is therefore less than that for creating the second-neighbor configuration, by 0.19 eV.

The repulsion found for the second-neighbor dimer, as against attraction in the first-neighbor geometry, is an example of an oscillatory adatom-adatom interaction, as has been predicted in phenomenological theories.[19] The fact that, in the second-neighbor configuration, the ad-Al's lie virtually on the fourfold symmetry lines in their respective hollows, displaced slightly higher above the substrate than they would be if isolated, is a manifestation of the "through-metal" nature of the interaction. The atoms of the dimer "know" that there is a neighbor present, but not in which second-neighbor site it is located. This contrasts with the off-symmetry sites of Al's in the first-neighbor geometry, where the is a direct adatom-adatom interaction.

In summary, first-principles total-energy calculations for single Al adatoms and Al dimers on Al(001) help explain two long-standing surprising results derived from field-ion microscope studies. They show that small pair-separation energies and pair-migration barriers are the result of rebonding to the surface when a dimer bond is stretched. In future work I will study the energetics of dissimilar atoms (e.g., modifiers and reactants) adsorbed on various metal surfaces, and hope to establish an understanding of trends in the energetics of adsorbed species.

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