Metal-on-Metal Bonding and Rebonding Revisited

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Density-functional calculations for a wide variety of metals show that, contrary to rebonding theory, ad-dimers do not have notably longer surface bonds than adatoms, do not reside farther above the surface, and do not meet the rebonding arguments for augmented mobility. Rebonding contributes to destabilize ad-dimers, but does not explain inherently weak ad-dimer bonds. [S0031-9007(99)09494-6]

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The bond-order–bond-length concept put forth by Pauling almost 70 years ago has greatly added to our intuitive understanding of atomic-scale bonding in molecules [1]. The basic idea is that the more bonds an atom makes, the weaker and longer each becomes. This principle is routinely used in molecular chemistry, and has also been applied to the gas-surface interface. Going one step further, Feibelman adopted similar arguments to interpret the stability and mobility of adsorbates in terms of "rebonding" [2]. At the heart of this model is the idea that an attractive interaction between adsorbates inevitably weakens their bonds to the surface. This leads to a number of important predictions [2]: (i) Ad-dimers are expected to bind farther above the surface than adatoms because they are more coordinated. (ii) Small ad-dimer binding energies (relative to per-bond bulk cohesive energies) result from "compensation between the cost of breaking an interadatom bond and the gain attendant on the simultaneous strengthening of adatom-surface bonds" [2]. (iii) Ad-dimers can be more mobile than adatoms because they reside in the less corrugated potential that exists higher above the substrate, and the atom not surmounting the barrier strengthens its bond to the surface as its partner moves away [2].

Although rebonding provides an appealing picture of adsorbate interactions, recent first-principles adsorption calculations for Al/Al(111) [3] disagree qualitatively with the rebonding view [4]. Since rebonding addresses fundamental issues in epitaxial growth and catalysis [3,5], it is of general interest to investigate this issue [2,3] in detail.

In this Letter, I show that the rebonding view of adsorbate bonding is oversimplified, and in many cases inappropriate. The notion of bond lengthening, increased resident height, and augmented mobility upon pair formation is not borne out by detailed calculations for a broad range of metal systems. The principal reason for this is that the main part of the rebonding energy lies in adsorbate and substrate relaxations that do not lengthen the adspecies-substrate bonds notably.

The calculations are based on density-functional theory (DFT) [6,7], using a pseudopotential method, as implemented in the VASP code [8], and applying both the local-density (LDA) [9] and generalized-gradient (GGA) [10] approximations for the exchange-correlation functional. Note that, unlike in the perturbative [11] "post-LDA/GGA" approach, these calculations are all fully self-consistent. Both approximations to DFT are employed for the purpose of generality, and to facilitate comparisons. The one-electron wave functions are expanded in a plane-wave basis with an energy cutoff of 9, 13, 14, 15, and 15 Ry for Al, Au, Pt, Ir, and Rh, respectively, using ultrasoft Vanderbilt pseudopotentials [12]. The Kohn-Sham equations are solved iteratively, and the atomic structure is optimized until the forces on all unconstrained atoms are less than 0.03 eV/Å. The (100) supercell is constructed of eight layers, each containing 20 atoms [the (111) cell has six layers with 30 atoms each]. Above an additional adsorbate layer [13], there is >10 Å of vacuum. The surface Brillouin zone is sampled using a dense (6×6) k-point mesh for good convergence [14]. This study focuses on the (100) face of fcc metals because rebonding effects are expected to be pronounced on this open surface. The results are as follows.

Bond lengths.—A simple observable manifestation of rebonding is that ad-dimers should reside farther above the surface than adatoms [2]. However, the present calculations, and inspection of two other unpublished studies on Pt/Pt(111) [15] and Cu/Cu(100) [16], argue otherwise: In all metal systems studied to date, dimers bind just as close to the surface as atoms within both the LDA and GGA. The actual adsorbate-surface bond lengths are equal for atoms and dimers to within 0.03 Å (Table I).

Dimer mobility.—If ad-dimers reside in a less corrugated potential than adatoms, it is not because of increased resident height. To test the other rebonding-model argument for enhanced ad-dimer mobility, I perform a calculation for Al/Al(100) in which one of the adatoms leaves the pair in a direction perpendicular to the dimer axis (as described in Ref. [2]). The activation barrier for this motion is 0.53 eV within the GGA. The adatom that is left behind relaxes towards the adatom diffusing away, so that the average bond length to the surface actually *increases* by $\simeq 0.01-0.02$ Å. Since the diffusion path for ad-dimers on (100) surfaces is currently unknown, this warrants further investigation. Still, neither of the two rebonding arguments for augmented ad-dimer mobility are supported by the present calculations. Experimentally, ad-dimers are most often found to be *less* mobile than adatoms [5,17]; the few exceptions are for heterogeneous systems [17],

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TABLE I. Adsorption parameters for adatom/ad-dimer systems within LDA and GGA: d denotes the adsorption height above the plane averaged over all surface atoms, r denotes the average bond length to the surface atoms, and r_l denotes the lateral bond length of the ad-dimer. All values are in angstroms.

	LDA			GGA		
	d	r	r_l	d	r	r_l
Al/Al(100)	1.69/69	2.67/69	2.62	1.72/70	2.72/73	2.66
Au/Au(100)	1.61/64	2.69/71	2.76	1.70/71	2.77/80	2.85
Rh/Rh(100)	1.63/64	2.49/51	2.57	1.68/69	2.55/57	2.64
Ir/Ir(100)	1.63/64	2.51/53	2.56	1.67/67	2.55/56	2.62
Au/Pt(100)				1.77/81	2.73/76	2.85
Pt/Au(100)				1.42/52	2.68/71	2.71
Al/Al(111)	2.03/1.98	2.65/65	2.61	2.05/00	2.69/68	2.64
Pt/Pt(111)[a]	1.96/96	2.56/56	2.63			

[a]Ref. [15].

which implicate the role of ad-dimer frustration (see below). It is possible, however, that rebonding is important for ad-dimer diffusion by exchange [as observed for Pt(100) [18]], but probably not in concerted sliding [as predicted for Al/Al(111) [3] and Pt/Pt(111) [15]].

Dimer stability.—Rebonding does contribute to lowering the ad-dimer binding energy E_d. In the few studies performed on dimer stability, $E_d = E_{\text{dimer}} + E_{\text{slab}} - 2E_{\text{atom}}$ is routinely compared with the per-bond bulk cohesive energy $E_c/6$ [2,17]. In this study, as in others, $x_2 = E_d/(E_c/6) < 1$ (Table II). An appealing feature of the rebonding model is that it suggests a simple explanation for this observation: Positive adatom-adatom interaction is gained at the expense of weakening adatom-surface bonds. Before assessing this effect, it is essential to realize that it is in fact *misleading* to expect that $E_d = E_c/6$ for two distinct reasons. First, any bond strength comparisons should include the actual ad-dimer bond strength E_{aa} rather than the ad-dimer binding energy E_d (see Fig. 1). Upon ad-dimer separation, each adatom retains its adatom-substrate bond E_{as}, augmented by the rebonding energy Δ, and hence $E_{aa} = E_d + 2\Delta$. Note that there is no such distinction in the gas and bulk phases, and that only in the limit of no rebonding does the ad-dimer binding energy equal its bond strength. Second, the ad-dimer bond is a tradeoff between the covalent bond of the gas dimer and the metallic bond in the bulk (see below). Neither the binding energy nor the bond strength of the ad-dimer should thus be expected to equal $E_c/6$, just as they should not equal the gas-phase dimer bond energy.

Rebonding.—To quantitatively assess rebonding effects, I decompose the total rebonding energy into three terms, $\Delta = \Delta_e + \Delta_a + \Delta_s$, where the respective components are due to electronic charge redistribution, adsorbate relaxations, and substrate relaxations. These terms are calculated for Al/Al(100), Au/Au(100), and Rh/Rh(100) according to $\Delta = E_1 - E_{21}$, $\Delta_e = E_1 - E_{11} - (E_{21} - E_{22})$, and $\Delta_s = (2E_{11} - E_0 - E_{22})/2$, where the first number in the subscript denotes the number of adsorbate atoms in a fully relaxed calculation, and a second number indicates the number of adsorbate atoms removed in a calculation where the atomic coordinates have been frozen. The term Δ_a is obtained by subtracting Δ_e and Δ_s from Δ. The results are displayed in Table III, and reveal that the *rebonding energy is predominantly elastic*, i.e., due to adsorbate and substrate relaxations. This explains why ad-dimers do not bind farther away from the surface than adatoms: The (mainly lateral) relaxations do not lengthen the bonds notably. Note that the adatom strain fields are repulsive for Al/Al(100) and Rh/Rh(100), and attractive for Au/Au(100) (Δ_s in Table III), which is likely to play a role in the adatom pair interaction oscillations observed on various metals [17].

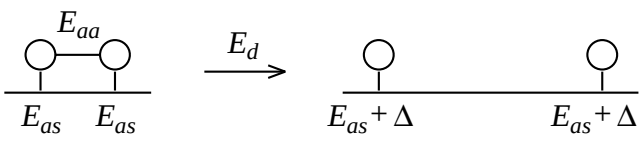

FIG. 1. The relation between the binding energy E_d, bond strength E_{aa}, and rebonding energy Δ of ad-dimers.

Direct evidence for the lack of electronic rebonding is found in charge-density analyses for Al/Al(100), Au/Au(100), and Rh/Rh(100). Figure 2 shows the charge redistribution when two adatoms meet to form an ad-dimer ($\rho_2 + \rho_{22} - \rho_{21} - \rho_{21}$). Note that there is practically no charge rearrangement at all in the directions towards the surface atoms (the rightmost cuts), in line with the observation that most of the rebonding is elastic. The (overall modest) charge redistribution exhibits bonding-orbital-like features, and is mostly in the plane of the dimer parallel to the surface, i.e., involves orbitals which are weak or nonbonding with respect to the substrate. The reason that Δ_e quite generally is so small is that the ability to form multidirectional bonds is limited both for the primarily s-d_σ bonded noble and transition metals, and the s-p bonded second-row element Al.

Substrate relaxations, not taken into account in rebonding theory [2], can be appreciable. The relative contributions of Δ_s and Δ_a to the rebonding energy Δ vary with the metal system (Table III), and indicate that neglecting substrate relaxations should be more important for the stiffer transition metals than for Al and Au. For direct verification, I have performed all calculations at three levels of atomic relaxation: In the *rigid* case, the adsorbates are allowed to relax onto the bulk-truncated metal surface. In the *frozen* case, the clean slab is first relaxed, and the adsorbates are then allowed to relax on this frozen-in surface. Finally, in the *relaxed* case (default), all atoms are allowed to relax, except for the bottom three [two for the (111) cell] layers, which are always kept at bulk positions. The results are displayed in Table IV, and show that substrate relaxations indeed are more important for transition metals than for Al and Au.

Returning to dimer stability, it is somewhat surprising that adatom-adatom bonds (E_{aa} in Table III) are weaker

TABLE II. Binding energies within the LDA and GGA. The lattice constant a is given in angstroms, the atomic adsorption energy E_a (calculated by subtracting the slab and spin-polarized atomic energies from the adatom system energy, cf. Ref. [11], and ad-dimer binding energy E_d in eV. The ratio between E_d and calculated bulk cohesive energies is given as a percentage in the last column: $x_1 = 6E_d/E_c$.

	LDA				GGA			
	a	E_a	E_d	x_1	a	E_a	E_d	x_1
Al/Al(100)	3.98	3.68	0.30	43%	4.04	3.28	0.26	43%
Au/Au(100)	4.07	3.83	0.27	37%	4.18	2.80	0.18	34%
Rh/Rh(100)	3.77	6.48	0.54	38%	3.85	5.25	0.39	32%
Ir/Ir(100)	3.82	8.33	0.75	44%	3.89	7.12	0.58	40%
Al/Al(111)	3.98	3.10	0.52	75%	4.04	2.71	0.45	74%
Au/Pt(100)					3.99	3.32	0.06	6%
Pt/Au(100)					4.18	5.45	−0.58	−109%

than bulk metal bonds, since they are shorter and partially covalent. Part of this oddity can be attributed to the higher kinetic energy associated with the more localized ad-dimer bond, but one cannot exclude ad-dimer "frustration" (a similar concept has been used previously in the context of cluster mobility [19]): Because of their intermediate coordination, ad-dimers strive towards a bond length somewhere between the one in the gas and bulk. Unlike in the latter two phases, however, ad-dimer relaxation is affected by the corrugation of the surface potential. It is therefore likely that the adatom-adatom bond is frustrated in many metal systems, especially for heterogeneous adsorption. Since both compressed and dilated ad-dimer bonds increase the system energy, the bond strength E_{aa} and binding energy E_d of a frustrated ad-dimer are always smaller than for the ideal tension-free ad-dimer. Support for this idea comes out of calculations for Au/Pt(100) and Pt/Au(100), where inspection of covalent and metallic radii suggests considerable frustration, and the E_d's are correspondingly extremely small or even negative (Table II). More work is currently underway to further assess this interesting problem.

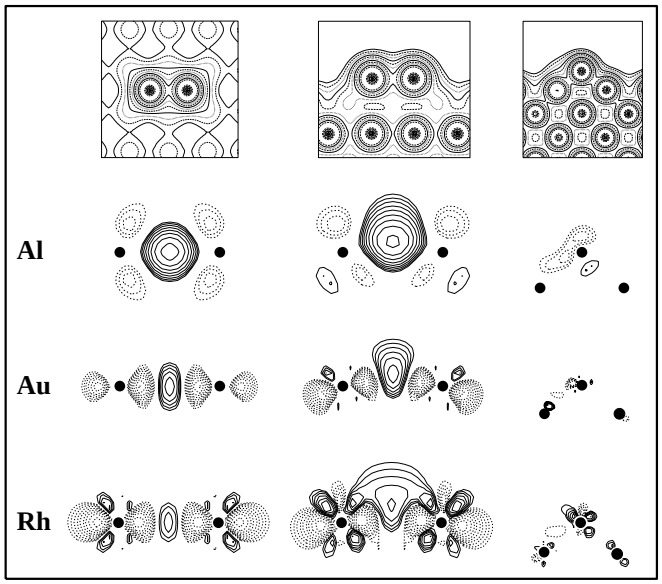

FIG. 2. Charge redistribution when two adatoms form an ad-dimer on Al/Al(100), Au/Au(100), and Rh/Rh(100). The topmost panels show the full charge density for Au to illustrate the geometry (relaxations sometimes prevent center cuts through all atoms simultaneously). In units of 10^{-3} electrons/Å^3, the charge-density range in the difference plots is $\rho = 10-79$ (Al), $\rho = 13-100$ (Au), and $\rho = 20-450$ (Rh), and changes by a factor of $10^{0.1}$ ($10^{0.15}$) for Al and Au (Rh) between successive contours. Solid lines indicate charge accumulation; dashed lines indicate depletion. The outermost contours are always for the lowest ρ, and successive contours always go towards increasing ρ. Atomic positions are marked by dots.

Beyond dimers.—As deposited adatoms aggregate to form clusters, these rise up from the surface. For the systems considered here, the adsorption height of a full monolayer is 10%–25% larger than for a single adatom. This difference is partly due to surface relaxations; the actual adspecies-surface bond lengths increase by 5%–6% during monolayer formation. From simple coordination considerations, one would expect the most pronounced changes in bond length at low coordination, i.e., for ad-dimer formation. To test this idea, I perform DFT-GGA calculations for compact Al clusters on Al(100) containing $n = 1$, 2, 3, 4, 6, 12, and 20 (a full monolayer) atoms. Figure 3 shows the average adsorption height above the surface plane d, the average adatom-substrate bond length r, and the average adatom-adatom bond length r_l in the clusters, normalized to bulk values. The most notable results are that bond lengthening proceeds rather smoothly and that the largest changes indeed do take place for small clusters, in line with the coordination view and related effective-medium theory [20]. Since the effect of rebonding on bond lengthening is negligible where it is most pronounced, in ad-dimer formation, it is of even less relevance to the formation of trimers, tetramers, etc. Only

TABLE III. Decomposition of the rebonding energy Δ, and comparison of the ad-dimer bond strength with the calculated bulk bond strength, $x_3 = E_{aa}/(E_c/6)$ for Al/Al(100), Au/Au(100), and Rh/Rh(100). All energies are in eV.

	Δ_e	Δ_a	Δ_s	Δ	E_{aa}	x_3
Al/Al(100)	33%	63%	4%	0.11	0.51	74%
Au/Au(100)	9%	97%	−6%	0.14	0.57	77%
Rh/Rh(100)	30%	41%	29%	0.10	0.74	52%

TABLE IV. Dimer binding energies in eV within LDA and GGA at three levels of relaxation (see main text) indicated by the superscript: rigid (r), frozen (f), and fully relaxed.

	LDA			GGA		
	E_d	E_d^f	E_d^r	E_d	E_d^f	E_d^r
Al/Al(100)	0.30	0.28	0.26	0.26	0.22	0.21
Au/Au(100)	0.27	0.28	0.27	0.18	0.17	0.18
Rh/Rh(100)	0.54	0.49	0.45	0.39	0.35	0.32
Ir/Ir(100)	0.75	0.62	0.60	0.58	0.46	0.38
Au/Pt(100)				0.06	0.09	0.08
Pt/Au(100)				−0.61	−0.62	−0.62
Al/Al(111)	0.52	0.48	0.48	0.45	0.41	0.41

through the integrated effect of a large number of individual aggregations is it even observed. For the elementary atomic processes that take place in nucleation and cluster formation, the rebonding model is thus of limited value.

At this point, one might wonder how these shortcomings of the rebonding model have remained undetected until now. The original DFT-LDA study for Al/Al(100) persuasively argues the rebonding view, which has played an important role in establishing credibility. However, this turns out to be due mainly to a rather restricted description of the Al system: The decade-old results are based on adsorption calculations using a thin two-layer rigid substrate (due to the limited computer power at the time) that is also strained (the experimental room-temperature lattice constant is used, resulting in a tensile strain of 1.9% for the otherwise LDA-described system) [2]. In the previous/present study, the ad-dimer–adatom height difference is substantial/nonexistent, $\delta d = 0.16/0.00$ Å, and the ad-dimer binding energy minute/"normal," $E_d = 0.07/0.30$ eV within the LDA. Using a two-layer rigid substrate without (with) 1.9% tensile strain, I find $\delta d = 0.16$ (0.18) Å, and $E_d = 0.34$ (0.23) eV. It is thus mainly the thin rigid slab that causes the misleadingly large δd.

In summary, I show that the rebonding view of adsorbate bonding is invalid for a wide range of metal systems.

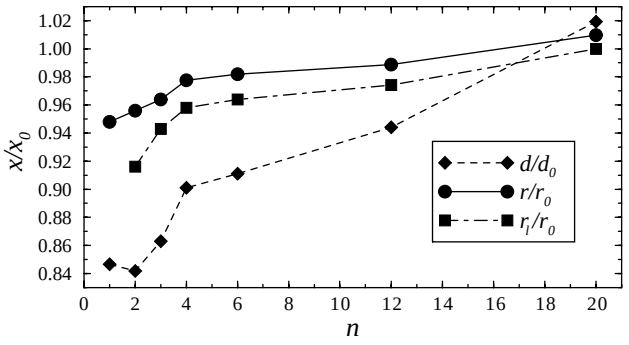

FIG. 3. Illustration of how Al clusters expand and lift off from the Al(100) surface as they grow. The notation is explained in the text; all bond lengths are normalized to bulk values (x on the y-axis label represents d, r, and r_l).

Compared with adatoms, ad-dimers do *not* have notably longer surface bonds, and do *not* bind farther above the surface. Regarding diffusion, ad-dimers do *not* experience a less corrugated potential due to increased resident height, and the atom left behind does *not* strengthen its surface bond as its partner moves away. Rebonding *does*, however, play a role for the stability of ad-dimers, but also here there is a misconception about how the bond strength should compare with bulk and gas-phase interatomic bonds. Evidence for ad-dimer frustration is presented, which impacts ad-dimer stability and mobility.

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