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Simple model explaining and predicting coverage-dependent atomic adsorption energies on transition metal surfaces

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The adsorption energies of simple atomic adsorbates are coverage dependent. We use density-functional theory to show that the coverage dependence is due to an adsorbate-induced modification of the surface *d*-band structure. We developed a simple model for predicting the *d*-band widths of clean and adsorbate-covered metallic surfaces using a tight-binding formalism. The new model can be used in conjunction with the *d*-band adsorption model to estimate adsorption energies as a function of coverage.

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One of the primary goals in computational surface science is developing a fundamental understanding of the reactivity of transition metal surfaces to guide the tailoring of surfaces to provide desired chemical properties and to tune the reactivity of catalyst surfaces.[1] Real catalytic systems are complex with effects due to adsorbate interactions and environmental conditions. Consequently it has proven to be extremely difficult to develop simple models that quantitatively account for all of these factors.

The adsorption properties are the key descriptors in many catalytic systems providing explanations of relative catalytic reactivity between different metals.[2] The variations in adsorption energies on different metal surfaces at low coverages have been explained by the *d*-band model developed by Hammer and Nørskov.[3,4] This model relates the surface reactivity to the surface *d*-band center (ε_d) and the model has been applied to many different systems including pure metals, surface alloys,[5,6] surfaces with strain,[7] poisons, promoters,[8] and electron-deficient sites.[7] Correlations between the surface *d*-band center (ε_d) and reactivity can dramatically reduce the computational cost associated with the density-functional theory (DFT) calculations, if a simple model for predicting the surface *d*-band center (ε_d) exists or if a large enough database of surface *d*-band centers exists. Although simple models[5] and databases[5,9] exist they are not complete, and they do not include the effects of coverage dependence on the surface reactivity.

In the current paper, we present a simple model for estimating the adsorbate-induced modifications in the surface *d*-band width due to electronic and geometric effects, and the effects of these modifications on the adsorption properties of these surfaces. The model is capable of parametrizing the coverage dependence of surface electronic-structure modifications over late transition metals. On the basis of tight-binding theory a *d*-band width formalism is developed by utilizing the correlations between the width of the surface *d*-band and the interatomic matrix elements between neighboring atoms.[5,10,11] A new solid-state table of the parameters used in the model for transition metals and for some adsorbates is developed. Finally, the *d*-band width formalism and the new solid-state table are utilized together to predict the *d*-band widths of clean-surface structures and surfaces with adsorbates as well as to estimate coverage-dependent adsorption energies on late transition metal (111), (100), and (110) surfaces through correlations between changes in the electronic structure due to coverage effects with shifts in the adsorption energies.

The study involves the low Miller index surfaces, i.e., (111), (100), and (110) of late transition metals (Cu, Rh, Pd, Ag, Ir, Pt, and Au) modeled using a four-layer slab that was repeated periodically in a supercell geometry with 10 Å of vacuum separating the slabs. C, N, O, and S adsorption were modeled within 2×2 unit cells considering only the fcc site. The Pd data are from our previous work.[12] Adsorption was allowed only on one side of the slabs where both the adsorbates and the top two layers were relaxed until the forces were less than 0.05 eV/Å. The DACAPO code[13] was utilized for all the DFT calculations in this work. The ionic cores were described by Vanderbilt ultrasoft pseudopotentials[14,15] and the one-electron valence eigenstates were expanded in a plane-wave basis set with a cut-off energy of 340 eV. The exchange correlation functional used was the Perdew-Wang 1991 (PW91) generalized gradient approximation.[16] Brillouin-zone integrations were performed using an $8\times8\times1$ Monkhorst-Pack grid for the 2×2 surface unit cell. The calculated C, N, O, and S adsorption energies were converged with respect to plane waves and *k*-point sampling until the variation was less than 0.02 eV/adsorbate. The atom-projected *d* bands were calculated by projecting the Kohn-Sham orbitals onto atomic orbitals localized on each atom. The extents of the atomic orbitals are infinite causing overlap of the orbitals on a particular atom with those of its neighbors and an overcounting of states attributed to that orbital. To limit the overlap and thus to limit the overcounting of the states, a cut-off radius may be used to truncate the orbitals. In general, however, we have found that the trends in the *d*-band properties are similar for a truncated orbital and for the full infinite extent. In this work we do not utilize a cut-off radius. The *d*-band width is calculated as the square root of the second moment of the *d* band with respect to the Fermi level as $W_d=\sqrt{\int\rho E^2 dE/\int\rho dE}$.

Adsorption energies are often correlated with the surface *d*-band center (ε_d). Based on the rectangular *d*-band model, the surface *d*-band center, however, is linearly correlated with the surface *d*-band width due to band-filling constraints.[5,10] For all of the adsorption systems examined in

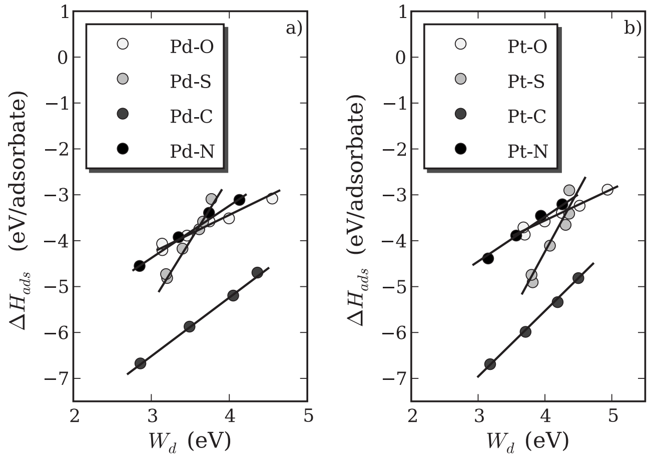

FIG. 1. Adsorption energies of C, N, O, and S at different coverages from 0.25 to 1 ML on (a) Pd and (b) Pt metal (111) facets as a function of *d*-band width. The *d*-band width was found to vary linearly with coverage, thus the curves are parametric in coverage. The low coverage results have the most negative adsorption energies and the narrowest *d* bands whereas the high coverage results show the weakest adsorption energies and the widest surface *d*-bands. Similar results were also found on other late transition metal (111) surfaces.

TABLE I. PW91-DFT parametrized solid-state table for transition metals and for some adsorbates including surface specific constants β and η.

Element/adsorbates		r_d	
C		1.25	
N		1.18	
O		1.01	
S		1.22	
Element/metals	r_d		W_o
Cu	2.68		1.09
Rh	3.32		0.36
Pd	3.38		0.05
Ag	3.34		2.44
Ir	3.72		0.24
Pt	3.79		0.04
Au	3.88		1.11
		β	
	111 facet	100 facet	110 facet
Noble TM	0.24	0.40	0.41
Other TM	0.30	0.41	0.50
		η	
	111 facet	100 facet	110 facet
Noble TM	−0.01	−0.06	−0.30
Other TM	0.07	0.25	−0.16

this work, the surface *d*-band center and width were linearly correlated with each other at all coverages, leading to linear correlations of the coverage-dependent adsorption energy with the surface *d*-band width [two examples are shown in Figs. 1(a) and 1(b)]. For the correlations we calculated C, N, O, or S adsorption energies on Pd [Fig. 1(a)] and Pt [Fig. 1(b)] (111) at different coverages ranging between 0.25 monolayer (ML) and 1 ML using the gas phase atom as the reference energy. Similar to our previous work,[12] linear correlations were obtained between adsorption energies and coverage. A linear relationship was also observed between the coverage and the surface *d*-band widths.[12] These linear correlations can be linked together to rationalize the coverage dependence of the adsorption energies in terms of an adsorbate-induced broadening of the surface *d* band. At higher coverages, the broader *d* bands have lower surface *d*-band centers and consequently interact more weakly with subsequent adsorbates.

Surface *d*-band widths for pure metals and alloys are proportional to the interatomic matrix elements that define the broadening of the bands due to orbital overlaps of neighboring atoms.[5,10] However, the incorporation of adsorption into the interatomic matrix elements and their effect on band broadening has not been reported before. Therefore, we next develop a *d*-band-width formalism based on interatomic matrix elements that accounts for the adsorbate-induced electronic-structure effects.

The *d*-band widths are correlated with interatomic matrix elements (V) (Refs. 5 and 10) that describe the bonding interactions between *d* states on two atoms in term of a characteristic orbital size, r_d. The matrix element is computed by summing over all the nearest neighbors as $V_i \approx \sum_j \frac{(r_d^{(i)} r_d^{(j)})^{3/2}}{d_{ij}^5}$, where d_{ij} represents the spacing between metal atoms i and j. This model accounts for the sharpening of the surface *d* band due to loss of coordination in the surface atoms through the sum over nearest neighbors, but it does not account for the redistribution of electron density near the surface due to loss of the bulk structure which also affects the surface *d*-band width. We correct the expression by adding a facet-specific constant β to arrive at a new expression for predicting the *d*-band width of a metal atom i in a clean metal surface in terms of the interatomic matrix elements between atom i and the j nearest neighbors

$$W_{d,i} = W_{o,i} + \sum_j \frac{(r_d^{(i)} r_d^{(j)})^{3/2}}{d_{ij}^5} + \beta. \tag{1}$$

$W_{o,i}$ is a constant accounting for the nonzero bandwidth of an atom i at infinite separation due to the atom-projected density of states algorithm and the equation used to compute the *d*-band width. d_{ij} represents the distance between ith and jth nearest-neighbor atoms. β is a surface term that accounts for surface-relaxation effects and has different values for non-noble and noble metals as well as for different Miller index facets (Table I). In Harrison's formulation,[11] there is a constant in front of the summation, which we have absorbed into the r_d values for notational simplicity, making our tabulated

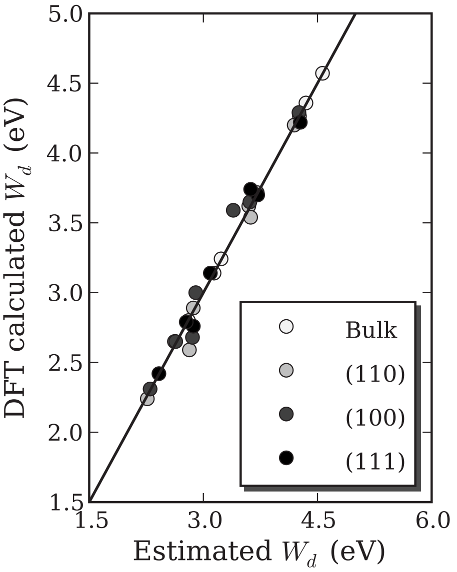

FIG. 2. Parity plot of d-band widths for clean-surface structures of Cu, Rh, Pd, Ag, Ir, Pt, and Au with different facets as well as for bulk systems for late transition metals.

radii differ in magnitude from expected sizes of atomic orbitals. We also note a crucial difference in the definition of bandwidth in our formulation and Harrison's: we use the square root of the second moment of the d band about the Fermi level as W_d whereas Harrison defines W_d in terms of the separation between band edges. Thus, we cannot directly compare effective orbital radii with Harrison's solid-state table radii.

The above-mentioned parameters were obtained from d-band widths calculated from bulk calculations in unit cells with varying volumes (not shown here) yielding to an expression of surface d-band widths as a function of the reciprocal of the distance to the fifth power. A plot of W_d vs $1/d_{ij}^5$ is linear from which r_d and W_o can be obtained for each metal from the slope and intercept, respectively. β was determined from d-band widths of clean, relaxed surfaces. Utilizing the characteristic lengths for each metal and the suggested model, good agreement has been achieved in predicting the d-band widths for clean surfaces of Cu, Rh, Pd, Ag, Ir, Pt, and Au for bulk structures as well as for three different low Miller index facets (Fig. 2).

The model for predicting surface d-band widths can be extended to include the effects of adsorption. The model for clean surfaces essentially accounts for changes in bandwidth due to d orbital overlaps with neighboring atoms and for surface-relaxation effects. We extend the clean-surface model by adding terms to account for the overlap of the adsorbate orbitals with the surface metal-atom orbitals and effects due to redistribution of the electron density at the surface. The expression predicting the d-band widths of surface atoms with adsorbates on them is assumed to be in the form of

$$W_{d,i} = W_{o,i} + \sum_j \frac{(r_d^{(i)} r_d^{(j)})^{3/2}}{d_{ij}^5} + \beta + \gamma\theta \frac{(r_d^{(i)} r_{ads})^x}{d_{i,ads}^y} + \eta, \qquad (2)$$

where the last two terms represent the contribution based on adsorption. The electronic effect due to the size of the orbitals is incorporated into the numerator though the r_d for the metal atom and r_{ads}, the characteristic size for the adsorbate orbitals, and the geometric contributions are included in the denominator through the distance between the adsorbate and the metal atoms. γ is introduced as a fitting factor and η represents an adsorbate-induced modification of the β factor; since β is a facet-specific term, so is η. θ incorporates the coverage of the adsorbates on the surface.

The parameters x and y were derived from several sets of data. In Eq. (1) the power in the denominator ($y=5$) was derived from the angular-momentum quantum number l of the d orbitals: $y=-(l+l'+1)$, where $l=2$ for d orbitals which leads to the d^{-5} dependence. Here, we develop a model based on a single, effective adsorbate orbital for simplicity. Consequently, there is no well-defined angular-momentum quantum number, and we will determine the parameters in the model by fitting. The surface d-band widths were calculated for different adsorbate heights above the surface and y was obtained from a linear fit of d-band widths vs $d_{i,ads}^{-y}$. Different metal surfaces were considered with the same adsorbate which led to coupled equations with constraints of the same unknown r_{ads} and the same power x allowing both parameters to be determined by nonlinear least-squares fitting. The value for x was found to be close to 1.5, so for consistency with the metal-metal matrix element form where $x=3/2$ represents the geometric average of the two orbital radii we set $x=3/2$. Similarly for y the value was found to be close to 2.5 and because we expect integer or halves from the physics,[11] we set $y=5/2$. The final model has the form

$$W_d = W_d^{clean} + \gamma\theta \frac{(r_d r_{ads})^{3/2}}{d^{5/2}} + \eta \qquad (3)$$

with γ being a proportionality factor of 1.189 and η being a facet-specific constant accounting for surface electron-density redistribution and modifications to surface relaxation. η has different values for non-noble and noble metals possibly due to Pauli repulsion effects that are more important for noble metals having completely filled d bands. The full set of characteristic orbitals and parameters for the metals and adsorbates investigated in this work are tabulated in a new solid-state table (Table I). These parameters are derived from calculations utilizing the PW91 exchange-correlation functional. Adsorption energies are sensitive to the choice of exchange-correlation functional, but the trends in coverage dependence are independent of the exchange-correlation functional. The solid-state table parameters, particularly the β term accounting for the electron-density redistribution and surface-relaxation effects of the clean facets, as well as, η parameter representing the adsorbate-induced modification of the β factor could be sensitive to the choice of the exchange-correlation functional.

Utilization of the DFT parametrized solid-state table enables one to estimate the d-band widths of metal surfaces (Cu, Rh, Pd, Ag, Ir, Pt, and Au) with different adsorbates at different coverage values. As seen from Fig. 3, the estimated and the DFT calculated d-band widths agree with each other reasonably well for all different low Miller index facets including the effects of coverage. The average error with respect to the DFT calculated values is less than 5% with the

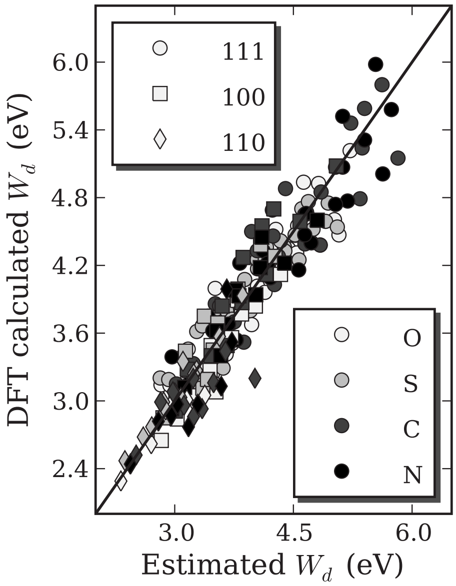

FIG. 3. Parity plot of DFT calculated and solid-state table estimated d-band widths for coverage-dependent adsorbate surface structures (0.25–1 ML) on Cu, Rh, Pd, Ag, Ir, Pt, and Au surfaces. Circles, squares, and diamonds correspond to (111), (100), and (110) facets, respectively. The outliers correspond to C adsorption on Pd(110) and C or N adsorption over Ir(111) where enlargement of the spacings between the top- and the second-layer metal atoms was observed.

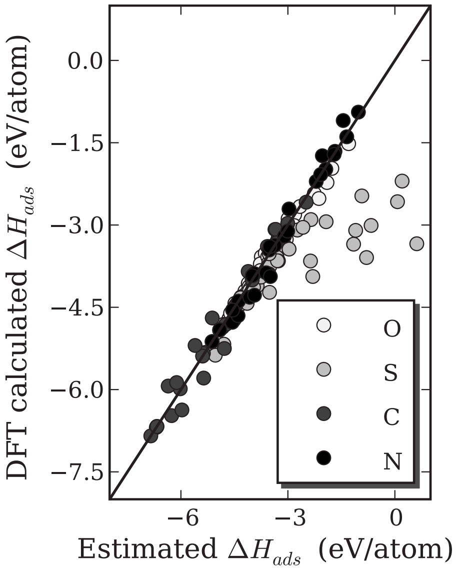

FIG. 4. Parity plot of DFT and estimated coverage-dependent adsorption energies for C, N, O, and S on Cu, Rh, Pd, Ag, Ir, Pt, and Au (111) surfaces.

largest error being 13% corresponding to noble-metal Ag surfaces. The data that show the most scatter include surfaces that reconstruct such as the Pd(110) facet with a monolayer of C adsorption. That surface formed a surface carbide which causes the top-layer Pd atoms to be separated from the rest of the bulk structure by a larger distance than on the clean relaxed Pd(110) facet. Similar structures were also observed for monolayer adsorption of C and N over Ir (111) surface. For these outliers, it has been observed that there is an enlargement of the spacings between the layers. These structures are outliers because we utilized the ideal atom separation values based on the bulk lattice constants for the estimation rather than the actual distances from the relaxed structures. Despite the outliers, the reasonable agreement between the model and DFT data set allows the coverage-dependent properties to be explained largely by adsorbate-induced changes in the electronic and geometric contributions as described in the model presented above.

The new solid-state table and the d-band formalism allow one to make predictions of adsorption energies as a function of coverage for any metal surface with any of the studied adsorbates. All that is needed is a single reference adsorption energy at a known coverage, the dependence of the adsorption energies on the surface d-band width and information about average bond lengths between the adsorbates and the metal surface. This dependence may be looked up in databases, derived from literature d-band correlations or estimated from a small number of calculations (e.g., Fig. 1). Excellent correlations have been achieved for all metals except for S adsorption energies over Cu, Ag, and Au. In these systems the deviation can be attributed to the completely filled d-band states of these noble metals resulting in different types of interactions with sulfur (e.g., Pauli repulsion or interadsorbate bonding) that are not accounted for in the simple d-band model or in our tight-binding model. Once the correlation between changes in adsorption energy and d-band width can be established by some means, e.g., from two DFT calculations at 0.25 and 1 ML or literature reports, the solid-state table enables the remaining coverage dependence to be rapidly estimated. An example of this approach is shown in Fig. 4 for (111) facets of all considered transition metals where the reference adsorption energy of 0.25 ML was used for each system. A similar approach is also applicable to other low Miller index facets where shifts in coverage-dependent adsorption energies are linearly correlated with the modifications in the d-band characteristics. For simplicity, we have shown the estimated and DFT-calculated adsorption energies over (111) facets.

The estimated C, N, and O adsorption energies are in reasonable agreement with the DFT-calculated values at all the coverages considered (Fig. 4). The most scattered data correspond to the systems where shifts in adsorption energies are not correlated with the shifts in electronic properties, e.g., noble-metal surface structures with adsorbed S at higher coverages. This shows that for noble-metal surfaces with S, the surface d-band characteristics are not the only descriptive factor to capture the reactivity of these surfaces, Pauli repulsion and the role of s and p electrons likely participate in determining catalytic activities.[17,18] Those effects are not captured in our model. The average error in estimating adsorption energies using the solid-state table is less than 4.3% excluding S adsorption energies over noble metals.

Our simple model suggests an explanation for the different coverage dependences of the adsorption energies for each adsorbate on different metal surfaces. The larger the adsorbate orbital radii are, and the closer they approach the surface, the greater the change in adsorbate-induced surface electronic modification. This leads to systems where adsorption energies change significantly with small changes in coverage. The highest coverage dependence is found for S due to its large characteristic orbital size. Conversely, O shows the smallest electronic and the greatest geometric contribution resulting in the smallest modifications in *d*-band characteristics with respect to coverage. Similar arguments can be derived for the other adsorbates, which finally results that the change in adsorbate-induced electronic modification follows the order of $S > N > C > O$.

The model presented here should also be applicable for alloy systems. Here, the alloying effects (strain, ligand, ensemble effects) are taken into consideration through the characteristic orbital sizes and distances between metal atoms in the alloy and adsorbates. Good agreement has been achieved between estimated and DFT-calculated *d*-band widths of impurities in the surfaces of close-packed (111) Pd-based alloys, as well as for the bimetallic systems with surface atoms of type A and substrate layer of type B (e.g., A and B being Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, and Au) (not shown here). A future manuscript will address these results.

The present paper demonstrates that the adsorbate-induced modifications of the surface *d*-band characteristics are due to the combined effects of electronic and geometric contributions due to overlap of adsorbate orbitals with surface *d* orbitals. The effects could be estimated using the correlations between *d*-band widths and interatomic matrix elements that incorporate the adsorbate contributions. We have proposed a simple, computationally inexpensive model that predicts *d*-band widths of clean-surface structures, pure metals, and bimetallic systems as well as of surface structures under adsorption with moderate accuracy. The parameters for our model were derived from an extensive set of DFT calculations and used to create a new solid-state table. The model, in conjunction with the solid-state table can be used to predict changes in the surface *d*-band width due to adsorption. Combined with correlations between adsorption energies and *d*-band widths or centers, the model can be used to predict adsorption energies of as a function of coverage. A reasonable agreement has been demonstrated in estimating the coverage-dependent adsorption energies of C, N, O, and S on late transition metals using the developed model. The correlations described in this paper could be used as a first step toward predicting the properties of both for pure metal or bimetallic systems and designing systems with desirable electronic and thus chemical properties without the need to perform expensive DFT calculations or to guide where expensive DFT calculations should be used.

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[1] B. Hammer and J. K. Nørskov, Adv. Catal. **45**, 71 (2000).

[2] T. Bligaard, J. K. Nørskov, S. Dahl, J. Matthiesen, C. H. Christensen, and J. Sehested, J. Catal. **224**, 206 (2004).

[3] B. Hammer and J. K. Nørskov, Surf. Sci. **343**, 211 (1995).

[4] B. Hammer and J. K. Nørskov, Nature (London) **376**, 238 (1995).

[5] J. R. Kitchin, J. K. Nørskov, M. A. Barteau, and J. G. Chen, J. Chem. Phys. **120**, 10240 (2004).

[6] J. Greeley and M. Mavrikakis, J. Phys. Chem. B **109**, 3460 (2005).

[7] M. Mavrikakis, B. Hammer, and J. K. Nørskov, Phys. Rev. Lett. **81**, 2819 (1998).

[8] J. J. Mortensen, B. Hammer, and J. K. Nørskov, Phys. Rev. Lett. **80**, 4333 (1998).

[9] A. Ruban, B. Hammer, P. Stoltze, H. L. Skriver, and J. K. Nørskov, J. Mol. Catal. A: Chem. **115**, 421 (1997).

[10] J. R. Kitchin, J. K. Nørskov, M. A. Barteau, and J. G. Chen, Phys. Rev. Lett. **93**, 156801 (2004).

[11] W. A. Harrison, *Electronic Structure and the Properties of Solids: The Physics of the Chemical Bond* (Dover, New York, 1989).

[12] J. R. Kitchin, Phys. Rev. B **79**, 205412 (2009).

[13] http://www.fysik.dtu.dk/CAMPOS

[14] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[15] K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, Phys. Rev. B **47**, 10142 (1993).

[16] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[17] M. P. Hyman, B. T. Loveless, and J. W. Medlin, Surf. Sci. **601**, 5382 (2007).

[18] H. Xin and S. Linic, J. Chem. Phys. **132**, 221101 (2010).