

Simple connections in alkali adsorption

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Stimulated by recent two-photon photoemission spectroscopy and density-functional theory studies by Petek and co-workers, a retrospective look at some fundamentals in the theory of ionic alkali adsorption on metal surfaces is presented that provides a simple correlation between free-atom ionization potentials, ionic size, adsorption heights, and spectroscopically observed alkali valence-electron binding energies.

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Since the classic study of Taylor and Langmuir¹ on the electronic properties of tungsten surfaces coated with partial Cs monolayers, the scientific and technological importance of alkali adsorption on metal surfaces has been universally recognized. They observed that the formation of roughly 0.6–0.7 of a monolayer of Cs on the W surface caused the work function of the composite system to be reduced by as much as 3 eV. This behavior was explained by Langmuir and associates in terms of a simple classical picture in which the alkali is adsorbed primarily as a positive ion since its ionization potential is less than the initial work function of the W substrate thereby facilitating adsorbate-to-substrate electron charge transfer. The resulting dipole layer formed by the positive ions together with their image charges within the metallic substrate produces the dipole layer potential drop responsible for the work function decrease. Gurney² then provided a quantum-mechanical conceptual framework in terms of broadened alkali valence levels which led to subsequent atomistic adsorption theories^{3–9} based on the Anderson-Fano model^{10–12} of a discrete state interacting with a continuum. Invariably these theories require the observed or computed spectroscopic data as input to specify the energetic positions and the widths of the adsorbed alkali valence levels. Since these levels are mostly unoccupied, experimental techniques such as inverse photoemission¹³ or two-photon photoemission (TPP)¹⁴ spectroscopies rather than the more prevalent (single photon) photoelectron spectroscopy¹⁵ of occupied states are required.

Throughout the past ten years, Petek *et al.*¹⁶ carried out an extensive series of time-resolved TPP studies largely involving excitation and desorption dynamics of alkali atoms adsorbed on noble-metal surfaces. Most recently they have presented the results of a combined experimental and theoretical inquiry of all the alkali atoms (Li to Cs) chemisorbed at low coverage (less than 0.1 monolayer) on Ag(111) and Cu(111) surfaces, finding that the unoccupied hydrogenic *ns* valence electron resonances of all the alkali species show a common binding energy of about 2.0 eV with respect to the vacuum potential in spite of the fact that the free-atom ionization potentials vary by as much as 1.5 eV.¹⁷ They note that

“The period-independent energy of the *ns* resonance of alkali atoms... suggest that the apparent universal behavior might be explained with a simple physical model. Therefore we undertook a calculation...”¹⁷

The main purpose of the present comment is to demon-

strate that indeed this universal (and some subsidiary) behavior is readily understood within the framework of computationally nonintensive simple physical models (SPM) that were popularized some 40 years ago. A secondary objective is to call attention, by example, to the important complementary roles of modeling versus computation. While each strategy may yield similar end results, considerations such as the relative transparency into physical insights and also the economy of effort required to attain these insights and numerical “answers” argue for public airing of both mutually reinforcing alternative approaches.

In the conventional terminology of a surface spectroscopist, the binding energy of an adsorbed alkali-atom valence electron is represented simply as

$$E_b = V_i - \Delta\varepsilon_{a-m}, \quad (1)$$

where V_i is the free-atom ionization potential and $\Delta\varepsilon_{a-m}$ is the shift of the energy level due to the atom-metal interaction. Note that this is the negative of the energy Zhao *et al.*¹⁷ referred to as the binding energy. Since the binding energy is here being referenced with respect to the vacuum potential just outside the surface, knowledge of φ_s , the work function of the substrate is not required.^{18,19} Historically the shift has been accounted for in terms of the system of image charges shown in Fig. 1 that replicate the fields due to the actual ionic bond polarization and screening charge induced within the metal by the alkali atom.²⁰ In the perfect-conductor limit,

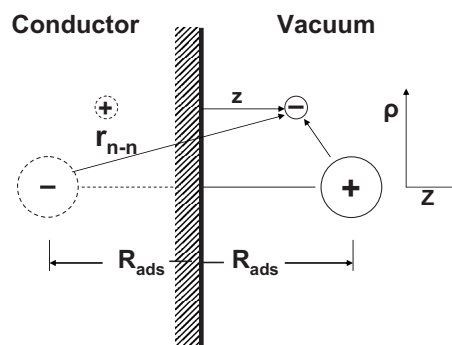


FIG. 1. Classical picture of the alkali “atom” (solid) and the image charges (dashed) it induces within the conductor. The positive alkali ion core and its negative image are centered at $z = \pm R_{\text{ads}}$ about the image plane. The distance between the valence electron and the ion core image is $r_{n-n} = [(R_{\text{ads}} + z)^2 + \rho^2]^{1/2}$. (See Fig. 6 in Ref. 20.)

the ns valence electron feels its own image potential attraction and also a repulsion due to the negative image charge (i.e., the screening) induced by the positive alkali ion core. This repulsion can be thought of as the perturbation of the local atomic potential when the alkali atom forms a strong ionic bond with the substrate. Consequently the total potential outside the metal seen by the atomic electron is

$$V_{\text{ads}}(\underline{r}; R_{\text{ads}}) = -\frac{e^2}{4z} + \frac{e^2}{[(R_{\text{ads}} + z)^2 + \rho^2]^{1/2}}, \quad (2)$$

where $\underline{r} = (\rho, z\hat{i}_z)$ is the electron coordinate and R_{ads} is the alkali-specific stabilization position with respect to “the” image plane or in other words the adsorbate ion-substrate separation. This distance is reasonably taken to be the ionic radius (as given say in the chemical rubber handbook²¹). The picture is thus one of a positively charged ball of radius $r_{\text{ion}} = R_{\text{ads}}$ sitting on a flat perfect conductor.

The potential $V_{\text{ads}}(\underline{r}; R_{\text{ads}})$ given by Eq. (2) when acting on the bound valence electron results in a perturbative energy-level shift,

$$\Delta\varepsilon_{\text{a-m}}(R_{\text{ads}}) = \int d\underline{r} |\psi_{\text{ns}}(\underline{r})|^2 V_{\text{ads}}(\underline{r}; R_{\text{ads}}),$$

which nicely reduces to

$$\Delta\varepsilon_{\text{a-m}}(R_{\text{ads}}) = e^2/4R_{\text{ads}} + \delta\varepsilon, \quad (3)$$

where $e^2/4R_{\text{ads}}$ follows in the $|\psi(\underline{r})|^2 \Rightarrow \delta^{(2)}(\rho)\delta(z - R_{\text{ads}})$ limit considered by Zhao *et al.*¹⁷ As detailed elsewhere,²⁰ $\delta\varepsilon \ll e^2/4R_{\text{ads}}$ is a small correction due to the finite extent and orientation of $\psi_{\text{ns}}(\underline{r})$, the actual alkali wave function, which can safely be neglected within the present context.

Next, the location of the relevant image plane for a real conductor with a finite screening length must be specified relative to either something physical in the substrate, perhaps the last layer of ion cores or that position plus $d/2$, with d as the interlayer spacing,²² or with respect to the “image plane” of the perfect conductor referred to in Eq. (2).^{23–25} One thing for sure is that finite screening will place the screening charge further into the substrate than is implied by the perfect-conductor result, thus lowering the magnitude of the image attraction, for fixed r_{ion} , with respect to the simple $e^2/4z$ relation.^{24,25} Also, the “correct” result must anticipate the possibility of merging into the bulk exchange-correlation potential as z becomes small.²⁶ Simple “solutions” to this aspect of the problem have been worked out²⁵ which provide a basis for the original proposal by Gomer and Swanson²⁷ that $V_{\text{image}}(z) \approx e^2/4(z + \kappa^{-1})$, where κ^{-1} is the screening length, a number that is a property of the substrate but not the alkali adsorbate. In other words, the image potential form is retained but with the position of the effective image plane displaced into the real conductor to account for the nonzero screening length. Hence the characteristic adsorption height for a given alkali-substrate combination is simply r_{ion} plus the same constant term for all alkalis.

Referring to Zhao *et al.*'s¹⁷ Fig. 4(b) showing alkali ionization potential vs the adsorption height, their R_{ads} calculated via density-functional theory (DFT) appears to vary linearly with $-V_i$. Likewise, when $z + \kappa^{-1} \Rightarrow r_{\text{ion}} + 0.8a_o$

TABLE I. Input data characterizing the Cu(111)-alkali systems and derived “adsorption heights.”

Alkali	V_i (eV) ^a	r_{ion} (a_o) ^a	R_{ads} (a_o) ^b	R_{ads} (a_o) ^c
Li	5.40	1.44	2.24	2.0
Na	5.12	1.89	2.69	2.60
K	4.32	2.60	3.40	3.40
Rb	4.16	2.87	3.67	3.65
Cs	3.89	3.15	3.95	3.95

^aReference 21.

^bThis work.

^cReference 17.

$\equiv R_{\text{ads}}$, with a_o as the Bohr radius, the same linear correlation between V_i and r_{ion} and thus R_{ads} is obtained here using the SPM. The numerical results presented in Table I show near-perfect agreement between the SPM and DFT anticorrelations. Upon reflection, at least qualitatively this should not be too surprising. The smaller atoms show the smallest adsorption heights for obvious geometric reasons. Another consequence of this smallness is that the tightly bound smaller-atom valence electron feels a more attractive Coulomb attraction hence a larger ionization potential than for the larger atoms. Thus the predicted anticorrelation between V_i and R_{ads} is intuitively demanded. Demonstrating that the anticorrelation appears linear required a mix of theory, modeling, and computation. With respect to the $0.8a_o$, if the Fermi-Thomas screening length is used then $\kappa^{-1} = 0.64r_s^{1/2}a_o$ which equals $0.8a_o$ if $r_s \approx 1.56$, characteristic of a somewhat higher-density electron gas than Cu or Ag for which $r_s \approx 2.5$ (r_s is the radius in units of a_o defining the average electron volume hence density and falls in the range $2 \lesssim r_s \lesssim 4$ for typical metals).²⁸ Still it is not too bad an estimate for something so simple. Moreover there is nothing sacred about Fermi-Thomas screening. The correlation between V_i and r_{ion} is

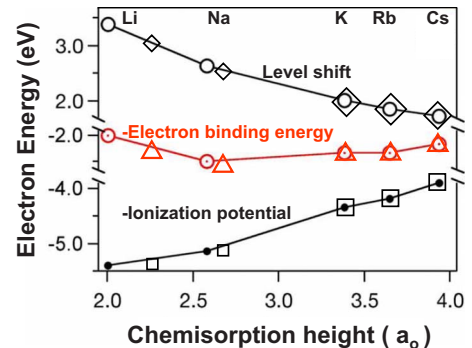


FIG. 2. (Color online) Various electron energies as a function of chemisorption heights calculated for the family of alkali atoms. The valence-electron ionization energy of the free alkali atom ($-V_i$; solid circles, squares) and the total level shift [$\Delta\varepsilon_{\text{a-m}}(R_{\text{ads}}) = e^2/4R_{\text{ads}}$; open circles, diamonds] together define the valence-electron resonance binding energy ($E_b = V_i - \Delta\varepsilon_{\text{a-m}}$ at R_{ads} ; bulls eye, triangles) for Li through Cs on Cu(111). The circle and bulls eye points are theoretical from Ref. 17, whereas the diamond and triangle points are from the present work. (See Fig. 4c in Ref. 17.)

purely an atomic physics issue and has nothing to do with adsorption. The “fact” that r_{ion} and R_{ads} are related by an additive constant independent of the particular alkali is the “wisdom” that emerged from the old-time adsorption “theory.” The computationally intensive DFT numbers are supportive of these results obtained from the simple physical model. While a more detailed view of the image plane issue could provide a more visible presence for the role of surface crystallography, the essential point here is that due to finite screening effects of real conductors, the effective image plane is displaced such that the image attraction is reduced from that implied by a perfect conductor model.^{22–28}

Finally, the commonality in the adsorbed alkali valence-electron binding energy first observed and then DFT-calculated by the Petek *et al.*¹⁴ is easily accounted for with the SPM. A period-independent binding energy defined by Eq. (1) requires that the period-dependent V_i is compensated by $\Delta\epsilon_{\text{a-m}}$ to realize an atom size-independent or R_{ads} -independent difference. Using Eqs. (1) and (3) with the SPM parameters displayed in Table I, the opposing $-V_i$ and $\Delta\epsilon_{\text{a-m}}$ values are displayed in Fig. 2 (reproduced from Ref. 17 retaining their sign convention) as a function of alkali R_{ads}

together with the consequent near-constant negative electron binding energy $-E_b$. These SPM results, in remarkable agreement with both the TPP experiments and DFT calculations of Zhao *et al.*,¹⁷ have been obtained with a minimum of current effort simply by exploiting some of our archival past. In response to some “puzzling why alkali atom unoccupied states fall at the same binding energy with respect to the work function of Cu(111) and Ag(111) independent of the size, can it be explained from some simple theoretical estimations, or is it just how it is?” it is felt that the present Brief Report answers this wondering in the affirmative, demonstrating that indeed simple physical models when judiciously and appropriately chosen can produce not only intuitive insights into venerable problems of contemporary interest²⁹ but also understandable numerics which should serve to enhance the confidence in output generated from procedures such as DFT.

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- ¹J. B. Taylor and I. Langmuir, Phys. Rev. **44**, 423 (1933).
- ²R. W. Gurney, Phys. Rev. **47**, 479 (1935).
- ³A. J. Bennett and L. M. Falicov, Phys. Rev. **151**, 512 (1966).
- ⁴J. W. Gadzuk, Surf. Sci. **6**, 133 (1967); J. W. Gadzuk, J. K. Hartman, and T. N. Rhodin, Phys. Rev. B **4**, 241 (1971).
- ⁵D. M. Newns, Phys. Rev. **178**, 1123 (1969); J. P. Muscat and D. M. Newns, Prog. Surf. Sci. **9**, 1 (1978).
- ⁶T. B. Grimley, J. Phys. C **3**, 1934 (1970); J. Vac. Sci. Technol. **8**, 31 (1971).
- ⁷J. R. Schrieffer, J. Vac. Sci. Technol. **9**, 561 (1972); T. L. Einstein and J. R. Schrieffer, Phys. Rev. B **7**, 3629 (1973).
- ⁸W. Brenig and K. Schönhammer, Z. Phys. **267**, 201 (1974).
- ⁹R. Gomer, Solid State Phys. **30**, 93 (1975).
- ¹⁰P. W. Anderson, Phys. Rev. **124**, 41 (1961).
- ¹¹U. Fano, Phys. Rev. **124**, 1866 (1961).
- ¹²G. D. Mahan, *Many-Particle Physics* (Plenum, New York, 1990), p. 272.
- ¹³N. V. Smith, Rep. Prog. Phys. **51**, 1227 (1988); D. A. Arena, F. G. Curti, and R. A. Bartynski, Phys. Rev. B **56**, 15404 (1997).
- ¹⁴M. Bauer, S. Pawlik, and M. Aeschlimann, Phys. Rev. B **55**, 10040 (1997); H. Petek and S. Ogawa, Prog. Surf. Sci. **56**, 239 (1997); H. Ueba and B. Gumhalter, *ibid.* **82**, 193 (2007).
- ¹⁵*Photoemission and the Electronic Properties of Surfaces*, edited by B. Feuerbacher, B. Fitton, and R. F. Willis (Wiley, Chichester, 1978); F. Reinert and S. Hüfner, New J. Phys. **7**, 97 (2005).
- ¹⁶S. Ogawa, H. Nagano, and H. Petek, Phys. Rev. Lett. **82**, 1931 (1999); H. Petek, M. J. Weida, H. Nagano, and S. Ogawa, Science **288**, 1402 (2000); J. Phys. Chem. B **105**, 6767 (2001); H. Petek and S. Ogawa, Annu. Rev. Phys. Chem. **53**, 507 (2002).
- ¹⁷J. Zhao, N. Pontius, A. Winkelmann, V. Sametoglu, A. Kubo, A. G. Borisov, D. Sanchez-Portal, V. M. Silkin, E. V. Chulkov, P. M. Echenique, and H. Petek, Phys. Rev. B **78**, 085419 (2008).
- ¹⁸J. W. Gadzuk, Phys. Rev. B **14**, 2267 (1976).
- ¹⁹Parenthetically note however that φ_s is a key ingredient in determining both the charge state of the adsorbate [basically positive (neutral) for $\varphi_s > (<) E_b$] and also the extension of the substrate electron wave functions into the vacuum [i.e., $\psi_{\text{sub}}(z) \sim \exp(-\alpha\varphi_s^{1/2}z)$, with α as a constant of order of 10 (eV^{1/2} nm)⁻¹]. While $\psi_{\text{sub}}(z)$ is important in determining the rate of electron transfer processes between substrate and adsorbate, this rate is not explicitly required for present considerations.
- ²⁰J. W. Gadzuk, Phys. Rev. B **1**, 2110 (1970).
- ²¹*Chemical Rubber Company Handbook of Chemistry and Physics*, 87th ed., edited by D. R. Lide (Taylor and Francis, Boca Raton, FL, 2006), pp. 12–11.
- ²²N. D. Lang, Phys. Rev. B **7**, 3541 (1973); P. J. Jennings and R. O. Jones, Adv. Phys. **37**, 341 (1988).
- ²³R. H. Ritchie and A. L. Marusak, Surf. Sci. **4**, 234 (1966); J. W. Gadzuk, *ibid.* **67**, 77 (1977).
- ²⁴J. W. Gadzuk, J. Phys. Chem. Solids **30**, 2307 (1969); D. M. Newns, Phys. Rev. B **1**, 3304 (1970).
- ²⁵D. M. Newns, J. Chem. Phys. **50**, 4572 (1969).
- ²⁶T. L. Loucks and P. H. Cutler, J. Phys. Chem. Solids **25**, 105 (1964); P. A. Serena, J. M. Soler, and N. Garcia, Phys. Rev. B **34**, 6767 (1986); A. Kiejna, *ibid.* **43**, 14695 (1991).
- ²⁷R. Gomer and L. W. Swanson, J. Chem. Phys. **38**, 1613 (1963).
- ²⁸J. W. Gadzuk, Surf. Sci. **23**, 58 (1970).
- ²⁹R. D. Diehl and R. McGrath, J. Phys.: Condens. Matter **9**, 951 (1997); M. Scheffler and C. Stampfli, in *Handbook of Surface Science: Electronic Structure*, edited by K. Horn and M. Scheffler (Elsevier, Amsterdam, 2000), Vol. 2.