Work Function and Bonding Energy of Rare-Gas Atoms Adsorbed on Metals

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It is shown that the substantial bonding-energy and work-function changes associated
with inert gases adsorbed on metal surfaces arise from an admixture of polar excited
configurations that occurs as the excited-state charge-transfer instability is crossed.

The surprisingly large work-function change
caused by rare-gas atoms adsorbed on certain
metal surfaces has remained a puzzle since its
first observation by Mignolet[1] over a quarter of
a century ago. These are among the simplest of
adsorbate complexes; they are prototype systems
for molecular physisorption, and a failure to un-
derstand their properties is a cause for concern
when one deals with more complicated molecular
adsorbates on which much current attention fo-
cuses. Saturation rare-gas coverages can change
the work function φ by a volt or more, corre-
sponding to dipole moments of ~ 0.3 debye/atom.
Engel and Gomer[2] and Mignolet,[1] following Mulli-
ken,[3] ascribe this effect to the admixture of polar
states; others[4] have discussed adsorbate polariza-
tion by the surface field. Ehrlich and Hudda[5] first
demonstrated that the bonding energy E_a of ad-
sorbed rare gases can also be considerable.
Neither E_a, nor the work-function change $\Delta\varphi$, is
large compared to values for chemically active
species. They are, however, unexpected for in-
ert atoms. In this Letter we show that the effects
do indeed arise from an admixture of charge-
transfer states. The interpretation rests on re-
cent progress in understanding the charge-trans-
fer instability of metals. Charge transfer be-
tween an atomic center and an embedding metal
has been observed both in the ground[6] and locally
excited configurations,[7] and for centers both in
the bulk metal and adsorbed on metal surfaces.[6,7]

Of principal concern here are the *excited* states
of rare-gas atoms adsorbed on metal surfaces.
To understand these complexes one must first
realize that rare-gas $p^5 s$ excited configurations
act chemically just like alkali $p^6 s$ ground con-
figurations.[8] Also like the alkalis,[9] they charge
transfer to $(p^5)^+$ adsorbed configurations when
the metal work function φ exceeds the adsorbate
potential I^* for $p^5 s \rightarrow (p^5)^+$ ionization. This is
established in detailed investigations by Cunning-
ham, Greenlaw, and Flynn.[7] A change of only
0.2 eV in φ suffices to cross the charge-transfer

instability and switch the system from the non-
polar configuration. There is no experimental
indication of an intermediate regime in which
both configurations are simultaneously accessible.

Methods due to Mulliken[3] can be used to explore
the consequences of this excited-state switching
for ground-state adsorbate properties. We write
ψ_a for the free-adsorbate ground state and ψ_m for
that of the metal. $\Psi = \mathcal{C}\psi_a\psi_m$ then provides one
good basis state for the complex, with $\mathcal{C}$ the anti-
symmetrization operator. Similarly, we write
$\Psi' = \mathcal{C}\psi_a'\psi_m'$ for the excited configuration (it is
not yet necessary to specify whether or not ψ_a'
and ψ_m' incorporate charge transfer). We as-
sume that Ψ and Ψ' are orthogonal or have been
orthogonalized. Then

$$\Phi = (1-a^2)^{1/2}\Psi + a\Psi' \tag{1}$$

gives a better approximation to the ground state
of the exact Hamiltonian H of the interacting sys-
tem. Here, $a \simeq t/\hbar\omega$, with $t = \langle \Psi'|H|\Psi'\rangle$ the hop-
ping matrix element and $\hbar\omega = \langle \Psi'|H|\Psi'\rangle - \langle \Psi|H|\Psi\rangle$
the approximate excitation energy. The energy
change caused by the interaction is

$$E_i = -t^2/\hbar\omega. \tag{2}$$

To find the polarization μ associated with each
adsorbate we need matrix elements of the dipole
operator $Z = \sum_i z_i$, in which the sum extends over
all particles. We find the *change* in surface di-
pole strength,

$$\mu/e = \langle \Phi|Z|\Phi\rangle - \langle \Psi|Z|\Psi\rangle$$
$$= a^2(\zeta' - \zeta) + 2a(1-a^2)^{1/2}\langle \Psi|Z|\Psi'\rangle, \tag{3}$$

with

$$\zeta = \langle \Psi|Z|\Psi\rangle \quad \text{and} \quad \zeta' = \langle \Psi'|Z|\Psi'\rangle. \tag{4}$$

For small admixtures we thus obtain

$$\mu/e = t^2(\zeta' - \zeta)/\hbar^2\omega^2 + 2t\langle \Psi|Z|\Psi'\rangle/\hbar\omega. \tag{5}$$

The second term is the first-order polarization
induced by the metal-adsorbate coupling; the

first arises from the admixture of an excited configuration possessing a different dipole moment.

When the excited state is nonpolar $(I^* > \varphi)$, so that $\zeta' - \zeta$ is small, the first term in Eq. (5) is unimportant because it is of second order in the small quantity $t/\hbar\omega$. As $\varphi - I^*$ passes through the charge-transfer condition, however, $\zeta' - \zeta$ changes to become the difference of moments between a polar and a nonpolar configuration, typically ~ 5 debye. Observed optical spectra[7] show that the order of magnitude of the z-dipole matrix element does not change. The hopping matrix element t most probably decreases because of a reduced overlap with the ionic configuration. From observed optical spectra, together with Eq. (5), one therefore expects the small first-order dipole moment, which occurs at small φ, to be augmented abruptly by a charge-transfer dipole contribution when the work function is increased to cross the approximate charge-transfer condition $\varphi - I^* = 0$.

The experimental data in Fig. 1, due mainly to Mignolet,[1] show that this is precisely what occurs in practice. For $\varphi - I^* < 0$, the dipole moment is negligibly small. As soon as the charge-transfer instability is passed there develops a substantial dipole moment which shows no further significant dependence on φ. Like the optical results, the work-function data are almost bimodal, without an extended intermediate regime. These results make clear that the first-order polarization must be quite small. The main effect, which switches on as the charge-transfer instability is crossed, arises directly from the admixture of the charge-transfer state. The switch mechanism itself ensures that either the polar or the nonpolar excited state is needed in Eq. (1), *not both*.

To proceed with quantitative comparisons we need experimental values of the dipole moment per adsorbate which are generally lacking because most work-function experiments have not determined absolute coverages. Optical data show that excited-state charge transfer remains complete for coverages up to at least 10^{15} cm^{-2}.[7] This value has therefore been employed to derive the moments for saturation coverage displayed in Fig. 1. Neglecting induced polarization, we now calculate from Eqs. (2) and (5) the energy change upon adsorption:

$$E_i = -t^2/\hbar\omega = -\hbar\omega\mu/(\zeta' - \zeta)e . \qquad (6)$$

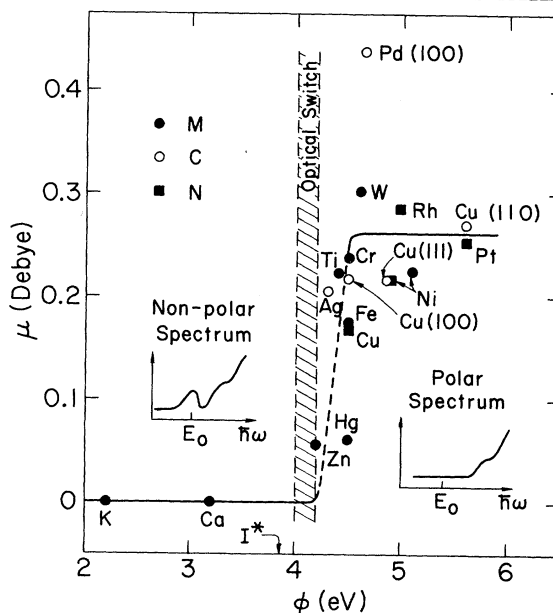Equation (6) successfully predicts the observed linear dependence of E_i on μ.[4] As a rough ap-

FIG. 1. Variation with substrate work function φ of the dipole moment per adsorbed xenon atom (Ref. 1). The dipole moment emerges at the optical charge-transfer instability (Ref. 7) (hatched band), which separates complexes giving polar optical spectra (lower right inset) from those giving nonpolar spectra (left) in which the atomic excitation at E_0 persists with full oscillator strength. The uncertainties in φ and μ are commensurate with the scatter of the points. Values of μ are obtained by assuming a surface density 10^{15} cm^{-2} of active adsorbates (see text) for cases of saturation coverage, and the observed coverages for the data of Chesters, Hussain, and Pritchard (Ref. 15). The code for the data points is as follows: C, Chesters, Hussain, and Pritchard (Ref. 15); M, Mingolet (Ref. 1); and N, Nieuwenhuys, Van Aardenne, and Sachtler (Ref. 4).

proximation we take $e(\zeta' - \zeta) = 8.6$ debye for Xe* (the observed value[10] for Cs$^+$), $\hbar\omega = 10$ eV, and $\mu \sim 0.3$ debye. The resulting energy $E_i = -0.35$ eV is in good agreement with the value[2,5] 8 kcal (0.3 eV) for the observed heat of adsorption on W. Evidently, Eqs. (2) and (5) are quantitatively consistent both with each other and with the data. Existing data for adsorbed Ar and Kr give equally satisfactory results.[2,5] For the hopping matrix element we obtain $t \sim 1$–2 eV, which also appears reasonable. It will be possible to explore the variation of t with substrate properties once work-function measurements are made with low, accurately known coverages. Experimental work of this type is under way in our laboratories.

From the present viewpoint one can discuss several fundamental issues that now appear open

to resolution. We comment on these in what follows. Each concerns the accessible spectrum of excited configurations. The present treatment has, of course, oversimplified the true physical situation by treating a single excited configuration. This deficiency is easily corrected in Eq. (1) by summing over all excited configurations containing, for example, differing core holes. To the extent that the excitation energies of the various holes are almost identical, this has little effect on the relationship (6) between E_a and μ; only the individual t for the separate contributing orbitals differ from the lumped t employed above.

Two phenomena that point to further rich structure are (a) the fact that the observed charge-transfer excitations and large work-function changes persist in all cases up to coverages $> 10^{15}$ cm^{-2}, which surely exceed one rare-gas monolayer as measured in specific cases[11]; and (b) the fact that the observed work-function changes caused by rare gases on W exhibit a remarkable dependence on the particular substrate crystal face.[5,2] The former result indicates that the photohole is trapped in the excited state, whether as an atomic or molecular ion[12] form, while the excited electron transfers to the metal over distances exceeding the nearest-neighbor spacing. The second result probably originates in the way the differing ridges on various crystal faces modify the efficiency and the orientation of the charge-transfer processes from the several core orbitals. In the first area, there is a need for experiments in which rare-gas monolayers of one species are buffered from the substrate by an intervening dissimilar layer, in order that the distance dependence of the process may be investigated. In the second, it is the polarization of the exciting light with respect to the surface structure that will reveal the origin of the surface-specific effects. These phenomena remain to be clarified by future research.

From the standpoint of fundamental metal physics a most important result of the present work is the confirmation that the excitation spectrum of a Fermi liquid interacting with an atomic center can contain a sharp charge-transfer instability. The observed switching cannot derive from energy denominators, which vary slowly with φ, but must instead arise from abrupt modifications of the excited-state wave functions. For the present simple system it appears likely that the accessible self-consistent excited configurations are either all polar or all nonpolar. Recent photoemission results for CO and N_2 give contrary

evidence that both polar and nonpolar final configurations occur.[13] It is conceivable that differing core configurations span the instability, thereby opening channels to both types of excitation, or, alternatively, that one or both excited states fall in the weak-coupling limit where $t = 0$ because of a correlation-induced decoupling of the local center from the metal.[14]

In summary, we have shown how the long-standing puzzle of inert-gas adsorbate properties on metal surfaces can be understood in terms of the charge-transfer instability of metals. Both the occurrence and the general magnitude of the "anomalous" effects are explained and, for certain cases, the bonding is related to the work-function changes in a simple way.

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