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OFFICE OF NAVAL RESEARCH

Contract No. N00014-91-J-1409

Technical Report No. 133

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Electrostatic-Field Effects on Adsorbate Bonding
and Structure at Metal Surfaces: Parallels Between
Electrochemical and Vacuum Systems

by

Michael J. Weaver

Prepared for Publication

in

Surface Science

Department of Chemistry

Purdue University

West Lafayette, Indiana 47907-1393

October 1992

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92-28549



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REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE OCTOBER 1992	3. REPORT TYPE AND DATES COVERED	
4. TITLE AND SUBTITLE ELECTROSTATIC-FIELD EFFECTS ON ADSORBATE BONDING AND STRUCTURE AT METAL SURFACES: PARALLELS BETWEEN ELECTROCHEMICAL AND VACUUM SYSTEMS			5. FUNDING NUMBERS CONTRACT NO. N00014-91-J-1409	
6. AUTHOR(S) MICHAEL J. WEAVER				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) PURDUE UNIVERSITY DEPARTMENT OF CHEMISTRY 1393 BROWN BUILDING WEST LAFAYETTE, IN 47907-1393			8. PERFORMING ORGANIZATION REPORT NUMBER TECHNICAL REPORT NO. 133	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) DIVISION OF SPONSORED PROGRAMS PURDUE RESEARCH FOUNDATION PURDUE UNIVERSITY WEST LAFAYETTE, IN 47906			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE AND SALE: ITS DISTRIBUTION IS UNLIMITED			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The observed effects of varying the surface potential, and hence the accompanying electrostatic fields, upon adsorbate bonding at ordered monocrystalline metals in electrochemical environments are summarized and discussed in comparison with field effects at related metal-vacuum interfaces for the specific case of carbon monoxide. The dependencies of the C-O stretching frequency, ν_{CO} , upon the electrochemical surface potential, E , (and interfacial field, \mathcal{E}) as evaluated for CO adlayers at a fixed coverage, θ_{CO} , and surface binding site are summarized as a function of θ_{CO} , the metal substrate, and the double-layer ionic environment, in order to illustrate the virtues of electrochemical systems for exploring such interfacial field effects. The increasing preference for multifold versus terminal CO binding commonly observed towards lower potentials (and at larger negative fields) is also noted. These findings are compared with related field-induced effects observed for metal-CO adlayers in vacuum and also for chargeable metal-carbonyl clusters in				
14. SUBJECT TERMS MONOCRYSTALLINE METALS, METAL-VACUUM INTERFACES,			15. NUMBER OF PAGES 30	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

13. ABSTRACT (continued)

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ABSTRACT

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Introduction

It has long been recognized that the surface electrical potential and the attendant electrostatic fields play an entirely central role in interfacial electrochemical phenomena. Thus the thermodynamics and kinetics of interfacial electron-transfer processes, as well as the binding of molecular and ionic chemisorbates, are well known to be sensitive to the metal-solution potential difference[1]. The longevity of this realization owes largely to the unique control as well as measurement of the interfacial potential available in electrochemical systems, together with the high electrostatic fields (typically ca 10^7 V cm⁻¹) generated at metal-solution interfaces by the free charge and oriented dipolar constituents of the so-called electrochemical double layer. Less evident, at least traditionally, however, has been the relation between such phenomena and those involving adsorbates at metal-vacuum interfaces. While the continuing developments in field ion microscopy and the accompanying fundamental interest in electrostatic-field effects has brought an acknowledgment of the importance of such phenomena in vacuum-based surface systems, a more comprehensive recognition of their common significance to metal interfaces in vacuum as well as electrochemical environments has largely been lacking.

A major factor contributing to this situation has been the paucity of physical measurements that are common to both types of interface. In contrast to metal-vacuum surfaces, until recently experimental investigations of electrochemical interfaces were limited to "macroscopic" techniques, primarily utilizing current-potential-time measurements. While a remarkable amount of fundamental insight concerning the nature of metal-solution interfaces, and the processes that occur there, has been (and continues to be) extracted from such conventional electrochemical methods, they tend to yield distinctly different

types of information from the microscopic techniques that are prevalent in vacuum surface science. Moreover, most fundamental electrochemical information has been gathered at polycrystalline, rather than ordered single-crystal, metal surfaces, contrasting the longstanding emphasis on the latter, sterically better defined, type of interface in vacuum-based studies.

Several factors, however, are conspiring increasingly to change this situation quite dramatically, leading to substantial new opportunities for understanding fundamental phenomena such as electrostatic-field effects at metal-solution and metal-vacuum interfaces on a genuinely unified basis. The last decade or so has seen an accelerating development of microscopic structural methods that are applicable to in-situ electrochemical as well as vacuum-based surfaces[2]. These techniques include vibrational (infrared, Raman) spectroscopies, x-ray diffraction and related methods, and scanning probe techniques, especially scanning tunneling microscopy (STM). Concurrently, increasingly reliable procedures for preparing ordered monocrystalline metal surfaces compatible with in-situ electrochemical environments have been devised[3-5]. Besides promoting their development, some of the former techniques (particularly STM) also allow the reliability of the surface preparative methods to be checked and the degree of structural order and uniformity assessed in an analogous fashion to vacuum-based strategies. As a consequence, information on adsorbate bonding and atomic structure at electrochemical surfaces is now emerging in a format and at a level of detail which is closely compatible with that obtained at metal-vacuum interfaces[6].

In addition, vacuum-based strategies have been developed which establish close experimental ties with corresponding electrochemical systems. In suitable cases, electrode surfaces may be emersed and transferred into ultrahigh vacuum

with at least part of the electrochemical double layer remaining intact[7]. These "ex-situ" tactics enable the electrochemical surface-adsorbate structures to be assessed by a full range of vacuum-based methods. A fruitful alternative approach, commonly dubbed "electrochemical modeling", involves dosing surfaces in vacuum with atoms and molecules that form anticipated components of the electrochemical double layer[8]. By including ionizable species (eg. alkali metal atoms, halogens), the surfaces can be charged electronically in a similar fashion to electrode-solution interfaces[8]. Besides such metal-vacuum surfaces, tailored specifically to mimic electrochemical interfaces, the examination of coadsorbate systems in general is attracting increasing attention. The influence of a second adsorbate upon the vibrational properties of a suitable "probe" molecule, especially CO or NO, has formed the subject of a number of recent studies (eg. refs. 9-14). The observed adsorbate vibrational frequency shifts can be understood at least partly in terms of electrostatic-field effects exerted by the dipolar or ionic coadsorbate[6,14,15]. The changes in surface potential attending such alterations in the interfacial composition can be evaluated readily by work-function measurements, extracted commonly from photoemission thresholds or by using a Kelvin probe. Such effects upon the vibrational frequencies of CO adsorbed at metal-vacuum interfaces have also been explored more directly by applying a variable external electrostatic field by means of a nearby counter electrode[16,17].

These findings are related closely to the adsorbate frequency shifts commonly induced in electrochemical systems by altering the electrode potential.⁶ We have recently undertaken a detailed series of infrared spectroscopic studies of carbon monoxide adsorbed on monocrystalline platinum, rhodium, iridium, palladium, and gold electrodes in a range of aqueous[6,18-30] and nonaqueous

electrolytes[31,32]. One objective is to understand how the CO adsorbate bonding is modified by the applied electrode potential in relation to the other influences exerted by the chemical and crystallographic nature of the metal surface[6,31,32]. Generally, decreasing the applied potential (corresponding to increases in the negative electronic surface charge) yields not only marked diminutions in the C-O stretching frequency, ν_{CO} , but in several cases triggers progressive shifts in the adsorbate binding geometry from atop to bridging (multifold) coordination[6]. The effects of varying the electrostatic field at a given applied potential by altering the size of the double-layer cation, and hence the inner-layer thickness, have also been explored[31-33].

Given the foregoing, it is clearly of interest to consider such electrochemical field effects in comparison with related observations and theoretical predictions for analogous metal-vacuum systems. Such an examination along these lines, involving the likely commonality of field effects in electrochemical and vacuum surface environments using CO as a probe molecule, is the primary objective of the present conference paper. Other roles of the surface potential in the chemistry and physics of such systems are noted briefly.

Electrochemical CO Frequency-Field Dependencies: Sensitivity to Interfacial Environment

In order to gain an appreciation of the observed dependencies of C-O adsorbate vibrational frequencies upon the electrode potential (E) and hence the surface electrostatic field (sometimes termed "Stark-tuning slopes" or "rates"), it is desirable to examine observed ν_{CO} - E data obtained at a fixed total CO coverage, θ_{CO} , and binding site occupancy[25]. This is because substantial ν_{CO} frequency enhancements commonly occur as θ_{CO} is increased at a fixed potential

(or surface charge), due in part to dynamic dipole-dipole coupling[19]. Even at a fixed θ_{CO} , such contributions can vary (and hence can distort the $\nu_{\text{CO}} - E$ slopes) unless the adsorbate site occupancy, as gleaned from the form of the infrared spectra, remains constant.

Table I contains a representative selection of Stark-tuning slopes for CO bound to atop (i.e. terminal) and twofold bridging sites, $d\nu_{\text{CO}}^t/dE$ and $d\nu_{\text{CO}}^b/dE$, respectively, obtained by infrared spectroscopy for saturated CO adlayers on Pt(111), Pt(110), and Rh(111) in aqueous and acetonitrile electrolytes. The latter solvent is representative of the several nonaqueous media studied[31,32]. As at metal-vacuum surfaces, the atop and bridging CO can readily be identified and distinguished by the markedly (ca 150-200 cm^{-1}) lower ν_{CO} frequencies characterizing the latter. Data for four electrolytes are contained in Table I, consisting of four different cations. As elaborated further below, over most of the experimentally assessible range of electrode potentials (ca -2.0 to 1.0 V versus saturated calomel electrode, SCE) the metal surface carries a varying negative electronic charge, countered by an excess cationic charge located outside the CO adlayer. This yields a variable "free-charge" contribution to the surface potential drop, and hence the electrostatic field, formed across the CO adlayer. Consequently, the nature of the electrolyte cation might be expected to influence the magnitude of the observed $\nu_{\text{CO}} - E$ response.

An illustrative example of the observed cation dependence (taken from ref. 32) is shown in Figure 1, which is a plot of the atop stretching frequency, ν_{CO}^t , versus the electrode potential for saturated CO adlayers ($\theta_{\text{CO}} = 0.75$) on Rh(111) in aqueous media (filled symbols) and in acetonitrile (open symbols). The open circles and squares refer to acetonitrile containing 0.1M tetrabutylammonium (TBA^+) and tetraethylammonium (TEA^+) perchlorate,

respectively. These two electrolytes are seen to yield divergent linear $\nu_{\text{CO}} - E$ plots, that intersect close to the high-potential limit, $E \approx 0.9$ V versus SCE. As outlined elsewhere[31,32], this intersection potential can be identified with the so-called "potential of zero charge," E_{pzc} , where the electronic surface charge density is zero. At this point, the free-charge contribution to the surface potential vanishes. In addition, conversion of this E_{pzc} estimate to the vacuum scale* yields an "absolute" surface potential, ϕ^{M} , value of 5.8V[32]. Interestingly, this value is similar to the surface potential, $\phi_{\text{V}}^{\text{M}}$, of the Rh(111)/CO($\theta=0.75$)-vacuum interface, 5.9V, as extracted from work-function data[32], indicating that the solvent dipolar contribution to the surface potential at E_{pzc} is small or negligible. A similar finding pertains to other metal/CO-nonaqueous interfaces examined in this manner[31,32]. As the electrode potential is adjusted below 0.9V versus SCE, the negative electronic charge density increases, mirrored by the cationic charge located at the so-called "outer Helmholtz plane" (oHp). At a given $(E - E_{\text{pzc}})$ value, the oHp formed from smaller TEA^+ cations is anticipated to be located closer to the metal surface than for TBA^+ , given their differing crystallographic radii (ca 4.0 and 5.0Å, respectively). The larger electrostatic field expected to be generated in the former case is consistent with the greater downshifts in $\nu_{\text{CO}}^{\text{t}}$, and hence larger $d\nu_{\text{CO}}^{\text{t}}/dE$ slope, observed in the presence of TEA^+ compared to TBA^+ (Figure 1).

Such cation effects upon the Stark-tuning rates are observed more readily in nonaqueous media[31-34]. Thus significantly larger $d\nu_{\text{CO}}^{\text{t}}/dE$ values are usually

* The conversion is undertaken by noting that the normal hydrogen electrode (NHE) has an electrode potential of about 4.6(± 0.2)V on the vacuum scale[6], and the aqueous SCE is about 0.25V more positive than the NHE.

observed for metal-acetonitrile systems containing TEA⁺ than TBA⁺ (Table I). More marked differences, however, are seen between $d\nu_{\text{CO}}^{\text{t}}/dE$ (and $d\nu_{\text{CO}}^{\text{b}}/dE$) values obtained for a given metal/CO adlayer in aqueous versus nonaqueous electrolytes[31,32]. This point can be discerned from Table I by comparing the data listed for water versus acetonitrile. For a given electrolyte cation (Na⁺ or TEA⁺), the $d\nu_{\text{CO}}/dE$ values tend to be significantly (even substantially) larger in aqueous than in acetonitrile electrolyte. This trend is observed more generally for aqueous versus nonaqueous media[31,32], and is also evident from Figure 1 in the larger $d\nu_{\text{CO}}^{\text{t}}/dE$ slopes observed for Rh(111)/CO in water versus acetonitrile containing TEA⁺ (filled, open squares) or Na⁺ (filled, open triangles).

These observations can be rationalized in terms of a simple electrostatic model describing the potential-distance (i.e. field) profile across the inner layer (i.e. between the metal surface and the oHp), bearing in mind that the C-O frequency should be responsive only to the potential component lying across the CO adlayer, $\phi_{\text{CO}}^{\text{M}}$. This quantity can be related most simply to the overall metal-solution potential drop, $\phi_{\text{s}}^{\text{M}}$, by[32,33]

$$\phi_{\text{CO}}^{\text{M}} = \phi_{\text{s}}^{\text{M}} [d_{\text{CO}} / (d_{\text{CO}} + r_{\text{c}})] \quad (1)$$

where d_{CO} is the thickness of the CO adlayer, and r_{c} is the radius of the oHp cation. This formula presumes that the metal-oHp potential drop is linear, i.e. that the inner-layer field is constant. However, given that the effective "dielectric constant" of the CO adlayer, ϵ_{CO} , is liable to differ from that between the adsorbate and the oHp, ϵ_{s} , since the latter contains solvent dipoles, one can modify Eq. (1) to read

$$\phi_{\text{CO}}^{\text{M}} = \phi_{\text{s}}^{\text{M}} [1 + (r_{\text{c}}/d_{\text{CO}})(\epsilon_{\text{CO}}/\epsilon_{\text{s}})]^{-1} \quad (2)$$

Given that $dE = d\phi_s^M$, the measured Stark-tuning slopes can be related to the fundamentally desired quantity $d\nu_{co}/d\phi_{co}^M$ by

$$(d\nu_{co}/dE) = [1 + (r_c/d_{co})(\epsilon_{co}/\epsilon_s)]^{-1} (d\nu_{co}/d\phi_{co}^M) \quad (3)$$

Strictly speaking, ϕ_s^M (and hence $d\phi_s^M$ and dE) also differ from ϕ_{co}^M by the potential drop across the diffuse layer (i.e., between the oHp and the bulk solution). It turns out, however, that the diffuse-layer contribution to at least the electrode potential derivatives considered here are typically small or negligible[32].

The observed variations in $(d\nu_{co}/dE)$ with the nature of the double-layer cation can usefully be described on the basis of Eq. (3). Thus the ca 10-20% differences in $(d\nu_{co}^t/dE)$ typically observed in nonaqueous TEA⁺ versus TBA⁺ media are approximately consistent with Eq. (3) if $\epsilon_{co} \sim \epsilon_s$. The larger $(d\nu_{co}^t/dE)$ values usually obtained for aqueous versus corresponding nonaqueous systems can also readily be rationalized on this basis since the excellent dielectric screening properties of water dipoles are expected to yield larger effective ϵ_s values, and hence measured $(d\nu_{co}/dE)$ values that approach more closely towards $(d\nu_{co}/d\phi_{co}^M)$. This expectation is also in harmony with the observed insensitivity of the Stark-tuning slopes observed in aqueous media to the nature of the double-layer cation[25], consistent with the suppression of the potential drop outside the CO adlayer by dielectric screening. Although hampered by uncertainties in $(\epsilon_{co}/\epsilon_s)$, Eq. (3) can enable rough estimates of $(d\nu_{co}/d\phi_{co}^M)$ to be extracted from the measured $(d\nu_{co}/dE)$ values[32]. One can estimate on this basis that the required estimates of $(d\nu_{co}/d\phi_{co}^M)$ are roughly 2-2.5 fold larger than the $(d\nu_{co}/dE)$ values measured in nonaqueous-tetraalkylammonium media[32], yielding typically $(d\nu_{co}^t/d\phi_{co}^M) \approx 40-50 \text{ cm}^{-1} \text{ V}^{-1}$ for the systems listed in Table I.

It is also appropriate to comment on the linearity of the observed $\nu_{\text{CO}} - E$ plots in this context. Decidedly nonlinear $\nu_{\text{CO}} - E$ plots, with slopes decreasing towards higher potentials, have been observed in several cases in aqueous media, even for systems having essentially E-independent CO adlayer structure[36]. A notable case is the saturated CO adlayer on Pt(110), for which $(d\nu_{\text{CO}}^{\text{t}}/dE)$ decreases by about one-third over a ca 0.5V potential range in aqueous media[36]. In nonaqueous media, however, the corresponding $d\nu_{\text{CO}}^{\text{t}} - E$ plots are essentially linear over a much wider potential range, from -2 to 1V versus SCE. Analysis of these differences with respect to the above considerations suggest that the nonlinear $\nu_{\text{CO}} - E$ plots may well reflect the presence of potential-dependent double-layer geometries arising from electrostriction[32]. One therefore needs to be wary of fundamental conclusions concerning the behavior of $(d\nu_{\text{CO}}^{\text{t}}/d\phi_{\text{CO}}^{\text{M}})$ that are drawn from such observations.

In addition to such double-layer effects, it is also of interest to examine the sensitivity of the Stark-tuning slopes to the adlayer coverage, θ_{CO} , as well as the binding geometry and the nature of the metal surface. Table II contains a brief selection of data selected for these purposes, obtained in aqueous 0.1M HClO₄ at 0V versus SCE. [From the above arguments, the desired $(d\nu_{\text{CO}}/d\phi_{\text{CO}}^{\text{M}})$ values are anticipated to be only about 20-30% larger than these measured $(d\nu_{\text{CO}}/dE)$ quantities in aqueous media.] Three general features become evident upon examining Table II. First, the $(d\nu_{\text{CO}}/dE)$ values consistently increase towards lower CO coverages, yielding values at low θ_{CO} that are as much as twofold larger than at the saturated coverages considered exclusively in Table I. Recent experiments involving saturated mixed ¹³CO/¹²CO adlayers on Pt(111) have shown that the frequency upshift due to dynamic dipole-dipole coupling, $\Delta\nu_{\text{D}}$, diminishes markedly towards lower potentials[36]. Given that the overall θ_{CO} -induced ν_{CO}

upshift due to adsorbate interaction effects, $\Delta\nu$, under these conditions, the former finding infers that these decreases in $(d\nu_{\text{co}}/dE)$ are associated with marked coverage-induced increases in the "chemical" (or "static") contribution[37] to $\Delta\nu$, $\Delta\nu_{\text{c}}$. A simple physical interpretation is that the θ_{co} -induced diminutions in the Stark-tuning slope arise from screening of the local electrostatic field by surrounding CO dipoles, and additionally perhaps to competition between neighboring adsorbate molecules for the surface charge density involved in the $d\pi-2\pi^*$ metal-CO backbonding anticipated increasingly towards lower potentials (vide infra).

A second significant feature seen in Table II is the larger Stark-tuning slopes observed for CO bound in twofold bridging, as compared with atop, coordination geometries. The question arises whether this difference reflects an intrinsic behavioral dissimilarity, or arises primarily from environmental factors. Evidence that the latter is at least partly the case is gleaned from the observation of comparable coverage-dependent Stark-tuning rates for atop and bridging CO on Pt(111) and Pd(111), respectively (Table II), for which these bonding modes predominate. The larger $(d\nu_{\text{co}}^{\text{b}}/dE)$ versus $(d\nu_{\text{co}}^{\text{t}}/dE)$ values observed, for example, for saturated CO adlayers on Pt(111) and Rh(111) (Table II) may therefore reflect chiefly the ca twofold smaller occupancies of bridging versus atop binding sites that characterize these systems[27,38].

A third feature of the data in Table II concerns the sensitivity of the Stark-tuning rates to the nature of the metal surface. Such considerations are complicated by the distinct adlayer structures formed on different metal surfaces even having the same crystallographic orientation. This difficulty is minimized by examining data at low adsorbate coverages. Examination of the data in Table II meeting this requirement (say, for $\theta_{\text{co}} \leq 0.25$), reveals the occurrence of some

variations, although both the $(d\nu_{co}^t/dE)$ and $(d\nu_{co}^b/dE)$ values lie mostly within the relatively narrow range 45–60 cm^{-1} .

Besides the C–O stretch, examination of the metal surface–CO vibration should provide particularly useful information on the specific role of the metal. Unfortunately, observation of the latter, ν_{M-C} , vibration by using infrared spectroscopy is made difficult by the low frequency (typically 400–500 cm^{-1}) as well as weak intensity of the mode[39]. However, such information can still be obtained even in electrochemical environments by means of surface-enhanced Raman spectroscopy (SERS), albeit only for polycrystalline metals. For example, we have recently obtained potential-dependent SERS data for CO on gold which shows small yet significant decreases of ν_{M-C} with electrode potential, yielding negative $(d\nu_{M-C}/dE)$ values, ca 7–9 $\text{cm}^{-1} \text{V}^{-1}$ [40]. Such effects can be understood in terms of potential-dependent surface bonding (vide infra).

Given the present overall objective, it is important to note the relation of such observed $(d\nu_{co}/dE)$ and $(d\nu_{M-C}/dE)$ values to corresponding band frequency-electrostatic field slopes, $(d\nu_{co}/d\mathcal{E})$. Provided that estimates of $(d\nu_{co}/\phi_{co}^M)$ can be obtained, the extraction of the corresponding $(d\nu_{co}/d\mathcal{E})$ values is straightforward given that the effective CO adlayer thickness, d_{co} , is of the order of 3Å, since

$$(d\nu_{co}/d\mathcal{E}) = d_{co}(d\nu_{co}/\phi_{co}^M) \quad (4)$$

The magnitude of \mathcal{E} values generated at the interfaces of concern here may readily be estimated as follows. The E_{pzc} values for the surfaces in Tables I and II lie in the range 0.7 to 1.0 V versus SCE[31,32]. Given that $(E - E_{pzc})$ values of at least -1.5 V are readily encountered experimentally in nonaqueous media (eg., Figure 1), if $d\phi_{co}^M \sim 0.5dE$ one deduces that fields of up to $2.5 \times 10^7 \text{ V cm}^{-1}$ are

present across the CO adlayers under these conditions. While not as large as those generated typically in vacuum field-emission experiments, such fields are clearly of sufficient magnitude to exert marked effects upon the adsorbate bonding.

As already mentioned, decreasing the electrode potential also leads in a number of instances to marked shifts in the predominant CO binding geometry from atop to multifold coordination[6,25,31-33]. Such site shifts are readily detected from the appearance of new bands at markedly (ca 150-200 cm^{-1}) lower frequencies (vide supra). For one system, Rh(111) in aqueous solution, the detailed potential-dependent CO adlayer structures were elucidated by means of a combined infrared spectral-STM analysis[38]. A specific role of the supporting-electrolyte cation in this site conversion is clearly implicated in several cases. Thus complete atop-bridge site conversion can be induced at large negative electrode potentials on Pt(110) as well as polycrystalline platinum in nonaqueous media containing alkali-metal cations, whereas no such site conversion occurs in the presence of the larger tetraalkylammonium ions[32,33]. These adsorbate coordination shifts can be considered to be driven by Lewis acid-base interactions between partly desolvated alkali cations and the CO adlayer[33]. In other cases, notably Rh(111), the potential-induced site conversion is sensitive to coupled solvent/cation effects[32]. Semi-empirical molecular-orbital theory can rationalize the observed sensitivity of this phenomenon to the crystallographic orientation as well as the nature of the metal; thus the observed greater propensity of Rh(111) versus Rh(100) towards potential-induced site conversion[25] can be accounted for on this basis[41].

Comparisons with Metal-Vacuum and Cluster Systems

Although conducted for only a single adsorbate, the foregoing results reveal a detailed picture of electrostatic field effects upon adsorbate bonding for structurally well-defined electrochemical interfaces. As such, the findings provide an interesting opportunity for undertaking comparisons with related field-induced phenomena at metal-vacuum interfaces[6]. As already noted, a number of studies of metal-vacuum interfaces have been undertaken recently where the effects of dosing a second dipolar or ionizable component upon the vibrational frequencies of CO adlayers have been examined[9-15]. Most of these additional components, such as water, ammonia, or alkali metals, are known to diminish the surface work function and hence lower the surface potential ϕ_V^M . Such coadsorbates usually produce substantial downshifts in the ν_{CO} frequencies, often together with alterations in the CO binding site towards multifold surface coordination[9-15]. Consequently, it is tempting to ascribe such effects to decreases in the surface potential and hence to increases in the local electrostatic field sensed by the CO molecules. This is especially appropriate for coadsorbates postdosed onto high or saturated CO coverages where the former species are unlikely to compete for surface coordination sites.

Unfortunately, the quantitative appraisal of this notion is thwarted in most cases by a paucity of the required work-function data. One recent exception is a study by Xu et al of progressive atop-bridging site conversion induced in a saturated CO adlayer on Ni(111) at 150K by various polar overlayers[14]. Interestingly, the degree of CO site conversion as deduced from the relative infrared band intensities correlates in a common fashion with the measured surface potential, irrespective of the chemical nature of the dipolar overlayer. These results, which are in harmony with semi-empirical MO predictions[14],

therefore support the perceived important role of the electrostatic field in controlling the adsorbate bonding in vacuum interfacial environments.

This finding is closely similar to the electrode potential-induced site conversion observed for saturated CO adlayers on Pt(111), which is observed to occur at closely similar potentials irrespective of the solvent medium[31]. (On the other hand, the occurrence of more dramatic potential-induced atop-bridge site conversion observed on Rh(111) electrodes is seen to be dependent upon the solvent as well as the electrolyte cation (vide supra)[32].) As discussed in ref. 6, however, it is important to recognize a fundamental difference between vacuum-based coadsorbate effects such as those described in ref. 14 and potential-induced electrochemical phenomena. In the former case, the alterations in surface potential are triggered by dosing differing amounts of overlayer dipolar species. While this strategy can yield substantial (up to ca 2-3V) changes in the surface potential, these alterations are associated with dipolar orientation and the consequent image interactions in the metal. In electrochemical systems, by contrast, the externally controlled variations in electrode potential at a given interface are triggered by a flow of electrons to (or from) the metal surface, with a consequent accumulation of excess ionic charge within the double layer. This *free-charge* component drives entirely the alterations in electrode potential. While the attendant changes in the solvent dipolar orientation may also contribute importantly to the surface potential, this component is usually expected to oppose the free-charge contribution, in that the alignment of the solvent dipoles will tend to diminish the electrostatic field thus created ("dielectric screening")[6]. In this regard, then, the effect of interfacial solvent dipoles in the electrochemical case is qualitatively different from their influence as coadsorbates upon metal-vacuum systems such as

in ref. 14.

While there is no reason to degrade the role of such electrostatic-field effects in metal-vacuum systems, the above considerations highlight the unique virtues of electrochemical interfaces for exploring their fundamental characteristics. The correlation of CO frequency shifts at constant site occupancy with the surface-potential changes induced by coadsorbates in metal-vacuum systems would nevertheless be of great interest for comparison with electrochemical results. Given the observed sensitivity of the electrochemical Stark-tuning slopes to the interfacial-potential profile as determined by the double-layer cation, one might expect a similar dependence on the spatial properties of the dipolar coadsorbate in such metal-vacuum systems. No quantitative studies of this type have apparently been reported to date. Some evidence, however, suggests that comparable effects can be obtained. For example, the ν_{CO} frequency downshifts observed for CO coadsorbed with potassium on Ni(111) in vacuum[42] yield $(d\nu_{\text{CO}}^{\text{t}}/dE) \sim 100 \text{ cm}^{-1} \text{ V}^{-1}$.

As noted above, the influence of external electrostatic fields on ν_{CO} frequencies has been pursued for adlayers at metal-vacuum interfaces by applying large-potential differences with respect to a nearby counter electrode[16,17]. Unlike metal-electrolyte interfaces where virtually the entire interfacial potential drop is located over molecularly short ($\geq 10\text{\AA}$) distances from the metal surface, the electrostatic field is expected to extend uniformly across the planar substrate-counter-electrode gap in such vacuum systems. Consequently, the fields attainable, ca $3 \times 10^4 \text{ V cm}^{-1}$, are much smaller than those, ca 10^7 V cm^{-1} , commonly generated at analogous electrochemical interfaces. Nevertheless, significant infrared ν_{CO} frequency shifts can still be detected[16].

This approach has recently been utilized to obtain $(d\nu_{\text{CO}}/d\mathcal{E})$ values for CO

adlayers at the Pt(111)-vacuum interface[17,43], enabling a direct comparison with analogous results for the Pt(111) electrochemical interfaces noted above. Values of $(d\nu_{\text{co}}^t/d\mathcal{E})$ and $(d\nu_{\text{co}}^b/d\mathcal{E})$ equal to ca 2.6×10^{-7} and $4 \times 10^{-7} \text{ cm}^{-1}/\text{V cm}^{-1}$, respectively, have been reported for a saturated ($\theta_{\text{co}} = 0.6$) adlayer on Pt(111) in vacuum[17]. (These quantities are defined in terms of the external, or apparent, electrostatic field; slightly (10-20%) higher estimates are obtained after correction for adsorbate screening so to extract the local fields[17].) Interestingly, the values are markedly smaller than the corresponding quantities estimated from electrochemical $(d\nu_{\text{co}}/dE)$ data. Thus assuming that $(d\nu_{\text{co}}/\phi_{\text{co}}^M) = (d\nu_{\text{co}}/dE)$ in aqueous media, and that $d_{\text{co}} \approx 3.5\text{\AA}$, given that $(d\nu_{\text{co}}^t/dE) \approx 30 \text{ cm}^{-1} \text{ V}^{-1}$ and $(d\nu_{\text{co}}^b/dE) \approx 50 \text{ cm}^{-1} \text{ V}^{-1}$ for a saturated ($\theta_{\text{co}} \approx 0.65$) CO adlayer on Pt(111) in aqueous 0.1M HClO_4 [25], we deduce that $(d\nu_{\text{co}}^t/d\mathcal{E}) \sim 1.0 \times 10^{-6} \text{ cm}^{-1}/\text{V cm}^{-1}$ and $(d\nu_{\text{co}}^b/d\mathcal{E}) \sim 1.75 \times 10^{-6} \text{ cm}^{-1}/\text{V cm}^{-1}$. These $(d\nu_{\text{co}}/d\mathcal{E})$ estimates are markedly (ca twofold) larger than the corresponding values noted above for the analogous metal-vacuum system. Even larger discrepancies are obtained if the likely inequality $(d\nu_{\text{co}}/\phi_{\text{co}}^M) > (d\nu_{\text{co}}/dE)$ is taken into account by means of Eq(3).

The factors responsible for this behavioral disparity between the Pt(111)/CO electrochemical and vacuum systems are unclear at present[17]. It is possible that the local field acting on the CO adsorbate in the Pt(111)-vacuum system is markedly smaller than the external field as a result of screening effects[17] (vide infra). Alternatively, the smaller $(d\nu_{\text{co}}/d\mathcal{E})$ estimates for the Pt(111)/CO-vacuum interface may reflect the much (ca 10^2 - 10^3) lower fields generated in comparison with the electrochemical system. The latter explanation requires, of course, that the $\nu_{\text{co}} - \mathcal{E}$ dependence is nonlinear over this range. Despite these disparities, the larger $(d\nu_{\text{co}}/d\mathcal{E})$ values deduced for the bridging versus terminal bands in the Pt(111)/CO-vacuum system are in harmony with the

corresponding electrochemical results. In addition, the $(d\nu_{\text{CO}}^t/d\mathcal{E})$ values in the former system have been observed to increase towards lower CO coverages in a similar fashion to the behavior of the electrochemical system (Table II)[6,43].

In addition to metal-vacuum systems, the comparison of the present electrochemical field effects with those observed in related metal clusters is of interest, especially given their relationship to the curved surfaces that constitute emitter tips in field ion microscopy. Information of this type for clusters in vacuum (or gas-phase) environments is apparently absent. Nevertheless, we have recently examined the infrared spectroscopy of high-nuclearity platinum carbonyl clusters such as $[\text{Pt}_{24}(\text{CO})_{30}]^n$ and $[\text{Pt}_{38}(\text{CO})_{44}]^n$ in various nonaqueous media, where n can be altered from 0 to at least -8 by electrochemical reduction [35,44]. As befits their well-defined crystallographic structure, clearcut terminal and bridging ν_{CO} bands are observed for the cluster solutes. Since the various electron additions occur reversibly at sequential formal potentials E_f , the dependence of the ν_{CO} frequencies upon potential (E_f) as well as cluster charge can be examined in a similar fashion to metal electrode surfaces. The observed $\nu_{\text{CO}}^t - E_f$ dependencies are nonlinear, reflecting in part quantum-size effects. Nevertheless, the average slopes in nonaqueous media such as acetonitrile, ca $50 \text{ cm}^{-1} \text{ V}^{-1}$, are significantly (2-3 fold) larger than those observed at analogous electrode-solution interfaces (Table I)[44]. These differences can be ascribed partly to the greater local electrostatic fields generated at the roughly spherical cluster surfaces[44a,45].

Comparison with Theoretical Expectations

Overall, the experimental electrostatic-field effects gathered for metal surfaces (and clusters) in electrolyte solutions and in vacuum display an

interesting sensitivity to the interfacial environment. We conclude with a brief comparison of these results with some extant theoretical expectations.

The simplest theoretical approach entails treating the adsorbed CO as oriented free (gas-phase) molecules influenced by the field via a first-order Stark effect [16,46,47]. This treatment yields $(d\nu_{\text{co}}/d\mathcal{E})$ values, ca 4×10^{-7} $\text{cm}^{-1}/\text{V cm}^{-1}$, that are noticeably (ca 3-5 fold) smaller than those typically observed at least at metal-electrolyte interfaces. According to Lambert[16], at least part of this discrepancy between theory and experiment is due to modification of the CO dipole oscillator properties by adsorption, along with differences between the "local" field acting on the adsorbate, \mathcal{E}_{loc} , and the externally applied field, \mathcal{E}_{ext} . (The latter is the measured field applied in the metal-vacuum experiments noted above.) The screening coefficient, $\gamma_0 = \mathcal{E}_{\text{loc}} / \mathcal{E}_{\text{ext}}$, can be significantly below unity, ca 0.3[16,17]; given that the electrochemical $(d\nu_{\text{co}}/d\mathcal{E})$ values as estimated above should refer approximately to \mathcal{E}_{loc} [16], the corresponding theoretical $(d\nu_{\text{co}}/d\mathcal{E})$ estimates derived in this fashion can approach the former values. However, the discrepancy noted above between the $(d\nu_{\text{co}}/d\mathcal{E})$ values extracted for the Pt(111)/CO electrochemical and vacuum systems are not necessarily accounted for on this basis, since $\gamma_0 \sim 0.7$ for this system[17].

An alternative theoretical approach involves asserting that the dependence of the ν_{co} frequency upon the surface potential arises from alterations in the extent of metal-adsorbate charge sharing, i.e. chemical bonding. One version along these lines, developed by A.B. Anderson, involves semi-empirical molecular orbital calculations where the effect of varying the surface potential is mimicked by alterations in the Fermi level for an appropriate metal cluster[48]. Results of such numerical calculations have been reported for several metal-CO

systems. For example, the observed electrode potential-dependent CO site occupancy on Rh(111) and differences Rh(100) noted above can be accounted for semiquantitatively on this basis[49]. The predicted $\nu_{\text{CO}} - E$ behavior for Pt(111)/CO [50] is of interest in the present context. The $\nu_{\text{CO}} - E$ slopes are predicted to increase towards more negative potentials, with $(d\nu_{\text{CO}}^t/dE)$ lying in the range ca 110 to 160 $\text{cm}^{-1} \text{V}^{-1}$ for potentials below E_{pzc} [50]. (Note that the "theoretical" potential scale given in ref. 50 refers essentially to $(E - E_{\text{pzc}})$ [49].)

These $(d\nu_{\text{CO}}^t/dE)$ estimates, which should essentially be equivalent to $(d\nu_{\text{CO}}^t/d\phi_{\text{CO}}^M)$, are instead markedly larger than the experimental values noted above. Moreover, even greater disparities with experiment are obtained for bridge-bound CO in that the MO theory predicts that $(d\nu_{\text{CO}}^b/d\phi_{\text{CO}}^M) \sim 250 \text{ cm}^{-1} \text{V}^{-1}$ at negative potentials, very much (4-5 fold) larger than the low-coverage experimental $(d\nu_{\text{CO}}^b/dE)$ values (Table II). These theory-experiment disparities probably reside at least partly in the neglect of field effects across the CO adlayer. Thus, by mimicking the variations in electrode potential by altering the metal Fermi level the MO calculations assume tacitly that the potential drop is discontinuous at the metal surface, rather than spanning the adlayer as in actuality.

Some ab initio MO calculations for Pd(100)/CO suggest that alterations in the extent of metal-CO charge sharing induced by changing the external field, as estimated by the Anderson semi-empirical MO treatment, provide only a minor contribution to the Stark-tuning slope[51]. Nevertheless, another analysis concluded that this "chemical bonding" component as well as classical electrostatic field effects is required to account for the experimental findings[52]. In any case, Lambert has pointed out that the interpretation of such Stark-tuning effects for adsorbed species by means of MO treatments are

ultimately equivalent to descriptions couched in terms of dipole moment/electrostatic-field effects with proper consideration of metal surface interactions[16]. It would nonetheless be of substantial interest to employ semi-empirical MO treatments in conjunction with proper consideration of external field effects for comparison with the extensive experimental data now available for well-defined electrochemical systems. The approach employed by Kreuzer et al[53] for analyzing some metal-gas systems[14] would appear to be especially useful in this regard.

Other Electrochemical Field Effects

While we have focussed here on a single non-traditional example of field effects in electrochemical systems in order to facilitate links with metal-vacuum surfaces, it is also appropriate to note briefly their more general significance to electrochemical phenomena. As in field ion microscopy, electron-transfer processes involving interfacial species are of central importance in electrochemistry. While such heterogeneous charge-transfer phenomena are inherently dependent upon the interfacial fields, it is usually more convenient to describe redox electrochemical systems in terms of the electrode potential. This is because the charge-transfer thermodynamics are dependent upon the entire metal-solution potential drop irrespective of the local electrostatic fields, and hence can be described precisely by the electrode potential (i.e. versus a reference redox couple). The kinetics of electrode reactions, on the other hand, are sensitive to the local electrostatic fields where the reacting species is located. Indeed, field- rather than potential, -based descriptions have their virtues for some electrode processes[54], even though the two approaches are formally equivalent.

In closing, we mention a distinctly different phenomenon which may turn out to exhibit related field effects in electrochemical and metal-vacuum systems, namely potential-induced surface reconstruction. Several in-situ microscopic techniques, primarily x-ray diffraction and scanning tunneling microscopy, have demonstrated recently that reconstruction is triggered on ordered low-index gold surfaces in nonadsorbing aqueous media at small negative electrode charges, and lifted at positive charges[55-59]. Similar reconstructions can be induced on silver and copper low-index faces in vacuum by charging the surfaces negative by dosing with low coverages of ionizable alkali metals[60]. It remains to be seen if such charge-induced reconstructions in electrochemical and vacuum-based systems have a related or even common origin: theoretical understanding of the phenomenon remains distinctly incomplete.

There are some reasons, then to anticipate that the commonality of phenomena observed at related metal-solution and metal-vacuum interfaces, spurred by an expanding array of spectroscopic and microscopic techniques applicable to both types of systems, will embrace an increasing recognition of the broadbased importance of electrostatic-field effects in surface science. The greater interaction, and cooperation, between experimentalists and theoreticians interested in electrochemical and vacuum-based surface phenomena would therefore seem not only desirable, but hopefully also inevitable.

Acknowledgements

The author's interest in the present topic was nurtured substantially by the industrious efforts of Dr. Si-Chung Chang. This work is supported by the National Science Foundation and the Office of Naval Research.

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TABLE I Stretching Frequency-Electrode Potential Slopes for Saturated CO Adlayers at Selected Ordered Metal-Electrolyte Interfaces (from refs. 25, 31 and 32).

Surface	Solvent	Electrolyte ^a	θ_{CO} ^b	Potential Range ^c vs. SCE	$d\nu_{\text{CO}}^t/dE$ ^d $\text{cm}^{-1}\text{V}^{-1}$	$d\nu_{\text{CO}}^b/dE$ ^e $\text{cm}^{-1}\text{V}^{-1}$
Pt(111)	Water	0.1M HClO ₄	0.65	0 to 0.3	29	55
		0.15M TEAP	0.65	0 to 0.3	18	45
	Acetonitrile	0.15M TEAP	0.65	0.2 to 1.0	22	21
		0.15M TBAP	0.65	0.2 to 1.0	20	23.5
Pt(110)	Water	0.1M HClO ₄	1.0	-0.2 to 0.25	-26 ^f	
		0.1M NaClO ₄	1.0	-0.2 to 0.25	-25 ^f	
		0.1M TEAP	1.0	-0.2 to 0.25	20	
	Acetonitrile	0.1M NaClO ₄	1.0	-1.5 to 1.0	21	
		0.1M TEAP	1.0	-1.5 to 1.0	21	
		0.1M TBAP	1.0	-1.5 to 1.0	17	
Rh(111)	Water	0.1M NaClO ₄	0.75	-0.1 to 0.25	30	46
		0.1M TEAP	0.75	-0.1 to 0.25	28	31
	Acetonitrile	0.1M NaClO ₄	0.75	0.2 to 1.0	22	
		0.1M TEAP	0.75	-2.0 to 1.0	18	22
		0.1M TBAP	0.75	-1.5 to 1.0	14	18

^a TEAP = tetraethylammonium perchlorate; TBAP = tetrabutylammonium perchlorate

^b Fractional surface coverage of saturated CO adlayer

^c Range of electrode potential over which the average $d\nu_{\text{CO}}/dE$ values quoted in the right-hand pair of columns refer.

^d Average ν_{CO} frequency-potential slope for terminal (i.e. atop) CO.

^e Average ν_{CO} frequency-potential slope for bridging CO.

^f Values depend significantly upon electrode potential within chosen range.

TABLE II Stretching Frequency-Electrode Potential Slopes for CO Adlayers at Varying Coverages on Ordered Metal Surfaces in Aqueous 0.1M HClO₄ at 0 V vs. SCE.

Surface	θ_{CO}^a	$d\nu_{\text{CO}}^t/dE^b$ cm ⁻¹ V ⁻¹	$d\nu_{\text{CO}}^b/dE^c$ cm ⁻¹ V ⁻¹
Pt(111) ^d	0.65	30	55
	0.1	45	
Pt(110) ^e	1.0	28	
	0.5	40	
Rh(111) ^{f, g}	0.75	30	47
Rh(100) ^h	0.75	34	37
	0.25		57
Rh(110) ^g	1.0	40	40
	0.65	52	48
Ir(111) ⁱ	0.6	20	
	0.15	50	
Pd(111) _j	0.65	30	
	0.35	45	
Au(110) ^k	-0.1	≈65	
Au(210) ^k	-0.05	≈60	

^a Fractional surface coverage of CO adlayer

^b ν_{CO} frequency-potential slope for terminal (i.e. atop) CO at 0V vs. SCE

^c ν_{CO} frequency-potential slope for bridging CO at 0V vs. SCE

Key to data sources: ^d ref. 19; ^e ref. 21; ^f ref. 23; ^g ref. 25; ^h ref. 24;
ⁱ ref. 28; ^j ref. 29; ^k ref. 30.

Figure Caption

Peak frequency of terminal C-O stretch, ν_{CO}^t , versus electrode potential for saturated ($\theta_{\text{CO}} = 0.75$) CO adlayer on Rh(111) in CO-saturated solvents as indicated: circles, acetonitrile + 0.1M tetrabutylammonium perchlorate; open squares, acetonitrile + 0.1M tetraethylammonium perchlorate (TEAP); open upright triangles, acetonitrile + 0.1M NaClO₄; filled squares, water + 0.1M TEAP; filled upright triangles, water + 0.1M NaClO₄; filled inverted triangles, water + 5mM HClO₄. (From ref. 32).

