Some dielectric solvation effects on the energetics of electrified metal interfaces and related molecular systems

Michael J. Weaver

Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA

Abstract

The sensitivity of the surface potential of metal-vacuum interfaces to the presence of molecular dielectric (solvating) species both with or without free ionic/electronic charge is discussed with the objective of comparing the behavior of such "electrified dielectric" interfaces with analogous metal-solution (i.e. electrochemical) systems. The close connection between "surface-potential" scales based on work function (Φ) and electrode-potential (E) measurements is outlined. The chief factors determining the surface potential are illustrated by means of composition-dependent Φ data for single-crystal metal surfaces modified by thin (1–3 monolayer) films of dipolar molecules along with ionizable species in relation to E values for corresponding in-situ electrochemical interfaces. The former Φ-composition measurements, for vacuum-based electrified dielectric interfaces, demonstrate how even primary solvation (i.e. a single molecular layer) is sufficient to engender substantial and electrochemical-like stabilization of interfacial ionic species. The essential nature of dielectric-induced modifications to electron-transfer energetics at metal-vacuum interfaces are considered, and also related to the observed marked solvation effects on the charging of metalliclike clusters, such as fullerenes. The potential value of such unified treatments of surface potential-charge relationships in vacuum and electrochemical systems is also sketched in more general terms. (Int J Mass Spectrom 182/183 (1999) 403–414) © 1999 Elsevier Science B.V.

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1. Introduction

Electrochemists have long been preoccupied with understanding the roles of solvation in modifying the structure and energetics of metal surfaces, especially with regard to electron transfer and other electrostatic charging processes. Perhaps surprisingly, then, the emergence of a microscopic-level experimental framework for describing and ultimately understanding such condensed-phase interfacial phenomena is of quite recent origin, chiefly within the present decade. A major reason for this upsurge in interest lies in the concerted development of in situ molecular spectroscopic and spatial microscopic methods applicable to metal-solution interfaces [1]. Concurrent with (and indeed stimulated by) these activities, there are increasing opportunities for interconnecting the properties of charged interfacial assemblies in vacuum, gas-phase, and conventional electrochemical environments. One aspect involves the use of ultrahigh vacuum (UHV) surface science tactics to both prepare and characterize electrochemically relevant inter-

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faces, along with the well-established application of UHV surface-transfer methodologies to examine their structure and composition [2].

A most welcome, if as yet only inadequately realized, consequence of such cross fertilization between these historically disconnected branches of interfacial science involves the emergence of a truly unified framework of interpretation and understanding. Thus surface-science studies of, for example, coadsorption of charged and dipolar species at metal-UHV interfaces bring a new dimension to elucidating electrochemical double-layer phenomena. Conversely, molecular structural and kinetic studies pursued at electrochemical interfaces, especially as a function of the applied electrode potential, can yield much information of value also to researchers (including mass spectrometrists) concerned with molecular phenomena at electrified interfaces in vacuum or gaseous environments. It should be noted that free (ionic) charge should commonly be present at metal-vacuum/gaseous interfaces, formed often by dosing ions or ionizable species, even though direct external control of the surface potential is only feasible in electrochemical systems. Such an interplay of experimental and conceptual information across these subdisciplines of interfacial science is very desirable, mutually stimulating, and distinctly overdue.

Furthermore, we believe that there is a more general motivation for pursuing such interrelationships. This is because electrochemical systems constitute versatile examples of a broad-based class of surfaces that might usefully be termed *electrified dielectric interfaces*, where the electronic/ionic charge is screened (and otherwise modified) by coadsorbed dielectric species. While this dielectric screening is usually accomplished by the solvent in electrochemical systems, inherently allied effects can be anticipated with numerous coadsorbates at electrified metal-gas interfaces, for example with substituted hydrocarbons or polar chemisorbates. In particular, coadsorbed dielectric should exert a marked influence on the surface potential of charged interfaces, and consequently can drastically alter the energetics (and dynamics) of electron-transfer processes, such as those involving species incident from the gas phase.

However, such effects at metal-vacuum interfaces are seldom discussed.

In our laboratory, we have a longstanding objective of relating the atomic, molecular, and electronic structure of electrochemical interfaces to their kinetic properties, especially involving electron-transfer and catalytic processes. This interest has recently led us to harness molecular-level information obtained for metal-UHV as well as metal-solution interfaces in order to aid interpretation of the latter, often more complex systems [3]. Among other attributes, the UHV environment offers the opportunity to "synthesize" models of electrochemical interfaces ("double layers") by the controlled stepwise dosing of individual components, including chemisorbates, ions, and solvent onto initially clean metal surfaces. This "UHV electrochemical modeling" approach, pioneered especially by Sass and co-workers in Berlin during the 1980s [4], enables the mutual influence of such different double-layer components on the electrostatic and molecular structural properties of electrified interfaces to be elucidated in unique detail.

In particular, we have been utilizing such UHV-based modeling tactics to explore the effects of surface charging on interfacial solvation, together with the synergetic effects of solvation/charging on chemisorbate vibrational properties [3]. The molecular vibrational data, obtained with infrared reflection-absorption spectroscopy (IRAS), are typically combined with work-function (Φ) measurements as a function of interfacial composition. One important reason for utilizing IRAS is the opportunity to compare directly such UHV-based information with vibrational data obtained with the same technique for related in situ electrochemical interfaces. The latter is providing important information concerning chemisorbate structure and bonding at electrodes [5,6]; such comparisons with UHV-based IRAS data can therefore aid the understanding of charge/solvation effects on chemisorbate properties in the electrochemical systems [5,6]. The Φ measurements, of particular relevance here, yield insight into how the surface potential is determined by the double-layer composition, and also provide the link between UHV-based and electrochemical potential scales, crucial for un-

derstanding the nature of interfacial charging and electron-transfer processes (vide infra) [3].

A primary objective of this overview article is to assess the type of insight into the energetics of electrified dielectric interfaces that can accrue by examining suitably solvated metal surfaces in both UHV-based and electrochemical environments. In addition, the connections between charge-potential relationships for solvated metal surfaces and for molecular systems, especially metallic clusters, are briefly examined. Such considerations may be relevant to charge-transfer processes that can occur in ionic "soft landing" and other experiments involving ion-surface interactions at metal-vacuum interfaces [7].

On a personal note, an indirectly related exploration of metallocene electron-exchange processes in the gas phase was the subject of an earlier study involving us and the Freiser group, spearheaded by Don Phelps and the redoubtable Jim Gord [8]. While constituting our only scientific collaboration, Ben Freiser's natural scientific and research group "management" (and delegating!) skills along with his sense of humor and the sheer enjoyment of life which were all part of Ben's remarkable persona, made this effort (as for our numerous other interactions over the years) notably more stimulating (and fun) for us.

2. Surface potentials in vacuum versus solution phases

An outwardly simple and centrally important concept which has engendered much discussion (and confusion!) is that of "surface potentials." Given its significance to the present discussion, some general comments are in order here. These quantities are commonly evaluated as surface work functions, Φ (eV), and electrode potentials, E (V), for vacuum-based and electrochemical interfaces, respectively. The Φ and E values for a given interface (or a pair of interfaces) are related by [9]

$$E = \Phi/e - E_k \tag{1}$$

where e is the electronic charge and E_k is the so-called "absolute" potential of the reference electrode. (The latter term can also be thought of as the "work function" of the reference electrode, Φ_{ref}, where $\Phi_{ref} = eE_k$.) This simple relationship therefore accounts for the different electron "reference" states, in vacuum or in the metallic phase of the reference electrode, necessarily employed for the Φ and E measurements, respectively, of the surface potential.*

There are at least two complications, however, when utilizing Eq. (1) in practice [10]. First, the Φ/e value for a metal surface covered by a monolayer or more of dielectric material (solvent or other species, such as a chemisorbed thioalkyl film) will contain a contribution from the potential drop at the solvent-vacuum as well as the metal-solvent interfaces, χ_s and ϕ_s^M, respectively. Depending on the film thickness, both χ_s and ϕ_s^M can influence charge-transfer processes at metal-vacuum interfaces, whereas only ϕ_s^M is present at the corresponding electrochemical surface. The magnitude of $|\chi_s|$ may approach several tenths of a volt [9,11,12]. The second, somewhat more insidious, problem is that the estimates of E_k, most commonly for the standard hydrogen electrode (SHE), obtained by various routes are significantly discrepant, values between about 4.4 and 4.8 V being obtained (and often vigorously defended!) by different workers [10]. Unfortunately, there is no clear resolution to this controversy at present, although the use of higher E_k values (say 4.6–4.8 V) appears to be more consistent with spectral and other data for related metal-vacuum and electrochemical interfaces [10,13]. Bearing these numerical uncertainties in mind, such a interrelationship between Φ and E for systems in vacuum and condensed-phase environments enables the sensitivity of the surface potential

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* It is worth mentioning that both Φ and E, as here, are often referred to as "surface potentials." Strictly speaking, the surface potential (ϕ) refers to the electrical potential drop across a single metal interface which, unlike Φ and E, is *not* measurable. (Thus, Φ contains a "bulk chemical" as well as interfacial contribution.) Nevertheless, the term "surface potential" is a convenient moniker for both Φ and E. Variations in Φ/e or E induced on a given metal by changes in surface composition will equal $\Delta\phi$.

to the composition and structure at these two types of metal interfaces to be examined *on a common basis*.

Given that the surface potential describes the energetics of electron transfer across the metal boundary, a knowledge of Φ and E has important ramifications for ionization and related interfacial redox processes in vacuum/gas as well as solution-phase environments. We now present a brief survey of the broad-based dependences of Φ (and E) on the chemical and electrostatic state of metal interfaces, culled partly from recent results in our laboratory, so to show the manner and extent to which the surface potential can be manipulated by chemical modification in such systems.

3. Sensitivity of surface potential to molecular adsorption

Fig. 1 shows experimentally determined surface potentials plotted schematically on a vertical "bar scale" for some selected "well-defined" metal interfaces in UHV and aqueous electrochemical environments as Φ and E values (left- and right-hand columns, respectively), adapted in part from [14]. The E_k value was taken as 4.5 V, hence determining the offset shown between the Φ and E scales from Eq. (1). The systems included in Fig. 1 were chosen so to illustrate several basic points. First, as is well known the work function of a "clean" surface (in UHV) is sensitive to both the metal and the surface crystallographic orientation. The Φ values for Pt(111) and Ag(110), for example, differ by over 1.5 eV, whereas the work functions for (110) planes are typically 0.2–0.3 eV lower than for (111) faces of the same metal. Second, such dissimilarities in Φ are roughly mirrored by offsets in the E values for the same metals in aqueous solution in the *absence* of a net surface charge, the so-called "potential of zero charge," E_{pzc}. Such correlations between Φ and E_{pzc} have been explored in detail especially by Trasatti [9,12,15]. Note, however, that the E_{pzc} values for the Ag(110) and especially the Pt(111) surface [9,16] correspond to markedly (ca 0.7–1 eV) lower Φ values than for the clean metals in UHV. These differences can be approximately ac-
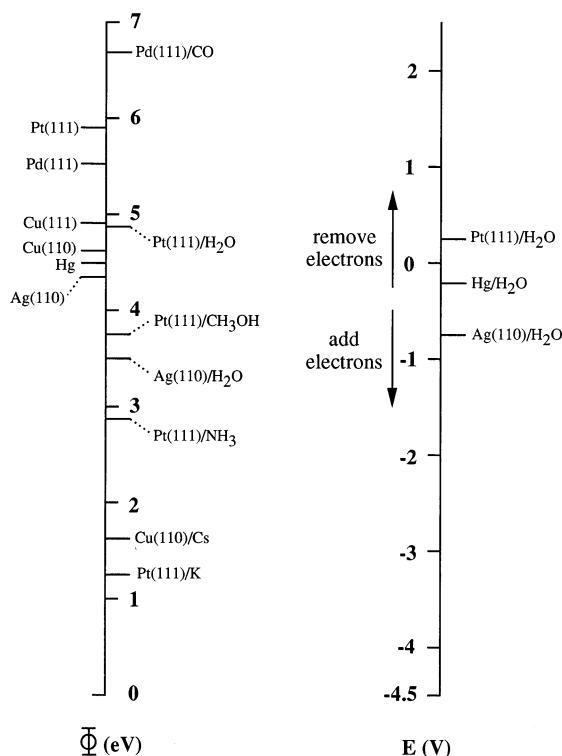

Fig. 1. Schematic "bar scale" representation of surface potentials for selected interfaces in vacuum and aqueous electrochemical environments, adapted in part from [14]. Left- and right-band vertical axes refer to work-function (Φ) and electrode potential (E) values, referenced to vacuum and the standard hydrogen electrode (SHE). The SHE scale is adjusted by 4.5 V so to provide an approximate alignment of the Φ and E values in terms of electron energies. (See text for further details.)

counted for from the similarly large (0.8–1.2 eV) Φ decreases observed upon adsorbing 1–2 monolayers of water in UHV, especially on transition metals [17]. In other words, the surface potentials of the corresponding uncharged *yet solvated* metals in UHV and electrochemical environments are closely similar (Fig. 1).

Interestingly, comparable or even larger alterations in Φ can be engendered by adsorbing other simple dipolar species onto clean metal surfaces. (As for water, such experiments are often undertaken at lower temperatures, $\leq$ 150 K, so to eliminate evaporation [4].) Fig. 1 shows two other examples on Pt(111), for methanol and ammonia [18]. Dosing 2–3 monolayers

of these species is seen to yield substantial Φ decreases, 1.8 and 3 eV, respectively; i.e. binding ammonia to Pt(111) essentially *halves* the very large (6 eV) Φ value for this metal! Although these dramatic effects may be due partly to adsorbate dipole orientation, they probably arise chiefly from alterations in the surface distribution of the metallic electrons, i.e. by changing the substrate $e\phi$ component [18,19]. The other example of "dipolar" surface modification included in Fig. 1 involves a saturated CO layer on Pd(111). In contrast to the dipolar solvents, this chemisorbate *increases* Φ, by about 1 eV. Such effects can be ascribed to surface-adsorbate charge polarization from $d\pi - \pi$ back donation [20], associated with the multifold CO coordination encountered for this (and related) systems [21].

Overall, then, adsorption of these weakly polar or dipolar molecules alone yield Φ variations on a given metal surface (or related surfaces) that span a wide range, over 4 eV. Such changes can therefore be expected to exert profound effects on the chemistry occurring at such modified interfaces, most obviously that involving charge-transfer processes. This is because the surface potential drop $\Delta\phi$ will be located molecularly close to the metal surface, so that the ϕ variations will cause similarly large changes in the energetics of interfacial electron transfer between the metal and nearby ions and molecules, even when imbedded in the dielectric film (vide infra). The presence of such dielectric layers can therefore greatly alter the surface electrostatic environments even in the *absence* of free ionic/electronic charges.

4. Influence of ionic/electronic charges on the surface potential

An essential part of electrochemical systems, and a common (although less celebrated) component of metal-vacuum interfaces, however, involves the additional presence of such free (unipolar) ionic and accompanying excess surface electronic charges. Admittedly, in the absence of coadsorbed dielectric many neutral atoms and small molecules will tend to adsorb on clean metal surfaces as largely uncharged

species i.e. surface ionization will not occur. This is because the work functions of "clean" metal surfaces (typically 4–6 eV) are lower than the ionization potentials (IP) and higher than the electron affinities (EA) of many uncharged gaseous species, so that adsorption in such cases will not yield ionization [22]. (Note that the metal work function can be considered equally as the IP *and* EA value of the surface [23].) The notable exceptions are species having relatively low ionization potentials or high electron affinities, these tending to form interfacial cationic or anionic species, respectively. An instructive example of such "surface ionizing" species are alkali metal atoms, which can be readily dosed onto a clean metal in UHV, forming essentially "soft-landed cations," or more precisely a "local ion-electron surface dipole," nonetheless featuring substantial electron transfer to the metal phase [24]. Such marked charge polarization upon alkali adsorption is signaled commonly by dramatic, $\sim$ 3–5 eV, Φ decreases at relatively low fractional coverages ($\theta \sim$ 0.1–0.3) before dipole-dipole depolarization develops at higher θ values [24]. A pair of examples, for cesium atoms on Cu(110) and potassium on Pt(111), are also included in Fig. 1, where the Φ entries refer to the minimum of the $\Phi - \theta$ curve, reached in both cases at $\theta \approx 0.2$ [14,25,26]. The dramatic electrostatic effect of binding K to Pt(111), yielding a work function (1.2 eV) distinctly lower than the K ionization potential, 4.3 eV, is clearly evident.

However, as might be expected, the presence of interfacial dielectric material produces substantial modifications to these electrostatic effects. This centrally important point is exemplified in Fig. 2, taken from [27], which shows the effects upon the work function of dosing increasing amounts of water onto a Pt(111) surface at 90 K predosed with the K coverages, θ_K, indicated (in fractional monolayers, ML). Note that the work-function changes, $\Delta\Phi$, on the y-axis are referenced to that for clean Pt(111) ($\Phi =$ 5.9 eV), and the water dosages are in "equivalent (close-packed) monolayers," EL (see [27]). (The $\Delta\Phi$ measurements utilized a Kelvin probe.) The (vertical) displacements of curves 1–4 on the y-axis reflect large K-induced Φ decreases (up to 3 eV), propor-
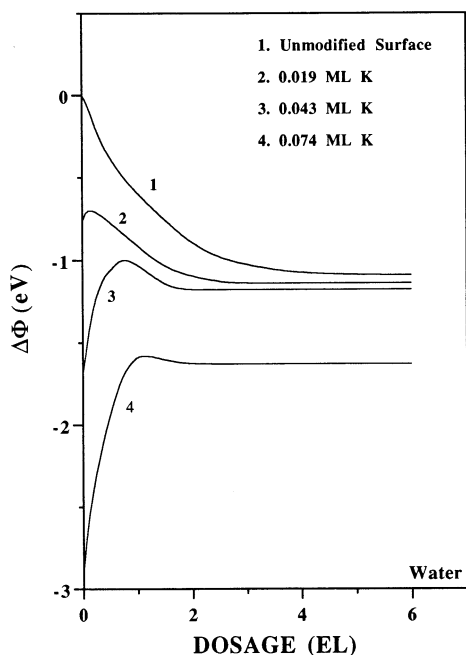
Fig. 2. Work-function ($\Delta\Phi$) changes induced on clean Pt(111) at 90 K in vacuum by initial adsorption of K at coverages as indicated, followed by progressive water dosing. See text and especially [27] for details.
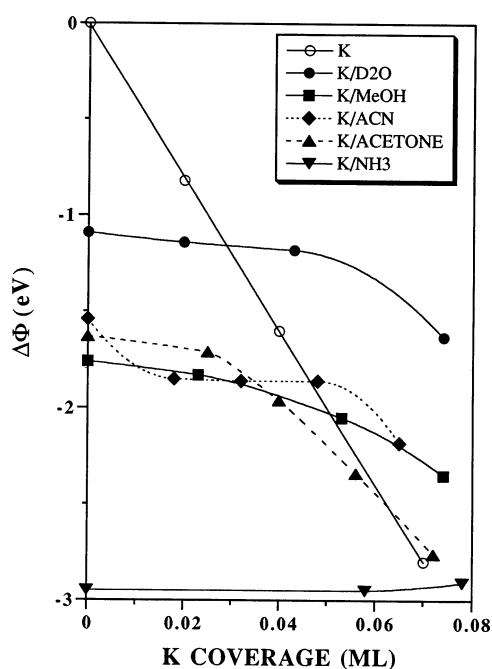

Fig. 3. Work-function changes ($\Delta\Phi$) referenced to the clean surface on Pt(111) at 90 K as a function of the K coverage (monolayers, ML) in the absence (circles) and presence of 2–4 monolayers of various solvents, as indicated (MeOH = methanol, ACN = acetonitrile). See text and especially [27] for details.

tional to θ_K. The progressive addition of $\leq$ 3 EL of water, however, is seen to yield marked alterations to Φ, so that these K-induced work function changes are considerably attenuated. Indeed, the marked monotonic Φ decreases seen upon water addition to clean Pt(111) (curve 1, vide supra) are replaced by large initial Φ *increases* on the K-modified surfaces followed by decreases at larger water dosages ($>$ 1 EL). These latter changes are seen on the basis of IRAS to be associated primarily with solvation of the interfacial K$^+$ species followed by the Pt(111) surface itself [28]. (Note that the anticipated chemical reduction of H$_2$O by K does not occur until higher θ_K, and hence lower Φ, values are reached [26].) In physical terms, the marked Φ increases seen upon K$^+$ interfacial solvation can be understood from the charge-induced water dipole reorientation, or, equivalently, from the dielectric screening of the K$^+$ . . . e^- "image dipole" by nearby water molecules [27,28].

Qualitatively similar behavior is obtained for the hydration of other alkali metal-modified surfaces,

such as Cu(110)/Cs [25,29], as well as Pt(111)/K solvation by several other dipolar species including methanol and ammonia [27]. The latter results are included in Fig. 3 (also taken from ref 27) which is a plot of the Φ changes induced on Pt(111) at 90 K as a function of the K coverage in the presence of $\leq$ 3 monolayers of water, methanol, acetonitrile, acetone, and ammonia, as indicated. These specific layers were chosen on the basis of their differing dielectric constant, solvation and dipolar properties.

Several points significant to the present discussion are evident in Fig. 3. First, all the solvents act to "buffer" the effect of adding K (and hence K$^+$) to the surface, especially at low θ_K ($\leq$ 0.04) the $\Phi - \theta_K$ slopes being 5–10-fold smaller than in the absence of dielectric. As for hydration, this attenuation can be taken as a measure of the degree to which the K$^+$ charge (or K$^+$ . . . e^- "image dipole") is screened by the surrounding adsorbate. Second, and perhaps more

surprisingly, the $\Delta\Phi - \theta_K$ profiles (with the exception of ammonia) are insensitive to the solvent, even though the trace for water is displaced upward due to the smaller Φ decrease engendered by water adsorption on clean Pt(111). This near-uniform $\Delta\Phi - \theta_K$ behavior suggests that the effective "dielectric constant" ϵ_s of the solvating films at low θ_K are within ca twofold of each other (roughly 5–10), and diminish similarly towards higher surface charges. The "bulk-phase" ϵ_s values are considerably larger (15–80) and markedly more solvent sensitive [27]. Interestingly, this behavior is closely reminiscent of the relatively solvent-insensitive charge-potential (i.e. capacitance) behavior of in situ electrochemical interfaces [27]. It is accounted for by a degree of "dielectric saturation" in the presence of the huge electrostatic fields ($\geq 10^6$ V cm^{-1}) generated at such charged surfaces, acting to "pin" the solvent dipole orientation and hence diminish the otherwise-dominant component of ϵ_s arising from orientational polarization. Smaller effective ϵ_s values (say 5–10), reflecting predominantly vibrational and electronic, rather than dipole reorientational, contributions are therefore obtained. An important consequence in the present context is that even relatively "nonpolar" molecular dielectrics such as hydrocarbons are anticipated to yield roughly comparable ϵ_s values, say ~ 5, in the high-field interfacial environment, so that their effective "dielectric screening" properties should not differ greatly from those for more polar molecules.

Indeed, the presence of coadsorbed CO also exerts a qualitatively similar yet milder "dielectric screening" effect compared to the dipolar solvents, the $\Delta\Phi - \theta_K$ slope being ca twofold smaller than for K adsorption on clean Pt(111) [27]. The smaller extent of charge screening by the chemisorbate compared to the multilayer solvents may be ascribed partly to the inability of the C–O dipole to reorient markedly in the vicinity of the K$^+$ charges, along with the absence of a second "solvating" layer. The behavior of the K$^+$-ammonia coadsorption system (inverted triangles, Fig. 3) is also noteworthy, in that the presence of K yields *virtually no* additional Φ changes i.e. the work function is *entirely* "buffered" towards charge addition in the presence of the ammonia film. This finding

is most likely due to the formation of solvated electrons, so that K ionization is not accompanied by interfacial electron transfer. Equivalently, the behavior can be considered to reflect "redox pinning" at the measured work function, ca 3 eV; this point corresponds roughly to the equilibrium potential anticipated for the formation of solvated electrons by transfer from the metal surface [27,30].

It is important to recognize that only relatively small quantities of such dielectric species are typically required to alter the electrostatic properties of interfacial ions to that corresponding to the "fully solvated" state. Thus the water-induced Φ changes for the Pt(111)/K system (Fig. 2) are largely complete by two monolayers or so, and similar results are evident with other systems [27]. Furthermore, various IRAS experiments provide microscopic-level evidence that the solvent-induced dielectric screening is provided chiefly by the first ("primary") solvation of interfacial ions and molecules [3,28,31]. For example, the C–O vibrational frequencies (ν_{CO}) on Pt(111) are affected in relatively complex fashion by coadsorbed K$^+$ alone, reflecting the presence of both "specific short-range" and "longer-range" ion dipole interactions [31–33]. However, addition of water or other dielectric sufficient *only* to provide *primary* ("first layer") solvation of the ionic charge essentially eliminates the presence of the ν_{CO} fingerprints associated with "specific" K$^+$–CO interactions [3,28,31]. This is consistent with the anticipated preferential solvation of the cations. Subsequent addition of sufficient dielectric to provide primary (i.e. monolayer) solvation also of the chemisorbate essentially completes the marked overall changes upon the ν_{CO} properties wrought by the ion/dielectric matrix, yielding vibrational behavior essentially identical to that observed for the corresponding metal-solution interfaces [31]. Consequently, while electrochemical systems necessarily feature huge solvent excesses, the essential chemical and electrostatic changes brought about at initially "dry" metal interfaces require the addition of only small quantities of dielectric molecules.

The presence of "short-range" charge-adsorbate interactions also recalls the issue of "local" versus "average" work functions (and hence surface poten-

tials). While most Φ measurements actually evaluate "macroscopic" or spatially averaged work functions, one anticipates the presence of substantial "local" variations in Φ parallel as well as normal to the metal surface, especially in the vicinity of immobile ions, and at surface steps or defects. The presence of moderate or even large microscopic-level variations in Φ across metal surfaces has been demonstrated experimentally for some UHV-based systems [34]. The presence of interfacial solvent is anticipated to diminish such Φ variations through dielectric screening. Nevertheless, the distinction between such "local" and "average" surface potentials should be borne in mind; the former may well be the more relevant quantity concerning interfacial electron-transfer process, especially involving charged species.

The inherently close relationship between "solvated ion" metal-vacuum and electrochemical interfaces is also worthy of more general clarification. In the former type of system, the interfacial ionic charge is either created by ionization of atoms/molecules, such as K, impinging on the surface, or by electron flow to or from a (grounded) metal upon dosing gaseous ionic species. In both cases, the surface potential is altered *in response to* a change in interfacial chemical/ electrostatic composition. At electrochemical interfaces, the opposite is usually the case in that externally applied alterations in the electrode potential, or electrode charge via controlled current flow, act to alter the surface ionic composition by migration/ diffusion of electrolyte ions (such as K^+). Nonetheless, in principle the structure and composition of such electrified dielectric interfaces in vacuum and solution-phase environments can be the same, despite these different mechanisms for their formation.

While we are chiefly concerned here with "ultra-thin" dielectric films, say ≤ 3 monolayers, emphasized in our UHV-based studies because of their close relationship to in situ electrochemical systems, it is also appropriate to mention the possibility of depositing ions (or ionizable species) on (and/or within) thicker films. Such dielectrically interesting materials can readily be grown in uniform fashion even for small-molecule systems (e.g. water) by low-temperature dosing. Indeed, dosing ionizable species such as

K *onto* water films (rather than in the reverse order) at low temperatures yields decidedly larger Φ responses due to the spatial charge separation within the dielectric "ice" layer [27]. Cowin and co-workers have recently pursued ion "soft-landing" experiments on very thick molecular films (up to 10^4 layers) over a range of cryogenic temperatures, and observe intriguing dynamic dielectric responses as monitored by Φ measurements [7b].

5. General consequences for interfacial ionization and electron transfer

It is evident from the foregoing that the presence of interfacial dielectric can markedly attenuate the surface-potential responses to the addition of ions. This observation might be construed as implying that the dielectric diminishes the surface energetic consequences of interfacial ionization. It is also important, however, to recognize that the presence of dielectric material also markedly *stabilizes* ionic states, so that interfacial ionization (either to form cations or anions) will be much more prevalent under these conditions. Furthermore, such marked stabilization of ionic species brought about by such "interfacial solvation" will strongly favor the occurrence of oxidative or reductive electron transfer to yield cations or anions, respectively, for molecules impinging from the gas phase when these species become at least partly solvated at the interface. In addition, alterations in surface potential engendered by surface charging brought about, for example, by ion dosing may well trigger redox chemistry involving the dielectric species as well as other coadsorbates. A simple example, mentioned above, concerns the reduction of adsorbed water by dosing ionizable K atoms [26,29]. The onset of this process at metal-gas interfaces can be thought of as being akin to electrochemical reduction triggered by suitable decreases in the surface potential, again brought about by ion charging (or to electrochemists, "double-layer" charging). More generally, there are a variety of chemical (including redox) processes known to be triggered at metal-vacuum/gas interfaces by ion dosing [35,36]. Indeed, one might

anticipate that at least some of this chemistry could be rationalized in terms of surface composition-dependent surface potentials.

To summarize, then, in the absence of dielectric one can envisage altering the work function substantially, say by 2–3 eV, by binding "bare" highly electropositive or electronegative species (e.g. potassium, oxygen atoms). These could then engender oxidative or reductive electron transfer for incoming gaseous species providing that Φ was lowered or raised to a point compatible with the ionization potential or electron affinity of the latter. However, quite apart from the large changes in Φ (typically several eV) necessary to achieve such redox chemistry for unsolvated species, it is likely that the product species would react with the ionic surface modifier, leading to "electron-transfer annihilation" and removal of the charged species. On the other hand, the presence of interfacial "solvation" leads not only to the stabilization of the "double-layer" charge (such as K^+) responsible in part for the Φ alterations, but also acts to favor charged states formed from impinging gas-phase species by interfacial electron transfer. The latter effect enhances markedly the types and extent of analyte ionization (oxidation or reduction) that can occur within a given Φ span, or, equivalently, range of surface potentials (i.e. electron energies). In addition, the dielectric will act to stabilize such cation/anion (and related redox-active) species from undergoing "self-annihilation" reactions.

This scenario, of course, is familiar to electrochemists concerned with electron-transfer chemistry. Thus the large majority of redox processes encountered in solution-phase chemistry exhibit "standard (or "formal") potentials," E^f, between, say $-$ 1.5 and 1.5 V vs SHE i.e. about 3 to 6 eV on the "vacuum" reference scale (cf. Fig. 1). This range of oxidation/reduction potentials is much smaller than that encountered for the corresponding processes for unsolvated species in vacuum (i.e. IP and EA values). As a simple contemporary example of the stabilization of ionic states rendered by such solvation, consider buckminsterfullerene (C_{60}). Even though negative ionization of this relatively large molecule yields somewhat delocalized electronic states [37], the first

and second (gas-phase) electron affinities are small and well separated: 2.65 and ca. 0 eV, respectively [38]. In contrast, the first two negative ionizations (i.e. reductions) of C_{60} even in nonpolar solvent media occur at markedly higher potentials, about 4.0 and 3.5 eV vs. vacuum. (These values were deduced from electrochemical data in [39] by presuming that E_k for the ferrocenium-ferrocene couple is 5.0 V [23]. Indeed, even the formation of C_{60}^{5-} can be observed in nonaqueous media, at ca. 2.0 eV versus vacuum [39]. Such marked stabilization of the multicharged anion states in nonpolar media is consistent with an effective ϵ_s value of about 6 [23].

More "specific chemical" ion-solvent interactions, of course, are also commonly important when considering the stabilization of smaller ionic species, especially systems where protonation or other donor-acceptor binding modes are present in addition to coulombic forces. Nevertheless, the relationships between the energetics of gas-phase and solvated redox couples (including partly solvated gaseous species) have been successfully explored along these lines for a variety of systems, for example organic radical anions [40]. Such links between the charging energetics of chemical systems, of interest to both mass spectroscopists and electrochemists, are therefore relatively well established, at least on a general conceptual level.

6. Dielectric charging of molecular clusters

The fullerene system mentioned above provides but one celebrated example of a diverse class of metallic-like molecular clusters that can readily undergo ionization in both isolated gas phase and solvated environments. In the context of the present discussion concerned with the interplay between the charging energetics of metal surfaces and molecular systems, it is useful to consider the inherently close connection between the electrostatics, specifically charge-potential relationships, describing planar metal surfaces and metallic clusters, and their modification by surrounding dielectric. Such a comparison is also interesting since the latter systems represent an

intermediate state of (ionizable) matter between bulk metals and small molecules. This issue has been examined in detail elsewhere [23], so that we briefly present here only some salient points.

Consider an uncharged (spherical) metallic cluster, MC, of radius r which can be reduced via successive electron transfers to form a series of anionic species, MC^n (n is negative):

$$MC^n + e^- \rightleftarrows MC^{n-1} \qquad (2)$$

Each step occurs at a standard (or formal) potential E_n^f. On the basis of the simple Born model, the E_n^f values for such successive electron transfer in either vacuum or a continuum dielectric medium (ϵ_s) are given by [23].

$$E_n^f = E(r \to \infty) + (n - 0.5)e^2/\epsilon_s r \qquad (3)$$

where $E(r \to \infty)$ is the corresponding potential that would be obtained for a cluster having the same chemical properties but an infinitely large radius (i.e. a planar surface). Essentially the same relationship applies to oxidations as well as reductions (i.e. formation of positive- rather than negative-charged clusters), by altering the charge sign. It should be noted that Eq. (3) neglects the presence of "quantum electronic" contributions to the energy difference between successive electron transfers, such as electron spin pairing and HOMO-LUMO separations, although these can be included as a n-dependent (but ϵ_s-independent) term [23].

The usefulness of Eq. (3) is that it links in a simple way the charging energetics of analogous metallic clusters and metal surfaces in the presence as well as absence of stabilizing dielectric. This point is illustrated in Fig. 4, which shows schematically the relation between E_n^f and $(\epsilon_s r)^{-1}$ for various cluster charges, n, according to Eq. (3). The separation in potential (i.e. electron energy) between successive electron transfers, ΔE, for a given metallic cluster radius (r) and dielectric solvating medium (ϵ_s) corresponds to the vertical displacement between the lines shown. In particular, ΔE diminishes linearly with increasing ϵ_s for a given r, so that the energetic ability to form successively more highly ionized states
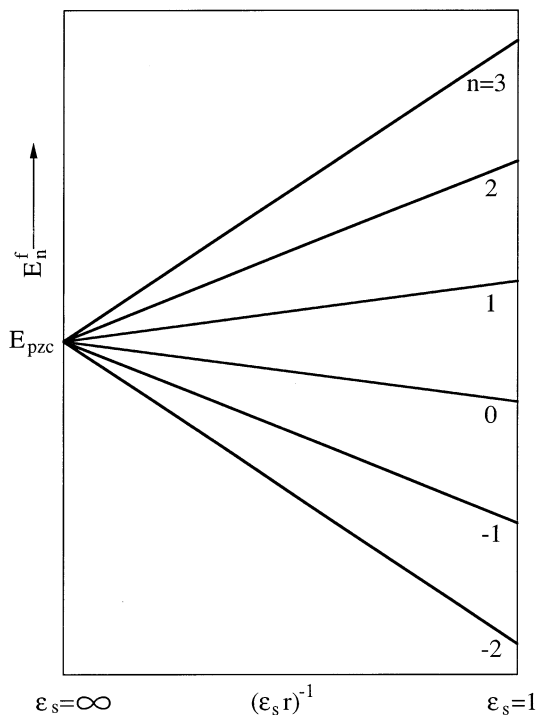

Fig. 4. Schematic dependence of formal potentials (E_n^f) for sequential electron addition to a metal cluster MC^n [Eq. (2)] as a function of $(\epsilon_s r)^{-1}$ (where r is the cluster radius, and ϵ_s is the medium dielectric constant), according to Eq. (3). See text and Ref. 23 for details.

will be markedly enhanced in the presence of solvating dielectric. Indeed, the application of Eq. (3) (and allied relationships) to experimental data for the C_{60}^n system, as well as to other metallic clusters, yields $\epsilon_s \sim 5$–10 in a range of common solvents i.e. the ΔE values are diminished typically by 5–10-fold compared to dielectric-free vacuum [23] (vide supra). The analysis can also be extended in some cases to "small-molecule" solutes, such as metallocenes, that can be ionized to form cation or anion species, with roughly concordant results [23].

This high degree of dielectric stabilization of the *molecular* ionic states is comparable to that noted above for the ionic/electronic charging of metallic *surfaces*. Indeed, a close formal correspondence between the charging of such small clusters and analogous planar surfaces can be established through the concept of "molecular capacitance," C_m, which refers

to the relation between the "surface" charge density, σ, and the successive electrode potentials, E_n^f, observed for the former system. Intriguingly, the C_m values ($= \Delta\sigma/\Delta E_n^f$) obtained specifically for fullerene and high-nuclearity platinum carbonyl clusters in this fashion, ca. 5–15 μF cm^{-2}, are numerically similar to "double-layer" capacitances (surface charge density-potential slopes) obtained for analogous electrified dielectric interfaces in both vacuum and conventional electrochemical environments [23,27]. These findings further emphasize the intrinsically close relationships between dielectric stabilization effects encountered for charged systems in different interfacial and molecular environments.

7. Concluding remarks

The foregoing discussion considers, albeit at a fairly qualitative and general level, how the electronic energetic properties of metal surfaces in vacuum/gas- and solution-phase systems can be described and treated in a common fashion. While the general notions utilized are straightforward, we suspect that the descriptions of these different types of metal interfaces usually found in the literature are more disparate than befits their inherently related physico-chemical properties. The close connections also evident between the dielectric stabilization afforded to charged interfaces and molecular clusters provides a further incentive to pursue such unified treatments.

In particular, it is felt that the role of the surface potential in driving redox chemical processes at dielectrically modified metal-vacuum interfaces in a similar fashion to electrochemical systems is yet to be fully appreciated, or at least commonly considered, by researchers concerned with the former type of systems. One obvious problem is that the work functions of metal-gas interfaces are often unknown. In this connection, we have recently estimated the surface potentials of some Pt-group metal-ambient pressure gas interfaces in relation to electrochemical systems by means of electrostatic Stark shifts on measured adsorbate vibrational frequencies [41]. The unexpectedly low (ca. 4.5 eV) work functions so deduced for these interfaces were surmised to be due to "redox-pinning" by impinging gas-phase species. Such notions are admittedly only suggestive or even speculative in the absence of quantitative surface analysis and physical characterization. Nonetheless, within the general framework of surface electrostatics outlined herein, they may prove insightful and ultimately beneficial in encouraging a more unified understanding of interfacial chemical phenomena.

References

[1] (a) M.J. Weaver, J. Phys. Chem. 100 (1996) 13079; (b) M.J. Weaver, X. Gao, Ann. Phys. Chem. 44 (1993) 459.
[2] A.T. Hubbard, Chem. Rev. 88 (1988) 633.
[3] I. Villegas, M.J. Weaver, J. Phys. Chem. B 101 (1997) 10166.
[4] For example, J.K. Sass, K. Bange, ACS Symp. Ser. 378 (1988) 54.
[5] S-C. Chang, M.J. Weaver, J. Phys. Chem. 95 (1991) 5391.
[6] M.J. Weaver, S. Zou, in Spectroscopy for Surface Science, Advances in Spectroscopy, Vol. 26, R.J.H. Clark, R.E. Hester (Eds.), Wiley, Chichester, UK, 1998, Chap. 5.
[7] (a) H. Luo, S.A. Miller, R.G. Cooks, S.J. Pachuta, Int. J. Mass Spect. Ion Processes 174 (1998) 193; (b) A.A. Tsekouras, M.J. Iedema, G.B. Ellison, J.P. Cowen, *ibid*. 174 (1998) 219.
[8] D.K. Phelps, J.R. Gord, B.S. Freiser, M.J. Weaver, J. Phys. Chem. 95 (1991) 4338.
[9] S. Trasatti, Electrochim. Acta 36 (1991) 1659, and previous references therein.
[10] For a particularly insightful discussion, see F.T. Wagner, in Structure of Electrified Interfaces, J. Lipkowski, P.N. Ross (Eds.), VCH, New York, 1993, Chap. 9.
[11] Z. Samec, B.W. Johnson, K. Doblhofer, Surf. Sci. 264 (1992) 440.
[12] S. Trasatti, Electrochim. Acta 32 (1987) 843.
[13] (a) I. Villegas, R. Gómez, M.J. Weaver, J. Phys. Chem. 99 (1995) 14832. (b) M.S. Weaver, S. Zou, C. Tang, submitted.
[14] J.K. Sass, D. Lackey, J. Schott, B. Straehler, Surf. Sci. 247 (1991) 239.
[15] S. Trasatti, in Advances in Electrochemistry and Electrochemical Engineering, Vol. 10, H. Gerischer, C.W. Tobias (Eds.) Wiley, New York, 1977, p. 213.
[16] M.J. Weaver, Langmuir 14 (1998) 3932.
[17] P.A. Thiel, T.E. Madey, Surf. Sci. Reports 7 (1987) 211.
[18] N. Kizhakevariam, I. Villegas, M.J. Weaver, Surf. Sci. 336 (1995) 37.

[19] (a) R.C. Baetzold, J. Phys. Chem. 87 (1983) 3858; (b) R.C. Baetzold, G. Apai, E. Stustorovich, Appl. Surf. Sci. 19 (1984) 135.

[20] B.E. Nieuwenhuys, Surf. Sci. 105 (1981) 505.

[21] (a) J. Szanyi, W.K. Kuhn, D.W. Goodman, J. Vac. Sci. Technol. A 11 (1993) 1969; (b) M. Tüshaus, W. Berndt, H. Conrad, A.M. Bradshaw, B. Persson, Appl. Phys. A 51 (1990) 91.

[22] R.I. Masel, Principles of Adsorption and Reaction on Solid Surfaces, Wiley, New York, 1996, p. 147–149.

[23] M.J. Weaver, X. Gao, J. Phys. Chem. 97 (1993) 332.

[24] (a) T. Aruga, Y. Murata, Prog. Surf. Sci. 31 (1989) 61; (b) K. Wandelt, in Physics and Chemistry of Alkali Metal Adsorption, H.P. Bonzel, A.M. Bradshaw, G. Ertl (Eds.), Elsevier, Amsterdam, 1989, p. 25.

[25] D. Lackey, J. Schott, B. Straehler, J.K. Sass, J. Chem. Phys. 91 (1989) 1365.

[26] H.P. Bonzel, G. Pirug, C. Ritke, Langmuir 7 (1991) 3006.

[27] M.J. Weaver, I. Villegas, Langmuir 13 (1997) 6836.

[28] N. Kizhakevariam, I. Villegas, M.J. Weaver, J. Phys. Chem. 99 (1995) 7677.

[29] G. Pirug, H.P. Bonzel, in [10], Chap. 5.

[30] I. Villegas, M.J. Weaver, Surf. Sci. 367 (1996) 162.

[31] I. Villegas, M.J. Weaver, J. Phys. Chem. B 101 (1997) 5842.

[32] G. Pirug, H.P. Bonzel, Surf. Sci. 199 (1998) 371.

[33] M. Tüshaus, P. Gardner, A.M. Bradshaw, Surf. Sci. 286 (1993) 212.

[34] K. Wandelt, in Electrified Interfaces in Physics, Chemistry, and Biology, R. Guidelli (Ed.), Kluwer, Dordrecht, 1992, p. 65.

[35] For example: B.H. Cooper, E.R. Behringer, in Low Energy Ion-Surface Interactions, J.W. Rabalais (Ed.), Wiley, Chichester, UK, 1994, p. 301.

[36] R.G. Cooks, T. Ast, T. Pradeep, V. Wysocki, Acc. Chem. Res. 27 (1994) 316.

[37] (a) S. Chakravarty, M.P. Gelfand, S. Kivelson, Science 254 (1991) 970; (b) V. de Coulon, J.L. Martins, F. Reuse, Phys. Rev. B 45 (1992) 13671.

[38] L-S. Wang, J. Conceicao, C. Jin, R.E. Smalley, Chem. Phys. Lett. 182 (1991) 5; (b) R.L. Hettich, R.N. Compton, R.H. Ritchie, Phys. Rev. Lett. 67 (1991) 1242.

[39] D. Dubois, G. Moninot, W. Kutner, M.T. Jones, K.M. Kadish, J. Phys. Chem. 96 (1992) 7137.

[40] (a) P. Kebarle, S. Chowdhury, Chem. Rev. 87 (1987) 513; (b) H. Shalev, D.H. Evans, J. Am. Chem. Soc. 111 (1989) 2667.

[41] M.J. Weaver, C.T. Williams, S. Zou, H. Chan, C.G. Takoudis, Catalysis Lett. 57 (1998) 181.