Surface potentials of metal–gas interfaces compared with analogous electrochemical systems as probed by adsorbate vibrational frequencies

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Received 15 December 1997; accepted 3 April 1998

The dependence of adsorbate vibrational frequencies on the surface potential, ϕ ("Stark-tuning" effect), observed in electrochemical systems is exploited for the same metal surfaces in contact with ambient-pressure gases so to estimate ϕ values in the latter environment. Saturated CO adlayers on palladium and platinum films are examined along these lines by using surface-enhanced Raman spectroscopy (SERS) to obtain frequencies for both the C–O (ν_{CO}) and metal–carbon stretching (ν_{M-CO}) vibrations in CO-containing aqueous electrochemical and gaseous environments. The effective gas-phase surface potentials extracted by matching the vibrational frequencies with the corresponding potential-dependent electrochemical spectra are substantially (ca. 1–1.5 V) lower than the work functions for such interfaces under "clean" (ultrahigh vacuum) conditions. These disparities are ascribed to the occurrence of electrochemical-like redox half-reactions in the ambient-pressure gas-phase environment, leading to surface charging, and, hence, marked alterations in the surface potential as controlled by potential-dependent redox kinetics. The possible implications of these and related findings to ambient-pressure adsorption and catalysis are discussed.

Keywords: chemisorption, catalysis, surface electronic phenomena, adsorbate vibrations, Raman scattering, work functions, solid–liquid interfaces

1. Introduction

Electrochemists have long recognized the exquisite sensitivity to the surface potential drop displayed by adsorption and reaction chemistry at metal–solution interfaces. This dependence is, of course, unsurprising itself, since the interfacial potential can readily be varied continuously by externally controlled alterations in the electrode potential, E. Substantial (10^7–10^8 V cm^{-1}) electrostatic fields can be developed as a consequence of the buildup of free charge and oriented solvent (or adsorbate) dipoles at the metal surface. The situation, however, is quite different to that commonly perceived for metal–gas (or –vacuum) interfaces. Although "surface potentials" (versus vacuum) are also definable at such interfaces via the work function, Φ, this quantity has tended to receive rather less attention in the heterogeneous chemistry literature concerned with gas-phase chemisorption and catalysis. While an obvious reason is undoubtedly the difficulty in controlling Φ externally, in comparison with the applied electrode potential, some electrochemists might react to this situation with surprise.

One of us has recently been examining in some detail the nature of "model electrochemical interfaces" in ultrahigh vacuum (UHV), formed by dosing chemisorbates, solvents, and ionizable species, in part by combined infrared spectroscopic and work-function measurements (for example, see [1–6]). One facet of these studies has been the demonstration that the vibrational frequencies (ν) of chemisorbed molecules, specifically CO and NO, are dependent upon the surface potential (ϕ) in a near-identical fashion for analogous UHV and electrochemical interfaces, once the offset between the vacuum and reference electrode potential scales is taken into account [1–4,6]. Such ν–ϕ dependencies, the so-called adsorbate "Stark-tuning" effect, are well known (for an insightful overview, see [7]) and can arise from chemisorbate–surface charge sharing as well as from a classical Stark effect (as in the gas phase) upon the bond force constants due to variations in the local electrostatic field [7,8]. Significantly, the vibrational frequency–potential dependencies for a given metal–chemisorbate system appear to be insensitive to the chemical nature of the field-inducing dipoles and ionic charges, at least if the latter are solvated so to suppress specific short-range chemisorbate–ion interactions [6]. Consequently, then one has at hand a straightforward, albeit perhaps rough, means of estimating surface potentials (or, equivalently, work functions) for metal/chemisorbate–gas interfaces by comparing the vibrational frequencies of suitable probe chemisorbates with ν–ϕ data obtained for the same adsorbate in electrochemical environments.

One might question the need for such a strategy with surfaces in UHV given the ease of work-function mea-

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surements and the ready control of the surface composition under such circumstances. While this is unassailably true, a rather different situation pertains for metal–ambient-pressure and other interfaces that are pertinent to "real-world" catalysis. For these systems, work-function measurements are less straightforward (indeed are seldom pursued), and yet the presence of adsorbed species such as oxides, volatile liquids, and diverse impurities might be anticipated to alter the interfacial electrostatic environment, and possibly even the surface chemistry, in a significant fashion.

Such issues have indeed recently been of interest to us in connection with a research program aimed at utilizing surface-enhanced Raman scattering (SERS) as a sensitive vibrational probe of adsorbates on transition-metal surfaces in ambient-pressure gas-phase reactors (for example, [9–13]). (The SERS probe is made applicable to transition metals by electrodeposition as ultrathin films on gold.) This approach enables us to monitor the vibrational properties of adsorbates over wide frequency ranges under equilibrium, steady-state, or transient reactor conditions [9–13]. Earlier and also concurrently, the Weaver group has scrutinized in detail the potential-dependent SER spectra of related electrochemical interfaces (for example, see [14–17]), thereby expediting the possible application of Stark-tuning effects to explore the behavior of the less well-understood metal–gas interfaces.

The present communication describes experimental findings along those lines, with the specific aims of deducing the effective surface potentials of representative metal–gas interfaces and examining possible chemical implications. The results demonstrate how the chemisorbate and reaction chemistry of some metal–ambient-pressure systems can be rationalized in markedly unconventional, yet possibly profound, electrochemical-like terms.

2. Experimental

Most details of the arrangements for electrochemical and gas-phase SERS and associated experimentation are given in [18] and [9–13], respectively. The Raman excitation was from a Spectra-Physics Stabilite 6W Kr^+ laser operated at 647.1 nm, collected into a SPEX Triplemate spectrometer equipped with a Photometrics PM512 CCD detector. The same SERS-active transition-metal surfaces were used for experiments in both gas-phase and electrochemical environments (*vide infra*). Briefly, these entailed roughening a 4 mm diameter gold disk (sheathed in Teflon) by electrochemical oxidation–reduction cycles, as detailed in [19]. Platinum films were formed by transferral to an aqueous solution of 4 mM H_2PtCl_6 in 0.7 M Na_2HPO_4 and passing 0.05 mA cathodic current for 40 s. Palladium films were deposited from 5 mM $PdCl_2$ in 1 M $HClO_4$ by using 0.02 mA for 10 s. These procedures yield essentially uniform pinhole-free films several monolayers thick, with excellent electrochemical and SERS characteristics [20]. Rhodium films were prepared as outlined in [15]. After transition-metal deposition, the surfaces were rinsed with water and transferred to 0.1 M $HClO_4$, holding the potential at -0.2 V versus SCE for ca. 5 s to remove residual adsorbed chloride, before rinsing again and transferring rapidly to the desired environment. Most experiments utilized 99.99% CO from an aluminum cylinder (Matteson), with doubly distilled perchloric acid, and ultrapure water from a Millipore system. All measurements were made at room temperature, $23 \pm 1\,^\circ\mathrm{C}$. Measured electrode potentials are quoted here versus the saturated calomel electrode (SCE). Note that this reference electrode has a potential that is about 0.25 V higher (more positive) than the normal hydrogen electrode (NHE) often used for comparisons between electrochemical and surface–vacuum systems (*vide infra*).

3. Results and discussion

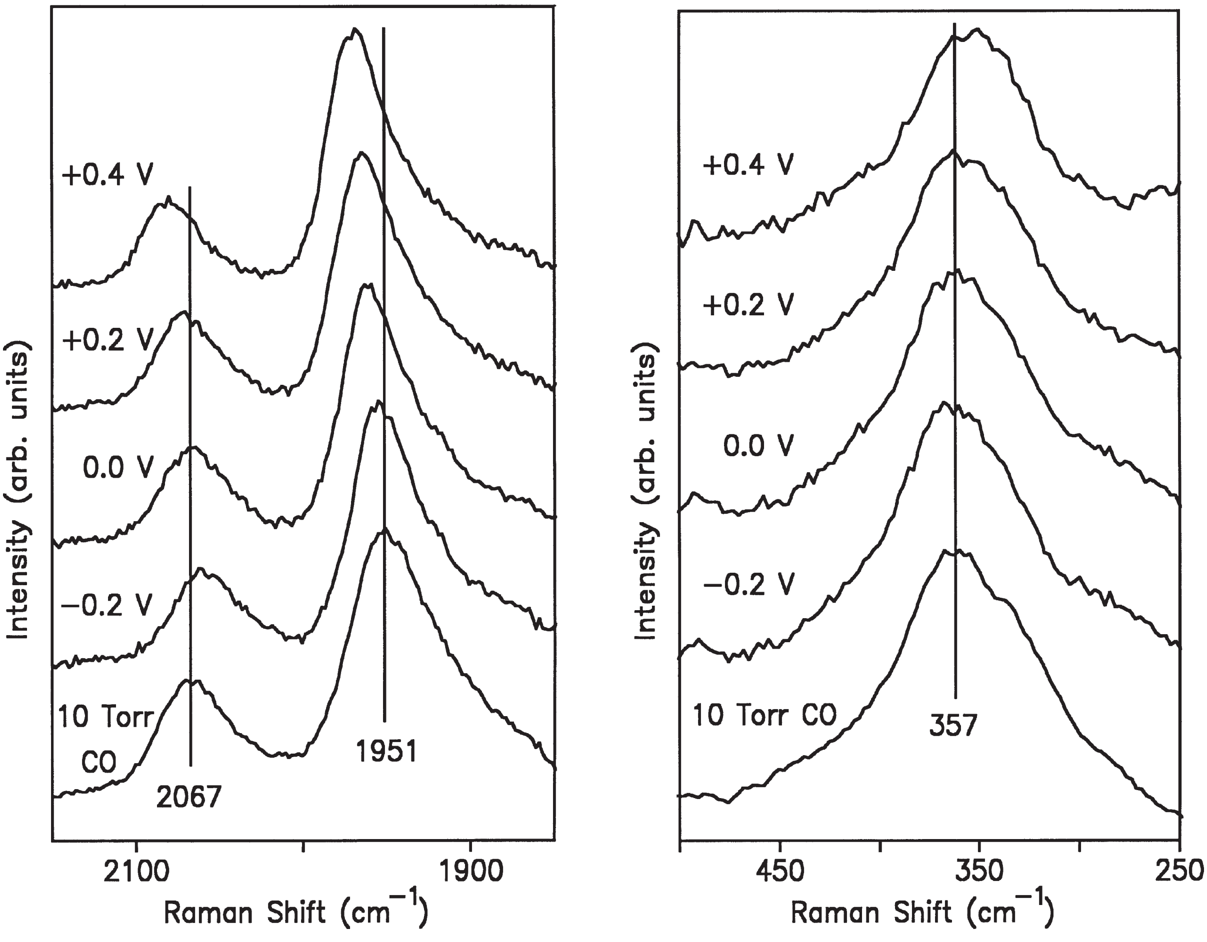
3.1. Gas-phase versus electrochemical surface potentials

As already mentioned, the basic experimental tactic pursued here entails comparing the potential-dependent vibrational frequencies for a given surface–chemisorbate system obtained in an electrochemical cell, i.e., displaying field-induced Stark shifts, with a spectrum for a corresponding gas-phase metal–chemisorbate interface, and matching the frequencies (along with bandshapes, etc.) so to estimate the surface potential for the latter system.

It is necessary, however, to comment first on the "surface-potential" scales of concern here. We have already, quite loosely, referred to electrode potentials (E), surface potentials (ϕ), and work functions (Φ). In actuality, however, only the first and third absolute quantities can be measured. Since ϕ also contains (unknown) bulk-phase metal contributions, only relative values ($\Delta\phi$) can strictly speaking be evaluated [21]. Nonetheless, for convenience, we can define (formally) $\phi = \Phi/e$, where e is the electronic charge. We will therefore undertake the analysis here in terms of E and Φ, yet bearing in mind that a "surface potential", ϕ, can loosely (yet usefully) be taken as Φ/e. Following Trasatti [22,23], one can relate the electrode potential, E, of an electrochemical interface with the work function, Φ, of the same system (i.e., on the vacuum scale) by

$$E = \Phi/e - E_{\mathrm{k}}, \tag{1}$$

where E_{k} is the so-called "absolute potential" of the reference electrode employed for the electrode-potential measurements, referring to an electron transferred from the metal phase of the reference electrode into vacuum. Since equation (1) is required to interrelate the electrochemical and vacuum (or gas-phase) surface-potential scales, E_{k} has been the source of considerable discussion (and some controversy) [24–26]. For the aqueous normal hydrogen electrode (NHE), two values, around 4.45 and 4.8 V, have been



(A) (B)

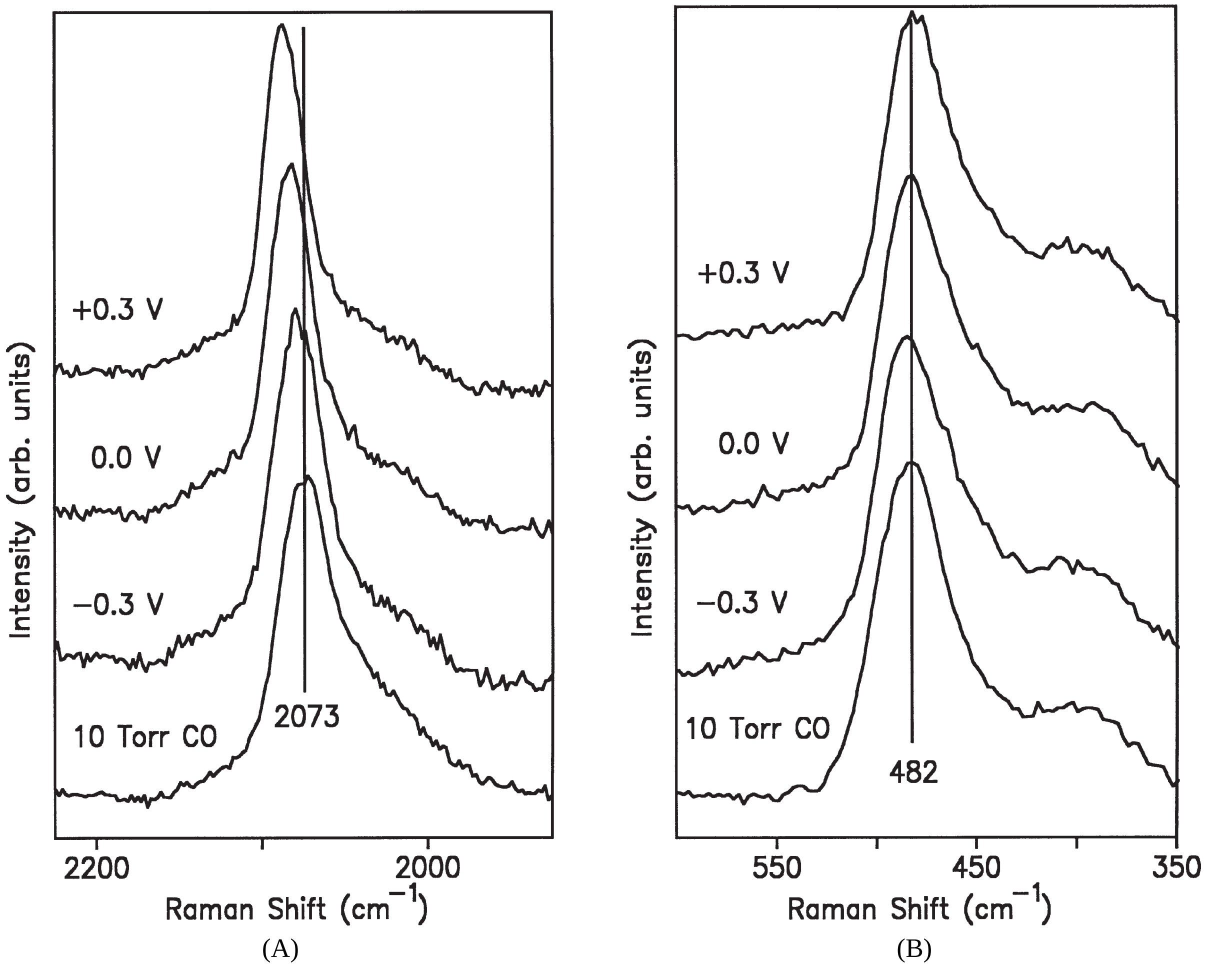
Figure 1. Set of electrochemical SER spectra for CO-saturated adlayer on Pd film in CO-sparged aqueous 0.1 M $HClO_4$ at electrode potentials, indicated in comparison with corresponding spectrum (bottom) obtained for CO adsorbed from the gas phase. (A) C–O stretching (ν_{CO}) region; (B) metal–CO stretching (ν_{M-CO}) region. Vertical lines denote peak frequency of vibrational bands obtained in gas phase. Laser power incident on the surface was 20–30 mW.

deduced (and defended!) [24,25]. It will suffice here, however, merely to note that the latter estimate is (for various reasons [4]) probably more suitable for the purposes of intercomparing electrochemical and vacuum-based interfaces by means of Stark tuning [1,4,6]. Converting this value to the SCE reference scale yields an E_k value of ca. 5.0 V. That is, a measured electrode potential of, say, 0 V versus SCE, should correspond to a work function, Φ, of around 5.0 eV.

3.2. Stark-tuning results

We are now in a position to intercompare the metal–solution and metal–gas vibrational data in terms of surface potentials. Figure 1(A) contains a set of electrochemical SER spectra at the four electrode potentials indicated for a saturated coverage of carbon monoxide on a palladium film electrode in CO-sparged aqueous 0.1 M $HClO_4$ in the frequency region, 1850–2150 cm^{-1}, where the C–O stretching (ν_{CO}) vibrations are located. The predominant lower-frequency band is probably due to two-fold bridging CO, whereas the weaker higher-frequency component is ascribed to atop (i.e., terminal) CO [17]. As outlined elsewhere [17], in addition to being familiar from *in situ* infrared spectral studies [27], the ν_{CO} frequencies are seen to upshift substantially with increasing electrode potential, so that $d\nu_{CO}/dE \approx 30$ cm^{-1} V^{-1}.

The bottom spectrum in figure 1(A) shows the ν_{CO} bands observed *for the same surface* following film deposition, emersion from 0.1 M $HClO_4$ at various potentials (−0.2 to 0.2 V), rinsing, and rapid transfer to the gas-phase cell containing 10 Torr carbon monoxide in ambient-pressure argon. The Pd film was, therefore, exposed to CO for the first time in the gas-phase reactor, rather than in the electrochemical cell. Identical electrochemical SER spectra were obtained, however, whether or not the surface had undergone gas-phase CO dosing in this fashion. (The CO partial pressure used matches the corresponding saturation concentration, ca. 1 mM, of CO in the aqueous electrolyte, but higher CO pressures give the same results.) The Raman spectral intensities and spectral form are very similar to the electrochemical SERS data. Comparing carefully the frequencies



(A) (B)

Figure 2. Similarly to figure 1 (A) and (B), but for CO-saturated adlayers on Pt film.

of both $\nu_{\rm CO}$ bands in the gas phase in comparison with the potential-dependent electrochemical spectra, it is evident that the former spectrum is indicative of a "surface potential" of the Pd–CO gas interface of about 0 to -0.2 V versus SCE; i.e., about 4.9 eV on the vacuum work-function scale.

This result is extremely surprising. Thus taking the work function of the "clean" Pd film (approximated roughly by the monocrystalline (110) surface) as ca. 5.2 eV [28], and given that adsorbing a CO monolayer *increases* Φ by about 1.0 eV [29], one would anticipate on this basis that the Pd–CO gaseous system would exhibit a work function of ca. 6.2 eV, i.e., almost 1.5 eV *higher* than that estimated by the above Stark-tuning analysis. One conceivable explanation is that the analysis contains a systematic error if the CO coverages in the electrochemical and gas-phase environments are different. Indeed, if the coverage is markedly smaller in the latter case, this could partly explain the discrepancy since the $\nu_{\rm CO}$ frequencies would then be significantly lower due to diminished dipole–dipole coupling [30]. However, this is extremely unlikely: the SER intensities tend to be *higher* in the latter case, even though the optical geometry is slightly different. Moreover, identical gas-phase SER spectra are observed if the surface is transferred to the electrochemical cell and back to the gas-phase reactor, or if the freshly prepared film is examined first in the former environment followed by transfer to the latter; i.e., the findings are independent of the order of the measurements.

Nevertheless, it is worthwhile also to examine the corresponding behavior of the metal–CO stretching ($\nu_{\rm M\text{–}CO}$) vibration. While the Stark-tuning slopes, $d\nu_{\rm M\text{–}CO}/dE$, are smaller (ca. -10 to -15 cm^{-1} V^{-1}) and of opposite sign to the corresponding $d\nu_{\rm CO}/dE$ values, the $\nu_{\rm M\text{–}CO}$ frequencies are affected little by dipole–dipole coupling and display only small increases with coverage (about 3 cm^{-1} upon doubling the coverage up to saturation). Figure 1(B) shows a set of four electrochemical SER spectra in the $\nu_{\rm M\text{–}CO}$ region for CO-saturated Pd in 0.1 M $HClO_4$ at the same potentials as in figure 1(A), again in comparison with the corresponding gas-phase spectrum. The major $\nu_{\rm M\text{–}CO}$ band at ca. 360 cm^{-1} corresponds to bridging CO, the corresponding atop feature appearing only as a weak high-frequency tail. While the potential-induced $\nu_{\rm M\text{–}CO}$ frequency shifts are only small, the gas-phase and electrochemical SER spectra are again seen to match well at a potential for the latter of about 0 V versus SCE.

We also performed similar experiments for saturated CO layers on Pt films. Aside from the archetypical importance of platinum in surface chemistry, one reason for this choice is that atop rather than bridging CO binding predominates under our interfacial conditions. Figure 2(A) shows, in similar fashion to figure 1(A), a trio of electrochemical SER spectra obtained in CO-saturated 0.1 M $HClO_4$ at the electrode potentials indicated, again in comparison with the corresponding gas-phase spectrum. (The latter was again obtained following transfer of a fresh metal film into the gas-phase reactor for initial CO dosing.) An atop ν_{CO} band at 2075–2085 cm^{-1} is seen in both interfacial environments, the frequency of which again increases with electrode potential so that $d\nu_{CO}/dE \approx 30\ cm^{-1}\,V^{-1}$. (We also observed a weak lower-frequency bridging ν_{CO} feature, consistent with an earlier study [17].)

Comparison between the atop ν_{CO} frequencies for gas-phase and electrochemical SERS in figure 2(A) again implies a very low effective potential for the former, ca. -0.3 V. This is roughly corroborated by the corresponding low-frequency comparison shown in figure 2(B), for which the atop $\nu_{M\text{–}CO}$ stretch at ca. 480 cm^{-1} in the gas-phase spectrum matches the electrochemical spectra for an electrode potential around 0 V versus SCE. (Similarly to the Pd case, the $\nu_{M\text{–}CO}$ stretching frequency for atop CO on the Pt film *decreases* significantly with increasing potential, with $d\nu_{M\text{–}CO}/dE \approx -10\ cm^{-1}\,V^{-1}$.) Electrochemical SER experiments on Pt were also conducted in neutral aqueous electrolyte, 0.1 M $NaClO_4$, chosen so to extend the accessible range of electrode potentials to lower values as well as check the possibility that the electrolyte cation might influence the results [17]. A typical set of potential-dependent ν_{CO} spectra are shown in figure 3, again in comparison with the gas-phase spectrum obtained either immediately before or after the former data. Once again, a good match between the gas-phase and electrochemical ν_{CO} frequencies is obtained at a low electrode potential, close to -0.1 V versus SCE.

Similarly to the Pd case, the surface potentials for the corresponding Pt–gas interface are substantially lower than anticipated for CO-saturated-Pt–vacuum interfaces. Thus the work function of clean Pt(110) (a reasonable model for polycrystalline Pt) is 5.7 eV [31]. Given that adsorption of a saturated CO layer onto Pt(110) yields only a small (<0.05 eV) Φ change [32], one would expect that the Pt–CO gaseous interface would exhibit $\Phi \sim 5.7$ eV. However, the E values noted above correspond, instead, to a work function below 5.0 eV.

A number of experiments were also performed that involved transferring the Pt electrode from the CO-saturated 0.1 M $HClO_4$ or 0.1 M $NaClO_4$ electrolyte *without* rinsing into the gas-phase reactor. The resulting gas-phase ν_{CO} frequencies tended to be slightly (5–10 cm^{-1}) higher under these conditions, in comparison with vibrational spectra obtained by initial gas-phase CO dosing or electrode transfer with rinsing (*vide supra*), especially for higher emersion potentials. Overall, these results suggest that retention of the double layer, presumably engendered by an absence of rinsing upon electrode transfer into the gas-phase cell, can influence the effective surface potential in the latter environment.

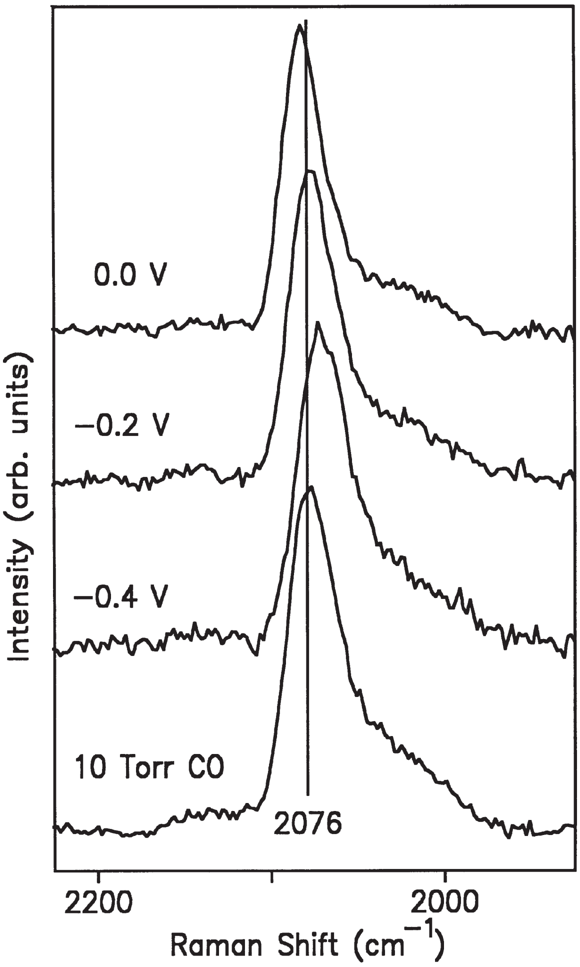


Figure 3. Similarly to figure 1(A), but electrochemical SER spectra for Pt film in CO-saturated aqueous 0.1 M $NaClO_4$.

The observation of unexpectedly low work functions (or surface potentials) for metal–gas interfaces is not limited to CO adlayers on transition metals. Figure 4 shows an example for chloride adsorbed on polycrystalline gold. The top two spectra were obtained at the pair of electrode potentials indicated in aqueous 0.1 M KCl. The vibrational band at ca. 265–280 cm^{-1} is due to Au–Cl stretching for near-saturated levels of adsorbed chloride, $\nu_{M\text{–}Cl}$ [14]. This band has a comparable intensity for $E \geqslant 0$ V under these conditions, the frequency increasing markedly with potential under these conditions so that $d\nu_{M\text{–}Cl}/dE \approx 35\ cm^{-1}\,V^{-1}$ [14]. The bottom spectrum in figure 4 shows the same frequency region after emersion from solution and transferral to the reactor in vacuum (10^{-6} Torr). The $\nu_{M\text{–}Cl}$ frequency obtained under the latter conditions, 263–265 cm^{-1}, was found *regardless* of the emersion potential over the range 0–0.5 V, and matches the electrochemical SERS frequency for $E \approx 0.1$ V versus SCE.

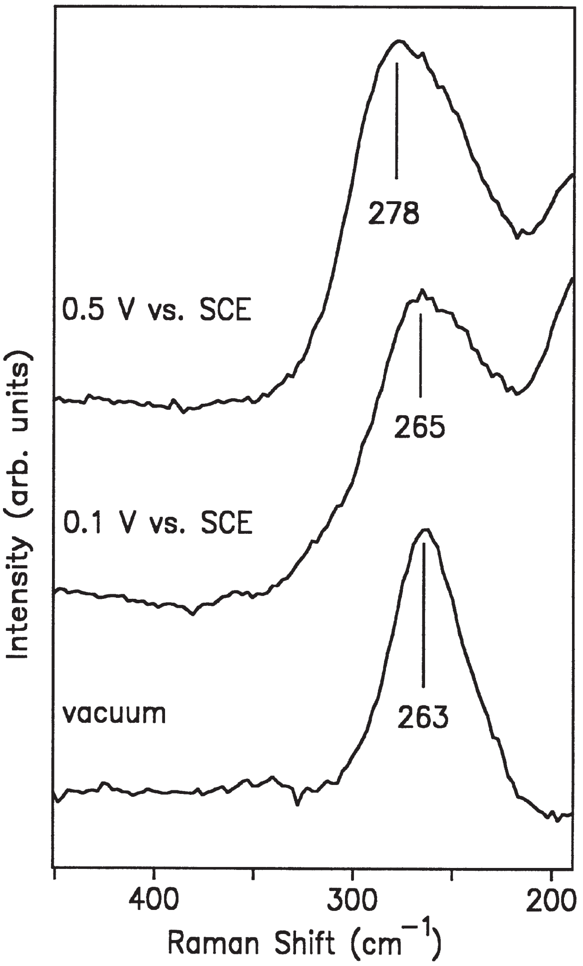


Figure 4. Electrochemical SER spectra for chloride adsorbed on gold (metal–Cl stretch) in 0.1 M KCl at the two electrode potentials, indicated in comparison with spectrum obtained after subsequent surface transfer into vacuum (see text for details).

This result appears distinctly different to that reported by Koetz et al. [33], who showed that emersing a polycrystalline gold electrode from aqueous 0.1 M $HClO_4$ into UHV yielded Φ values in the latter environment that "tracked" well the varying electrode potentials at which the transfer took place [33]. Although the intercept found in this Φ–E correlation is controversial (*vis-à-vis* E_k estimates, *vide supra*) [24], the essential point is that such "clean UHV transfer", in contrast to the present aerated ambient-pressure, conditions result in the retention of at least some electrostatic double-layer properties in the emersed state.

3.3. Rationalization of gas-phase surface potentials

Even though the above data are gathered for only a small group of interfacial systems, a common feature is that the "effective surface potential" of all three metal–gas interfaces is relatively low, in the vicinity of 0 V versus SCE, corresponding to ca. 5.0 eV (or lower) on the vacuum scale. This is most striking for the Pt–CO and especially the Pd–CO interfaces in that they feature surface potentials that are around 1.0–1.5 V lower than expected on the basis of "clean" surface science expectations. Although one might surmise that the presence of the underlying gold substrate could exert an effect, this appears unlikely given that the transition-metal films are several monolayers thick. Moreover, varying the film thickness has no significant influence on the adsorbate vibrational properties.

What, then, are the likely reasons for this ostensibly surprising behavior? A reasonable explanation can be found by considering the reaction chemistry, especially redox processes, that can occur *after* emersion of the surface into the gas phase. Metal surfaces transferred into controlled ambient-pressure environments will inevitably be exposed to a number of gas-phase species, in addition to the intended gas (or gases). Thus common impurities in supposedly "pure" (99.99%) CO include water, hydrogen, oxygen, CO_2, and hydrocarbons at ppm levels. Similarly, the argon carrier gas commonly contains ppm levels of such impurities.

As a consequence, a number of redox processes can be envisaged to proceed on the metal surface *in the ambient-pressure gas phase*, such as

$$CO + H_2O \rightarrow CO_2 + 2e^- + 2H^+ \tag{2}$$

$$H_2 \rightarrow 2e^- + 2H^+ \tag{3}$$

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \tag{4}$$

where the protons are assumed to be hydrated (or, otherwise, stabilized by an alternate acceptor). While other redox processes can certainly be envisaged (e.g., hydrocarbon oxidation), reactions (2)–(4) serve to illustrate the principles involved.

Starting with, say, an uncharged metal surface, the occurrence of the oxidation "half-reactions" (2) and (3) would generate surface electronic charge, thereby lowering the surface potential to the point where these processes are no longer kinetically and/or thermodynamically feasible. (Recall that the kinetics and thermodynamics of such "electrochemical" redox processes are inherently very sensitive to the potential, so that the rates typically vary by at least 10 fold every 0.1 V or so; for example, see [34].) The oxygen reaction (4), on the other hand, will consume electrons from the metal, so that the occurrence of this process will *increase* the surface potential, again to the point where it is no longer favorable. Consequently, the effect of these reactions will be to (a) shift the surface potential either to a value where the process ceases, or, additionally, (b) to a common point where appropriate combinations of oxidation and reduction half-reactions can proceed at an equal rate. The occurrence of (b) can lead to a net heterogeneous catalysis since the electrons required by the reduction half-reaction will then be supplied by the oxidation half-reaction, even though these steps are microscopically separate (*vide infra*). Such heterogeneous "catalytic cycles" based on redox reactions are well known to be engendered by metal particles or surfaces in solution (for a review, see [35]) and, indeed, form the basis of metal corrosion, where the oxidation half-reaction is anodic dissolution of the surface itself (for an insightful overview, see [36]).

The occurrence of only (a), however, is required to rationalize the above results. That only a very small extent of reaction is sufficient to shift substantially the surface potential to values around those implied by the Stark-tuning findings is illustrated by the following. Imagine, say, an initially uncharged Pd–CO surface, presumably thereby having a work function of around 6.0 eV (*vide supra*). (In electrochemical terms, the potential for such an uncharged interface is referred to as the "potential of zero charge", E_{pzc}, or the "electrochemical work function" [37].) The presence of even slightly damp CO can trigger the occurrence of reaction (2), yielding electrons and (hydrated) protons. In the absence of a reduction half-reaction, these electrons will build up metal electronic charge, countered by hydronium cation countercharge, i.e., double-layer charging takes place. This charging will diminish the surface potential by an amount $\Delta\phi$, which is inversely proportional to the surface capacitance, C_{d} ($=\mathrm{d}\sigma/\mathrm{d}\phi$, where σ is the surface electronic charge density). The effective values of C_{d} are sensitive to the presence of interfacial solvent as well as being (less) dependent on its nature, as shown most directly by recent observations with model electrochemical interfaces, including CO-saturated Pt(111), in UHV [2,38]. These measurements yield C_{d} values around 10 $\mu\mathrm{F\,cm^{-2}}$ for this system in the presence of solvents [38]. One, therefore, only requires the passage of only 10 $\mu\mathrm{C\,cm^{-2}}$ of charge to shift the surface potential by 1 V, an almost infinitesimal extent of reaction (therefore requiring only very small reaction rates).

However, besides the marked progressive attenuation of the reaction rate for (2) with decreasing potential, this condition will encourage increasingly the occurrence of *reduction* half-reactions, such as O_2 reduction (4). Consequently, the surface potential will settle eventually at a value determined either by the effective cessation of reaction (2), or the point where the rates of reactions (2) and (4) become equal for the particular interfacial conditions encountered. The latter, and even the former, condition can therefore usefully be thought to involve "redox-pinning" of the surface potentials at some intermediate value between the regions where reactions (2) and (4) readily proceed. Providing that both oxidation and reduction half-reactions can occur, the same final "redox-pinned" potential will be obtained *regardless* of the initial surface charge state prior to gas exposure. This accounts for the present observation of a near-constant surface potential in the gas phase irrespective of the metal-surface history. (Variations in the chemical interfacial composition are presumably responsible for the differences noted above, when electrode emersion into the gas phase was undertaken *without* surface rinsing.)

The above arguments are bolstered, for example, by a consideration of the voltammetric kinetics of reactions (2) and (4) on Pd. Linear sweep voltammograms were measured on Pd films for the electrooxidation of solution CO in aqueous 0.1 M $NaClO_4$ under acidic (pH 1–3) and basic (pH 11) conditions. As expected [39], the onset potential for detectable CO electrooxidation (as evaluated from the "foot" of the voltammetric wave) is strongly pH-dependent, being about 0.6 and -0.4 V versus SCE under acidic and basic conditions, respectively. While the effective pH conditions for a water film on the metal in the gas phase are not well defined, one can certainly envisage on such a basis an "onset potential" for "gas-phase CO electrooxidation" within this potential range. In addition, the onset of detectable oxygen reduction from O_2-saturated solution on Pd in mildly basic media is around 0.1 V versus SCE, and at more positive potentials in acidic solution. Therefore, the presence of trace amounts of oxygen along with gaseous carbon monoxide could indeed yield surface potentials on Pd in the range, say, -0.3 to 0 V, as a result of "redox pinning". Similar comments apply to Pt, which yields comparable pH-dependent kinetics for CO oxidation and oxygen reduction.

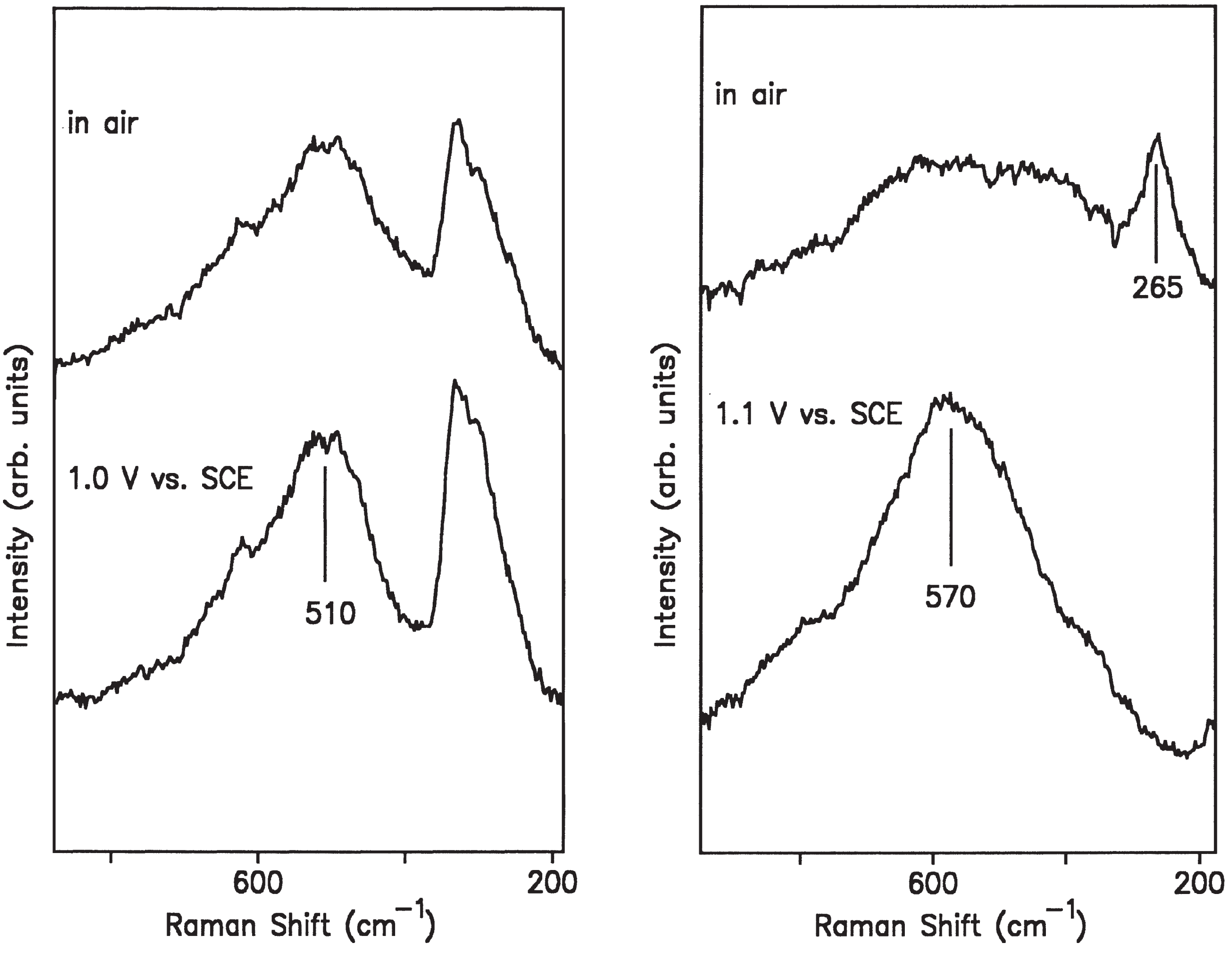
The situation for the gold surface, also examined above, is more cloudy. Certainly transferring Cl-modified Au through air to the vacuum cell will create ample opportunity for surface contamination with oxygen, for example, and the latter environment undoubtedly contains traces of H_2, CO, hydrocarbons, and probably other oxidizable species. The electrooxidation of CO is particularly facile on gold, the voltammetric onset occurring even by -0.3 V or so in neutral aqueous media (pH $\sim$ 7) on Au(110) and (210) [39,40]. The present observation of effective surface potentials around 0.1 V on gold is, therefore, not surprising on this basis.

3.4. Stability of electrochemically formed oxides in air

So far, we have noted the persistent occurrence of effective surface potentials for metal–gas interfaces around 0 V versus SCE, or below, and rationalized the observation on the basis of interfacial redox processes. Another likely manifestation of this chemistry is to be found in the stability of electrochemically formed metal oxides upon subsequent transfer to air.

The lower spectrum in figure 5(A) was obtained for a rhodium film in deaerated aqueous 0.1 M $HClO_4$ at 1.0 V versus SCE. This relatively oxidizing condition yields an anodic oxide film, as signaled by the characteristic SERS features observed around 510 and 290 $\mathrm{cm^{-1}}$, associated with Rh–O vibrations [16]. Essentially the same spectrum was obtained after transferring the surface from the electrochemical cell into air, as seen in figure 5(A) (top), indicating that the oxide is stable in this environment. The same results were obtained whether or not the surface was rinsed upon transfer.

Markedly different findings, however, were obtained for an anodic oxide film formed on gold. Figure 5(B) shows the vibrational spectrum for an electrooxidized gold surface in aqueous 0.1 M $HClO_4$ at 1.1 V versus SCE, the



(A) (B)

Figure 5. Electrochemical SER spectra in metal-oxide stretch region for (A) rhodium and (B) gold obtained in 0.1 M $HClO_4$ at electrode potentials, indicated in comparison with corresponding spectra obtained after surface transfer into air (see text for details).

broad feature centered around 570 cm^{-1} being characteristic of electrochemical gold oxide [16,41]. In contrast to the rhodium case, transferring this surface into air, either with or without rinsing, yielded the virtual *removal* of the oxide, as seen in the top spectrum in figure 5(B). (The identity of the 265 cm^{-1} band observed under these conditions is unclear, although it may well to due to the presence of residual chloride; cf. figure 4.)

A likely reason for this behavioral difference can again be found by considering the occurrence of redox half-reactions in the metal–gas environment. Inspection of cyclic voltammograms for electrochemical oxide formation and removal on the rhodium and gold surfaces (see figures 7 and 1, respectively, in [16]) shows that the latter oxide is reduced at substantially (ca. 0.5–0.7 V) higher potentials than is the former. Thus, in acidic electrolyte, for example, these reduction processes on Rh and Au occur at ca. 0.15 and 0.8 V versus SCE, respectively.

This stability difference makes the latter oxide much more susceptible to reductive removal by adventitious gas-phase components for two reasons. First, any gas-phase species capable of undergoing electrooxidation on gold below 0.8 V or so in acidic environments will, by the above arguments, effectively trigger removal of the gold oxide by forcing the surface potential to lower values. (This oxide reduction potential decreases by about 60 mV per pH unit since protons are involved in the reaction.) While the actual reducing agent(s) involved is unclear, plausible candidates again include CO or H_2; note that the presence of a surface water film is very likely in ambient air. Indeed, gold is a *uniquely* good catalyst for CO electrooxidation in aqueous environments [39,40]. By contrast, such oxidation half-reactions must proceed at substantially (at least 0.5 V) lower potentials on rhodium in order to remove the oxide. The second factor, which probably contributes importantly to the stability of the rhodium oxide film in air, is the additional occurrence of oxygen electroreduction (reaction (4) above). While the onset of this reaction on gold occurs at potentials well below where oxide reduction occurs in aqueous media, the opposite is typically the case on rhodium, oxygen reduction proceeding at *higher* potentials than surface oxide reduction. Consequently, from the above arguments, the abundance of oxygen in air should act to “redox pin” the rhodium surface potential at values where the oxide is stable, even in the presence of powerful reducing agents (i.e., oxidation half-reactions that occur at lower potentials).

This electrochemical reasoning can readily account in broader terms for the observed wide variations in the stability of different metal oxides in air or related ambient-pressure environments. Indeed, related arguments involving oxidation and reduction half-reactions constitute the commonly accepted description of metal-corrosion phenomena [36].

3.5. More general implications

The foregoing provides direct evidence that the effective surface potential of metal–ambient-pressure-gas interfaces tends to acquire low values, ca. 0 V versus SCE ($\equiv$5.0 eV versus vacuum or below), as a consequence of "electrochemical redox pinning". The situation is in a sense not particularly well defined, since the identity of the redox half-reactions involved and the actual surface state (presence of water film, etc.) tends to be uncertain for metals in contact with ambient-pressure gases. (Indeed, one could argue that the chemical and physical state of the surface is *only* known with confidence either in UHV or clean electrochemical environments.) Nonetheless, on this basis, one might anticipate that the surface potential of metals exposed to higher-pressure gaseous environments, as in "real-world" catalysis, would commonly lie in the range, say, from -0.5 to 0.5 V versus SCE. The reason for this assertion is that the majority of likely redox half-reactions tend to exhibit onset potentials within this range, so that redox pinning should typically yield stable potentials not greatly different to 0 V versus SCE. Indeed, the common electrochemical observation of open-circuit (or "rest") potentials for solid noble metals around 0 V versus SCE arises for the same reason. One, therefore, can reasonably refer to such a situation as yielding "terrestrial surface potentials", given the propensity towards water/oxygen-based redox chemistry in ambient or related environments.

What then are the possible implications of such findings to our understanding of metal–gas surface chemistry, including catalysis? Admittedly, the present systems are not catalysts *per se*, even though the vibrational spectral data provide clear evidence that some reaction chemistry is occurring on them. More generally, the acceptance of the above hypothesis has two possible consequences. First, even in the absence of catalytic chemistry, altering the surface potential can incur substantial changes in the stability of adsorbates and the surface composition in coadsorbate systems, as deduced directly from electrochemical observations. An interesting likely example of this stability effect is to be found in a recent study of the Pt(111)/CO system by Stuve and coworkers [42]. They observed that CO adlayers transferred to UHV by emersion from electrochemical cells exhibited markedly higher stabilities (and saturation coverages) when coadsorbed electrolyte species remained along with the chemisorbate. This difference, which was attributed to the diminution of CO–CO repulsion by coadsorbed electrolyte, probably also reflects the influence of the latter on the surface potential.

A second, and more profound, consequence is that one can envisage redox half-reactions as being involved directly in heterogeneous catalysis at metal–gas interfaces under some circumstances. Thus, if a pair of oxidation and reduction half-reactions can proceed at least at moderate (and equal) rates at a common surface potential on a given metal, those processes coupled together can constitute an effective "redox catalytic cycle", yielding an overall gas-phase chemical reaction (cf. [35]).

A plausible example of such "redox catalysis" is CO oxidation by O_2 on palladium. As already noted, the onset potentials for CO electrooxidation on Pd tend to be rather more negative than for O_2 electroreduction at a given pH in aqueous media. Consequently, feeding a suitable (damp) CO/O_2 mixture onto Pd should yield a surface potential where the net reaction

$$CO + (1/2)O_2 \rightarrow CO_2 \qquad (5)$$

is achieved via *microscopically separate* oxidation and reduction half-reactions. (Note that reaction (5) can be obtained from the sum of reactions (2) and (4), so that water and protons serve only as "surface intermediates" in the overall process.) Whether this two-stage "electrochemical" pathway provides the preferred route to CO_2 formation depends, of course, on the energetics of alternative "non-electrochemical" mechanisms involving, for example, reaction between adsorbed CO and coadsorbed oxygen atoms. However, a potential advantage of the redox–catalytic route is that the activation energies of electrochemical processes are commonly smaller than their chemical counterparts because heterogeneous electron transfer inherently requires activation of only one reactant, rather than a pair of reactants as in the latter case [34].

An interesting phenomenon which may well be relevant to the above notions is the so-called "nonfaradaic electrochemical modification of catalytic activity" (NEMCA) examined extensively by Vayenas and coworkers [43,44]. This effect involves the often-substantial alterations in catalytic activity of metal–gas interfaces seen upon altering the surface potential by means of contact with a solid–electrolyte electrochemical cell [43,44]. While the observations have been interpreted chiefly in terms of potential-induced alterations in the surface–chemisorbate bond strengths, they may well also arise from "redox half-reaction" considerations as outlined above.

Consequently, then it is distinctly possible that such electrochemical-like considerations as manifested in redox catalytic cycles, in addition to "redox pinning" of surface potentials, could provide a useful basis for understanding chemical processes at some metal–gas as well as metal–solution interfaces. We are aware, of course, that the above hypotheses are partly speculative at present, and some surface scientists may even react to them with discomfort. Nevertheless, experiments aimed at testing these notions further in quantitative fashion, although not straightforward, are certainly feasible.

Acknowledgement

This work was supported by grants to MJW and CGT from the National Science Foundation.

References

[1] N. Kizhakevariam, I. Villegas and M.J. Weaver, Surf. Sci. 336 (1995) 37.
[2] N. Kizhakevariam, I. Villegas and M.J. Weaver, J. Phys. Chem. 99 (1995) 7677.
[3] I. Villegas, N. Kizhakevariam and M.J. Weaver, Surf. Sci. 335 (1995) 300.
[4] I. Villegas, R. Gómez and M.J. Weaver, J. Phys. Chem. 99 (1995) 14832.
[5] I. Villegas and M.J. Weaver, J. Phys. Chem. B 101 (1997) 10166.
[6] I. Villegas and M.J. Weaver, J. Phys. Chem. B 101 (1997) 5842.
[7] D.K. Lambert, Electrochim. Acta 41 (1996) 623.
[8] M. Head-Gordon and J.C. Tully, Chem. Phys. 175 (1993) 37.
[9] A.A. Tolia, C.T. Williams, C.G. Takoudis and M.J. Weaver, J. Phys. Chem. 99 (1995) 4599.
[10] C.T. Williams, A.A. Tolia, M.J. Weaver and C.G. Takoudis, Chem. Eng. Sci. 51 (1996) 1673.
[11] C.T. Williams, A.A. Tolia, H.Y.H. Chan, C.G. Takoudis and M.J. Weaver, J. Catal. 163 (1996) 63.
[12] C.T. Williams, C.A. Black, M.J. Weaver and C.G. Takoudis, J. Phys. Chem. B 101 (1997) 2874.
[13] C.T. Williams, C.G. Takoudis and M.J. Weaver, J. Phys. Chem. B 102 (1998) 406.
[14] P. Gao and M.J. Weaver, J. Phys. Chem. 90 (1986) 4057.
[15] L.-W.H. Leung and M.J. Weaver, J. Am. Chem. Soc. 109 (1987) 5113; Langmuir 4 (1988) 1076.
[16] Y. Zhang, X. Gao and M.J. Weaver, J. Phys. Chem. 97 (1993) 8656.
[17] S. Zou and M.J. Weaver, J. Phys. Chem. 100 (1996) 4237.
[18] X. Gao, Y. Zhang and M.J. Weaver, Langmuir 8 (1992) 668.
[19] P. Gao, D. Gosztola, L.-W.H. Leung and M.J. Weaver, J. Electroanal. Chem. 233 (1987) 211.
[20] S. Zou and M.J. Weaver, Anal. Chem., in press.
[21] E. Stuve, personal communication.
[22] S. Trasatti, J. Electroanal. Chem. 150 (1983) 1; 139 (1982) 1.
[23] S. Trasatti, Surf. Sci. 335 (1995) 1.
[24] W.N. Hansen and G.J. Hansen, ACS Symp. Ser. 378 (1988) 166.
[25] F.T. Wagner, in: *Structure of Electrified Interfaces*, eds. J. Lipkowski and P.N. Ross (VCH, New York, 1993) chapter 9.
[26] S. Trasatti, Electrochim. Acta 36 (1991) 1659.
[27] M.J. Weaver, Appl. Surf. Sci. 67 (1993) 147.
[28] K. Wandelt and J.E. Hulse, J. Chem. Phys. 80 (1984) 1340.
[29] H. Conrad, G. Ertl, J. Koch and E.E. Latta, Surf. Sci. 43 (1974) 462.
[30] A. Ortega, F.M. Hoffman and A.M. Bradshaw, Surf. Sci. 119 (1982) 79.
[31] H.H. Rotermund, S. Jabubith, S. Kubala, A. Von Oertzen and G. Ertl, J. Electron. Spectr. Related Phenom. 52 (1990) 811.
[32] R. Imbihl, S. Ledas and G. Ertl, Surf. Sci. 206 (1988) L903.
[33] E.R. Koetz, H. Neff and K. Mueller, J. Electroanal. Chem. 215 (1986) 331.
[34] M.J. Weaver, in: *Comprehensive Chemical Kinetics*, Vol. 27, ed. R.G. Compton (Elsevier, Amsterdam, 1987) chapter 1.
[35] M. Spiro, in: *Comprehensive Chemical Kinetics*, Vol. 28, ed. R.G. Compton (Elsevier, Amsterdam, 1989) chapter 2.
[36] J.O'M. Bockris and S.U.M. Khan, *Surface Electrochemistry* (Plenum Press, New York, 1993) chapter 8.
[37] S. Trasatti, in: *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 10, eds. H. Gerischer and C.W. Tobias (Wiley, New York, 1977) p. 213.
[38] M.J. Weaver and I. Villegas, Langmuir 13 (1997) 6836.
[39] G.J. Edens, A. Hamelin and M.J. Weaver, J. Phys. Chem. 100 (1996) 2322.
[40] S.-C. Chang, A. Hamelin and M.J. Weaver, J. Phys. Chem. 95 (1991) 5560.
[41] J. Delsilvestro and M.J. Weaver, J. Electroanal. Chem. 209 (1986) 377.
[42] R.L. Borup, D.E. Sauer and E.M. Stuve, Surf. Sci. 374 (1997) 142.
[43] C.G. Vayenas and S.G. Neophytides, in: *Catalysis – A Specialist Periodical Report*, Vol. 12 (Royal Society of Chemistry, Cambridge, 1996) chapter 6.
[44] C.G. Vayenas, M.M. Jaksic, S.I. Bebelis and S.G. Neophytides, in: *Modern Aspects of Electrochemistry*, Vol. 29, eds. J.O'M. Bockris, B.E. Conway and R.E. White (Plenum Press, New York, 1996) chapter 2.