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Semiconductor Electrodes. 59. Photocurrent Efficiencies at p-InP Electrodes in Aqueous Solutions

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The quantum efficiency for photoelectrochemical reactions at bare and Pt and Au catalyst incorporated p-InP electrodes in 1.0 M H₂SO₄ and bare and Ru/p-InP in 0.05 M Eu³⁺ in 1.0 M HClO₄ has been studied as a function of potential and wavelength of incident light. As opposed to a previous report, quantum efficiency (ϵ) values above 1 were not obtained. Rather an ϵ of 0.65 was found for the hydrogen evolution reaction in 1.0 M H₂SO₄ at Pt/p-InP and $\epsilon \approx 0.8$ for Eu³⁺ reduction on Ru³⁺-treated p-InP electrodes. The flat-band potentials of bare, Pt-, and Au-plated p-InP electrodes were determined by impedance measurement and were independent of the nature of the plated metal (Pt, Au).

Introduction

Its favorable band gap (1.35 eV) and stability to photocorrosion have made p-InP an attractive choice for photoelectrochemical (PEC) applications. The PEC performance of this electrode was reported for several redox systems in nonaqueous solutions^{1,2} and for the V³⁺/V²⁺ couple and hydrogen evolution reaction (her) in aqueous solutions.³⁻⁹ Heller and co-workers studied Rh-, Ru-, and Pt-plated p-InP electrodes and reported quantum efficiencies (ϵ) of up to 0.8 for the her in 3 M HCl^{7,8} with Ar ion laser irradiation and ϵ 's of 0.64-0.83 for V³⁺ reduction in sunlight.^{3,6} However, Szklarczyk and Bockris⁹ recently reported ϵ -values significantly larger than one (up to 1.6) for the her on catalyst-plated p-InP and suggested possible processes by which photon energy greater than that of the bandgap can result in multiple electron transfer per incident photon. Since such processes are generally unprecedented in PEC cells (in the absence of current-doubling processes^{10,11}) and could be of significance in the development of efficient PEC cells, we reinvestigated p-InP to obtain further information about the mechanism of this process. To this end, we studied bare, Pt-, and Au-plated p-InP electrodes in 1.0 M H₂SO₄ and bare and Ru-treated p-InP electrodes in 0.05 M Eu³⁺ in 1.0 M HClO₄ under carefully controlled conditions. In no case did we find ϵ -values above 1, and for both the her and Eu³⁺ reaction, ϵ was generally the same as that reported by earlier workers. We also studied the effect of plated metal on flat-band potential (V_{fb}) and briefly searched for possible current-doubling reactions at p-InP. Details of these experiments are given below.

Experimental Section

Zinc-doped p-InP (dopant concentration, $(2-3) \times 10^{17} \text{ cm}^{-3}$), generously provided by Drs. W. A. Bonner and B. Miller of Bell Laboratories, was used in the present studies. Electrical contact to the single crystals was provided by heating In-Zn (98% In) alloy over a freshly abraded (with 320 grade sand paper) single crystal surface at 600 °C for 15 min under a hydrogen atmosphere. After confirming the ohmic nature of the contact, a copper wire

was soldered to the In-Zn alloy layer with In solder. The front surface of the crystal was polished with alumina powder of successively decreasing particle size down to 0.05 μm . The back surface and sides of the crystal were covered with a thin layer of 5-min epoxy (Devon Corp., USA) and the crystal was mounted in 6-mm-diameter glass tubing with silicone sealant (Silastic 732 RTV, Dow Corning Corp., USA). The epoxy cement was also covered with the silicone, leaving an InP area of ca. 0.1 cm² exposed. This procedure for preparing semiconductor electrodes has been used successfully in numerous previous studies from our laboratory with both aqueous and nonaqueous solutions.¹²

The crystal surface was etched with a HNO₃:HCl:H₂O (2:2:1) mixture for 10 s and thoroughly washed with Millipore water. For studies with Au- and Pt-deposited electrodes, the electrodeposition of a few monolayers of the respective metals was carried out potentiostatically under 50-mW white light illumination of the electrode from either a gold cyanide bath (pure gold SG-10 Transene Co., Inc., Rowley, MA) or a chloroplatinic acid solution. The amount of metal deposited was determined from the number of coulombs, under the assumption of 100% current efficiencies in the plating process.

Reagent grade H₂SO₄, HNO₃, and HCl (Fisher), HClO₄ (MCB) and 99.9% pure EuCl₃ (Johnson Matthey) were used as received. Test solutions were prepared with Millipore water and deaerated with nitrogen for 1 h before the experiments.

A conventional single compartment cell with a flat Pyrex glass window for illumination of the semiconductor electrode was used. A Pt gauze electrode was used as the counter electrode. The reference electrode was a saturated calomel electrode (SCE) with saturated KCl agar bridge.

A 2500-W Xe lamp (Schoeffel Instrument Co., Westwood, NJ) combined with lens and Jarrel Ash monochromator (Waltham, MA) served as the light source. The light flux was measured with an EG&G Model 550 radiometer. The radiometer was calibrated by actinometry using aqueous KCr(NH₃)₂(NCS)₄ following the procedure described in the literature.¹³ The flux determined by actinometry was within 15% of the nominal readings of the radiometer. Based on this calibration, the white light power at the electrode surface was adjusted to $50 \pm 1 \text{ mW/cm}^2$.

Current-potential curves were recorded with a PAR Model 173 potentiostat, a Model 179 digital coulometer, Model 175 programmer (Princeton Applied Research, Princeton, NJ), and Model 2000 X-Y recorder (Houston Instruments, Austin, TX).

For ac impedance studies of the p-InP electrodes, a 12-mV peak-to-peak ac sinusoidal signal, obtained from a Hewlett-Packard wide range oscillator (Model 200 CD), was superimposed on a slow (5 mV/s) dc potential ramp. The output from the potentiostat was separated into in-phase and out-of-phase com-

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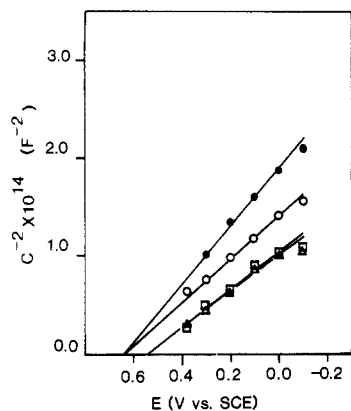


Figure 1. Mott-Schottky plots for p-InP electrodes at 50-Hz ac input signal: (O) bare, (□) Pt-plated, (Δ) Au-plated electrode in 1.0 M H₂SO₄ and (●) bare electrode in 0.05 M Eu³⁺ in 1.0 M HClO₄.

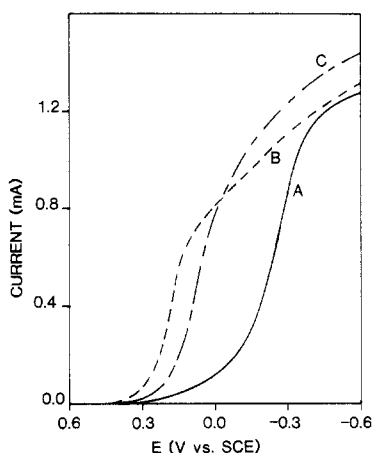


Figure 2. *i*-*E* curves for p-InP electrodes in 1.0 M H₂SO₄ under 50-mW white light illumination: (A) bare, (B) Pt-plated, and (C) Au-plated electrode.

ponents with respect to the input sine wave signal by a PAR Model 5204 lock-in amplifier and recorded on a Soltec X-Y₁-Y₂ recorder (Model 6432). The measurements were carried out in the frequency range 35–500 Hz.

Results and Discussion

Plots of $1/C^2$ (C , capacitance) vs. electrode potential (E) (Mott-Schottky plots) for bare, Pt-plated, and Au-plated p-InP electrodes in 1.0 M H₂SO₄ and a bare electrode in 0.05 M Eu³⁺ in 1.0 M HClO₄ at frequencies of the input signal of 35–500 Hz were straight lines. The values of $1/C^2$ at a fixed potential were, however, frequency-dependent. Although, in the lower frequency range (35–100 Hz), the $1/C^2$ vs. E lines converged to a single point on the potential axis, in the higher frequency region the plots exhibited parallel shifts. As suggested by Dutoit et al.,¹⁴ the flat-band potential (V_{fb}) can be estimated from Mott-Schottky plots that are frequency-dependent but converge on the potential axis. Hence, the data in the lower frequency range of the input ac signal were used to obtain V_{fb} . A typical set of Mott-Schottky plots obtained at 50 Hz are shown in Figure 1. V_{fb} was $+0.6 \pm 0.1$ V vs. SCE for bare, Pt-, and Au-plated p-InP, so that, within experimental error, V_{fb} is unaffected by metal deposition.

Photoelectrochemistry in H₂SO₄. The current-potential (*i*-*E*) curves for bare and plated p-InP in 1.0 M H₂SO₄ under illumination with 50 mW/cm² white light, 550-nm monochromatic light, and in the dark are shown in Figures 2 and 3. A notable feature of these plots is that the potential of onset of photocurrent due to the her (V_{on}), as opposed to the potential to sustain a larger photocurrent, is spaced within about 100 mV for all three elec-

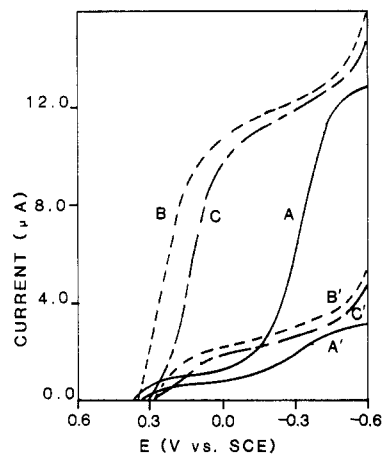


Figure 3. *i*-*E* curves for p-InP electrodes in 1.0 M H₂SO₄ under dark and 550-nm monochromatic light illumination: A(A') bare, B(B') Pt-plated, and C(C') Au-plated electrode under illumination (dark).

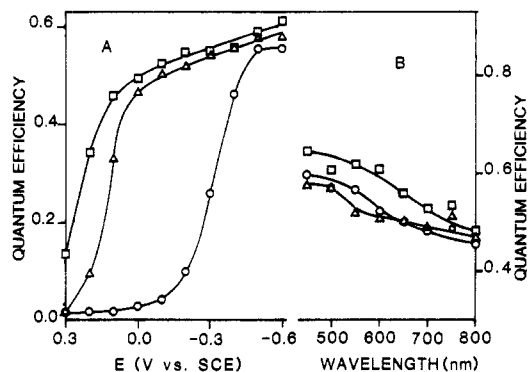


Figure 4. (A) Quantum efficiency vs. potential for p-InP electrodes in 1.0 M H₂SO₄ at 550-nm monochromatic illumination: (O) bare, (□) Pt-plated, and (Δ) Au-plated electrode. (B) Quantum efficiency vs. wavelength for p-InP electrodes (biased at -0.5 V vs. SCE) in 1.0 M H₂SO₄: (O) bare, (□) Pt-plated, and (Δ) Au-plated.

trodes. Similarly Heller et al.⁸ reported that the open circuit photopotentials (ΔV_{oc}) at bare p-InP electrodes (untreated, etched, or dipped in AgNO₃) and Pt-, Rh-, or Ru-deposited or evaporated films were all the same, within ± 100 mV. This similarity of V_{on} and V_{fb} for the three different electrodes is consistent with the model of Heller and co-workers that involves a decrease in the work function of the metal overlayer by adsorption of hydrogen leading to a small barrier at the metal/semiconductor junction. At higher photocurrent levels the rate of the her becomes important and the catalytic role of the metal in promoting the electron transfer determines the potential; hence, in this region at a given current density below saturation, the potentials are in the order Pt-plated > Au-plated > bare InP. The lower saturation current on the Pt-plated electrode under white light illumination can be attributed to the attenuation of light by the thicker Pt film compared to the Au-plated electrode. For a thinner Pt coating under monochromatic illumination, the saturation current was higher than that for the Au-plated electrode.

To obtain the quantum efficiency (ϵ) vs. potential curves for 550-nm monochromatic illumination of the electrodes, the dark current values were subtracted from the observed photocurrents at 100-mV intervals of potential and the corresponding electron flux ($e\text{ s}^{-1}\text{ cm}^{-2}$) was divided by the incident photon flux (photons $\text{s}^{-1}\text{ cm}^{-2}$). For comparison with the values reported by Szklarczyk et al.,⁹ no correction was made for the absorption of light by the solution and reflection by cell walls or electrode surface in calculating the photon flux. The resulting ϵ -*E* curves are shown in Figure 4A. Measurement of the solution absorption and reflectance by the cell walls by determining the ratio of light incident to that transmitted through the cell demonstrated that light attenuation by these factors was <4% with 50-mW white light and <2% with monochromatic light at 550 nm. The etched

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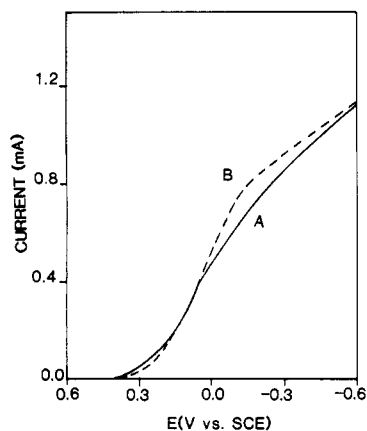


Figure 5. i - E curves for p-InP electrodes in 0.05 M Eu^{3+} in 1.0 M HClO_4 under 50-mW white light illumination: (A) bare and (B) Ru(III)-treated electrode.

and catalyst-coated surfaces do not reflect light in amounts that will substantially change ϵ . For the bare p-InP electrodes, ϵ was low at positive potentials but increased rapidly about -0.2 V vs. SCE. For Pt- and Au-plated electrodes, however, ϵ increased at potentials 0.4–0.5-V positive of the standard potential for proton reduction and approached saturation at more negative potentials. To evaluate the dependence of ϵ on the wavelength of incident light (λ), the potential of the electrode was held at -0.5 V vs. SCE and the i vs. λ curves were recorded. From the observed current values the dark current of the respective electrode at -0.5 V vs. SCE was subtracted and the quantum efficiency was calculated. Typical ϵ vs. λ plots are shown in Figure 4B.

Note that we never obtained ϵ -values > 1 for either bare or catalyst-coated p-InP electrodes in contrast to the report of Szklarczyk and Bockris⁹ but consistent with the earlier studies of Heller et al.⁸ Note that the dopant (Zn) level used in these studies and those of Heller et al. was $(2-3) \times 10^{17} \text{ cm}^{-3}$, while Szklarczyk and Bockris had a Zn dopant density of 10^{18} cm^{-3} . However, Grätzel et al.,¹⁵ in the study of the reduction of MV^{2+} (MV = methylviologen) in 0.1 M HCl at p-InP, noted a strong decrease in ϵ for monochromatic irradiation at 550 nm when the Zn dopant density increased from 7.1×10^{17} to $2.3 \times 10^{18} \text{ cm}^{-3}$. This decrease in ϵ with doping density has also been found with other semiconductor electrodes, such as n-Si,¹⁶ so the differences between the results here and the previous report probably cannot be ascribed to this factor. The slightly smaller values of ϵ observed for the Au-plated electrodes compared to the bare electrode at $\lambda < 650$ nm (Figure 4B) may be due to the reflection of light by the Au-plated surface of the electrode. Note that the ϵ - λ plots obtained at a potential of -0.5 V vs. SCE yield ϵ -values of comparable magnitude irrespective of plating.

PEC Cells with Eu^{3+} . To examine if higher ϵ -values might be obtained with an electron acceptor different than H^+ and V^{3+} , and to calibrate the system with a redox couple that can clearly only involve a single-electron transfer without the possibility of current-doubling effects,^{10,11} the PEC reduction of Eu^{3+} at bare and Ru(III)-treated p-InP electrodes was examined. The Ru(III) treatment involved etching in $\text{HNO}_3\text{:HCl:H}_2\text{O}$ (2:2:1), followed by rinsing with water, immersion of the electrode in 0.01 M Ru^{3+} in 0.10 M HNO_3 solution for 1 min, and washing with water.

The i - E curves for bare and Ru(III)-treated electrodes in 0.05 M Eu^{3+} in 1.0 M HClO_4 under 50-mW white light, 550-nm monochromatic illumination, and in the dark are shown in Figures 5 and 6. At positive potentials the magnitude of current for the bare and Ru-treated electrodes was similar, but at negative potentials, the Ru-treated electrode yielded a higher current. Heller et al.⁶ showed the beneficial effect on p-InP of surface oxidation and a CN^- treatment in removing surface states, and a Ru(III)

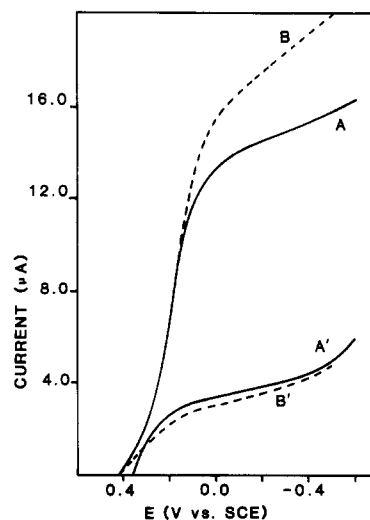


Figure 6. i - E curves for p-InP electrodes in 0.05 M Eu^{3+} in 1.0 M HClO_4 under dark and 550-nm monochromatic illumination: A(A') bare and B(B') Ru(III)-treated electrode under illumination (dark).

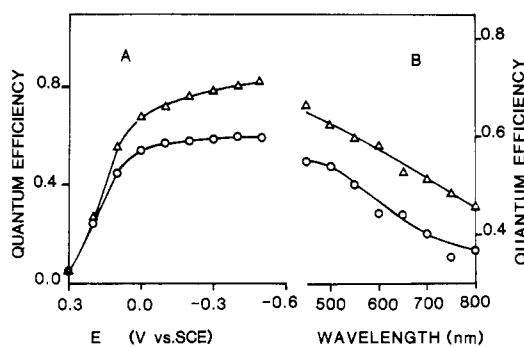


Figure 7. (A) Quantum efficiency vs. potential for p-InP electrodes in 0.05 M Eu^{3+} in 1.0 M HClO_4 at 550-nm monochromatic illumination: (O) bare and (Δ) Ru(III)-treated electrode. (B) Quantum efficiency vs. wavelength for p-InP electrodes (biased at -0.5 V vs. SCE) in 0.05 M Eu^{3+} in 1.0 M HClO_4 : (O) bare and (Δ) Ru(III)-treated electrode.

treatment had earlier been proposed for improving n-GaAs.¹⁷ In our case the Ru(III) treatment may also passivate surface states and decrease recombination; possibly Ru^{3+} adsorbed on the electrode surface may be photoreduced to Ru metal which can catalyze reduction of Eu^{3+} (and also protons).

ϵ vs. E and ϵ vs. λ curves, constructed following the procedure given earlier, are shown in Figure 7A,B. Higher quantum efficiencies at negative potentials in the ϵ vs. E plots and higher ϵ -values at all wavelengths in the ϵ vs. λ plots were found for the ruthenium-treated electrode. Again ϵ values greater than 1 were not observed. The fact that the ϵ for Eu^{3+} reduction was slightly greater at short circuit than the corresponding value for reduction of protons suggests that there is no current-doubling mechanism present for H_2 evolution on p-InP electrode.

There are several possible factors that might cause apparent ϵ -values > 1 . If photocurrent measurements at the semiconductor are taken at potentials where the reaction is thermodynamically allowed and occurs at a conductive electrode, it is possible that currents under irradiation would include both photodriven and thermal components. This effect could not occur at "underpotentials" where dark current contributions are not possible. Apparent quantum efficiencies > 1 have been observed in the case of some photoelectrochemical systems through current-doubling mechanisms.^{10,11} For example, at a p-GaP electrode¹⁸ in H_2SO_4 , current doubling during O_2 reduction through the intermediacy of $\text{HO}_2\cdot$ has been proposed for low photon flux densities (below about $10^{14} \text{ cm}^{-2} \text{ s}^{-1}$) at 430 nm incident light.

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To study whether a similar current doubling could be observed in the case of p-InP electrodes, experiments were carried out in O₂-saturated 1.0 M H₂SO₄ with 550-nm monochromatic light irradiation of the electrode with a photon flux density of 3×10^{13} cm⁻² s⁻¹. However, no photocurrent enhancement was noted. Addition of 50 mM peroxydisulfate or 10 mM maleic acid as current-doubling mediators to deaerated H₂SO₄ solution was also tried. Again no current enhancement was observed.

Conclusions

(1) The onset of the her occurs at comparable potentials for bare, Pt-, and Au-plated electrodes. Deposited catalyst metals improve the kinetics of her in H₂SO₄. (2) The flat-band potentials

of the bare, Pt-, and Au-deposited electrodes are independent of the nature of the deposited metal. (3) The maximum quantum efficiency for the her at the Pt/p-InP electrode was about 0.65; for Eu³⁺ reduction it was ≈ 0.8 , at Ru³⁺-treated p-InP electrode.

Acknowledgment. We thank Drs. W. A. Bonner and B. Miller of Bell Laboratories for their generous gift of p-InP single crystals. N.C. thanks ICSU/UNESCO for award of the Distinguished Fellowship in Science. The support of the National Science Foundation (CHE8304666) is gratefully acknowledged.

Registry No. InP, 22398-80-7; H₂, 1333-74-0; Pt, 7440-06-4; Au, 7440-57-5; Ru, 7440-18-8; Eu, 7440-53-1; HClO₄, 7601-90-3; H₂SO₄, 7664-93-9.

Surface-Enhanced Raman Spectroscopy as a Probe of Adsorbate-Surface Bonding: Benzene and Monosubstituted Benzenes Adsorbed at Gold Electrodes

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Surface-enhanced Raman spectra of benzene and eight monosubstituted benzenes adsorbed at gold electrodes have been examined in order to probe the nature of adsorbate-surface bonding for simple aromatic molecules. Benzene appears to adsorb flat via π adsorbate-surface interactions as evidenced by the significant (20–30 cm⁻¹) downshifts in the symmetric ring breathing mode (ν_1) and the absence of other ring modes in the SER spectra. Similar results were obtained by using gold surfaces prepared by electroplating or by anodic-cathodic potential sweeps in chloride, although much more stable SERS was obtained by using the latter procedure. The ring substituents -CH₃, -CH(CH₃)₂, -C(CH₃)₃, -Cl, -Br, -CN, -NO₂, -COO⁻, and -CHO were chosen so to provide steric perturbations or alternative binding modes to the metal surface. With the alkyl, benzoate, and aldehyde substituents, small yet significant (ca. 5–15 cm⁻¹) decreases in the ν_{12} and ν_{18a} characteristic ring modes along with band broadening were observed upon adsorption, consistent with attachment via the benzene ring. For the halogen substituents, smaller such downshifts were obtained along with the appearance of low-frequency modes associated with halogen-surface vibrations, implicating the role of substituent bonding in the adsorption. For the nitrile and nitro substituents, the ring modes were unaltered in frequency or bandshape upon adsorption while intense internal substituent modes were observed. The frequency shifts obtained for the latter modes along with the appearance of substituent-surface vibrational bands indicate that surface binding occurs entirely via the substituent rather than the benzene ring. Studies with deuterium-labeled adsorbates indicate that the adsorption-desorption kinetics were rapid on the time scale required to obtain the surface Raman spectra.

A major application of vibrational spectroscopies at metal surfaces is to gain information on the nature of adsorbate-surface interactions from differences in the form of the spectra, especially frequencies and bandshapes, for species in bulk and interfacial environments. A potentially valuable such technique, especially at electrochemical interfaces, is surface-enhanced Raman scattering (SERS).¹ Although limited to polycrystalline, mildly roughened surfaces (most prominently at silver, copper, and gold), absolute spectra can rapidly be obtained with high resolution (~ 1 cm⁻¹) over wide frequency ranges, enabling a variety of vibrational bands associated with internal and adsorbate-surface modes to readily be detected.

We have recently reported a straightforward procedure by which gold surfaces can be prepared so to yield extremely stable as well as intense SER spectra for a miscellany of adsorbates.² In particular, stable SER spectra can be obtained at gold for adsorbates such as oxyanions,² ethylene,³ carbon monoxide,⁴ etc., that yield weak or even undetectable signals at the traditionally preeminent SERS metal, silver.² This is attributed in part to a greater stability of the SERS-active sites (probably large metal

clusters^{1a}) at gold, so that their survival does not require the presence of high adsorbate coverages as appears to be the case at silver.^{1a,5}

We report here a study of potential-dependent SERS for benzene adsorbed at gold-aqueous interfaces. Benzene is of interest in view of its simple symmetric structure, and the likely involvement of π orbitals in the surface bonding. The influence of metal-benzene π bonding upon the vibrational spectra has been examined for bulk-phase arene complexes.⁶ A number of vibrational studies of benzene adsorbed at metal surfaces have been reported.^{7,8} These include several SERS studies,⁸ although only

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