

Notes

Theoretical Considerations of Electroreflectance Effect of Au(111) on Potential Modulated Differential Reflectance Spectroscopy of Adsorbed Species

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It has been well known that for a number of solids, the reflectance in an optical frequency range can be modulated when a strong electric field is applied across the interface.^{1,2} This phenomenon known as electroreflectance (ER) has been adapted, for example, to the determination of band structure of semiconductors. Since Feinleib³ observed ER at metal-electrolyte interfaces, many have employed ER to study electrochemical interfaces such as double-layer structure.⁴⁻⁶ Since the Helmholtz layer thickness is about an angstrom order in an ordinary electrochemical environment, the electric field intensity easily becomes as high as 10^7 V/cm by simple double-layer charging and this is responsible for the electro-modulation of UV-visible light.

ER coefficient, ρ , defined as a normalized electromodulation of reflectance, R , by surface charge, σ , (or equivalently electrode potential, E) is expressed by the equation,

$$\rho = -1/R (\partial R / \partial \sigma) \quad (1)$$

The magnitude of ρ for bare metals is usually an order of 10^{-4} and the model based on field-induced change of free electron concentration of metals has been used to explain electromodulation mechanism.⁷ When a molecular overlayer forms on a metal electrode surface, a new ER feature appears although potential is modulated within a double-layer region where the molecule does not undergo any electrochemical reactions.^{8,9} For example, when adsorbed, *p*-nitroaniline¹⁰ on platinum gives a reflectance peak at 670 nm which is quite away from an absorption maximum at 380 nm in a transmission spectrum. The explanation thus far has been concentrated on the field-dependence of optical properties, called electrochromic (Stark) effect,⁸ of an overlayer. According to this explanation, the complex optical constant of an overlayer, n_2 is modulated by E . In this paper, however, a simulation is presented to explain the same observations in which the emphasis has been placed on an intrinsic optical modulation of a substrate by the applied electric field, which in turn affects resulting spectra. Tetraphenyl porphyrin (TPP) on Au(111) face was chosen as a model system mainly because gold is one of the most common substrates in electrochemistry with a precisely known ER effect over UV and visible region, and TPP is a typical dye molecule with a large extinction coefficient.¹¹

Theoretical Considerations

Integration of Eq. (1) gives the relationship between reflectance and charge, relative to the reflectance at a potential of zero charge (pzc),

$$R_v^\sigma = R_v^{pzc} \cdot \exp\left(-\int (\rho_v(\sigma) d\sigma)\right) \quad (2)$$

where v is either p- or s-polarized light. Equation 2 tells that if $\rho(\sigma)$ is known, the reflectance at a specified charge is readily obtained from R_v^{pzc} and $\rho(\sigma)$. Optical data (refractive index, n and extinction coefficient, k) for polycrystalline gold¹² were employed in this simulation because they are readily available and indistinguishable from those of single crystal gold. ρ_p and ρ_s for Au(111) were taken from Hinnens data¹³ who reported at two different charge state (pzc and $-22 \mu\text{C}/\text{cm}^{-2}$) at 62° as a function of wavelength. It is now straightforward to calculate R_p and R_s at $-22 \mu\text{C}/\text{cm}^{-2}$ from Eq. (2). In principle, it is possible to calculate (n, k) at any incidence angle from R_p and R_s using Fresnel equations¹⁴ for two phase systems except at 45° because an infinite pairs of (n, k) satisfy the same R_p and R_s at that angle from the fact that $R_p = R_s^2$.

In real experiments in the presence of an overlayer, potential modulated differential reflectance spectra (PMDRS), $\Delta R_{123}/R_{123}$ are recorded, where the difference in R between at the sample and reference potential, E_{sample} and E_{ref} is normalized by R at the reference potential. Subscripts 1, 2 and 3 mean ambient phase, overlayer, and substrate, respectively. In the present work, potentials giving $-22 \mu\text{C}/\text{cm}^{-2}$ and pzc were arbitrarily set as E_{sample} and E_{ref} . In order to obtain R_{123} , $\Delta R/R (= R_{123}/R_{13}-1)$ was first calculated, and R_{123} was then simply given by $(\Delta R/R + 1) \cdot R_{13}$. $\Delta R/R$ for the three layer system has been well formulated by McIntyre and Aspin¹⁵ when each boundary of the electrolyte/overlayer/metal system is sharp and the dimension of the second phase is much smaller than the wavelength of the light. Then Fresnel equations for $\Delta R/R$ can be linearized giving much simpler forms. The expressions of $\Delta R/R$ for s- and p-polarized light are given by

$$\left(\frac{\Delta R}{R}\right)_s = \frac{8\pi d n_1 \cos\phi_1}{\lambda_0} \text{Im}\left\{\frac{\hat{\epsilon}_2 - \hat{\epsilon}_3}{\epsilon_1 - \hat{\epsilon}_3}\right\} \quad (3)$$

$$\left(\frac{\Delta R}{R}\right)_p = \frac{8\pi d n_1 \cos\phi_1}{\lambda_0} \text{Im}\left\{\frac{\hat{\epsilon}_2 - \hat{\epsilon}_3}{\epsilon_1 - \hat{\epsilon}_3}\right\} \left[\frac{1 - (\epsilon_1/\hat{\epsilon}_2\hat{\epsilon}_3)(\hat{\epsilon}_2 + \hat{\epsilon}_3)\sin^2\phi_1}{1 - (1/\hat{\epsilon}_3)(\epsilon_1 + \hat{\epsilon}_3)\sin^2\phi_1}\right] \quad (4)$$

The parameters used in these equations are defined as follows: d , overlayer thickness; ϕ_1 , angle of incidence; λ_0 , wavelength of the light; $\hat{\epsilon}$, complex dielectric constant ($=\hat{n}^2$).

Results and Discussion

In the simulation, some assumptions have been made. Fi-

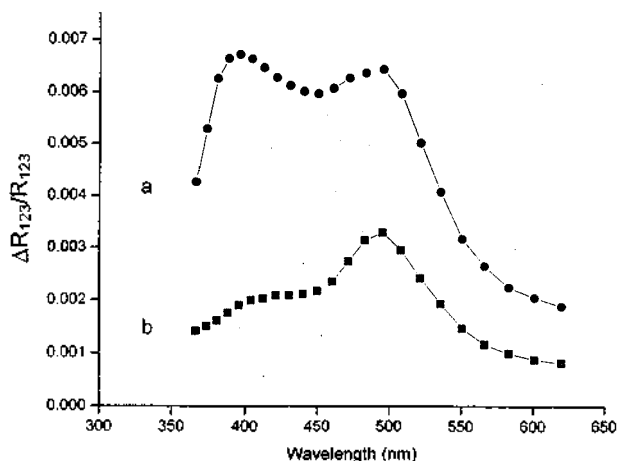


Figure 1. Simulated PMDRS, $\Delta R_{123}/R_{123}$ ($= (R_{-22\mu C} - R_{pzc})/R_{pzc}$), of tetraphenyl porphyrin on Au(111) face with (a) p- and (b) s-polarized light. Simulation parameters: $d=1$ nm, $\phi_1=62^\circ$, $n_1=1.333$.

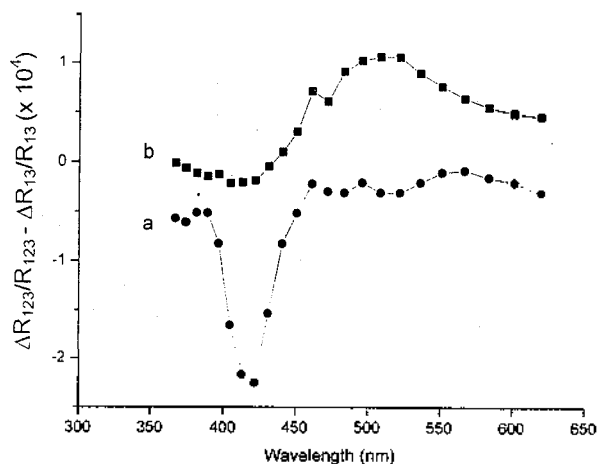


Figure 2. Difference in $\Delta R/R$ ($= \Delta R_{123}/R_{123} - \Delta R_{13}/R_{13}$) with and without an overlayer with (a) p- and (b) s-polarized light. Simulation parameters are the same as in Figure 1.

rst, as stated in **theoretical considerations**, each interface was regarded as having a sharp boundary. Second, no optical interactions between phases and no alteration of optical properties of an overlayer by the applied field were assumed to be present. The reflectance obtained at $-22 \mu\text{C}/\text{cm}^{-2}$ was always larger by less than 1% than at pzc, regardless of wavelength examined. This is quite consistent with experiments¹⁶ in which gold reflectance decreases as potential is positively scanned. The theoretical PMDRS when TPP is covered on Au(111) are shown in Figure 1. Optical constants of TPP were taken from ref. 11. To resemble a real system, 1.333 for n_1 , 1 nm for d were used in the simulation. These values represent typical numbers for the refractive index of an aqueous electrolyte and the thickness of organic monolayers, respectively. 62° was given to the incidence angle because ER data of Au(111) were obtained at that angle.

The resulting spectra show unexpected features at 495 nm, and 396 nm and 495 nm for s- and p-polarized light, respectively, which do not resemble a transmission spectrum

of TPP in a solution phase whose maximum absorption occurs at 440 nm. This can explain why electromodulation of an adsorbate gives rise to unexpected peak(s) although the species is not electrochemically active within potential examined. What is more surprising is that almost identical spectra came out when PMDRS were simulated *without* TPP. This must mean that the intrinsic ER effect of gold dominates optical properties even when a dye molecule is adsorbed. Care, therefore, must be exercised when interpreting ER spectra of an adsorbed layer on metallic substrates. This is true at least for gold since gold has been known as having a large ER coefficient.⁶

To evaluate relative contribution of an overlayer optical constants to overall spectral feature with respect to those of a substrate, the difference in PMDRS with and without TPP, $\Delta(\Delta R/R)$ both for p- and s-polarized light, were recorded (Figure 2). Different spectral shapes were observed with each polarization state of light. However it is not straightforward to predict them from equations. Since the magnitude is an order of 10^{-4} , in most cases the overlayer effect is buried under ER of metallic substrates with a large ER coefficient.

Conclusion

With assumptions made above and from a strictly optical point of view, the substrate ER effect on PMDRS of a molecular monolayer has been examined. The result shows that the intrinsic ER of a metallic substrate cannot be ignored, but actually dominates the spectra. Therefore, one has first to take substrate ER effect into consideration when interpreting reflectance spectra of adsorbates. It may be suggested that in order to detect an overlayer of a monolayer coverage by ER technique, a material of small ER coefficient such as graphite be used.

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L-Methionine and L-Methioninesulfenate Cobalt (III) Complexes of N,N'-dimethylethylenediamine-N,N'-diacetic Acid

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The cobalt(III) complexes of the N,N'-dimethylethylenediamine-N,N'-diacetic acid (H₂dmedda)¹⁻⁵ and the N,N'-dimethylethylenediamine-N,N'-di- α -butyric acid (H₂dmedba)⁶ have been found to yield the *s-cis* (symmetric) geometrical isomers only. Sloan and Krueger,⁷ and Deutsch, *et al.*^{8,9} have shown that in the cobalt(III) complexes such as [Co(en)₂(SCH₂CH₂NH₂)₂]²⁺, [Co(en)₂(SCH₂-CH(COO)NH₂)₂]⁺, and [Co(en)₂(SCH₂COO)]⁺ the controlled oxidation of thiol which are coordinated to cobalt(III) ion leads to the coordinated, S-bonded sulfenatos.

We have been interested in the oxidation of sulfur to the sulfenate stage in an uncoordinated sulfur atom in a metal complex of an amino acid containing a sulfur atom, it appeared that the methionine cobalt(III) complex of dmedda would be a useful choice for such a study, for such cobalt(III) complexes containing the oxidized methionine will likely be resulted in possessing the uncoordinated sulfur atom as desired in this study.

Experimental

s-Cis-Sodium Carbonato(N,N'-dimethylethylenediamine-N,N'-diacetato) cobaltate(III), s-cis-Na[Co(dmedda)CO₃] (1). 1.70 g (5.0 mmol) of Ba(dmedda)¹ was added to 20 mL of water and stirred. 5.6 mL of a solution prepared by diluting 5 mL of conc H₂SO₄ in 100 mL of water was added slowly to this solution. The solution was heated 50 °C and stirred for 30 min. The solution was filtered while hot to remove BaSO₄. 1.81 g (5.0 mmol) of Na₂[Co(CO₃)₂] \cdot 3H₂O

dissolved in 20 mL of water was slowly added to the filtrate with vigorous stirring. The solution was heated to 50 °C and stirred for 1 hr, during which period the solution change to violet color. The solution was filtered and the filtrate was concentrated to one half of its original volume. 25 mL of absolute ethanol was added to this solution, which was filtered. The filtrate was concentrated to 5 mL and 25 mL of absolute ethanol was added. The resultant solution was stored in a refrigerator for 1 day. The precipitates formed was filtered and the violet product was recrystallized from water and ethanol. Yield: 0.72 g (42%). Anal Calcd for NaCoC₉H₁₄O₇N₂: C, 31.41; H, 4.10; N, 8.14 Found: C, 30.19; H, 3.98; N, 8.25.

Δ -s-cis-N,N'-dimethylethylenediamine-N,N'-diacetato (L-methioninato)cobalt(III), Δ -s-cis-[Co(dmedda)(L-met)] (2). 1.72 g (5.0 mmol) of 1 was dissolved in 30 mL of water and heated at 60 °C for 30 min with stirring. 0.74 g (5.0 mmol) of L-methionine was added. 4.2 mL of a solution prepared by diluting 1 mL of conc HCl in 10 mL of water was slowly added to this solution. The pH of the solution was adjusted to 8.5 and 0.1 g of activated carbon was added. The reaction mixture was heated at 60 °C for 5 hrs. The reaction mixture was heated at 60 °C for 5 hrs. The reaction mixture was filtered and the filtrate was concentrated to 5 mL. 50 mL of absolute ethanol was slowly added and filtered. The filtrate was concentrated to 5 mL, which was admitted to a column packed with Dowex 50 W-X4 cation exchange resin (200-400 mesh, H⁺ form). Two bands were detected by elution with water. The violet first band fraction was the unreacted reactant. The red violet second band fraction was collected and evaporated to obtain the red violet product, which was recrystallized from water and ethanol, and vacuum dried. Yield: 0.84 g (41%). Anal Calcd for CoC₁₃H₂₄O₆N₃S: C, 38.15; H, 5.91; N, 10.42; S, 7.95 Found: C, 37.87; H, 5.77; N, 10.52; S, 7.77.

Δ -s-cis-N,N'-dimethylethylenediamine-N,N'-diacetato(L-methioninesulfenatonato) cobalt(III), Δ -s-cis-[Co(dedda)(L-met-O)] (3). *via* oxidation of 2. 0.41 g (1.0 mmol) of 1 was dissolved in 15 mL of water and stirred at room temperature for 30 min. 1.3 mL (1.0 mmol) of a solution prepared by adding 1 mL of 30% H₂O₂ to 10 mL of water was added to this solution dropwise for 50 min. Stirring was continued at room temperature for 1 hr. The solution was concentrated to 5 mL and filtered. The filtrate was admitted to a column packed with Dowex 50W-X4 cation exchange resin (200-400 mesh, H⁺ form). Two bands were detected by elution with water. The red violet second band fraction was collected and concentrated until precipitates were formed. The red violet product was obtained by filtration and vacuum dried. Yield: 0.30 (70%). Anal Calcd for CoC₁₃H₂₄O₇N₃S: C, 36.71; H, 5.69; N, 9.88; S, 7.52. Found: C, 36.66; H, 5.56; N, 10.01; S, 7.46.

L-Methioninesulfenate (5). 4.48 g (30 mmol) of L-methionine was dissolved in 60 mL of acetic and cooled to 12 °C. 3.5 mL of 30% H₂O₂ was slowly added for 4 hrs. The solution was filtered and filtrate was concentrated to 30 mL. 30 mL of acetone was slowly added and the solution was stored in refrigerator for 1 day. The white precipitates were collected by filtration, recrystallized once from water and ethanol, and vacuum dried. Yield: 2.64 g (53%).