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Technical Report No. 10

Modelling the In Situ Infrared Reflection-Absorption Spectra of the Diffuse Layer

by

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Prepared for Presentation

at

The Electrochemical Society Meeting
Los Angeles, CA, May 1989

May 1, 1989

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REPORT DOCUMENTATION PAGE	1. REPORT NO. 10	2.	3. Report's Accession No.
4. Title and Subtitle Modelling the In Situ Infrared Reflection-Absorption Spectra of the Diffuse Layer			5. Report Date May 1, 1989
7. Author(s) P.W. Faguy, S. McCullough and W.R. Fawcett			6.
9. Performing Organization Name and Address Department of Chemistry University of California Davis, CA 95616			8. Performing Organization Report No. 1
			10. Project/Task/Work Unit No.
			11. Contract(G) or Grant(G) No. N00014-87-K-0541
12. Sponsoring Organization Name and Address Office of Naval Research 800 N. Quincy Arlington, VA 22217-5000			13. Type of Report & Period Covered
			14.
15. Supplementary Notes Prepared for Presentation at: The Electrochemical Society Meeting, Los Angeles, CA, May 1989			
16. Abstract (Limit 200 words) Using a stratified medium model for the electrochemical interface and Gouy-Chapman-Stern theory of the double layer, a method to model infrared reflection-absorption spectra of the diffuse layer is developed. This method is applied to spectra obtained in the double layer region for aprotic, organic electrolytes on gold electrodes. <i>Keywords: Infrared spectroscopy; Raman spectroscopy; Electrode/electrolyte interface; Electrochemistry; (eds)</i>			
17. Document Analysis a. Descriptors			
b. Identifiers/Open-Ended Terms			
c. CBATI Field/Group			
18. Availability Statement		19. Security Class (This Report) Unclassified.	20. No. of Pages
		21. Security Class (This Page)	22. Price

75-Word Abstract Form

Extended Abstract must be submitted with the 75-Word Abstract by December 1, 1988

Los Angeles, California—May 7-12, 1989

Submit to: The Electrochemical Society, Inc.
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of the Diffuse Double Layer.

Authors (Underline name of author presenting paper.) P.W. Faguy, S. McCullough, W.R. Fawcett

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Modelling the *In Situ* Infrared Reflection-Absorption Spectra of the Diffuse Double Layer.

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The sensitivity of *in situ* IRRAS techniques¹ such as EMIRS and SNIFTIRS to molecular structure at the electrode / electrolyte interface arises from the coupling of two physical phenomena: the local increase in the electric field strength for parallel polarized light reflect at the surface of the electrode² and the potential drop across the double layer. In the EMIRS or SNIFTIRS experiment there is enhanced sensitivity to species present within a few wavelengths of the IR radiation from the electrode surface and only to those species which change due to the applied electrochemical potential. As the diffuse layer is typically 10 - 100 Å for these experiments³ and as the large electromagnetic field at the metal surface decays over much longer distances², 2 - 20 μm, the resultant *in situ* spectra will be a function of the product of these two effects integrated over the complete diffuse layer. Thus with such techniques the diffuse layer is probed to almost the same extent as is the electrode surface.

This paper presents a method for calculating the *in situ* infrared reflection-absorption spectra for species present in the diffuse layer based on a stratified media model of the electrode / electrolyte interface, Gouy-Chapman-Stern theory and the attenuated total reflection IR spectra of the electrolyte solutions.

In order to calculate reflection-absorption spectra it is necessary to construct an optical model of the interface. Figure 1 is a schematic drawing showing an N layer system consisting of a non-absorbing semi-infinite initial phase, N-2 planar finite strata and an absorbing semi-infinite final phase. This approach assumes that the media are isotropic, homogeneous, linear and that the dielectric constant is independent of position within an individual layer.^{4,5} Calculations of optical parameters for the *in situ* experiment, based on similar models, have been reported.^{6,7}

In this treatment, the matrix formalism developed by Hansen⁵ for the N layer system will be apply to a stratified medium where the 3rd through N-2 components represent the diffuse layer as is shown in Figure 1. Each of these N-4 strata will have a dielectric constant and characteristic thickness associated with it, obtained from bulk solution and solvent values and GSC theory. The real and the imaginary components of the dielectric constants are calculated using ATR measurements of the bulk components and the appropriate Fresnel equations.^{8,9}

Modelled and measured spectra for gold electrodes, using alkali perchlorate salts in dimethylformamide and acetonitrile solutions will be presented.

Acknowledgements

We gratefully acknowledge the support of the Office of Naval Research, Washington.

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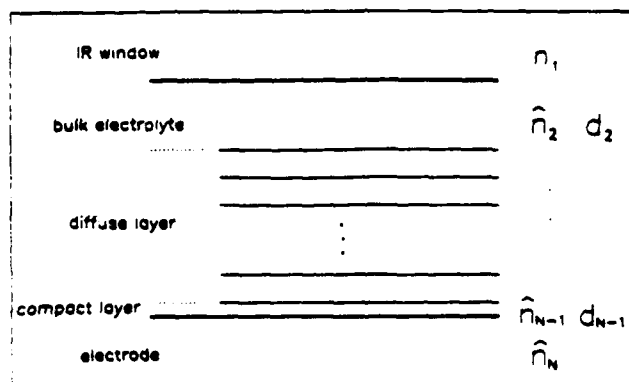


Figure 1. Multiple layer optical model of the electrode / electrolyte interface.