Potential Modulation of Equilibrium and Excitation Phenomena at the Electrolyte-Solid Interface

Progress Report

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by

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Abstract

This progress report covers the work accomplished from the beginning of Oct.. 1991, through the end of Sept. 1992.

During the reporting period we have concentrated on performing and interpreting well-defined experiments which have helped advance the understanding of the nonlinear optical properties of metal surfaces. This is associated with a class of techniques of fundamental interest in Materials Science with a broad range of potential applications involving characterization of buried interfaces. These include following the progression of events in the corrosion of a metal, designing conditions under which fuel cells might be made more efficient, and optimizing electrochemical processing. However, unlike the linear optical techniques of ellipsometry, for example, the nonlinear technique of optical second harmonic generation (SHG) is, at present, poorly understood. In spite of this, SHG has already been demonstrated to be particularly well suited for interfacial studies. The strongest nonlinear response is intrinsically surface sensitive and is rich in its information content.

In our experiment the sample is made to be an electrode in an electrochemical cell. This is for two reasons: First, the large interfacial electric field introduces a controlled perturbation that allows separation of the surface and bulk signals. Part of the complication associated with SHG is one of competition among the surface signal and weaker higher order bulk effects. Second, we are particularly interested in applying optical SHG as a probe of the electrolyte-solid interface. At this point in our program we are still establishing the fundamental understanding of the technique itself. In the future, we hope to apply what we have learned to diagnose some important problems in electrochemical science. One of the major distinguishing features of our approach is our use of a wide range of incident photon energies (unlike the more common practice of using a monochromatic source). This allows us to probe a variety of elementary excitations in the surface and the bulk of the metal, as well as to provide data that can be compared to theories in which the photon energy may be an important variable. In any nonlinear optical experiment we seek the surface susceptibilities that govern the strength of conversion of the incident light to second harmonic light. These are directly related to the geometrical and electronic structure of the system.

During the reporting period we completed a series of experiments on Ag(001). We learned some important information about the bulk isotropic (γ) and anisotropic (ζ) susceptibilities that can now be translated to other orientations of Ag. In addition, we found that the only allowed surface susceptibility, $\chi(zxx)$, was only negligible as long as the surface remained uncharged. On charged surfaces we measured a strong effective $\chi(zxx)$. This is important since virtually all theoretical approaches to optical SHG have ignored $\chi(zxx)$. In an effort to explain these results we developed a new

phenomenological model for four-field mixing. We treat the effect of the static electrochemical field as a third "incoming field" (together with the two optical fields of SHG) that mix via a third-order surface susceptibility. This picture successfully accounts for all that we have seen on Ag(001).

Although we are, at present, primarily interested in learning to understand optical SHG, occasionally, we stumble onto a previously unknown phenomenon associated with the electrolyte-solid interface itself. This was the case last year, when we reported a potential-induced surface reconstruction on Ag(111) [an orientation that was previously thought to be stable]. The reconstruction was identified through a symmetry analysis of the crystal orientation dependence of the optical SHG. We attributed this effect to strongly adsorbed sulfate ions. These were a component of our electrolyte. We have devoted a reasonable amount of time during the reporting period to improving our surface preparation methods and to experiments in other electrolytes in an effort to identify the conditions under which the reconstruction can be observed. We continued to detect a *trend* toward the fully reconstructed surface without reproducible results. The reproducibility problem was earlier associated with the random nature of the equivalent domains of the reconstructed phase. Only when one of the domains dominates the sampled region of the surface would we have seen the full transformation. Now we are exploring alternate explanations of the apparent symmetry change. These include the four-field mixing mechanism that was found to be useful on Ag(001).

In other work, we continued to improve the detection system on our new surface Raman facility. In the future, we hope to develop surface plasmon enhanced Raman scattering as the most sensitive method for studying vibrational spectroscopy of the liquid side of the electrolyte-solid interface. When the instrumentation portion of that aspect of our program is complete, we will look at interfacial water as a function of the applied potential. This year we reconfigured the optics in the monochromator to reduce scattered radiation and performed several sensitivity tests on prototypical samples. However, this aspect of our overall plan was impacted by a budget reduction. It was only possible to devote three months to this effort.

Although our goals have been scaled down from those of the original proposal, we are pleased with our progress. We continue to occupy an important position as one of the primary groups concerned with interfacial optical spectroscopy. In that regard, DOE continues to receive the benefit of our best ideas that are on the forefront of this field.

Bibliography of Publications, Reports, and Presentations

Publications:

1. "Surface Plasmon Assisted Raman Scattering from Electrochemically Controlled Adsorbates on Flat, Single Crystal Silver", S. P. Byahut and T. E. Furtak, *Electrochimica Acta* **36**, 1879 (1991).
2. "Study of Underpotential Deposition of Metals Using the Quartz Crystal Microbalance", Yeke Tang and T. E. Furtak, *Electrochimica Acta* **36**, 1873 (1991).
3. "Ag(111) Surface Reconstruction Studied by Optical Second Harmonic Generation", Yeke Tang, L. J. Simpson, and T. E. Furtak, *Physical Review Letters* **67**, 2814 (1991).
4. "Optical Second Harmonic Electroreflectance from Ag(111)", T. E. Furtak, Yeke Tang, and L. J. Simpson, *Physical Review* **B46**, 1719 (1992).
5. "Surface Plasmon Assisted Raman Scattering from Adsorbates on Flat Metal Surfaces", *Fundamentals and Applications of Surface Raman Spectroscopy*, T. M. Cotton, R. L. Garrell, and J. E. Pemberton (editors), (VCH Publishers, New York, in press), Chap. **B10**. T. E. Furtak and S. P. Byahut.
6. "Electric Field Induced Perturbation of the Nonlinear Optical Properties of Ag(001) in Contact With an Aqueous Solution", *Journal of the American Vacuum Society* (submitted), L. J. Simpson and T. E. Furtak.

Invited Presentation:

7. "Optimizing Surface Sensitivity in Raman Characterization of Buried Interfaces", *Seiler Laboratory Seminar*, United States Air Force Academy, Colorado Springs, CO, April 21, 1992, T. E. Furtak.

Contributed Presentations:

8. "Nonlinear Optical Reflectance Spectroscopy of a Single Crystal Metal Electrode", *Electrochemical Society, National Meeting*, Phoenix, AZ, Oct. 13, 1991. T. E. Furtak, Yeke Tang, and L. J. Simpson.

9. "Optical Second Harmonic Electroreflectance Spectroscopy from Ag(111)", *38th Annual American Vacuum Society Symposium*, Seattle, WA, Nov. 11, 1991. T. E. Furtak, L. J. Simpson, and Yeke Tang.
10. "Potential Dependent Resonant Second Harmonic Generation from Ag(001)", *American Physical Society*, March Meeting, Indianapolis, IN, March 16, 1992. L. J. Simpson and T. E. Furtak.
11. "Nonlinear Optical Characterization of Metal Surfaces", DOE Corrosion Contractors Meeting, University of Illinois, Sept. 10, 1992. T. E. Furtak and L. J. Simpson.

Summary of Published Work

Reproductions of already published work appear as Bibliography items 1-3. These were presented in reprint form as part of last year's Annual Progress Report. Notable among these is the article that was printed in *Physical Review Letters* last November. For a complete description of that result see DOE/ER/45253-6.

Second Harmonic Electroreflectance Spectroscopy [Bibliography items 4, 8, 9]

It is important to be able to perform tests of theoretical models that contain predictions about the characteristics of optical SHG and how it depends upon changes in the system. Only by this means do we actually verify our understanding of a new phenomenon. In the case of metals, reasonably complicated models have been presented for the "free electron" contribution to optical SHG. We have studied this as a function of the applied potential, which alters the ground state charge distribution, and as a function of the incident photon energy. Our object was to provide a quantitative test of the most sophisticated time dependent local density functional theory for metal electrodynamics in the nonlinear response regime. Prior to our work, a group in France had tested the model using an electrochemically perturbed Ag(111) sample, however their experiment was only performed at one incident photon energy, at 1.17 eV. We have covered the entire range of important elementary excitations in Ag with our results. To avoid the problems associated with normalization from energy to energy, we expressed our data in terms of the zero charge condition of the sample. This sample-normalized differential reflectance spectrum depends only upon the linear optical properties of bulk Ag (which we obtain from handbook data), and the nonlinear source terms which we have extracted from the local density functional theory. Our results show that the theory works much better than expected when $\Delta Q > 0$, provided the region around the interband transitions are avoided. Since the theory was contrived in the jellium approximation, which does not allow for band structure effects, this is not unexpected. The correlation is much worse when $\Delta Q < 0$. We were unable to get the theory to fit our data in any part of the spectral range, even when the nonlinear source terms were adjusted by a scale factor. As part of our analysis of these data we made the standard assumptions regarding the role of bulk susceptibilities. We also ignored $\chi(zxx)$, as has been the practice in all previous work.

Isolated Susceptibility Characterization [Bibliography items 6, 10, 11]

In spite of the fact that Ag(111) is a relatively simple system on which to study the mechanisms of optical SHG, it is still complex. Progress in the analysis has been made by some careful assumptions regarding several of the susceptibilities. However, the validity of these assumptions has never before been tested. In view of the lack of

correlation between the time dependent local density functional model and our Ag(111) data, it was essential that these tests be performed. For this task we designed a set of experiments on Ag(001). The surface symmetry of Ag(100) includes the inversion operation parallel to the surface. This means that, as is true for the bulk of a centrosymmetric material, second harmonic susceptibilities whose components are in the direction of the inversion must be zero--in the electric dipole limit. Contributions from the bulk are still possible due to much weaker higher order source terms (magnetic dipole and electric quadrupole) when integrated over the penetration depth of the optical radiation. These can be independently studied on Ag(100) without the relatively strong competition from the dipole allowed surface terms. By measuring the anisotropic contribution to the second harmonic reflectance as functions of the applied potential and the incident photon energy, we have been able to map some remarkable characteristics of these phenomena.

The conclusions to date are as follows: The bulk isotropic susceptibility (χ) is very small (most likely negligible) as long as the harmonic photon energy is below the bulk interband transition threshold. The bulk anisotropic susceptibility (χ_z) is also small. However, it can, in general, not be completely ignored. This is because of the manner in which the anisotropic contribution combines with other terms. It is possible that a mixing could occur that would lead to a relatively large second harmonic signal, in spite of the small magnitude of (χ_z) by itself. These results can be carried over to other orientations of Ag. The most striking finding was that $\chi(zxx)$, which has been previously ignored, can be appreciable. This only occurs, however, on a positively charged surface. On the neutral and negatively charged surfaces $\chi(zxx)$ can be considered to be zero.

In an effort to understand the origin of the potential dependence of $\chi(zxx)$ we undertook the development of a complete theory of four-field mixing. This is a concept that had originally been introduced by Bloemgrgen and his colleagues nearly two decades ago. However, never before have the full implications of the symmetry of the sample been brought out. The essence of the idea is that the interfacial field (at zero frequency) can be considered one of three fields (the other two being the incoming optical fields) that mix in the sample through a third order dipole allowed susceptibility. The fourth field is that of the outgoing second harmonic light. Our approach tells us which susceptibilities will have a static field dependent contribution. We find that, under the s-to-p configuration of the Ag(001) experiment, it is $\chi(zxx)$ that is modified. This is another way of saying that the field alters the electron density distribution at the surface so as to expose corrugation parallel to the surface plane. This corrugation represents a parallel gradient in electron density that must contribute to optical SHG. The "free electron" models had never considered this to be important since there is no structure parallel to the surface in a free electron solid. The role of the field is to push the screening electron density back beyond the equilibrium location so as to enhance the lattice potential effects.

Of even greater significance is the implications that the four-field mixing concept has on the Ag(111) experiments. In that system there is no inversion symmetry parallel to the surface. For this reason the third order susceptibility contains extra terms. One of these enters into the phenomenological expression for SHG signal in exactly the same way as an altered surface symmetry. This means that, upon the action of an applied static electric field, there is a mechanism leading to an "apparent" surface phase transition. This result was totally unexpected. Previous literature have indicated that there could never be a change in apparent symmetry if the static field is always perpendicular to the surface. On the contrary, because of the lack of inversion parallel to the surface, this effect is quite possible using the third order susceptibility. We are exploring this development with a new set of experiments.

Surface Plasmon-Polariton Assisted Raman Scattering. [Bibliography Items 5,7]

In addition to nonlinear optical spectroscopy at the electrolyte-solid interface the other major component of our program has been surface Raman spectroscopy in the same environment. These methods are complementary in that the former is primarily an electronic state probe while the latter samples the vibrational states. When coupled with the interfacial potential modulation method, one can learn a great deal about the influence which the electrochemical field has on the properties of the system by developing and studying these techniques simultaneously. Our efforts in surface Raman scattering have been scaled down from the original proposal because of budget restrictions. However, we are continuing to maintain a small program that exploits the uniqueness of our particular experimental device.

Our concept of surface Raman scattering has evolved into a sophisticated approach exploiting optical phase matching on a smooth surface of silver. This was accomplished using our unique "Kretschmann configuration" surface plasmon coupling device and multichannel detection. The apparatus has been described in previous Progress Reports. It exploits the large surface optical fields which are associated with surface plasmon-polariton waves on Ag. The Raman effect is driven at the surface by the very large fields. In the second step of the scattering, the emission of the energy shifted radiation, we also couple to surface plasmon-polaritons. This double coupling process results in very high efficiency for getting the optical energy into and out of the monolayer.

During the reporting period wrote an invited comprehensive review of this technique [Bibliography Item 5]. It traces the history of the development of the Kretschmann method applied to Raman scattering. As part of the explanation we have produced original theoretical modeling of the effect under a variety of conditions. Notable among these are configurations that involve use of Ag as the surface plasmon medium with a different material coated as a thin layer on top of that. This should make it possible to study the Raman spectra of adsorbates on oxides and foreign metals. In the case of Pt, for example, an enhancement factor of over 60 can still be realized under conditions where

most of the adsorption would be taking place on the Pt. Other predictions involve manipulation of the detected radiation distribution so as to selectively sample different components of the Raman polarizability tensor. Experiments of that type could be used to directly identify the orientation of a species.

Summary of Progress on Other Projects

Multichannel Photon Counting Surface Raman Spectrometer

We completed some important modifications of our instrumentation on the Raman experiment. These were necessary to reduce the overall level of scattered radiation in side of the monochromator. We reconfigured the optics and installed baffles at critical places. The monochromator is coupled to our multi-channel-plate photomultiplier. This device is capable of single photon counting in each of 512 different wavelengths in parallel. The multiplex advantage offered by this approach makes it possible to observe very weak Raman signals. Our plan is to couple this instrument to the Kretschmann phase matching device to achieve unprecedented detection sensitivity for an adsorbed monolayer. The eventual goal is to be able to observe the vibrational spectrum of water at the electrolyte-solid interface. Preliminary tests on the reconfigured system show outstanding dark signal behavior--close to 10^{-4} counts per channel per second. Additional work on this project will proceed as permitted by future resources.

Statement of PI Involvement

The principal investigator, Professor Tom Furtak, devoted 25% of his time during the summer, charged to the grant. He also devoted approximately 20% of his time to this project during the academic year, of which 10% was charged to the grant.

Statement of Student Involvement

During the grant period Lin Simpson was supported as a full-time graduate research associate (50% during the AY, 100% during the summer). Lin is a candidate for a Ph. D. in Materials Science at CSM. He has passed the Materials Science Comprehensive Examinations last November. His area of emphasis is Solid State Physics. Lin is primarily responsible for the experimental aspect of the surface nonlinear optical spectroscopy program.

During the summer 1992 a junior graduate student, Bin Qui, worked on the surface Raman apparatus. He completed all of the optical modifications and the sensitivity tests.

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