1989

Study of electrodeposition of a single monolayer of copper onto a polycrystalline gold electrode surface using second harmonic generation

Mark Bennahmias
San Jose State University

Follow this and additional works at: https://scholarworks.sjsu.edu/etd_theses

Recommended Citation

Bennahmias, Mark, "Study of electrodeposition of a single monolayer of copper onto a polycrystalline gold electrode surface using second harmonic generation" (1989). *Master's Theses*. 3177.
DOI: <https://doi.org/10.31979/etd.453n-6zzc>
https://scholarworks.sjsu.edu/etd_theses/3177

This Thesis is brought to you for free and open access by the Master's Theses and Graduate Research at SJSU ScholarWorks. It has been accepted for inclusion in Master's Theses by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.

INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

Order Number 1339603

**Study of electrodeposition of a single monolayer of copper onto
a polycrystalline gold electrode surface using second harmonic
generation**

Bennahmias, Mark Joseph, M.S.

San Jose State University, 1989

U·M·I

**300 N. Zeeb Rd.
Ann Arbor, MI 48106**

**STUDY OF ELECTRODEPOSITION OF
A SINGLE MONOLAYER OF COPPER
ONTO A POLYCRYSTALLINE GOLD
ELECTRODE SURFACE USING
SECOND HARMONIC GENERATION**

A Thesis
Presented to
The Faculty of the Department of Physics
San Jose State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

By
Mark Bennahmias
December 1989

**APPROVED FOR THE DEPARTMENT OF
PHYSICS**

Dr. H. Sarma Lakkaraju

Dr. Bradley M. Stone

Dr. Gareth T. Williams

APPROVED FOR THE UNIVERSITY

ACKNOWLEDGEMENTS:

The author owes a debt of gratitude to several people for their contributions in the preparation of this manuscript. I especially want to thank my two graduate thesis advisors, Professors H. Sarma Lakkaraju and Bradley M. Stone, to whom I am forever deeply indebted. They provided a constant source of encouragement and guidance both in the laboratory and in generating the body of this thesis. I am also extremely indebted to Professor Kevin Ashley for the many hours of invaluable discussions we shared on the principles and laboratory techniques involved in the Electrochemistry portion of this project. I also thank Dr. M.R. Philpott of IBM Almaden Research Center for the loan of a spectroelectrochemical cell that was used in these experiments. I would also like to express my deepest appreciation to Robert Ettelbrick and Jeremy Weston for many hours of technical assistance in working with the Quantel Nd:YAG laser. I also wish to thank Dr. Gareth T. Williams for participating as a member of my graduate committee and providing several valuable suggestions along the way. Finally, I wish to thank my wife, Andrea Bennahmias, for her infinite patience and understanding during those long hours I spent away from home working in the laboratory.

DEDICATION:

I would like to dedicate this thesis to my newborn son, Daniel Aaron Bennahmias, who has filled me with new inspirations, hope, and joy.

CONTENTS

1	INTRODUCTION	7
2	EXPERIMENTAL METHODS	20
2.1	Experimental Apparatus.....	20
2.2	Experimental Targets.....	23
2.2.1	Quartz Crystal.....	23
2.2.2	Spectroelectrochemical Cell.....	24
3	BULK SECOND HARMONIC GENERATION IN QUARTZ	26
3.1	Justification.....	26
3.2	Experimental Concerns.....	27
3.3	Experimental results.....	29
3.4	Discussion.....	30

4	SECOND HARMONIC GENERATION AT AN INTERFACE	3 4
4.1	Justification.....	3 4
4.2	Electrode/Electrolyte Interface.....	3 6
4.3	Underpotential Deposition.....	4 0
4.4	Experimental Concerns.....	4 3
4.5	Experimental Results.....	4 7
	4.5.1 CV Characteristics.....	4 7
	4.5.2 SHG Characteristics.....	4 8
	4.5.3 Blank Cell Characteristics.....	5 0
4.6	Discussion.....	5 1
5	CONCLUSIONS	5 5
6	APPENDIX	5 7
7	FIGURES	7 5

CHAPTER ONE

INTRODUCTION

Although it has been generally known since Maxwell's time that most materials respond nonlinearly to electromagnetic radiation, it was for the most part not possible to experimentally observe a great many nonlinear phenomena in the optical domain until the advent of the laser in the early 1960s. It had been previously well established from the classical theory of optics that the strength of a nonlinear optical response from a given material tended to be significantly smaller than the corresponding linear optical response. In fact, typical conversion efficiencies, providing an indication of the extent of coupling of the incident energy into nonlinear optical processes, fall within the range of 10^{-7} to 10^{-8} . As a result, most ordinary sources can not meet the enormous energy demands required to sufficiently excite optical nonlinearities to the point where they can be experimentally detected. For example, the electric field of sunlight at the surface of the earth has an amplitude on the order of 10 volts/cm, enough to change the refractive index of glass in the optical Kerr effect by only one part in 10^{15} . Similarly, the magnetic field of sunlight is about 1/30 gauss, enough to change the refractive index of glass in the Faraday effect by only one part in 10^{12} . Both the Faraday and Kerr nonlinear optics experiments were among the first to indicate that by virtue of its own electric and magnetic field, light of

sufficient intensity can change the refractive index of the medium supporting it, directly affecting its own propagation and that of other light beams present¹. Fortunately, today's lasers are able to provide light that is coherent, monochromatic, of high intensity, and embodying large electric and magnetic fields. Without them, much of the work that has since been accomplished in the field of nonlinear optics would not have been possible.

The physical principles involved in generating bulk and surfacial nonlinear optical signals by materials can be understood at the microscopic level. Simply stated, a free atom consists of a positively charged nucleus surrounded by a cloud of one or more electrons. These electrons form a series of discrete shells. The electrons in the outermost shells are loosely bound and are called valence or optical electrons. Electrons orbiting in shells much closer to the nucleus are much more tightly bound and are called core electrons. When atoms are close to one another, as in the case of a crystal, the valence electrons from each of the atoms are available to be shared by, or transferred to, other neighboring atoms. The result of this process is to completely fill the outer shells of adjacent atoms, thereby bonding all the atoms together. When a light wave interacts with a transparent crystal, the nuclei of the material atoms are too heavy to respond to the rapidly alternating electric field. The weakly bound valence electrons, however, redistribute themselves in step with this field. Their redistribution involves a polarization, or a displacement of

negative charge, inside the crystal. The periodically changing polarization within the crystal corresponds to a dipole oscillating motion of the negative charge density and therefore to a weak alternating current at the light frequency. As long as the optical electric field is small compared with the cohesive electric field within the crystal, the polarization current faithfully follows the electric field of the light wave. The crystal now behaves like a highly directional antenna, supporting a wave of current radiating, via optical transitions within the dipole approximation ($k \cdot r \ll 1$), precisely in step with the parent light wave. This wave of current is created by either transmission of the light wave through the bulk crystal or upon reflection of the light by surfacial or interfacial layers. Typically, the energy in the incident light wave will not significantly change; the only effect of the polarization and subsequent re-radiation is to slow down the velocity of the light propagating within the medium, i.e. dispersion.

On the other hand, the situation is quite different for intense light. For instance, focusing the light from a pulsed YAG laser down to a one micron spot size can produce an electric field as strong as 10^9 volts/cm. Such strong fields are comparable to the cohesive Coulombic electric fields in the crystal, which are in the range of 10^8 to 10^{10} volts/cm. Consequently when these intense laser beams enter a transparent crystal, they cause a sudden massive redistribution of the optical electrons such that the resultant polarization no longer leads to atoms radiating exactly in

step with the parent light wave, but rather these atoms will now also radiate light that contains higher order harmonics of the fundamental excitation field, as depicted in figure (1.1). This distorted polarization wave, will in principle travel through the crystal at nearly the same velocity as the incident light wave, with individual components differing by at most a few percent over the entire harmonic frequency range. A direct analogy to the nonlinear polarization of optical electrons can be found in studying the subsequent motion of a "soft" spring, which does not obey Hooke's law, initially displaced from its equilibrium and then released.

The simplest case of nonlinear optical wave interactions deals with second order effects. Of these nonlinear optical phenomenon, bulk second harmonic generation (SHG) was the first ever observed in which a coherent input generated a coherent output. In the summer of 1961, the experimental verification of the existence of bulk SHG was successfully undertaken by P.A. Franken, A.E. Hill, C.W. Peters, and G. Weinreich at the University of Michigan². They focused the red light ($\lambda = 6943 \text{ \AA}$) of a 3kW ruby laser onto a quartz crystal and were subsequently able to detect an optical signal with a magnitude attributable to one part in 10^8 of the incident light striking the crystal being converted to SHG light ($\lambda = 3471.5 \text{ \AA}$); this SHG wavelength which lies in the ultraviolet (uv) region of the spectrum, was exactly half the fundamental wavelength and therefore twice the frequency of the incident laser light. The

possibility that the emitted light might have been some kind of uv fluorescence induced by the laser beam was ruled out by the experimentalists because the signal was sharply tunable with respect to wavelength and was emitted in as highly directional beam as the incident light.

The experiments that soon followed strongly indicated that bulk SHG seemed to occur only in crystals that had a "one-wayness" in their structure, or, to be more precise, crystals that lacked a center of symmetry³. It was theoretically demonstrated that for centrosymmetric crystals, the second-order, nonlinear, electrical susceptibility coefficients $\chi_{ijk}^{(2)}$ vanished and therefore these crystals, to first order, were incapable of generating any bulk SHG signal. The electric susceptibility coefficients provide a sense of measure of the strength of a nonlinear interaction of the constituent atoms in a medium with an externally applied electric field. This characteristic of centrosymmetric materials can best be illustrated by the following train of thought. The relationship governing the components of the nonlinear polarization induced via the coupling of the components of the electric field is given by,

$$P_i^{(2)} = \chi_{ijk}^{(2)} E_j E_k \quad (1.1)$$

where $P_i^{(2)}$ = the i th second order nonlinear polarization coefficient,
 E_j, E_k = magnitudes of the j th and k th components of the electric field,

and where the Einstein summation convention has been adopted. In reversing the direction of the applied electric field, E_j becomes $-E_j$, and E_k becomes $-E_k$. Since the crystal is assumed to be centrosymmetric, the reversed field "sees" a crystal identical to the original one. Consequently, the polarization produced by the reversed electric field should bear a similar relationship, except for sign, to that of the original electric field; that is, the new polarization is simply $-P_i^{(2)}$. Modifying equation (1.1) accordingly,

$$-P_i^{(2)} = \chi_{ijk}^{(2)}(-E_j)(-E_k) \quad (1.2)$$

It should be clear that in order for equations (1.1) and (1.2) to be simultaneously satisfied, the coefficients $\chi_{ijk}^{(2)}$ would all have to be identically zero. The same arguments do not apply in materials that lack this kind of inversion symmetry. The importance of the statement, *SHG is electric dipole forbidden in crystals possessing an inversion symmetry*, signifies the underlying reason for the popularity of SHG as an optical microprobe of the internal structure of nonlinear materials. However one should always keep in mind that in all real materials, centrosymmetric, or not,

contributions to the second order, nonlinear, electrical susceptibility from electric quadrupole and magnetic dipole terms, from field discontinuities in the bulk medium, and at the surface, will generally exist^{4,5}. Experimental work in the area of bulk SHG has established reliable techniques that are currently in use today to measure, with a high degree of accuracy (<5%), the nonlinear optical coefficients of materials used as standards.

Current research into nonlinear optical effects occurring at surfaces and interfaces has for the most part proceeded along two lines: first, to obtain a more fundamental understanding of the nonlinear interactions, and second, to look into the possibility of exploiting these effects as new optical surface microprobes that are very different from, but complementary to, current conventional methods of surface characterization. Unlike many of the conventional surface probes, which rely strictly on emission, absorption, or scattering of massive particles in a ultra-high vacuum or a low temperature environment, optical techniques have the definite advantages of being nondestructive, capable of in-situ remote sensing, ultrafast, exhibiting high spatial and temporal resolution, and applicable to any interface accessible by light. However, the primary limitation of a large number of linear and nonlinear optical methods often lies in the lack of surface specificity and sensitivity. Fourier-transform infrared (FTIR)⁶ reflectance-absorbance measurements, surface enhanced Raman scattering (SERS)⁷, and Coherent anti-Stokes Raman scattering

(CARS)⁸ for example, can be employed for surface studies only if the dominant bulk contribution to the signal can be discriminated against.

Since inversion symmetry is necessarily broken at the boundary between two different media, it quickly became obvious to many researchers that SHG could be applied as an optical microprobe in experiments designed to study interfacial and surfacial phenomenon. Figure (1.2) depicts the physical model of SHG from an interface between two isotropic, non-magnetic, homogeneous media. The multilayer geometry indicates that the surface atomic layers of thickness, $d \ll \lambda$, will generally have optical properties different from those of either bulk material. Here medium 1 is taken to be strictly linear with dielectric constant ϵ_1 . Medium 2 is characterized by a linear dielectric constant ϵ_2 and second-order nonlinear electrical susceptibility $\chi_2^{(2)}$ tensor. The interface between medium 1 and medium 2 is characterized by the same index of refraction as medium 2, but with a different second order, nonlinear, electrical susceptibility $\chi_s^{(2)}$. A monochromatic plane wave at frequency ω , incident from medium 1, induces a nonlinear source polarization in the surface layers and in the bulk of medium 2, via non-vanishing electric quadrupole and magnetic dipole terms. The source polarization then radiates, and harmonic waves at 2ω emanate outwards from the boundary in both reflected and transmitted directions.

An estimate for the strength of the SHG radiation generated from an interface, considered to behave like a sheet of oscillating dipoles, is given approximately by ⁹

$$S \approx (128\pi^4\omega/hc^3)|X_s^{(2)}|^2 P^2 \tau_p / A_0 \tau_r \quad (1.3)$$

where S = number of photons per laser pulse

P = pump laser power [watts],

A₀ = spot size at target surface [cm²],

τ_p = laser pulsewidth [seconds],

τ_r = pulse repetition time [seconds],

ω = fundamental frequency [rad/sec],

c = speed of light [cm/sec],

h = Planck's constant [J-sec],

X_s⁽²⁾ = surface second order nonlinear electrical

susceptibility tensor [esu].

One important feature of equation (1.3) is the quadratic dependence of the output SHG signal on the input power.

By considering the simple case of a monolayer of noninteracting molecules, or atoms, it is possible to write X_s⁽²⁾ as a sum of the nonlinear polarizabilities of individual molecules over a unit surface area¹⁰:

$$\chi_s^{(2)} = \sum_{i=1}^N \alpha_i^{(2)} \quad (1.4)$$

where $\alpha_i^{(2)}$ = second order polarizability tensor for the i th species adsorbed in the interfacial region,

N = total number of adsorbates .

With surface densities representative of a single atomic or molecular monolayer on the order of 10^{13} to 10^{15} molecules/cm², typical values for nonlinear molecular polarizabilities ranging from 10^{-29} to 10^{-30} esu/molecule, characteristic 10 to 12 ns pulsewidths and 4 to 8 mJ peak energy/pulse values for a pulsed Nd³⁺:YAG laser of fundamental wavelength of 1.064 μ m focused down to a spot size of .1 cm², the SHG signal will range from 10^2 to 10^6 photons/pulse. Such a signal is readily detectable in a laboratory. This simple estimate does not take into account the possible enhancement of SHG from induced dipole - induced dipole interactions nor does it account for local field corrections due to surface roughness^{11,12}. In fact, SHG enhancement due to rough metal surfaces can be quite significant, often ranging over several orders of magnitude.

In general, $\chi_s^{(2)}$ will not only contain contributions from surface layers but contributions from adsorbates that may reside in the interfacial region as well. In light of this, the expression for

the second-order susceptibility due to electronic contributions of adsorbates at an interface may be written as^{13,14}

$$\chi_s^{(2)} = \mu_{gi}\mu_{ij}\mu_{jg}/(\omega_{gi} - \omega)(\omega_{jg} - 2\omega) + \text{o.t.} \quad (1.4)$$

where μ_{kl} is the electric dipole transition matrix from state ψ_k to state ψ_l for a given specie,

$$\mu_{kl} = -e \int \psi_k^* \mathbf{r} \psi_l d\mathbf{v} \quad (1.5)$$

and o.t. refers to other terms including contributions from higher-order multipole term transitions. It can be seen that as the pump frequency approaches a resonant electronic excitation at ω_{gi} or ω_{jg} , uniquely characteristic of a given adatom specie, the denominator of one of the $\chi_s^{(2)}$ terms will approach zero, giving rise to an enhancement of the SHG signal that is specific to the respective specie in resonance. Consequently, researchers have found that they can use SHG as a spectroscopic tool in a natural way in gathering information about the structure of an interface¹⁵⁻³⁵. In a relatively short time, the use of SHG for interface/surface phenomenology investigations has become an important tool within the areas of Electrochemistry and the thin-film industry.

In this thesis both SHG from bulk quartz and from an interface formed by a copper monolayer electrodeposited onto gold are investigated. In particular, previously published results for Maker

fringes, generated from bulk quartz, are experimentally reproduced and original experimental data reported from the results of the SHG study of the formation of a copper monolayer onto a polycrystalline gold working electrode during an underpotential deposition (UPD) process .

references

1. J.A. Giordmaine, **Laser Focus**, April 1981.
2. P.A. Franken, A.E. Hill, C.W. Peters and G. Weinreich, **Phys. Rev. Lett.** 7,118 (1961).
3. N. Bloembergen,NONLINEAR OPTICS, W.A. Benjamin Inc. publishers, Massachusetts, 1965
4. R.M. Corn, M. Romagnoli, M.D. Levenson and M.R. Philpott, **J. Chem. Phys.** 81,4127 (1984).
5. P. Guyot-Sionnest, W. Chen and Y.R. Shen, **Phys. Rev. B** 33, 8254 (1986).
6. J.K. Foley and S. Pons, **Anal. Chem.** 57, 945A (1985).
7. M. Moskovits, **Rev. Mod. Phys.** 57,783 (1985)
8. T.F. Heinz, H.W.K. Tom and Y.R. Shen,**Laser Focus** , May 1983, pp 101-104,106.
9. G.T. Boyd, Y.R. Shen and T.W. Hansch, **Opt. Lett.** 11,97 (1986).

10. T.F. Heinz, H.W.K. Tom and Y.R. Shen, International Conference on Surface Studies with Lasers, Mauterndorf, Austria, March 9 - 11, 1983.
11. C.K. Chen, T.F. Heinz, D. Ricard and Y.R. Shen, **Phys. Rev. B** 27, 1965 (1983).
12. T.T. Chen, K.U. Von Raben, D.V. Murphy and R.K. Chang, **Surf. Sci.** 143, 369 (1984).
13. B.M. Biwer, M.J. Pellin, M.W. Schauer and D.M. Gruen, **Langmuir** 4, 121 (1988) 377
14. C. Cohen-Tannoudji, B. Diu and F. Laloe, QUANTUM MECHANICS Volumes 1 & 2, John Wiley & Sons publishers, New York, 1977.
15. M.J. Bennaïmias, H.S. Lakkaraju, B.M. Stone and K. Ashley, **J. Electroanal. Chem.**, to be published (1989)
16. B.M. Biwer, M.J. Pellin, M.W. Schauer and D.M. Gruen, **Surface Science** 176, 377 (1986)
17. D.J. Campbell and R.M. Corn, **J. Phys. Chem.** 91, 5668 (1987).
18. D.J. Campbell and R.M. Corn, **J. Phys. Chem** 92, 5796 (1988)
19. D.J. Campbell and R.M. Corn, **J. Amer. Chem. Society**, in press (1989)
20. C.K. Chen, T.F. Heinz, D. Ricard and Y.R. Shen, **Phys. Rev. Lett.** 46, 1010 (1981) .
21. T.E. Furtak and J. Reyes, **Surf. Sci.** 93, 351 (1980)
22. C.D. Marshall and G.M. Korenowski, **J. Chem. Phys.** 85, 4172 (1986).

23. J. Miragliotta and T.E. Furtak, **Phys. Rev. B** 37, 1028 (1988).
24. G.L. Richmond, H.J. Rojhantalab, J.M. Robinson and V.L. Shannon,
J. Opt. Soc. Amer. B 4, 228 (1987).
25. G.L. Richmond, **Chem. Phys. Lett.** 106, 26 (1984).
26. G.L. Richmond, **Chem. Phys. Lett.** 110, 571 (1985).
27. G.L. Richmond, **Surf. Sci.** 147, 115 (1984).
28. G.L. Richmond, **Langmuir** 2, 132 (1986).
29. V.L. Shannon, D.A. Koos and G.L. Richmond, **J. Chem. Phys.** 87,
1440 (1987).
30. V.L. Shannon, J.M. Robinson and G.L. Richmond, **Spectroscopy**
3, 44 (1989).
31. Y.R. Shen, The Principles of NONLINEAR OPTICS, John Wiley &
Sons publishers, New York, 1984.
32. Y.R. Shen, **J. Vac. Sci. Technol. B** 3, 1464 (1985).
33. Y.R. Shen, **Ann. Rev. Mater. Sci.** 16, 69 (1986).
34. Y.R. Shen, **Nature**, in press (1989)
35. D.F. Voss, K.A. Bunding, M. Nagumo and L.S. Goldberg, **J. Chem.**
Phys. 90, 1834 (1986).
36. A. Yariv, OPTICAL ELECTRONICS, Holt, Reinhart & Winston
publishers, New York, 1985.

CHAPTER TWO

EXPERIMENTAL METHODS

2.1 Experimental Apparatus

The laser used for all the experiments was a Quatel 400 series Q-switched Nd³⁺:YAG laser. The fundamental wavelength of the laser is 1.064 μm . The maximum average output power that the laser was capable of providing was 4 Watts when run at a repetition rate of 10 Hz and the flashlamp voltage was set to 1.65 kV. Each laser pulsewidth is approximately 12 ns. A schematic picture of the experimental setup that was used is illustrated in figure (2.1). The output from the laser was passed through two Glan-Air type polarizing cubes that provided the capability of variable attenuation of the incident beam intensity and a means of polarization control. Subsequently, the beam was transmitted through a 50:50 2" beamsplitter that was fixed at 45° relative to the direction of propagation. The reflected beam was used to establish the reference signal and the transmitted beam was used to generate the target signal. Two separate Scientech detector heads, interfaced to the same Scientech power meter model # 362, were used to measure beam power; one head was used to monitor the output of the laser, and the other for measuring the beam intensity at various points along the target and reference lines.

The reference beam was first passed through a Corning Glass 7-54 filter to remove any green light that may have been present from the flashlamp discharges that could contaminate the experimental results. The beam was then softly focused onto the center of a 1" Quartz crystal with the aid of a positive lens having a focal length of 175 mm. The beam then passed through an IR reflector, at almost normal incidence, in order to remove 99.99% of the fundamental light and select out only the desired SHG signal. Next, the SHG beam was imaged onto the entrance slit of a Hilger & Watts F/4 monochromator, by means of a 100 mm focal length positive lens. The width of the entrance and exit slits were both kept at 1.5 mm. The purpose of the monochromator was twofold; first to provide additional filtering, and second to provide a means of establishing signal tunability with wavelength. A Hamamatsu model # R212 side-viewing photomultiplier detected the output from the monochromator. The photocathode of the photomultiplier was blind to the fundamental wavelength.

The target beam was passed through a Galilean telescope, to reduce the diameter of the beam from 1 cm to .33 cm and to collimate the beam. The optical elements used to make the telescope were a 150 mm focal length positive lens and a - 50 mm negative lens. The negative lens was placed 100 mm directly behind the positive lens. The demagnification produced by the use of these two particular lenses was 1/3. Similar to the reference beam, the target beam was filtered with a Corning Glass 7-54

filter. After the beam had interacted with the target, as described in sections 2.2.1 and 2.2.2, the SHG light was incident on the entrance slit of a Bausch & Lomb F/3 monochromator. The width of the entrance slit was 1.78 mm and that of the exit slit was 1.68 mm. A Hamamatsu photomultiplier, identical to the one used for the reference monochromator, was used to receive the output from the target monochromator.

The outputs from the reference and target photomultipliers were fed along 50 Ω BNC cables to a Stanford Research System (SRS) gated integrator/boxcar averager system. The SRS package consists of an amplifier module, model # SR 240, two gated integrator modules, model # SR 250, a function module, model # SR 260, and a power supply and display module, model # SR 280. One of the gated integrators, designated as channel A, was attached to the target photomultiplier, and the other gated integrator, channel B, was connected to the reference photomultiplier. Each of the gated integrators was triggered by the same TTL logic pulse, carried along 50 Ω BNC cables, provided by the Quantel Q-switch electronics board. The onset and width of the signal integration gate was adjusted externally using the trigger delay and gate width switches, respectively. Data accumulation during the integration was 300 pulses per average. A signal output and gate output BNC coupler allowed a standard 60 MHz laboratory scope to be used to monitor and align the gate with the signal.

2.2 Experimental Targets

2.2.1 Quartz Crystal

The target quartz crystal specimen was cut along a (010) crystallographic orientation in order that the optic axis would be parallel to the crystal faces. The dimensions of the thin quartz disk were 2.54 ± 0.001 cm in diameter by $.1 \pm 0.001$ cm thick. A mount was constructed for the quartz element to provide complete 360° of rotational freedom along a direction perpendicular to the crystal faces and about the optic axis.

Since the quartz crystal target was to be used for bulk SHG experiments, it had to be integrated into the experimental setup, described in section 2.1, such that the crystal faces would be perpendicular to the target beam. This was accomplished by placing a dielectric YAG mirror, at 45° with respect to the direction of the incident beam, directly behind the Corning Glass 7-54 filter in the target optics line. In turn, the target monochromator was then aligned along a 45° direction with respect to the mirror normal. The quartz crystal was then mounted between the mirror and the target monochromator. The beam was carefully centered on the input face of the quartz specimen in order to avoid any obscuration of the beam that might occur during the full rotational swing of $\pm 40^\circ$ about the optic axis. The beam after exiting the back face of the quartz crystal was passed

through an IR reflector that removed 99.99% of the fundamental light while effectively selecting out the SHG signal.

2.2.2 Spectroelectrochemical Cell

The housing for the spectroelectrochemical cell was fabricated from KEL-F plastic, a relatively inert material. Figure (2.2) provides an illustration of the spectroelectrochemical cell housing. The cell window (fused quartz) was transparent to light in the VIS/NIR region. The cell design utilized a three electrode system: reference, working, and auxiliary. The reference electrode was a Ag/AgCl, saturated in 3 M KCl, microreference tip (Microelectrodes, Inc.), and was placed 1-2 mm from the edge of the working (mirror) electrode . A shaft on top of the cell allowed the reference electrode to be inserted into the solution. The solution composition was 1.0 mM CuSO_4 in 0.10 M H_2SO_4 (aqueous). The working electrode was a polycrystalline gold (Au) disk with dimensions 25.4 mm in diameter by 1 mm thick. A micrometer allowed for lateral adjustments of the cylindrical piston in which the working electrode was embedded, providing a means of controlling the electrolyte thin layer depth. The thin layer depth between the cell window and working electrode surface for these SHG experiments was approximately 1 mm. A thin platinum auxiliary electrode was positioned in close proximity to

the working electrode. A vent screw was provided on the spectroelectrochemical cell housing for use when purging the cell with nitrogen gas. The three electrodes configuration of the cell was controlled by a JAS Instrument systems K-1000 potentiostat/waveform programmer unit. The output from the potentiostat/waveform programmer was connected, via 50 Ω BNC cables, to the input BNC couplers of a Hewlett-Packard XY recorder, model # HP 7044A.

As the spectroelectrochemical cell target was to be used for interfacial SHG experiments, it had to be integrated into the overall experimental setup, see section 2.1, such that the mirrored face of the working electrode was at 45° to the direction of the target beam. The cell was mounted after the Corning Glass 7-54 filter. The position of the target monochromator was adjusted so that it was at 45° relative to the normal of the face of the gold electrode. The mount for the cell allowed for 360° angular rotation about an axis perpendicular to the base, single-axis translation, and tilt adjustments for performing "fine tuning" optical alignment of the cell with the monochromator. The light incident on the spectroelectrochemical cell was p-polarized. The diffusely reflected light off the gold surface was passed through an IR reflector, judiciously placed to take into account all geometric considerations (i.e. solid angle) required to avoid any obscuration of the beam, in order to filter out most of the fundamental light. The transmitted SHG signal was collected with

a 152.4 mm focal length positive lens. The placement of the collection lens was optimized so that a point source at the target would be perfectly imaged onto the entrance slit of the target monochromator.

CHAPTER 3

BULK SECOND HARMONIC GENERATION IN QUARTZ

3.1 Justification

Several research studies to date have been published that fully characterize the second-order nonlinear optical nature of bulk quartz¹⁻⁴. These results demonstrate that bulk quartz produces a strong and easily detectable SHG signal. It was decided that accurately reproducing at least one of the better known nonlinear optical attributes of quartz would provide a sufficient experimental foundation for validating the rest of our SHG work. Previous investigations into the physical nature of bulk SHG had identified the presence of an interference pattern, first successfully produced in the laboratory by P.D. Maker and R.W. Terhune⁵, resulting from more than one source of second harmonic waves being generated in the bulk medium and interacting with each other. In a relatively short period of time thereafter, the generation of these "Maker fringes" became a standard laboratory procedure for measuring or comparing nonlinear optical coefficients, because it was not restricted to materials that were phase matchable. Producing a Maker fringe pattern for quartz,

similar to that found in the literature, was chosen as the best candidate for an easy and fast verification of our ability to conduct reliable SHG experiments.

3.2 Experimental Concerns

In order to produce a "clean" trace of the bulk quartz Maker Fringe interference pattern, several experimental considerations were taken into account: (1) presence of surface defects in the quartz crystal, (2) establishing that the input and the output faces of the quartz sample were parallel, (3) minimal laser beam divergence, (4) centering of the laser beam onto the quartz sample, (5) allowing for unobscured $\pm 40^\circ$ rotations, (6) p-polarize the incident light, (7) accurately define the axis of rotation to be the optic axis, (8) removal of any long term temperature drifts in the laser output, and (9) optimize photomultiplier detector sensitivity . In answer to the first two of these concerns, the (010) quartz sample was specified by the supplier as having a surface roughness better than $\lambda/20$, parallel faces to within $\pm .5$ arcsec, and for the most part free of scratches and digs. With respect to the third concern, the Galilean telescope in the experimental layout helped to provide a fairly collimated beam of laser light with a divergence half-angle of about $.1^\circ$. The fourth concern was critical because it related directly to obtaining a symmetric interference pattern. The rotation axis had to be centered on the laser beam,

perpendicular to it, at the beam waist. Otherwise, the power density on the crystal would not have been the same for positive and negative rotations. The fifth concern was automatically satisfied by proper optical alignment of the quartz crystal mount with the laser beam. The physical size of the clear aperture of the mounted quartz crystal with respect to the spot size of the laser insured unobscured $\pm 40^\circ$ rotations. Regarding the sixth concern, a Glan-Air type polarizing cube insured that the light at the target was p-polarized. It was important that the direction of the electric field polarization be perpendicular to the optic axis for this experiment as expressed by the seventh concern. The actual direction of the optic axis, parallel to the faces of the crystal, was provided by the supplier to within $\pm 1^\circ$. As a supplementary verification that the optic axis was indeed located where it was supposed to, the following procedure was used: (1) light from a 632.8 nm He-Ne laser was linearly polarized in a given fixed direction, (2) a second polarizer was placed in the path of the beam and oriented 90° with respect to the orientation of the first polarizer, (3) a detector was used to verify that no light passed through the second polarizer, (4) the mounted quartz crystal was inserted between the two polarizers and rotated about an axis perpendicular to the faces of the crystal, (5) the light output from the second polarizer was constantly monitored and the four orientations of the crystal where complete light extinction

occurred was noted. Figure 3.1 illustrates the experimental set-up used to ascertain the location of the optic axis.

In order to remove long term drifts in the laser due to temperature fluctuations, as expressed by the eighth concern, a second quartz crystal was used as a reference. Since the reference would be subject to the same dc temperature drifts, the ratio of target and reference SHG signal outputs would tend to cancel out this effect. Finally, in response to the ninth concern, diagnostics were performed on both the reference and target photomultipliers, using neutral density filters, to insure that the signal levels were not saturating the detectors. The baseline SHG signal levels were adjusted so that the detectors were operating in a linear region and therefore affording optimum sensitivity. The same average laser power, 150mW, was provided to both the reference quartz crystal and target quartz crystal. Simple diagnostics were performed on the output signal to make sure that it correlated well with the square of the input power and was sharply peaked about the SHG wavelength. The results from these diagnostics are presented in figures 3.2 and 3.3, respectively. The background noise level, determined by blocking the beam in front of the target quartz crystal, has been subtracted from the data.

3.3 Experimental Results

The experimental results from the generation of the Maker Fringe pattern from quartz are presented in figure 3.4. Here again, the background noise level, determined by blocking the beam in front of the target quartz crystal, has been subtracted from the data. Both the corrected and uncorrected data points appear in a table in figure 3.5. The data points clearly show the SHG intensity minima and maxima as a function of the incidence angle of the laser beam with respect to the normal of the input face of the crystal. The range of angular rotation spans $\pm 40^\circ$. As desired, the measurements came out to be nearly symmetric about normal incidence. Maxima peaks occur at $\pm 13^\circ$, $\pm 28^\circ$, and $\pm 38^\circ$. Five minima peaks can be clearly seen in the data, one at normal incidence, two at $\pm 22^\circ$, and the remaining two at $\pm 34^\circ$. The error in determining the maxima and minima peak positions is $\pm 1^\circ$. An important feature of the data is that successive maxima are decreasing in intensity following a cosine squared distribution. This cosine squared envelope is characteristic of typical interference patterns. Another observation is that the minima are not going all the way down to zero. This suggests that there may have been some slight variations in the background noise level over the extent of the experiment.

3.4 Discussion

The situation of interest is the following: a laser beam of fixed power, P_ω , electric field, $\mathbf{E}_\omega$, and wave vector, $\mathbf{k}_\omega$, is incident on a thin, non-absorbing, non-magnetic, dielectric crystal of thickness L , as shown in figure 3.6. The electric field is p-polarized so that it is perpendicular to the optic axis. The crystal is rotated about the optic axis. The angle of incidence θ of the laser beam is measured relative to the surface normal of the input face of the crystal. As the laser light propagates inside the crystal, the electric field $\mathbf{E}_\omega$ induces a second order nonlinear polarization $\mathbf{P}_{2\omega}$ that radiates ordinary electromagnetic waves of angular frequency 2ω . These waves are considered to be of the "bound" wave type. In addition, a second source of ordinary electromagnetic radiation of angular frequency 2ω arises because of the boundary conditions existing between the two different mediums at the input surface. These waves are considered to be of the "free" wave type. These bound and free waves in general will exhibit different velocities as they propagate through the crystal, giving rise to interference fringes as they superimpose with one another. Maxima and minima for this interference fringe pattern will then be a strong function of the angle of incidence of the laser light corresponding to a variation in the effective thickness of the crystal.

The normalized Maker fringe equation, for a (010) quartz crystal rotated about the optic axis, with the incident electric field polarized perpendicular to the optic axis, is given by

$$P_N = [(n_{2\omega}\cos\theta_\omega + n_\omega\cos\theta_{2\omega})\cos^4\theta\cos\theta_{2\omega}(n_{2\omega} + 1)^3(n_\omega + 1)^3 \cdot \cos^2(3\theta_\omega)\sin^2\{(\pi L/2)(4/\lambda)(n_\omega\cos\theta_\omega - n_{2\omega}\cos\theta_{2\omega})\} / (n_\omega\cos\theta + \cos\theta_\omega)^3(\cos\theta_{2\omega} + n_{2\omega}\cos\theta)^3(n_\omega + n_{2\omega})] \quad (3.1)$$

where n_ω = index of refraction for the ordinary wave at the
fundamental harmonic
 $n_{2\omega}$ = index of refraction for the ordinary wave at the
second harmonic
 θ = angle of incidence
 θ_ω = angle of refraction for the fundamental wave
 $\theta_{2\omega}$ = angle of refraction for the second harmonic wave
 L = thickness of crystal
 λ = wavelength

A detailed derivation of equation (3.1) has been provided as an appendix (chapter 6). A plot of equation (3.1) versus angle of incidence, θ , is presented in figure 3.7. The refractive index values, obtained from the table in figure 3.8, for an ordinary wave at the fundamental (1.064 μm) and SHG (.532 μm) wavelengths, used in generating figure 3.7, were 1.53413 and 1.54702, respectively. For comparative purposes, the corrected experimental data is also plotted in figure 3.7. The experimental data points agree

reasonably well with the theoretical curve to within $\pm 6\%$ over the full extent of the crystal rotation. This estimate was obtained by computing the root mean square deviation of the difference between the theoretical curve and the data points. One source of error is attributed to the coarse accuracy with which the positions of the maxima and minima were able to be determined. The uncertainty in the angle of incidence is estimated to be $\pm 1^\circ$. This particular source of error could be significantly reduced if a rotation stage providing more precise angular increments were to be used. Similarly, there is a $\pm 1^\circ$ uncertainty in the direction of polarization of the input. Here again, mounts for the polarizing cubes with more accurate angular divisions would help eliminate this contribution to the total error. Another source of error is believed to be due to the $\pm 0.5^\circ$ uncertainty in the extinction technique used to determine the exact orientation of the optic axis. Yet another source of error comes from the fact the laser beam is slightly divergent. Consequently, every point across the laser beam does not see the same effective coherence length of the crystal. However, the latter only accounts for at most about 1% of the total error, even for large incidence angles, $\theta > 30^\circ$.

A good check for self consistency in this experiment is to back out from the data an estimate for the thickness of the crystal and compare it to the measured value. Examination of equation (3.1) shows that the positions of the minima are exactly determined by the equation

$$\sin^2\{(\pi L/2)(4/\lambda)(n_{\omega}\cos\theta_{\omega} - n_{2\omega}\cos\theta_{2\omega})\} = 0 \quad (3.2)$$

and therefore depend only on the thickness of the sample and the normal dispersion of the light in the medium. The zeros of equation (3.2) for two successive minima will occur at

$$\pi L/2l_c(\theta_1) = n\pi \quad (3.3)$$

and

$$\pi L/2l_c(\theta_2) = (n + 1)\pi \quad (3.4)$$

respectively, where a coherence length

$$l_c(\theta) = \lambda/4|n_{\omega}\cos\theta_{\omega} - n_{2\omega}\cos\theta_{2\omega}| \quad (3.5)$$

has been defined for each value of θ that the minima occurred. Subtracting equation (3.3) from equation (3.4) and solving for the length of the crystal yields the result

$$L = 2/|1/l_c(\theta_2) - 1/l_c(\theta_1)| \quad (3.6)$$

The estimated thickness from the experimental measurements comes out to be about $0.977 \pm .005$ mm. The error in this estimate is on the order of 3%, which shows excellent agreement with the actual measured value as given in section 2.2.1. The findings from

this bulk SHG experiment compare quite well with the results of similar studies in the literature when differences in crystal thickness and in laser characteristics are accounted for.

references

1. P.A. Franken, A.E. Hill, C.W. Peters and G. Weinreich, **Phys. Rev. Lett.** 7,118 (1961).
2. J. Jerphagnon and S.K. Kurtz, **J. of App. Phys.** 41, 1667 (1970).
3. Y.R. Shen,The Principles of NONLINEAR OPTICS, John Wiley & Sons publishers, New York,1984.
4. F. Zernike and J.E. Midwinter,APPLIED NONLINEAR OPTICS, John Wiley & Sons, New York, 1973.
5. P.D. Maker, R.W. Terhune, M. Nisenhoff and C.M. Savage,**Phys. Rev. B** 128,606 (1962).

CHAPTER 4

SECOND HARMONIC GENERATION AT AN INTERFACE

4.1 Justification

A natural environment to exploit the surface SHG technique is in the field of Electrochemistry. This field is almost entirely devoted to studying interfacial and surfacial phenomenon. Often, the interfaces of interest to electrochemists are those formed by an electrolyte/electrode junction. However, suprisingly very little information has been obtained from conventional electrochemical methods, i.e. current-voltage and capacitance techniques, about the true nature of the electrode surface, the electrical double layer existing at the interface, the dynamics of adsorption on the electrode surface, and the mechanisms of charge transfer across an interface. Although relatively a new spectroscopic tool, the use of SHG in the study of these physical processes is already providing researchers in electrochemistry with many important answers . The SHG technique has already been used by electrochemists to examine transient phenomena in electrochemical surface processes¹. A few of these researchers have demonstrated that interfacial SHG signals from nonfaradic processes correlate linearly with the square of the electrode free surface charge density²⁻³. Others have shown that the field distribution within the electrical double layer can lead to a field

induced SHG signal, originating within the interface, that varies with the bias potential applied to the electrode surface⁴. In fact, they show that field-induced SHG can be quite significant as the interfacial electric field strength may become as high as 10^8 V/cm due to the limited dimensions of the electric double layer⁵. SHG has also been used in situ to monitor adsorption⁶⁻⁷, molecular orientation⁸, and surface symmetry⁹ of various noble metal electrode/liquid interfaces formed through underpotential deposition (UPD) processes. UPD is the stepwise deposition of a foreign metal overlayer, on an electrode surface, at potentials positive of the Nernstian potential for the initiation of electrochemical bulk deposition. SHG is especially useful for these in situ UPD studies because of its submonolayer sensitivity to molecular adsorbates. A summary of these experiments, as surveyed from the available literature, is provided in a table in figure 4.1. The majority of UPD work published so far involves single crystal, polycrystalline silver, and polycrystalline platinum electrodes. The study reported within the text of this thesis, represents an effort, for the first time, to use SHG as a probe of UPD of copper on a polycrystalline gold surface in situ. The results from these experiments have been accepted for publication¹⁰.

4.2 Electrode/Electrolyte Interface

Almost always, one of the two phases contributing to an interface of interest in electrochemistry will be an electrolyte, which is merely a phase through which charge is carried by the movement of ions, and the second will be an electrode, which is a phase through which charge is carried by electronic movement. Although it is natural to think about events occurring at a single interface, one must experimentally study the properties of collections of interfaces called electrochemical cells. The overall chemical reactions that take place in these cells is made up of several independent half-reactions. Most of the time, however, it is only of interest to observe one such reaction, and the electrode at which this occurs is called the working electrode. To focus on this specific interface, the rest of the cell is standardized by using a reference electrode made up of phases having constant composition. A third electrode, called the auxiliary electrode, often is used to supply a current to the cell. The auxiliary electrode is usually chosen so as not to produce substances by electrolysis that can contaminate the working electrode surface.

Since the reference electrode has a constant makeup, its potential is fixed. Therefore any changes in the cell are ascribable to the working electrode. The potential of the working electrode is controlled with respect to this reference electrode. Changing the applied potential on the working electrode essentially changes the energy states of the free electrons present on the working

electrode surface. By driving the electrode to more negative potentials the energy of the electrons is increased, and they will eventually reach a level high enough to occupy vacant energy sites on species in the electrolyte. In this case, a flow of electrons from electrode to solution (a reduction current) occurs. Similarly, the energy of the electrons can be lowered by imposing a more positive potential, and at some point electrons on solutes in the electrolyte will find a more favorable energy state on the electrode and will transfer there. Their flow from solution to electrode, is an oxidation current. In general, when the potential of an electrode is moved from its equilibrium (or its zero current) value toward more negative potentials, the substance that will be reduced first is the oxidant in the electrochemical system with the least negative (or most positive) standard reduction potential. When the potential of the electrode is moved from its zero current value towards more positive potentials, the substance that will be oxidized first is the reductant in the electrochemical system of least positive (or most negative) standard oxidation potential. Monitoring these oxidation /reduction currents, as a function of the applied working electrode potential, is a means used in electrochemistry for tracking individual electroactive species participating in the kinetics of interfacial phenomena. This method is called cyclic-voltammetry (CV).

An electrode at which no charge transfer across the metal-solution interface can occur regardless of the potential imposed by

an outside source of voltage is called an ideal polarized electrode (IPE). While no real electrode can behave as an IPE over an unlimited potential range, some electrode-solution electrochemical couples, over certain limited potential ranges, can approximate an IPE. When a metal electrode is biased in a simple aqueous electrolyte at potentials within the ideally polarizable region, to a first approximation, the interface will charge like a capacitor. In the absence of interfacial electron transfer, a charge Q_m , accumulates on the metal surface as the bias is varied. An equal and opposite charge, Q_s , also builds on the solution side of the junction forming what is typically called the electrical double layer. The solution side of the double layer is thought to be made up of several sections. Figure 4.2 provides a physical model of the electrical double layer. The layer closest to the electrode contains solvent molecules and sometimes other species (electroactive ions or molecules) that are considered to be specifically adsorbed. The locus of the electrical centers of these specifically adsorbed ions, located at a distance x_1 from the electrode surface, is referred to as the inner Helmholtz plane (IHP). Due to Coulombic repulsion with the ions in the IHP, solvated ions are limited in their approach towards the metal surface to within a distance x_2 . The locus of centers for these solvated ions is termed the outer Helmholtz plane (OHP). The interaction of the solvated ions with the free surface charges on the metal electrode surface involves only long-range electrostatic forces, so that their interaction is essentially

independent of the chemical properties of the ions. In this respect, the solvated ions are said to be non-specifically adsorbed. Because of thermal agitation in the solution, non-specifically adsorbed ions are distributed in a three-dimensional region, called the diffuse layer, that extends from the OHP into the bulk of the solution. The structure of the double layer directly affects the rates of electrode/electrolyte junction processes.

Equilibrium, for an electrode reaction, is governed by the Nernst equation,

$$E = E^0' + (RT/nF)\ln(C_O(x=0)/C_R(x=0)) \quad (4.1)$$

where E = electrode potential,

E^0' = formal potential of an electrode,
 $= E^0 + (RT/nF)\ln(a_O/a_R)$,

E^0 = electrode standard potential,

a_O = oxidant activity coefficient,

a_R = reductant activity coefficient,

R = universal gas constant,

T = temperature,

n = number of electrons per molecule oxidized or reduced,

C_O = bulk oxidant concentration at the electrode surface,

C_R = bulk reductant concentration at the electrode surface,

F = Faraday's constant

The above equation applies for the half-reaction,

assuming both the oxidants (O) and reductants (R) are soluble species. In general, the current (or electrode reaction rate) is governed by the rate of processes such as: (1) mass transfer, (2) electron transfer, (3) chemical reactions preceding or following the electron transfer, and (4) other surface reactions, such as adsorption, desorption, or crystallization (electrodeposition).

4.3 Underpotential Deposition

Underpotential deposition (UPD) is the stepwise deposition of a foreign metal on an electrode surface at potentials more positive of the Nernstian potential expected for the onset of bulk electrodeposition. UPD in many systems has been well correlated with electronegativity differences between the substrate atom and

the adsorbed atom¹¹. The UPD process tends to modify the nonlinear susceptibility of the metal electrode surface¹². UPD processes depend on the nature of the substrate (material and pretreatment) and on the adsorption dynamics of the oxidant. A simple, first order, model can be derived that describes the mechanisms of UPD kinetics. For the reaction given in equation (4.2), when more than a monolayer of R is electrodeposited onto an inert electrode (e.g. copper on a gold electrode), the activity of R, a_R , is constant and equal to unity at the completion of the electrolysis. Thus the Nernst equation (4.1) becomes

$$E = E^{0'} + (RT/nF)\ln[\alpha_O C_i(1 - x)] \quad (4.3)$$

where C_i = initial concentration of O,
 x = fraction of O reduced to R,
 R = universal gas constant ,
 F = Faraday's constant ,
 n = number of electrons per molecule oxidized or reduced,
 T = temperature,

$E^{0'}$ = formal potential of an electrode,
 $= E^0 + (RT/nF)\ln(\alpha_O/\alpha_R)$,
 E^0 = electrode standard potential,
 α_O = oxidant activity coefficient,

α_R = reductant activity coefficient

When less than a monolayer of R is electrodeposited on an inert substrate, $a_R \neq 1$, an expression for a_R as a function of coverage by R, i.e. an isotherm providing the steady-state description of the thermodynamic adsorption process, must be used in the Nernst equation. The Langmuir isotherm¹³, applicable to submonolayer coverage, assumes that a_R is linearly proportional to the fraction, β , of the electrode surface covered with R. Thus,

$$a_R \approx \alpha_R \beta = \alpha_R (A_R/A) = \alpha_R N_R A_0/A \quad (4.4)$$

where A_R = area occupied by R,

A = electrode area,

A_0 = molecular cross-sectional area,

N_R = number of molecules of R deposited onto the electrode,

α_R = reductant activity coefficient

At equilibrium, N_R is given by

$$N_R = V_S C_i \times N \quad (4.5)$$

where N = Avogadro's number,

V_S = solution volume

Substituting equation (4.5) and (4.4) into equation (4.3) yields,

$$E = E^{0'} + (RT/nF) \ln(\alpha_O A / \alpha_R V_S N_{AO}) + (RT/nF) \ln(1-x/x) \quad (4.6)$$

Consequently, given the area of the electrode, the type and amount of the electroactive specie present in the electrolyte, the solution volume, the estimated values for the activity coefficients, and the fraction of the oxidant reduced on the electrode surface, an estimate for the corresponding UPD potential can be made. Figure 4.3 provides a plot of estimated cathodic deposition potential versus fractional electrode surface coverage using equation (4.6), assuming equal activity coefficients, for the copper/gold UPD electrochemical system studied in this thesis. Note, however, that this simple treatment assumes the formation of a second adlayer does not begin until the first layer is complete. Frequently metallic atoms will aggregate, rather than deposit on a foreign surface, and dendrites will form¹⁴.

4.4 Experimental Concerns

The three main considerations in carrying out the interfacial SHG experiments were: (1) contamination, (2) laser heating of the gold metal electrode, and (3) maximizing the SHG signal throughput. In order to minimize the possibility of contamination from trace impurities (i.e. trace amounts of polishing compound)

and unwanted electroactive species (i.e. oxygen ions) from participating during the redox process, three steps were taken. The first was to prepare all aqueous solutions with deionized, triply distilled water. The second was to thoroughly wash the entire spectroelectrochemical cell, both the housing and the electrode, for a minimum of one hour with deionized, triply distilled water, after the gold mirror electrode had been mechanically polished with successively smaller grades of polishing alumina (Beuhler) of $1.0\mu\text{m}$, $0.3\mu\text{m}$, and $0.05\mu\text{m}$. Finally, the solution was purged, for about thirty minutes, with nitrogen gas. The nitrogen gas was first passed through a gas purifier. Latex gloves were worn at all stages of handling the electrochemical cell to maintain a clean gold electrode surface, free of oily amino acids.

Sustained laser pulse heating of the gold electrode surface could have adversely affected the thermodynamics of the interfacial region under study in two ways: (1) promote laser damage of the surface, and (2) induce desorption. The latter of these effects could significantly alter the copper electrodeposition rate onto the gold. In order to avoid any laser damage to the surface, the electrode was frequently monitored by visual inspection throughout the experiment. No damage was detected on the electrode surface throughout any of the SHG experiments. An estimate for the maximum temperature rise on

the surface of the electrode due to pulsed laser heating is given by¹⁵,

$$\Delta T = \frac{4}{3} \left(\frac{1}{4 - \tau_r/\tau_0} \right)^{1/2} [2(F_0/K)(k\tau_0/\pi)^{1/2}] \quad (4.7)$$

where τ_r = pulse rise time [seconds],
 τ_0 = pulse full width half maximum [seconds],
 F_0 = maximum absorbed laser power density
[Watts/cm²],
 K = thermal conductivity [W cm⁻¹ °K⁻¹],
 k = thermal diffusivity [cm²/sec]

Given the typical rise time for a YAG laser pulse is 100 ps, the FWHM of the pulse is about 10 ns, the absorbed peak power density is 1.5×10^5 W/cm², the thermal conductivity of gold is 3.18 W cm⁻¹ °K⁻¹, and the thermal diffusivity of gold is about 1 cm²/sec, the rise in temperature per pulse is approximately 3.5 °K. This kind of a temperature rise will not impact the adsorption kinetics occurring at the electrode surface. Since the numbers used in this estimate are representative of the actual experimental parameters, negligible heating of the gold surface was expected. Moreover, the estimate does not include the thermally dissipative nature of the aqueous solution enveloping the electrode that would tend to reduce the maximum rise in temperature at the electrode surface. The time necessary for the gold electrode surface to completely radiate away the heat, assuming that the heat is

flowing in only one direction, is on the order of 0.2 milliseconds, providing sufficient time for the electrode surface to cool down between pulses.

The important factors involved in maximizing the SHG output signal throughput were: (1) optimizing the reference optical line, (2) optimizing the target optical line, (3) not operating at signal levels that saturated the photomultiplier detectors, and (4) provide p-polarized light at the target. The alignment of the reference and target line optics was performed according to the following guidelines: (a) the beam was centered onto the entrance slit of the monochromator without any optical elements in the path of the beam, (b) pupils were mounted along the path of each beam to provide a reference height and direction for additional optical elements, and (c) each optical elements was placed into the path of the beam in a step-wise fashion. It was also necessary to rotate the reference quartz crystal until a maximum peak for the Maker fringe SHG signal (see section 3.3) was observed. To establish that the photomultipliers were not saturated, the SHG signal, as recorded by the boxcar averager, was compared before and after the use of a neutral density filter with O.D. of 1.0. For both photomultipliers, the detected SHG signal was seen to decrease to approximately one-tenth of its original value after the insertion of the neutral density filter. As described in section 2.1, a Glan-Air type polarizing cube provided the polarization control for this experiment. In principle, since only an electric field normal to a

smooth metal electrode surface can generate surface/interface SHG, the logical choice was to make the incident electric field p-polarized for the experiment. However in practice, due to surface roughness and non-normal orientations of molecular adsorbates, there can also be a contribution to the surface SHG signal from s-polarized light. Diagnostics were performed on the interfacial SHG signal to demonstrate the linear correlation with the square of the input power (figure 4.4) and wavelength tunability (figure 4.5). An evaluation was done to compare the value of the SHG signal for p-polarized and s-polarized light. As expected, the SHG signal from the s-polarized light was at least two orders of magnitude less than the SHG signal from the p-polarized light.

4.5 Experimental results

4.5.1 CV results

The external waveform programmer was programmed to ramp the potential from +0.8 V to -0.2 V, relative to the reference electrode, at a sweep rate of 10 mV/sec. Several redox cycles were initiated to ascertain the repeatability of the scans, a good indication of whether the solution was relatively free from contamination. The resulting CV is presented in figure 4.6. At very high potentials ($> +0.4$ V), the CV does not indicate any copper

adsorption activity is happening on the gold surface. As the potential is swept in an increasingly cathodic direction, reduction of copper, governed by UPD kinetics, can be observed. The copper UPD is initiated around +0.4 V and steadily increases until an ill-defined peak appears around +0.14 V. Increasing the cathodic potential still further indicates that copper reduction significantly decreases until bulk electrodeposition occurs at around -0.03 V. There are no sharp UPD peaks in this particular electrochemical system, as has been previously determined in combined cyclic voltammetry/in situ quartz crystal microbalance studies in perchlorate¹⁶ and sulfate media¹⁷. On the return sweep, two stripping peaks are observed. These two anodic peaks clearly show the separation between bulk and UPD electrodeposition. The more negative anodic peak, due to bulk oxidative desorption, occurs around +0.02 V. The UPD stripping peak occurs at about +0.31 V. Over the potential range for UPD, about 0.98 ± 0.06 of a monolayer of Cu is deposited on the gold substrate. The commensurate coverage of the copper overlayer was confirmed by an in situ quartz crystal microbalance measurement¹⁷. This copper adlayer corresponds to a surface charge density of about $430 \mu\text{C}/\text{cm}^2$. Figure 4.7 provides a plot of the cumulative surface charge density profile during the redox scan. All of the copper that was reduced during the cathodic scan was removed during the anodic scan.

4.5.2 SHG Results

The laser energy available at the electrode surface was about 7.7 mJ/pulse provided at a 5 Hz repetition rate. The area of the beam at the gold electrode was determined to be .07 cm². The energy density of the beam at the gold electrode surface, accounting for all of the propagation losses (a total factor of 6.5 attenuation throughout the experiment), was 110 mJ/cm². The potentiostat/external programmer was manually operated for this part of the experiment. The potential range covered was from +0.5 V to -0.1 V. The potential was applied to the working electrode in increments of 20 mV at three minute intervals. The three minute time interval facilitated the rate at which the data was being taken. Unlike the CV sensitivity for transient responses, the three minute duration per potential step provided ample time for the electrode/electrolyte interface to achieve steady-state. Fortunately, the differences in the temporal characteristics for the two sets of measurements affected only the electrode charging current profiles and not the amount of copper adsorbed on the gold surface, which is strictly a function of the applied potential. Therefore a direct correspondence between the results of the SHG experiment can be made with the results of the CV. Figure 4.8 presents the results from tracking the SHG signal over the full redox cycle. The background level, determined by blocking the beam in front of the spectroelectrochemical cell, has been

subtracted from the data. The corrected and uncorrected experimental data are provided in a table in figure 4.9. Starting around the initiation of copper UPD (+0.4 V), during the reduction sweep, the SHG signal begins to decrease in intensity from that recorded for the bare gold value, measured before starting the experiment. As the potential continues to be stepped towards more cathodic values, the SHG signal continues to decrease, reaching a constant value in the neighborhood of the onset of bulk electrodeposition. On the reverse path, the SHG signal gradually increases, as the UPD copper overlayer is stripped off the gold surface, until it reaches the original value that it had at the start of the experiment. However, the signal from the return sweep does not trace out the same curve as that for the forward sweep; this probably reflects the peak separation between deposition and stripping peaks observed in the CV experiment. The fact that the SHG signal returns to the original value observed prior to the cathodic excursion indicates that the nature of the gold surface does not change significantly during the oxidation-reduction scan (i.e. the adsorption process is reversible).

4.5.3 Blank Cell Results

As an additional diagnostic check, the SHG profile from a blank cell containing only 0.5 M H_2SO_4 electrolyte was examined.

The results from both the CV and SHG experiments are provided as figures 4.10 and 4.11, respectively. Here again, the background level, determined by blocking the beam in front of the spectroelectrochemical cell, has been subtracted from the data. The corrected and uncorrected experimental data are provided in a table in figure 4.12. The relatively flat and featureless CV indicates that any adsorbed bisulfate on the electrode surface probably did not desorb at any potential within the applied +0.5 V to -0.04 V range under study. This observation is consistent with results from an ex situ ultra-high vacuum study of bisulfate adsorbed on a single crystal Au[111] surface¹⁸. Bisulfate specific adsorption has been confirmed previously on silver¹⁹ and on platinum²⁰.

The SHG signal, in the absence of copper sulfate, remained constant through the entire redox cycle. The fact the SHG signal did not change during the blank cell experiment also suggests that there was no desorption activity of sulfate ions during the potential cycling. This is in contrast with what has been observed on platinum²¹ and silver²². The SHG signal level from the blank cell test was used to establish the background noise level of the system .

4.6 Discussion

The conclusion that has been drawn from previous interfacial SHG studies performed on UPD electrochemical systems was that the SHG signal intensity increases or decreases depending upon the contribution to the free electron density on the metal electrode surface from the foreign metal overlayer being deposited. Since the free electron density of copper ($8.45 \times 10^{22} \text{ cm}^{-3}$) is larger than the free electron concentration of gold ($5.9 \times 10^{22} \text{ cm}^{-3}$), one would expect the SHG signal to increase from the bare gold value during the reduction of copper. However, our experimental findings show that the SHG signal decreases during the cathodic potential scan. A decrease in the SHG signal during the UPD of copper onto gold is consistent with an analysis that was performed using surface-extended X-ray absorption fine structure (SEXAFS) spectroscopy of copper UPD on single crystal gold²³⁻²⁴. These workers suggested that rather than being in a pure metallic form, copper atoms are deposited onto the gold substrate in a tetrahedral geometry with three gold atoms in the (111) plane forming the base, a copper atom in the center, and an oxygen atom at the apex. This deposition configuration is shown in figure 4.13. This structure implies that the oxygen atoms covering the copper atoms, comprising the UPD adlayer, will reduce the delocalization of the d-electrons of the copper adlayer, through partial charge transfer, thus offering a possible explanation for the decrease we

observed in the SHG signal. The electrosorption valency characterizing this partial charge transfer between the oxygen and copper atoms²⁵ is 1.4. In this respect, our experimental findings are consistent with the results from other UPD/SHG studies in the literature.

references

1. R.M. Corn, M. Romagnoli, M.D. Levenson and M.R. Philpott, **J. Chem. Phys.** 81,4127 (1984).
2. D.J. Campbell and R.M. Corn, **J. Phys. Chem.** 91,5668 (1987).
3. D.J. Campbell and R.M. Corn, **J. Phys. Chem** 92,5796 (1988)
4. G.L. Richmond, H.J. Rojhantalab, J.M. Robinson and V.L. Shannon, **J. Opt. Soc. Amer. B** 4,228 (1987).
5. V.L. Shannon, J.M. Robinson and G.L. Richmond, **Spectroscopy** 3,44 (1989).
6. T.E. Furtak and J. Miragliotta, **Phys. Rev. B**35,2569 (1987)
7. D.J. Campbell and R.M. Corn, **J. Amer. Chem. Society**, in press (1989)
8. V.L. Shannon, D.A. Koos and G.L. Richmond, **J. Chem. Phys.** 87, 1440 (1987).
9. C.A. Paddock, G.F. Russell and R.B. Miles, **Surf. Sci.** 172,578 (1986).
10. M.J. Bennahmias, H.S. Lakkaraju, B.M. Stone and K. Ashley,

- J. Electroanal. Chem.**, to be published (1989)
11. H. Gerischer, D.M. Kolb and M. Przasnyski, **Surf. Sci.** 43, 662 (1974) .
 12. D.M. Kolb, D. Leutloff and M. Przasnyski, **Surf. Sci.** 47, 622 (1975).
 13. R.J. Elsey, **J. Vac. Sci. Technology** 25, 299 (1974).
 14. A.J. Bard and L.R. Faulkner, ELECTROCHEMICAL METHODS. Fundamentals and Applications. John Wiley & Sons publishers, New York, 1980.
 15. P.C. Stair and Eric Weitz, **J. Opt. Soc. Amer. B** 4, 255 (1987).
 16. M.R. Deakin and O.R. Melroy, **J. Electroanal. Chem.** 239, 321 (1988)
 17. M. Lazaga, K. Ashley, G.L. Borges, and J.G. Gordon, to be published
 18. M.S. Zei, D. Scherson, G. Lempfuhl, and D.M. Kolb, **J. Electroanal. Chem.** 229, 99 (1987)
 19. G. Valette, **J. Electroanal. Chem.** 122, 285 (1981)
 20. K. Kunimatsu, M.G. Samant and H. Seki, **J. Electroanal. Chem.** 258, 163 (1989)
 21. G.L. Richmond, **Chem. Phys. Lett.** 106, 26 (1984).
 22. T.F. Heinz, H.W.K. Tom and Y.R. Shen, **Phys. Rev. A** 28, 1883 (1983).
 23. O.R. Melroy, M.G. Samant, G.L. Borges, J.G. Gordon II, L. Blum, J.H. White, M.J. Albarelli, M. McMillan and H.D. Abruna, **J. Electroanal. Chem.**, to be published (1990)

24. L. Blum, H.D. Abruna, J. White, J.G. Gordon II, G.L. Borges, M.G. Samant and O.R. Melroy, **J. Chem. Phys.** 85, 6732 (1986).
25. M.R. Deakin and O.R. Melroy, **J. Electroanal. Chem.** 239, 321 (1988)
26. K. Ashley and S. Pons, **Chem. Rev.** 88, 673 (1988)
27. D.R. Crow, PRINCIPLES OF ELECTROCHEMISTRY, Chapman and Hall publishers, London, 1988.
28. J.C. Farmer, **J. Electrochem. Soc.** 132, 2640 (1985).
29. J.D. Jackson, CLASSICAL ELECTRODYNAMICS, John Wiley & Sons publishers, New York, 1975.
30. C.H. Lee, R.K. Chang and N. Bloembergen, **Phys. Rev. Lett.** 18, 167 (1967).
31. S. Swathirajan and S. Bruckenstein, **Electrochim. Acta.** 28, 865 (1983).

CHAPTER FIVE

CONCLUSIONS

The experimental findings of this thesis show that interfacial SHG has the sensitivity to observe the surface coverage of copper UPD onto polycrystalline gold. Thus the interfacial SHG signal can be used to quantify the degree of coverage of the copper UPD overlayer. This type of information would prove very advantageous for the thin-film industry in preparing a better grade of metallic foils. Consequently, It would be of great benefit and interest to expand the scope of this present study by the following future set of interfacial SHG experiments: (1) copper UPD onto single crystal gold, (2) other metal UPD onto various polycrystalline metals, and (3) other metal UPD onto a variety of single crystal metals. The results from this matrix of experiments would provide a good data base from which to learn about the nature of the various metal UPD-metal substrate bonds. Also, since the results reported here depend on the nature of the metal electrode surface, it would be useful in future tests to examine the changes observed in the interfacial SHG profile as a function of the surface roughness. By using an ultrafast laser instead of the YAG laser, with pulsewidths on the order of picoseconds, the interfacial SHG signal could be monitored on a real-time basis during the formation of the interface, providing a deeper insight into the UPD dynamics. In addition, the results reported in this thesis suggest that

structural information about the metal UPD adlayer could also be obtained from interfacial SHG. To this end, angle resolved interfacial SHG experiments on these UPD electrochemical systems would prove useful. As it stands now, the experimental set-up could be very easily modified for conducting angle resolved SHG studies by adding a third polarizing cube, as an analyzer, just before the entrance slit of the target monochromator (see chapter 2). The polarization of the incident beam could then be varied in an experiment and the subsequent polarization of the interfacial SHG signal determined. The use of the analyzer would facilitate this capability for measuring the mean orientation and structural configuration of the metal UPD adsorbates on the metal electrode surface.

It is worthwhile to mention in these closing remarks that the work reported here represents only a brief perspective of the many advantages of using the bulk and interfacial SHG techniques. SHG can be used to monitor the growth of many kinds of crystals. It can be used in situ for monitoring thin-film plasma vapor deposition or chemical vapor deposition processes. SHG has uses in monitoring particulate and molecular contamination levels in superconductor and semiconductor industrial manufacturing processes. SHG can be utilized to observe thermodynamic phase changes. Overall, optical

methods such as the SHG technique, will continue to play an important role in the development of new and improved optical materials.

CHAPTER SIX

APPENDIX

The physical situation of interest is depicted in figure 3.6. In a nonlinear medium, the constitutive relation between the electric induction $\mathbf{D}$ and the electric field $\mathbf{E}$ must include the existence of a nonlinear polarization $\mathbf{P}_{NL}$. In the present case, the second-order nonlinear polarization acts as a source term in the wave equation

$$\begin{aligned}\nabla \times \nabla \times \mathbf{E}_{2\omega}(\mathbf{r},t) + (\epsilon - \partial^2 \mathbf{E}_{2\omega}(\mathbf{r},t)/\partial t^2)/c^2 \\ = -4\pi /c^2 \partial^2 \mathbf{P}_{2\omega}(\mathbf{r},t)/\partial t^2\end{aligned}\quad (6.1)$$

In general, a simplified solution may be obtained for equation (6.1) by taking the following approximations into consideration: (1) all the waves are infinite plane waves, (2) depletion of energy from the pump wave can be neglected, (3) the non-linear medium is a finite slab with plane boundary surfaces, (4) the beam is propagating along a symmetry axis, and (5) the energy transfer among waves is only significant after the waves travels a distance much longer than their wavelengths . The solution can then be written in the form

$$\begin{aligned}\mathbf{E}_{2\omega}(\mathbf{r},t) &= \mathbf{e}_f E_f \exp(i\mathbf{k}_f \cdot \mathbf{r} - 2i\omega t) \\ &+ \mathbf{e}_b E_b \exp(i\mathbf{k}_b \cdot \mathbf{r} - 2i\omega t)\end{aligned}\quad (6.2)$$

where $\mathbf{e}_f$ = unit vector in the direction of the 'free' wave
solution resulting from applying the boundary
conditions

$\mathbf{e}_b$ = unit vector in the direction of the 'bound' wave
solution driven by the bulk medium
 $= \mathbf{p} - [\mathbf{k}_b(\mathbf{k}_b \cdot \mathbf{p})/|\mathbf{k}_f|^2]$

$\mathbf{p}$ = unit vector in the direction of the nonlinear
polarization

E_f = amplitude of free wave solution electric field
component determined from the boundary
conditions at the input face of the crystal

E_b = amplitude of bound wave solution electric field
component determined from the nonlinear
polarization
 $= 4\pi P_{2\omega}/(n_{\omega}^2 - n_{2\omega}^2)$

$P_{2\omega}$ = amplitude of second-order nonlinear polarization
 $= \chi^2_{ijk} E_i E_j$

χ^2 = second-order susceptibility tensor

n_{ω} = index of refraction for the fundamental wave in
the medium

$n_{2\omega}$ = index of refraction for the second harmonic wave
in the medium

$\mathbf{k}_f$ = wave vector for the free wave

$$\begin{aligned}
&= n_{2\omega}(2\omega/c) \\
\mathbf{k}_b &= \text{wave vector for the bound wave} \\
&= n_{\omega}(2\omega/c) \\
\omega &= \text{fundamental frequency of laser} \\
t &= \text{time}
\end{aligned}$$

The corresponding magnetic field $\mathbf{H}$, for the transverse plane wave, will be given by

$$\begin{aligned}
\mathbf{H}_{2\omega}(\mathbf{r},t) &= c/2\omega[(\mathbf{k}_f \times \mathbf{e}_f)E_f \exp(i\mathbf{k}_f \cdot \mathbf{r} - 2i\omega t) \\
&+ (\mathbf{k}_b \times \mathbf{e}_b) E_b \exp(i\mathbf{k}_b \cdot \mathbf{r} - 2i\omega t)] \quad (6.3)
\end{aligned}$$

All that remains is to apply the appropriate boundary conditions at the $w=0$ and $w= L$ input faces of the finite medium to solve for the various specific coefficients which are required to describe the exact nature of the wave solution. These boundary conditions require that the tangential components of the electric and magnetic field be continuous across the boundary. At the input face $w=0$, the reflected second harmonic wave in air, present because of the source term in equation (6.1), is given by the components

$$\mathbf{E}_{2\omega}^R(\mathbf{r},t) = \mathbf{e}_R E_R \exp(i\mathbf{k}_R \cdot \mathbf{r} - 2i\omega t) \quad (6.4)$$

$$\mathbf{H}_{2\omega}^R(\mathbf{r},t) = c(\mathbf{k}_R \times \mathbf{e}_R) E_R \exp(i\mathbf{k}_R \cdot \mathbf{r} - 2i\omega t)/2\omega \quad (6.5)$$

where $\mathbf{e}_R$ = unit vector in the direction of the reflected
second harmonic wave from the boundary at
 $z = 0$
 $\mathbf{k}_R$ = wave vector for reflected second harmonic
wave

At $r = 0$,

$$\mathbf{E}_{2\omega}(0,t) = (\mathbf{e}_f E_f + \mathbf{e}_b E_b) \exp(-2i\omega t) \quad (6.6)$$

$$\begin{aligned} \mathbf{H}_{2\omega}(0,t) = & (c/2\omega)[(\mathbf{k}_f \times \mathbf{e}_f) E_f \\ & + (\mathbf{k}_b \times \mathbf{e}_b) E_b] \exp(-2i\omega t) \end{aligned} \quad (6.7)$$

$$\mathbf{E}_{2\omega}^R(0,t) = \mathbf{e}_R E_R \exp(-2i\omega t) \quad (6.8)$$

$$\mathbf{H}_{2\omega}^R(0,t) = c(\mathbf{k}_R \times \mathbf{e}_R) E_R \exp(-2i\omega t)/2\omega \quad (6.9)$$

According to the coordinate system (X,Y,Z) indicated in figure 3.6,
the continuity relations are

$$\mathbf{X} \cdot \mathbf{e}_R E_R = \mathbf{X} \cdot (\mathbf{e}_f E_f + \mathbf{e}_b E_b) \quad (6.10)$$

$$\mathbf{k}_R \times \mathbf{e}_R \cdot \mathbf{X} E_R = \mathbf{X} \cdot [(\mathbf{k}_f \times \mathbf{e}_f) E_f + (\mathbf{k}_b \times \mathbf{e}_b) E_b] \quad (6.11)$$

$$\mathbf{Y} \cdot \mathbf{e}_R \mathbf{E}_R = \mathbf{Y} \cdot (\mathbf{e}_f \mathbf{E}_f + \mathbf{e}_b \mathbf{E}_b) \quad (6.12)$$

$$\mathbf{k}_R \times \mathbf{e}_R \cdot \mathbf{Y} \mathbf{E}_R = \mathbf{Y} \cdot [(\mathbf{k}_f \times \mathbf{e}_f) \mathbf{E}_f + (\mathbf{k}_b \times \mathbf{e}_b) \mathbf{E}_b] \quad (6.13)$$

Assigning the projections on $\mathbf{X}, \mathbf{Y}, \mathbf{Z}$ of $\mathbf{e}_b, \mathbf{e}_f, \mathbf{e}_R$, and $\mathbf{p}$ the following matrix of symbols,

$$\begin{array}{ccccc} & \mathbf{e}_b & \mathbf{e}_f & \mathbf{e}_R & \mathbf{p} \\ \mathbf{X} & b_x & f_x & R_x & p_x \\ \mathbf{Y} & b_y & f_y & R_y & p_y \\ \mathbf{Z} & b_z & f_z & R_z & p_z \end{array} \quad (6.14)$$

equations (6.10) - (6.13) become

$$R_x \mathbf{E}_R = f_x \mathbf{E}_f + b_x \mathbf{E}_b \quad (6.15)$$

$$R_y k_{Rz} \mathbf{E}_R = f_y k_{fz} \mathbf{E}_f + b_y k_{bz} \mathbf{E}_b \quad (6.16)$$

$$R_y \mathbf{E}_R = f_y \mathbf{E}_f + b_y \mathbf{E}_b \quad (6.17)$$

$$\begin{aligned} (R_x k_{Rz} - R_z k_{Rx}) \mathbf{E}_R &= (f_x k_{fz} - f_z k_{fx}) \mathbf{E}_f \\ &+ (p_x k_{bz} - p_z k_{bx}) \mathbf{E}_b \end{aligned} \quad (6.18)$$

where the fact the wave vectors lie entirely in the (X,Z) plane has been taken into account, i.e $k_{Ry} = k_{fy} = k_{by} = 0$. If the relationship between the crystal system (u,v,w) and the laboratory system (X,Y,Z) is

$$u = X \quad v = Z \quad w = -Y \quad (6.19)$$

the nonlinear polarization will be parallel to the plane of incidence. Taking into account that quartz belongs to the trigonal Bravais lattice type, specifically the point group 32 where the w crystallographic axis is a threefold axis, and the u crystallographic axis is a twofold axis, the induced nonlinear polarization will have the components

$$P_u = d_{11}(E_x^2 - E_y^2) \quad (6.20)$$

$$P_v = -2d_{11}E_xE_y \quad (6.21)$$

$$P_w = 0 \quad (6.22)$$

If we now assume that the incident laser beam is p-polarized, the geometry of figure 3.6 dictates that

$$p_y = 0 \quad (6.23)$$

$$b_x = p_x - (n_\omega^2/n_{2\omega}^2)\sin\theta_\omega(\sin\theta_\omega p_x + \cos\theta_\omega p_z) \quad (6.24)$$

$$b_y = 0 \quad (6.25)$$

$$b_z = p_z - (n_\omega^2/n_{2\omega}^2)\cos\theta_\omega(\sin\theta_\omega p_x + \cos\theta_\omega p_z) \quad (6.26)$$

where θ_ω is determined by using Snell's law of refraction

$$\sin\theta_\omega = \sin\theta/n_\omega \quad (6.27)$$

Equations (6.15) - (6.18) then become

$$R_x E_R = f_x E_f + b_x E_b \quad (6.28)$$

$$R_y k_{Rz} E_R = f_y k_{fz} E_f \quad (6.29)$$

$$R_y E_R = f_y E_f \quad (6.30)$$

$$\begin{aligned} (R_x k_{Rz} - R_z k_{Rx}) E_R = & (f_x k_{fz} - f_z k_{fx}) E_f \\ & + (p_x k_{bz} - p_z k_{bx}) E_b \end{aligned} \quad (6.31)$$

The coefficients R_y and f_y can only satisfy both equations (6.29) and (6.30) if they are identically zero. Also, in terms of the angles from figure 3.6, the direction cosines and wave numbers are

$$R_x = -\cos\theta \quad (6.32)$$

$$f_x = \cos\theta_{2\omega} \quad (6.33)$$

$$R_z = -\sin\theta \quad (6.34)$$

$$f_z = -\sin\theta_{2\omega} \quad (6.35)$$

$$k_{Rx} = 2\omega\sin\theta/c \quad (6.36)$$

$$k_{Rz} = -2\omega\cos\theta/c \quad (6.37)$$

$$k_{fx} = 2\omega n_{2\omega}\cos\theta_{2\omega}/c \quad (6.38)$$

$$k_{fz} = 2\omega n_{2\omega}\sin\theta_{2\omega}/c \quad (6.39)$$

$$k_{bx} = 2\omega n_{\omega}\sin\theta_{\omega}/c \quad (6.40)$$

$$k_{bz} = 2\omega n_{\omega}\cos\theta_{\omega}/c \quad (6.41)$$

where again Snell's law of refraction should be used to determine $\theta_{2\omega}$

$$\sin\theta_{2\omega} = \sin\theta/n_{2\omega} \quad (6.42)$$

Substitution of (6.32) through (6.41) into (6.28) and (6.31) yields

$$\begin{aligned} -E_R \cos \theta &= E_f \cos \theta_{2\omega} \\ &+ [p_x - (n_\omega^2 / n_{2\omega}^2) \sin \theta_\omega (\sin \theta_\omega p_x + \cos \theta_\omega p_z)] E_b \end{aligned} \quad (6.43)$$

and,

$$E_R = n_{2\omega} E_f + n_\omega (p_x \cos \theta_\omega - p_z \sin \theta_\omega) E_b \quad (6.44)$$

Solving equations (6.43) and (6.44) for E_f ends with the result

$$\begin{aligned} E_f &= -E_b [(b_x + n_\omega \cos \theta (p_x \cos \theta_\omega - p_z \sin \theta_\omega)) \\ &/ (\cos \theta_{2\omega} + n_{2\omega} \cos \theta)] \end{aligned} \quad (6.45)$$

Using the value for E_f coming from (6.45) into (6.2) and (6.3) provides one part of the complete solution, mainly the electric and magnetic field components of the second harmonic wave as it propagates through the bulk of the quartz crystal. The result is

$$\begin{aligned} E_{2\omega}(r,t) &= [-e_f (b_x + n_\omega \cos \theta (p_x \cos \theta_\omega - p_z \sin \theta_\omega)) \\ &/ (\cos \theta_{2\omega} + n_{2\omega} \cos \theta) \\ &\cdot \exp(ik_f \cdot r - 2i\omega t) + e_b \exp(ik_b \cdot r - 2i\omega t)] E_b \end{aligned} \quad (6.46)$$

and,

$$\begin{aligned}
H_{2\omega}(\mathbf{r},t) = & \quad c/2\omega[-(\mathbf{k}_f \times \mathbf{e}_f)(b_x + n_\omega \cos\theta(p_x \cos\theta_\omega - p_z \sin\theta_\omega)) \\
& / (\cos\theta_{2\omega} + n_{2\omega} \cos\theta) \cdot \exp(i\mathbf{k}_f \cdot \mathbf{r} - 2i\omega t) \\
& + (\mathbf{k}_b \times \mathbf{e}_b) \exp(i\mathbf{k}_b \cdot \mathbf{r} - 2i\omega t)] E_b
\end{aligned} \tag{6.47}$$

In order to describe the results given by equations (6.46) and (6.47) in terms of the electric field E_0 incident onto the crystal, the Fresnel transmission coefficient has to be evaluated, the form of which can be found in any good modern optics textbook,

$$t_\omega = 2\cos\theta/(n_\omega \cos\theta + \cos\theta_\omega) \tag{6.48}$$

such that,

$$|E_0|t_\omega = |E_\omega| \tag{6.49}$$

where E_0 as mentioned previously is polarized parallel to the plane of incidence. Keep in mind that E_ω is the electric field propagating inside the crystal at the fundamental frequency inducing the nonlinear polarization $P_{2\omega}$.

At the output face of the crystal, i.e. $w = L$, the bound and free waves are transmitted in air. So long as the reflections of E_ω at $w=L$ are neglected, there is no reflected bound second harmonic wave. Usually this is a good theoretical assumption to make because the intensity of the bound wave upon each successive

reflection diminishes very rapidly. For example only about 4% of the light is reflected on the first pass. However, there will be a reflected free second harmonic wave back into the crystal because of the physical presence of the boundary between the two different media. Proceeding in an analogous fashion to that used to establish the form of the solution at the $w=0$ boundary, the continuity relations are

$$E_{2\omega}^{\dagger} \cos\theta \exp(2ik_{\omega} \cdot ZL - 2i\omega t) = \cos\theta_{2\omega} E_f \exp(ik_f \cdot ZL - 2i\omega t) + b_x E_b \exp(ik_b \cdot ZL - 2i\omega t) - \cos\theta_{2\omega} \cdot E_R^{\dagger} \exp(-ik_f \cdot ZL - 2i\omega t) \quad (6.50)$$

and

$$E_{2\omega}^{\dagger} \exp(ik_{2\omega}^{\dagger} \cdot ZL - 2i\omega t) = E_f n_{2\omega} \exp(ik_f \cdot ZL - 2i\omega t) + n_{\omega} E_b (\cos\theta_{\omega} p_x - \sin\theta_{\omega} p_z) \cdot \exp(ik_b \cdot ZL - 2i\omega t) + n_{2\omega} \cdot E_R^{\dagger} \exp(-ik_f \cdot ZL - 2i\omega t) \quad (6.51)$$

where $k_{2\omega}^{\dagger}$ = the wave vector for the free second harmonic wave at the output face of the crystal
 $= 2 \cdot k_{\omega} = 2n_{\omega}\omega/c$

k_ω = the wave vector for the wave propagating through the crystal at the fundamental frequency

$E_R^\dagger$ = the amplitude for the electric field of the reflected free wave back into the crystal at the output face

$E_{2\omega}^\dagger$ = the amplitude for the electric field component of the free second harmonic wave exiting the output face of the crystal

Solving the system of equations (6.50) and (6.51) for the two unknowns $E_R^\dagger$ and $E_{2\omega}^\dagger$ results in the following two expressions

$$\begin{aligned} E_{2\omega}^\dagger \exp(2ik_\omega \cdot ZL) &= [2n_{2\omega} \cos \theta_{2\omega} / (n_{2\omega} \cos \theta + \cos \theta_{2\omega})] E_f \exp(ik_f \cdot ZL) \\ &+ [(n_{2\omega} b_x + n_\omega \cos \theta_{2\omega} \{ \cos \theta_\omega p_x - \sin \theta_\omega p_z \}) \\ &/ (n_{2\omega} \cos \theta + \cos \theta_{2\omega})] \\ &\cdot E_b \exp(ik_b \cdot ZL) \end{aligned} \quad (6.52)$$

$$\begin{aligned} E_R^\dagger \exp(-ik_f \cdot ZL) &= [1 - 2n_{2\omega} \cos \theta_{2\omega} / (n_{2\omega} \cos \theta + \cos \theta_{2\omega})] \\ &\cdot E_f \exp(ik_f \cdot ZL) + [b_x \cos \theta / \cos \theta_{2\omega} \\ &- (\cos \theta / \cos \theta_{2\omega}) (n_{2\omega} b_x + n_\omega \cos \theta_{2\omega} \\ &\cdot \{ \cos \theta_\omega p_x - \sin \theta_\omega p_z \}) / (n_{2\omega} \cos \theta + \cos \theta_{2\omega})] \\ &\cdot E_b \exp(ik_b \cdot ZL) \end{aligned} \quad (6.53)$$

Equation (6.52) is more important because that directly relates to the second harmonic power that is measured experimentally. However, for completeness in the predictions both fields must be accounted for.

The intensity of the second-harmonic light at the output face of the crystal is given by the amplitude of the complex Poynting vector,

$$I_{2\omega} = c/8\pi |(\mathbf{E}_{2\omega}^\dagger \times \mathbf{H}_{2\omega}^{\dagger*})| = c/8\pi |\mathbf{E}_{2\omega}^\dagger|^2 \quad [\text{cgs}] \quad (6.54)$$

Substitution of (6.52) into (6.54) results in the lengthy expression

$$\begin{aligned} I_{2\omega} = & (c/8\pi) \{ [2n_{2\omega} \cos \theta_{2\omega} / (n_{2\omega} \cos \theta + \cos \theta_{2\omega})]^2 E_f^2 \\ & + [(n_{2\omega} b_x + n_{\omega} \cos \theta_{2\omega} \{ \cos \theta_{\omega} p_x - \sin \theta_{\omega} p_z \}) / (n_{2\omega} \cos \theta \\ & + \cos \theta_{2\omega})]^2 E_b^2 + [2n_{2\omega} \cos \theta_{2\omega} / (n_{2\omega} \cos \theta + \cos \theta_{2\omega})] \\ & \cdot [(n_{2\omega} b_x + n_{\omega} \cos \theta_{2\omega} \{ \cos \theta_{\omega} p_x - \sin \theta_{\omega} p_z \}) \\ & / (n_{2\omega} \cos \theta + \cos \theta_{2\omega}) E_f E_b [\exp(i(\mathbf{k}_f - \mathbf{k}_b) \cdot \mathbf{Z}L) \\ & + \exp(-i(\mathbf{k}_f - \mathbf{k}_b) \cdot \mathbf{Z}L)] \} \end{aligned} \quad (6.55)$$

Now, making use of the following items: (1) the expression found in (6.45) for E_f , (2) the expression for E_b given in the beginning of this appendix, and (3) the following trigonometric identity,

$$[\exp(i(\mathbf{k}_f - \mathbf{k}_b) \cdot \mathbf{Z}L) + \exp(-i(\mathbf{k}_f - \mathbf{k}_b) \cdot \mathbf{Z}L)] = 2\cos[(\mathbf{k}_f - \mathbf{k}_b) \cdot \mathbf{Z}L]$$

$$= 2-4\sin^2[(k_f-k_b)\cdot ZL/2] \quad (6.56)$$

where

$$(k_f-k_b)\cdot ZL/2 = (\pi L/2)(4/\lambda)(n_\omega \cos\theta_\omega - n_{2\omega} \cos\theta_{2\omega}) \quad (6.57)$$

it is possible to recast equation (6.55) into the slightly modified expression

$$\begin{aligned} I_{2\omega} = & (c/8\pi)[4\pi|P_{2\omega}|/(n_\omega^2 - n_{2\omega}^2)]^2 \{ 8n_{2\omega} \cos\theta_{2\omega} \\ & \cdot (b_x + n_\omega \cos\theta(p_x \cos\theta_\omega - p_z \sin\theta_\omega))(n_{2\omega} b_x + n_\omega \cos\theta_{2\omega} \\ & \cdot \{\cos\theta_\omega p_x - \sin\theta_\omega p_z\}) \\ & \cdot \sin^2[(\pi L/2)(4/\lambda)(n_\omega \cos\theta_\omega - n_{2\omega} \cos\theta_{2\omega})] \\ & / (\cos\theta_{2\omega} + n_{2\omega} \cos\theta)^3 \\ & + [2n_{2\omega} \cos\theta_{2\omega}(b_x + n_\omega \cos\theta(p_x \cos\theta_\omega - p_z \sin\theta_\omega)) \\ & / (\cos\theta_{2\omega} + n_{2\omega} \cos\theta) \\ & - (n_{2\omega} b_x + n_\omega \cos\theta_{2\omega} \{\cos\theta_\omega p_x - \sin\theta_\omega p_z\}) \\ & / (\cos\theta_{2\omega} + n_{2\omega} \cos\theta)]^2 \} \quad (6.58) \end{aligned}$$

$I_{2\omega}$ can be seen to be the sum of two terms: one is dependent on the angle defined by equation (6.57) and the other depends only on the angle of incidence and the polarization of the incident light. The second term has an amplitude several orders of magnitude, i.e. $\sim 10^{-4}$, smaller than the maximum of the first term and therefore can be neglected. Moreover equation (6.58) can be further

simplified by noting that in materials for which dispersion is not very important ,i.e. $n_{\omega} \equiv n_{2\omega}$, like in quartz where the two indices differ by only 9%,

$$b_x \equiv \cos\theta_{\omega}(p_x\cos\theta_{\omega} - p_z\sin\theta_{\omega}) \quad (6.59)$$

Substitution of (6.59) back into (6.58) and factoring out the $b_x/\cos\theta_{\omega}$ term leads to a new expression

$$I_{2\omega} = (c/8\pi)[4\pi|\mathbf{P}_{2\omega}|/(n_{\omega}^2 - n_{2\omega}^2)]^2$$

$$\cdot \{8n_{2\omega}\cos\theta_{2\omega}(p_x\cos\theta_{\omega} - p_z\sin\theta_{\omega})$$

$$\cdot (\cos\theta_{\omega} + n_{\omega}\cos\theta)(n_{2\omega}\cos\theta_{\omega} + n_{\omega}\cos\theta_{2\omega})$$

$$\cdot \sin^2[(\pi L/2)(4/\lambda)(n_{\omega}\cos\theta_{\omega} - n_{2\omega}\cos\theta_{2\omega})]$$

$$/ (\cos\theta_{2\omega} + n_{2\omega}\cos\theta)^3 \quad (6.60)$$

Equation (6.60) can be further simplified by noting that the nonlinear polarization term $|\mathbf{P}_{2\omega}|$ can be related to the electric field $|\mathbf{E}_{\omega}|$ inside the crystal, via the nonlinear optical coefficient tensor $\mathbf{d}$ and the so-called "projection factor" $p(\theta)$. The projection factor depends on the specific form of the nonlinear optical coefficient tensor $\mathbf{d}$ and on the direction of the nonlinear polarization unit vector $\mathbf{p}$ compared with the plane of incidence.

The projection factor is the result of the multiplication of two quantities p_1 and p_2 . The term p_1 can be directly deduced by a comparison of the amplitude of the nonlinear polarization, for a p-polarized laser beam, as dictated by equations (6.20) through (6.22) with the corresponding terms in the following equation

$$|P_{2\omega}| = p_1 d |E_\omega|^2 \quad (6.61)$$

The result of such a comparison leads directly to the conclusion that p_1 must equal unity. The term p_2 can be shown to be given by

$$p_2 = \cos(\theta_\omega - \eta) \equiv b_x / \cos\theta_\omega \quad (6.62)$$

where η is the projection angle between the direction of the nonlinear polarization and the plane of incidence. As can again be inferred from figure 3.6,

$$p_x = \cos 2\theta_\omega \quad (6.63)$$

and,

$$p_z = \sin 2\theta_\omega \quad (6.64)$$

Therefore, from equations (6.59), (6.63), and (6.64), the result one can obtain for the value of p_2 , after some algebraic manipulations, is

$$p_2 = \cos 3\theta_\omega \quad (6.65)$$

The projection factor by the definition given above is then simply equivalent to just p_2 .

Now, the transmission factor at the exit face of the crystal is given by the expression

$$t_\omega^\dagger = \frac{[2n_{2\omega}\cos\theta_{2\omega}(n_\omega\cos\theta + \cos\theta_\omega) \cdot (n_{2\omega}\cos\theta_\omega + n_\omega\cos\theta_{2\omega}) / (n_{2\omega}\cos\theta + \cos\theta_{2\omega})^3]}{\quad} \quad (6.66)$$

Making use of equation (6.49) and equation (6.66), equation 6.60 can be simplified to the following form,

$$I_{2\omega} = [8\pi c|E_0|^4 / (n_\omega^2 - n_{2\omega}^2)^2] d^2 t_\omega^\dagger \rho^2(\theta) t_\omega^4 \cdot \sin^2[(\pi L/2)(4/\lambda)(n_\omega\cos\theta_\omega - n_{2\omega}\cos\theta_{2\omega})] \quad (6.67)$$

The power of the second harmonic light along the Z direction is then simply the integral of the flux of the intensity $I_{2\omega}$ across the plane $Z = \text{a constant}$. Therefore,

$$P_{2\omega} = \iint I_{2\omega} dX dY \quad (6.68)$$

Since the electric field can be considered constant to first order across the cross-sectional area of a pulsed YAG laser beam, equation (6.68) simply integrates to

$$P_{2\omega} = I_{2\omega} A_0 \quad (6.69)$$

where A_0 is the cross-sectional area of the beam.

At this point, let the normalized Maker Fringe equation be defined as the ratio

$$P_N = P_{2\omega}(\theta)/P_{2\omega}(0) \quad (6.70)$$

Evaluating equation (6.67) at normal incidence, $\theta = 0$, and then applying the definition given in equation (6.70), yields the desired outcome of this whole derivation

$$\begin{aligned} P_N = & [(n_{2\omega} \cos \theta_{2\omega} + n_{\omega} \cos \theta_{\omega}) \cos^4 \theta \cos \theta_{2\omega} (n_{2\omega} + 1)^3 \\ & \cdot (n_{\omega} + 1)^3 \cos^2(3\theta_{\omega}) \\ & \cdot \sin^2\{(\pi L/2)(4/\lambda)(n_{\omega} \cos \theta_{\omega} - n_{2\omega} \cos \theta_{2\omega})\} \\ & / (n_{\omega} \cos \theta + \cos \theta_{\omega})^3 \\ & \cdot (\cos \theta_{2\omega} + n_{2\omega} \cos \theta)^3 (n_{\omega} + n_{2\omega})] \end{aligned} \quad (6.71)$$

All that remains is to look at the effect of beam divergence on the result given in equation (6.71). Near a minimum the harmonic power is

$$P_{2\omega} = C \sin^2\{(\pi L/2)(4/\lambda)(n_{\omega} \cos \theta_{\omega} - n_{2\omega} \cos \theta_{2\omega})\} \quad (6.72)$$

where C can be considered as essentially a constant for small variations of θ . The measured power is in fact

$$\Delta P_{2\omega} = 2(\Delta\theta)^{-1} \int_{\theta-\Delta\theta}^{\theta+\Delta\theta} P_{2\omega} d\theta \quad (6.73)$$

averaged over the the variation $2\Delta\theta$ for the angle of incidence. If ϵ is the beam divergence(half-angle) of the laser at the sample, the amplitude $\Delta P_{2\omega}$ of the minimum compared to the amplitude $P_{2\omega}$ of the next maximum is, for small values of θ ,

$$\Delta P_{2\omega}/P_{2\omega} = (\pi^2 L^2 / 12 n^4 l_c^2) \epsilon^2 \theta^2 \quad (6.74)$$

where l_c is the coherence length of the light inside the crystal. Assuming $L = .1$ cm, $l_c = 21$ μ m, $n = 1.5$, $\epsilon = 1.75 \times 10^{-3}$ rad, and $\theta = 40^\circ$, the estimate of the error due to beam divergence is according to equation (6.74) only .05% and is therefore negligible.

CHAPTER SEVEN

FIGURES

$\overline{E}_{out}$

ATOM / MOLECULE
RESPONSE

$\overline{E}_{in}$

ROTATION ANGLE	RAW SHG (a.u)	CORRECTED SHG(**)	ROTATION ANGLE	RAW SHG (a.u)	CORRECTED SHG(**)
-40	4.80E-01	7.00E-02	1	8.30E-01	4.20E-01
-39	5.30E-01	1.20E-01	2	8.60E-01	4.50E-01
-38	5.50E-01	1.40E-01	3	8.90E-01	4.80E-01
-37	5.40E-01	1.30E-01	4	9.10E-01	5.00E-01
-36	4.70E-01	6.00E-02	5	9.40E-01	5.30E-01
-35	4.50E-01	4.00E-02	6	9.90E-01	5.80E-01
-34	4.10E-01	0.00E+00	7	1.03E+00	6.20E-01
-33	4.70E-01	6.00E-02	8	1.08E+00	6.70E-01
-32	5.30E-01	1.20E-01	9	1.14E+00	7.30E-01
-31	6.10E-01	2.00E-01	10	1.18E+00	7.70E-01
-30	6.90E-01	2.80E-01	11	1.21E+00	8.00E-01
-29	7.80E-01	3.70E-01	12	1.23E+00	8.20E-01
-28	7.90E-01	3.80E-01	13	1.21E+00	8.00E-01
-27	7.70E-01	3.60E-01	14	1.18E+00	7.70E-01
-26	6.80E-01	2.70E-01	15	1.11E+00	7.00E-01
-25	5.40E-01	1.30E-01	16	1.01E+00	6.00E-01
-24	5.10E-01	1.00E-01	17	8.80E-01	4.70E-01
-23	4.60E-01	5.00E-02	18	7.70E-01	3.60E-01
-22	4.40E-01	3.00E-02	19	6.50E-01	2.40E-01
-21	4.40E-01	3.00E-02	20	5.00E-01	9.00E-02
-20	5.30E-01	1.20E-01	21	4.40E-01	3.00E-02
-19	6.40E-01	2.30E-01	22	3.40E-01	0.00E+00
-18	7.70E-01	3.60E-01	23	4.40E-01	3.00E-02
-17	9.00E-01	4.90E-01	24	4.80E-01	7.00E-02
-16	1.05E+00	6.40E-01	25	5.50E-01	1.40E-01
-15	1.10E+00	6.90E-01	26	6.40E-01	2.30E-01
-14	1.14E+00	7.30E-01	27	7.20E-01	3.10E-01
-13	1.15E+00	7.40E-01	28	7.20E-01	3.10E-01
-12	1.17E+00	7.60E-01	29	7.10E-01	3.00E-01
-11	1.16E+00	7.50E-01	30	6.50E-01	2.40E-01
-10	1.13E+00	7.20E-01	31	5.60E-01	1.50E-01
-9	1.11E+00	7.00E-01	32	4.80E-01	7.00E-02
-8	1.09E+00	6.80E-01	33	4.20E-01	1.00E-02
-7	1.04E+00	6.30E-01	34	4.50E-01	4.00E-02
-6	9.60E-01	5.50E-01	35	4.70E-01	6.00E-02
-5	9.20E-01	5.10E-01	36	5.00E-01	9.00E-02
-4	9.10E-01	5.00E-01	37	5.30E-01	1.20E-01
-3	8.80E-01	4.70E-01	38	5.30E-01	1.20E-01
-2	8.50E-01	4.40E-01	39	5.20E-01	1.10E-01
-1	8.40E-01	4.30E-01	40	4.90E-01	8.00E-02
0	8.30E-01	4.20E-01			

3.5

(**) The background remained constant at 0.41 a.u.

NORMAL DISPERSION CURVE FOR QUARTZ

λ nm	n_o	n_e
185	1.65751	1.68988
198	1.65087	1.66394
231	1.61395	1.62555
340	1.56747	1.57737
394	1.55846	1.56805
434	1.55396	1.56339
508	1.54822	1.55746
589.3	1.54424	1.55335
768	1.53903	1.54794
832.5	1.53773	1.54661
991.4	1.53514	1.54392
1150.2	1.53283	1.54152
1307.0	1.53090	1.53951
1395.8	1.52977	1.53832
1479.2	1.52865	1.53716
1541.4		1.52781
1681.5		1.52583
1761.4		1.52468
1945.7		1.52184
2053.1		1.52005
2300.0		1.51561
2600.0		1.50986
3000.0		1.49953
3500.0		1.48451
4000.0		1.46617
4200.0		1.4569
5000.0		1.417
6450.0		1.274
7000.0		1.167
		1.53630
		1.53422
		1.53301
		1.53004
		1.52823

SUMMARY OF SHG/ELECTROCHEMISTRY LITERATURE SURVEYED

NO.	INVESTIGATOR(s)	AFFILIATION AT TIME OF RESULTS	LASER USED	WAVELENGTH [μm]	ENERGY [mJ/pulse]	SPOT SIZE (ϕ TARGET) [cm^2]	REPETITION RATE (Hz)	REFERENCE ELECTRODE	WORKING ELECTRODE	ELECTROLYTE(S)	APPLIED POTENTIAL RANGE (Volts)	SWEEP RATE [mV/s]
1.	B.J. BOWER et. al.	ARGONNE NATIONAL LABORATORIES	FREQUENCY DOUBLED Nd:YAG	0.532	0.44	0.01	1700	SCE	POLYCRYSTALLINE IRON	.1 M NaOH & .05M .25 M NaCl, .05M/Na .1 M KCl .1 M H2SO4	-1.2 to 0.2 -1.1 to -0.5 -0.7 to -0.4 -0.5 to -0.6	2 1 1 1
2.	D.J. CAMPBELL et. al.	UNIVERSITY OF WISCONSIN	Nd:YAG	1.064	2 to 6	NOT PROVIDED	10	Ag/1 M AgNO3	POLYCRYSTALLINE SILVER	.1 M TBAPF4 + .35 M ACETIC ACID ACETONITRILE SOLN	-2.0 to -0.4	10
3.	D.J. CAMPBELL et. al.	UNIVERSITY OF WISCONSIN	Nd:YAG PUMPED PYLON	0.578	1 to 12 [mJ/cm ²]	NOT PROVIDED	10	SCE	POLYCRYSTALLINE PLATINUM	.5 M H2SO4 .35 M HClO4	-0.3 to 1.1	10
4.	D.J. CAMPBELL et. al.	UNIVERSITY OF WISCONSIN	Nd:YAG	1.064	NOT PROVIDED	NOT PROVIDED	10	Ag/1 M AgNO3 SCE	POLYCRYSTALLINE SILVER POLYCRYSTALLINE PLATINUM	.1 M H2SO4 .1 M H2SO4 + .25 M HClO4 ACETONITRILE SOLN	-2.55 to -1.05 -1.15 to -0.3	10 20
5.	C.K. CHEN et. al.	UNIVERSITY OF CALIFORNIA, BERKELEY	Nd:YAG	1.064	< 0.6	0.2	10	SCE	POLYCRYSTALLINE SILVER	.1 M KCl .1 M KCl + 50 mM PYRIDINE	-1.1 to 0.08	STATIC STEPS
6.	T.T. CHEN et. al.	YALE UNIVERSITY	Nd:YAG	1.064	1.4	0.003	20	SCE	POLYCRYSTALLINE SILVER	1 M H2SO4 1 M H2SO4 + .25 M HClO4 1 M H2SO4 + .25 M HClO4 1 M H2SO4 + .25 M HClO4 + 50 mM PYRIDINE	-0.9 to 0.5	5
7.	R.M. CORN et. al.	IBM RESEARCH LABORATORIES	Nd:YAG	1.064	2 [mJ/cm ²]	NOT PROVIDED	2	Ag/AgCl SATD IN 3 M KCl	POLYCRYSTALLINE SILVER	.1 M H2SO4 NOT PROVIDED SPE (+) SPECIES	-1.25 to -0.75 -0.45 to -0.25	10
8.	T.F. HEINZ et. al.	UNIVERSITY OF CALIFORNIA, BERKELEY	Nd:YAG	1.064	0.2	0.2	10	SCE	POLYCRYSTALLINE SILVER	.1 M KCl .1 M KCl + .25 M C6H5N	-1.1 to 0.08	STATIC STEPS
9.	C.D. MARSHALL et. al.	RENSSELAER POLYTECHNIC	Nd:YAG	1.064	3.0 to 6.9 [mJ/cm ²]	0.2	10	SCE	POLYCRYSTALLINE SILVER	.1 M KCl	-0.4 to 0.2	5
10.	T.E. FURTAJ et. al.	COLORADO SCHOOL OF MINES	Nd:YAG	1.064	10 [mJ/cm ²]	2*10 ⁻² (-3)	CW	SCE	SINGLE CRYSTAL SILVER(111)	NOT PROVIDED (C6H5N) (electroactive species)	-0.65 to -0.4	NOT PROVIDED
11.	S.L. RICHMOND	BRYN MAWR COLLEGE	Nd:YAG	1.064	1 to 2	1	10	SCE	POLYCRYSTALLINE SILVER	.1 M H2SO4 .1 M HCl .1 M H2SO4	-1 to 0.5	10
12.	D.F. VOSS et. al.	NAVAL RESEARCH LABORATORIES	Nd:YAG	1.064	NOT PROVIDED	NOT PROVIDED	CW	Ag/AgCl SATD IN 3 M KCl	POLYCRYSTALLINE SILVER	10 mM 0.4% - 80 mM 0.2% + .1 M H2SO4	-1.2 to 0.0	10

CV GRAPH FOR COPPER UPD ONTO POLYCRYSTALLINE GOLD

SHG GRAPH FOR COPPER UPD ONTO POLYCRYSTALLINE GOLD

APPLIED POTENTIAL	CATHODIC SHG(a.u.)	CORRECTED SHG(**)	APPLIED POTENTIAL	ANODIC SHG(a.u.)	CORRECTED SHG(**)
0.5	-0.38	-0.34	0.5	-0.38	-0.34
0.48	-0.39	-0.35	0.48	-0.38	-0.34
0.46	-0.38	-0.34	0.46	-0.37	-0.33
0.44	-0.38	-0.34	0.44	-0.37	-0.33
0.42	-0.37	-0.33	0.42	-0.38	-0.34
0.4	-0.35	-0.31	0.4	-0.39	-0.35
0.38	-0.31	-0.27	0.38	-0.38	-0.34
0.36	-0.24	-0.2	0.36	-0.38	-0.34
0.34	-0.16	-0.12	0.34	-0.38	-0.34
0.32	-0.15	-0.11	0.32	-0.38	-0.34
0.3	-0.14	-0.1	0.3	-0.38	-0.34
0.28	-0.13	-0.09	0.28	-0.39	-0.35
0.26	-0.14	-0.1	0.26	-0.38	-0.34
0.24	-0.14	-0.1	0.24	-0.38	-0.34
0.22	-0.13	-0.09	0.22	-0.37	-0.33
0.2	-0.13	-0.09	0.2	-0.36	-0.32
0.18	-0.13	-0.09	0.18	-0.35	-0.31
0.16	-0.13	-0.09	0.16	-0.35	-0.31
0.14	-0.13	-0.09	0.14	-0.31	-0.27
0.12	-0.12	-0.08	0.12	-0.27	-0.23
0.1	-0.13	-0.09	0.1	-0.26	-0.22
0.08	-0.13	-0.09	0.08	-0.22	-0.18
0.06	-0.13	-0.09	0.06	-0.19	-0.15
0.04	-0.14	-0.1	0.04	-0.15	-0.11
0.02	-0.13	-0.09	0.02	-0.14	-0.1
0	-0.13	-0.09	0	-0.13	-0.09
-0.02	-0.13	-0.09	-0.02	-0.14	-0.1
-0.04	-0.13	-0.09	-0.04	-0.13	-0.09
-0.06	-0.12	-0.08	-0.06	-0.14	-0.1
-0.08	-0.12	-0.08	-0.08	-0.12	-0.08
-0.1	-0.12	-0.08	-0.1	-0.13	-0.09

(**) The background for the entire redox cycle remained constant at -0.04 a.u.

APPLIED POTENTIAL	CATHODIC SHG(a.u.)	CORRECTED SHG(**)	APPLIED POTENTIAL	ANODIC SHG(a.u.)	CORRECTED SHG(**)
0.5	-2.7	-2.65	0.5	-2.68	-2.63
0.48	-2.69	-2.64	0.48	-2.69	-2.64
0.46	-2.68	-2.63	0.46	-2.69	-2.64
0.44	-2.69	-2.64	0.44	-2.69	-2.64
0.42	-2.69	-2.64	0.42	-2.71	-2.66
0.4	-2.68	-2.63	0.4	-2.69	-2.64
0.38	-2.67	-2.62	0.38	-2.7	-2.65
0.36	-2.69	-2.64	0.36	-2.69	-2.64
0.34	-2.69	-2.64	0.34	-2.7	-2.65
0.32	-2.71	-2.66	0.32	-2.69	-2.64
0.3	-2.68	-2.63	0.3	-2.69	-2.64
0.28	-2.68	-2.63	0.28	-2.7	-2.65
0.26	-2.69	-2.64	0.26	-2.68	-2.63
0.24	-2.7	-2.65	0.24	-2.67	-2.62
0.22	-2.67	-2.62	0.22	-2.68	-2.63
0.2	-2.68	-2.63	0.2	-2.69	-2.64
0.18	-2.7	-2.65	0.18	-2.69	-2.64
0.16	-2.69	-2.64	0.16	-2.68	-2.63
0.14	-2.68	-2.63	0.14	-2.67	-2.62
0.12	-2.7	-2.65	0.12	-2.69	-2.64
0.1	-2.67	-2.62	0.1	-2.71	-2.66
0.08	-2.69	-2.64	0.08	-2.7	-2.65
0.06	-2.68	-2.63	0.06	-2.7	-2.65
0.04	-2.67	-2.62	0.04	-2.68	-2.63
0.02	-2.66	-2.61	0.02	-2.7	-2.65
0	-2.68	-2.63	0	-2.7	-2.65
-0.02	-2.68	-2.63	-0.02	-2.69	-2.64

(**) The background through the entire redox cycle remained constant at -.05 a.u.