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Raman spectroscopy of carbon electrode surfaces

Fryling, Mark Aaron, Ph.D.
The Ohio State University, 1994
RAMAN SPECTROSCOPY OF CARBON ELECTRODE SURFACES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Mark Aaron Fryling

The Ohio State University

1994

Dissertation Committee:

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Department of Chemistry
To my Family
ACKNOWLEDGEMENTS

Many people deserve thanks for contributions towards my reaching this milestone in my career. Though it is not practical to list everyone who has had influence in this part of my life, my sincere gratitude extends to all of you for your help and support. I could not have completed this work without the support of my family, friends and colleagues.

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Many thanks also go to "the Group" from 420 McPherson. First, thanks to the "old guard" who helped me get up to speed that first summer in the lab: Dan Alsmeyer, Nick Pontikos, Christie McDermott, Mark McDermott and Kristen Kneten-Cline. The lion’s share of the thanks goes to my contemporaries in the
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Finally, I must acknowledge my fiancé, Beth, for adding so much to my life in our two years together. The relationship that we are building is one based on friendship and respect and I think has the potential to be tremendously rewarding. I look forward to creating the rest of my life with you.
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Major Field: Chemistry
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CHAPTER I

INTRODUCTION

Surfaces

The interface that exists between a solid electrode surface and a surrounding electrolyte solution is a region which has been studied extensively. Heterogeneous reactions such as those that occur in many catalytic and energy conversion processes are of enormous economic importance but have previously been understood on an almost exclusively empirical basis. Of particular interest are the atomic scale heterogeneities which exist at the electrode interface. The surface atoms will profoundly influence the physical and chemical interactions which may occur between an electrode surface and electrochemically active species surrounding it. It is anticipated that improved understanding of the physiochemical interactions that occur within the few atomic layers existing on each side of the electrode-solution interface will allow for design of more efficient devices for electroanalysis, energy conversion and electrosynthesis.

In recent years, rapid instrumental improvements in a number of areas have made accessible previously impossible analyses such as the imaging of single atoms on ordered surfaces and the probing of the molecular dynamics of sub-monolayer quantities of surface adsorbates. By combining these direct probes of the structure of
the electrode-solution interface with the more classical approach of the observation of rates of various heterogeneous electron transfer (ET) reactions, one can begin to construct a detailed model of the chemical interactions occurring at that interface and how they affect observed ET reactions. Our laboratory and others have spent considerable effort toward the goal of understanding the atomic level structure of both electrode and electrolyte and how these affect the observed electrochemical activity. This thesis will be primarily concerned with probing the surface and near-surface microstructure of carbon electrodes by a variety of analytical techniques including Raman spectroscopy, scanning tunnelling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). The ultimate goal of these studies is to gain further insight into structural parameters such as the electrode microstructure and surface heteroatoms, which may influence electrochemical rates. Where possible, direct correlations will be drawn between the structural observations and electrochemical results.

Carbon electrodes have been the subject of much surface analysis for the purpose of elucidating structure-reactivity relationships and their effect on ET [1-17]. Graphitic carbon in many forms has become a popular electrode material for many applications ranging from laboratory electroanalysis to energy storage and conversion because of its relatively low cost, machinability and wide potential window. Despite the extensive use of carbon based electrodes, however, the rich surface chemistry of the native material has been only partially characterized and in many ways remains an enigma. This lack of understanding persists despite the numerous studies of graphite surfaces which have included everything from wet chemical analyses in the early part
of this century to careful study in recent years using sophisticated ultra-high vacuum (UHV) spectroscopic techniques [18-27]. Problems remain in the understanding of the different ways in which various electrode preparation procedures alter the atomic scale structure of the carbon electrode material at the interface and how the various functional groups that are introduced by these procedures affect the specific interactions that may occur between an approaching electroactive species and the electrode itself.

This work will focus on the analysis of functional groups which exist at carbon electrode surfaces and their relationship to the bulk carbon microstructure and observed ET rates. In order for this analysis to be possible, the development and application of novel techniques in the area of Raman spectroscopy which exploit recent improvements in spectroscopic hardware were necessary. These novel techniques will be discussed extensively in a later chapter. First, however, a description of the basic elements of Raman spectroscopy and some background on carbon electrode structure will be of use.

**Raman Spectroscopy - Background**

The Raman effect involves the inelastic scattering of light by sample molecules. The frequency difference between the inelastically scattered light and a monochromatic excitation source corresponds to the energy of a vibrational transition for the molecule. Figure 1 illustrates the classical description of the origin of the Raman effect [28,29]. When electromagnetic radiation having electric vectors in the
Figure 1. Classical description of the Raman event. $\nu_\text{ex}$ is the frequency of the excitation source, $\nu_v$ is the frequency of the Raman active vibration, $\nu_s$ is the frequency of the stokes shifted photon and $\nu_a$ is the frequency of the anti-stokes shifted photon.
xy plane and propagating along the z axis strikes a polarizable sample, the electron cloud is deformed at an oscillation frequency matching that of the incident radiation, \( \nu_{\text{inc}} \). This oscillating electron cloud is capable of immediately radiating light of frequency matching that of the excitation in all directions; this is known as elastic, or Rayleigh scattering. However, because the scattering body is not just a polarizable electron cloud, but has quantized vibrational modes of its own, a small fraction of the scattered light may be shifted from the frequency of the incident light by an energy corresponding to that of a vibrational mode of the molecule, \( \nu_v \). The intensity of the observed Raman active vibrational mode will depend directly on the polarizability of the electron cloud associated with vibrating bond(s). Figure 2 is a states diagram which illustrates some possible transitions, including Raman, which may occur when light interacts with a molecule [28]. When a Raman transition begins in the ground vibrational state of the ground electronic state of the molecule, the resulting scattered photon has less energy than that of the incident photon by an amount corresponding to a particular vibrational transition. This is known as a Stokes shifted Raman transition. When a molecule is in an excited vibrational state previous to the scattering event however, the resulting Raman scattered photon will have more energy than the incident photon and this process is known as anti-Stokes Raman scattering. Boltzmann distribution reveals that at room temperature most molecules will be in the ground vibrational state so that most Raman events will be of the Stokes variety. Another important observation is that the absolute energy of the inelastically scattered
Figure 2. Energy level diagrams for several possible photon-molecule interactions.
photon depends on the frequency of the excitation photon. This fact can lead to some interesting experimental difficulties that will be treated extensively at a later time.

Several other points associated with figure 2 are worth mentioning. The first is that when the frequency of the laser is such that an electronic transition can occur, the major competing process for Raman is fluorescence. This can lead to significant interference or in some cases complete masking of the weak Raman signal because the quantum yield for fluorescence is often $10^4 - 10^6$ times greater than that for Raman. Efforts to avoid this source of interference have led to the use of near IR excitation for many recent Raman applications [30, 31]. A second important point associated with figure 2 is that as the laser energy approaches that of an electronic transition for the material, an enhancement in the Raman efficiency of as much as $10^6$ may occur by a process known as resonance Raman (RRS). This enhancement is due to coupling of the vibrational and electronic transitions and is specific to vibrational modes of the chromophoric functional group(s) associated with the electronic transition. RRS has been useful as a technique for the analysis of relatively dilute biological samples which often exist in complex matrices [32,33].

Normal Raman, unfortunately, is an exceedingly weak effect with only approximately 1 in every $10^{10}$ incident photons being inelastically scattered. Therefore, since the introduction of the laser, all practical Raman spectroscopy has been performed using these intense, monochromatic sources to achieve excitation. Those photons not giving rise to Raman can be elastically scattered, reflected or transmitted in such a way that the very weak Raman signal may be only a very small
fraction of the total collected light. This fact imposes strict spectrometer requirements. Effective rejection of the intense laser-wavelength radiation is absolutely critical if one hopes to observe the very weak Raman signal since it is generally more than $10^3$ times less intense than the elastically scattered and reflected light. The situation is often at its worst in the case where the analyte is a low concentration adsorbate on a surface of high reflectivity. Consequently, surface Raman spectroscopy has traditionally been performed using high intensity excitation coupled with multi-stage spectrographs for efficient stray light rejection. This approach has been effective in many instances for the observation of molecules on substrates where Surface Enhanced Raman (SERS) is possible, but unenhanced surface Raman at sub-monolayer coverages has proven difficult in part because of the inefficiency of multi-stage spectrographs and older photon-counting detectors [34]. The only reported examples of unenhanced surface Raman to date has been on single crystal metal surfaces under UHV conditions [35-38]. To date, no reports have been published regarding the detection of monolayer or submonolayer quantities of adsorbates on carbon using Raman. Recently, however, high optical density, holographic Rayleigh line rejection filters have made possible the use of efficient single stage spectrographs which have much higher transmission efficiency than the multi stage spectrographs used in the past. Advances in filter technology coupled with the advent of shot-noise limited, multichannel, Charge Coupled Device (CCD) detectors have brought Surface Unenhanced Raman (SUERS) on carbon surfaces into the realm of practicality.
As an illustration of the improvements that have occurred in the instrumentation used for Raman spectroscopy, a theoretical comparison of two generations of spectrometers is helpful [39]. Spectrometer A, the Spex 1403, was state of the art in 1985 and consists of a relatively long focal length (1m), f/8 scanning double monochromator coupled to a photon counting photomultiplier tube (PMT). The second system, spectrometer B, is the current high-end instrument and consists of a short focal length (640mm), f/5.6 spectrograph and a multichannel CCD detector. The comparison of these systems will be based on the time required to achieve a signal to noise ratio (SNR) of 3 for a monolayer of benzene on an atomically smooth surface.

For the observation a Raman scatterer adsorbed onto a surface, the expected signal, S can be expressed as follows [40]:

\[ S = P_D \beta D_S \Omega A_D T(\lambda) Q(\lambda) t \]  

(1.1)

For the purposes of this comparison, a more convenient form of the expression above is:

\[ S = L_s Et \]  

(1.2)

where,

\[ L_s = P_D \beta D_s \]  

(1.3)

and
\[ E = \Omega A_D T(\lambda) Q(\lambda) \]  \hspace{1cm} (1.4)

\(^L_a\), the sample specific intensity, can be considered to depend only on the sample and the excitation source and will be the same regardless of the spectrometer that is used to observe the Raman signal. In the case of a monolayer of benzene \((D_a = 3 \times 10^{14} \text{ molecules cm}^{-2})\) adsorbed on an atomically flat surface and being excited by 10 mW of 515 nm laser light focused to a 60 \(\mu\text{m}\) spot \((P_o = 9.2 \times 10^{29} \text{ photons s}^{-1} \text{ cm}^{-2})\), the specific intensity from the sample for the 992 cm\(^{-1}\) mode of benzene \((\beta = 2 \times 10^{-29} \text{ cm}^{2} \text{ molecule}^{-1} \text{ sr}^{-1})\) will be \(L_a = 5.5 \times 10^4 \text{ photons s}^{-1} \text{ sr}^{-1} \text{ cm}^{-2}\) assuming the cross section of the surface bound benzene is the same as that determined in the gas phase [41].

The spectrometer efficiency \(E (\text{sr cm}^2 \text{ e}^{-1} \text{ photon}^{-1})\), contains all of the parameters associated with collection, dispersion and detection of the Raman generated photons. These include: \(\Omega\), the solid angle over which the spectrometer optics collect light (sr); \(A_{on}\), the area of the sample that the spectrometer optics monitor (cm\(^2\)); \(T(\lambda)\), the transmission efficiency of the spectrometer as a function of wavelength (unitless); and \(Q(\lambda)\) the detector quantum efficiency as a function of wavelength (e\(^-\) photon\(^{-1}\)). Table 1 gives some representative values for the two spectrometers under consideration [42].

For a rigorous comparison of Raman systems, one must generally pay close consideration to all possible noise sources in the system. Background processes such as continuum luminescence from the substrate or from the sample \(\phi_n\), detector dark counts \(\phi_d\) and detector read out noise \(\sigma_r\), all will limit the ultimate ability of a
Table 1: Efficiency comparison for two generations of Raman spectrometers.

<table>
<thead>
<tr>
<th>System</th>
<th>A_d (cm^2)</th>
<th>Ω (sr)</th>
<th>T(λ) (unitless)</th>
<th>Q(λ) (e^- phot^-1)</th>
<th>E (e^- cm^2 sr phot^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A^a</td>
<td>6x10^-4</td>
<td>0.78</td>
<td>0.1</td>
<td>0.2</td>
<td>9.4x10^-4</td>
</tr>
<tr>
<td>B^b</td>
<td>2.3x10^-3</td>
<td>0.045</td>
<td>0.3</td>
<td>0.5</td>
<td>1.6x10^-7</td>
</tr>
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Table 2: Calculated detection times for a monolayer of benzene using two generations of Raman spectrometers.

<table>
<thead>
<tr>
<th>System</th>
<th>L_e (phot s^-1 sr^-1 cm^-2)</th>
<th>E (e^- cm^2 sr phot^-1)</th>
<th>( \phi_e ) (e^- s^-1)</th>
<th>( \phi_b ) (e^- s^-1)</th>
<th>( \sigma_r ) (e^-)</th>
<th>t (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A^a</td>
<td>5.5x10^6</td>
<td>9.4x10^-3</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>186</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B^b</td>
<td>5.5x10^4</td>
<td>1.6x10^-7</td>
<td>0.1</td>
<td>0</td>
<td>6</td>
<td>27</td>
</tr>
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a: Spex 1403 f/8 scanning double monochromator with photon counting PMT detection.
b: ISA HR-640 f/5.6 single spectrograph with PM512 CCD detection.
c: Spex 1403 uses "f/ matching" to match f/1 collection optics to f/8 monochromator.
spectrometer to achieve a minimum SNR in a particular integration time. Considering all of the potential noise sources, the SNR expression is:

$$\text{SNR} = \frac{L_s E \tau}{\left[ (L_s E \tau) + (\phi_b \tau) + (\phi_d \tau) + \sigma^2 \right]^{1/2}} \quad (1.5)$$

Table 2 shows the results of using expression 1.3 to calculate the time required to achieve a SNR of 3 under conditions of increasing background signal. It should be said that SNR comparison shown here uses the integrated peak area as a measure of signal and that this may be a somewhat optimistic measurement since the noise is often determined by measuring the signal standard deviation on a per-resolution element basis. Nevertheless, there are several important points to be made regarding table 2. First is the observation that on a per-resolution element basis, spectrometer B will attain a given spectral SNR at least four times faster than the scanning instrument for the conditions considered here. Second, if one includes the fact that a CCD is a multichannel detector that generally has between 500 and 1200 channels along the dispersion axis, the full-range spectrum will actually be acquired in a time that is another 500 to 1200 times shorter than that required for the scanning instrument. Obviously this fact is important in a case where one is pushing the limits for practical observation times. The recent advances in spectrometer design have been critical in making SUERS a practical possibility under any conditions, and especially under conditions other than the UHV conditions that it has been previously limited to.
Graphitic Electrodes

Most carbon electrodes in common use are to some degree graphitic; that is they are made up of stacked laminar sheets of \( sp^2 \) bonded carbon. Although the carbon-carbon bonding in all of these materials is similar, the bulk properties can vary widely depending on the relative size and orientation of the graphite microcrystallites [43]. The structural parameters used to describe graphite microcrystallites which make up the bulk material are the C-C bond length, the intraplanar microcrystallite size \( L_x \), the interplanar spacing \( (d_{in}) \) and the interplanar microcrystallite size \( L_x \) [43, 45-49]. Carbons having different structural parameters will display different physical characteristics such as hardness, density and conductivity [49]. The structural parameters for a number of common graphitic electrode materials are summarized in table 3.

Table 3: Structural parameters for some common carbon electrode materials (49)

<table>
<thead>
<tr>
<th>Material</th>
<th>Density ((g , mL^{-1}))</th>
<th>(d_{in}) ((\AA))</th>
<th>(L_x) ((\AA))</th>
<th>(L_x) ((\AA))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOPG</td>
<td>2.26</td>
<td>3.354</td>
<td>(&gt;10^4)</td>
<td>(&gt;10^3)</td>
</tr>
<tr>
<td>GC 20</td>
<td>1.5</td>
<td>3.5</td>
<td>25</td>
<td>12</td>
</tr>
<tr>
<td>Carbon Fiber</td>
<td>1.8</td>
<td>3.4</td>
<td>(&gt;100)</td>
<td>40</td>
</tr>
<tr>
<td>(typical)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Two common graphitic electrode materials; Highly Oriented Pyrolytic Graphite (HOPG) and Glassy Carbon (GC) are illustrated in figure 3. HOPG is a large microcrystallite graphite prepared by high temperature decomposition of gaseous hydrocarbons on a flat surface [50]. As the decomposition temperature increases, so does the degree of ordering in the material. Because of the large microcrystallites, HOPG shows a high degree of anisotropy in its physical characteristics. The material exhibits very distinct basal and edge planes with the individual "sheets" of carbon rings being only weakly associated to one another via Van der Waals forces [49]. Because of the weak association between the graphite sheets and due to the highly delocalized nature of the pi electron clouds within a single sheet, the resistivity along the c axis of HOPG is approximately 4000 times greater than that exhibited along the a axis [51]. Studies using low-defect basal plane HOPG as an electrode material have shown it to have a low density of electronic states so that most redox systems display very slow ET kinetics at this surface [17]. Recently Kneten et. al. have shown that "pure", defect-free basal plane HOPG is essentially inert towards both physisorption and chemisorption [16]. When one creates edge sites on an HOPG surface however, the electronic structure of the material is disrupted in such a way that the surface may become quite active both electrochemically and toward adsorption [10,11,15,16].

GC has found much favor as an electrode material because of its hardness, it's high degree of machinability and because of its relatively low cost. GC, in contrast to HOPG, is an isotropic material on most scales of measurement. With L₄ values on the order of 10-100 Å, GC exhibits none of the physical anisotropy that is
Figure 3. Structural models for highly oriented pyrolytic graphite (HOPG) and glassy carbon (GC).
characteristic of more highly ordered graphite [49,51]. Because the very small microcrystallites are basically randomly oriented, the ratio of edge sites to basal sites on a GC surface will be much greater than that for the corresponding HOPG surface. The disordered nature of GC leads to an increase in electronic states which is manifested by relatively high reactivity of GC surfaces both toward adsorption and ET reactions.

An excellent technique for differentiating between large and small microcrystallite carbons is Raman spectroscopy. An infinitely large, perfect graphite crystal belongs to the \( D_{6h}^1 \) space group which has the following possible vibrational modes which are illustrated in figure 4:

\[ 2B_{2g} + 2E_{2g} + A_{1u} + E_{1u} \]

The two \( E_{2g} \) modes are predicted to be Raman active and in fact the Raman spectrum of basal plane HOPG shows a strong, sharp band at approximately 1582 cm\(^{-1}\) [44,45]. Figure 5 shows the first order Raman spectra for both HOPG and GC in the range of 900 - 1700 cm\(^{-1}\). A group of weaker bands observed above 2000 cm\(^{-1}\) have been assigned to overtones and combinations [45,46]. As the microcrystallite size decreases in graphitic carbon, another band which is not predicted by graphite symmetry appears at about 1360 cm\(^{-1}\). This band, which is commonly referred to as the D or disorder band, has been assigned to an \( A_{1g} \) mode which becomes allowed as the symmetry of the "perfect" graphite sheets is destroyed. Tuinstra and Koenig found a linear correlation between the ratio of the 1360 cm\(^{-1}\) to the 1580 cm\(^{-1}\) bands and \( 1/L_e \), for a variety of carbon materials [44]. Obviously, this relationship has
Figure 4. Graphite vibrational modes.
Figure 5. First order Raman spectra of HOPG and GC.
limits, but in several cases the ratio of these bands has been used as an indication of changes in graphite microstructure following various treatment procedures [9-13]. Additionally, the 1582 cm\(^{-1}\) band broadens and shifts to higher frequency as the graphite microstructure is damaged and L\(_s\) and L\(_c\) are reduced. Though the Raman spectrum of a particular graphite material may be useful in assessing the condition of the near surface microcrystallites, Raman has generally not been useful in directly probing the oxides that exist at the electrode interface.

**Surface Oxides on Graphitic Electrodes**

Wherever a graphitic sheet terminates, there will exist carbon atoms which have unsatisfied valences. Though there are likely to be many ways for these carbon radicals to be terminated, it is generally believed that a substantial fraction of these sites are terminated by reacting with oxygen to form one of a variety of possible functional groups. Clearly, with its high edge to basal site ratio, GC surfaces would be expected to have a higher native oxide density than basal plane HOPG surfaces. Figure 6 illustrates some of the oxygen containing functional groups that are believed to exist at graphitic edges. Because of its relatively high surface reactivity, GC electrodes generally require some surface pretreatment procedure before acceptable voltammetric results may be obtained. These pretreatment procedures include, but are not limited to, polishing with alumina slurry, exposure to high power density laser pulses, UHV heat treatment, and electrochemical oxidation [5,6,10,11,52-58]. Though each of these pretreatment procedures may not always have the stated goal of
Figure 6. Oxygen containing function groups thought to exist at graphite edges.
producing surface oxides, each of them, with the possible exception of UHV heating, has the potential to introduce some degree of surface oxidation. Also, though creation of surface oxides may not be the primary activation mechanism for all redox couples, direct catalysis by specific surface oxide functionalities is believed to be important for electrochemical activation of some systems [17,57-59]. Inner sphere catalysis, redox mediation, proton transfer and chemisorption have all been reported to involve oxygen containing functional groups on carbon [2,7,8,17]. For these reasons characterization of the chemical identity and local environment of surface oxides is of interest.

A variety of analytical techniques have been used to characterize oxides on carbon surfaces, including acid/base titrations, X-ray Photoelectron Spectroscopy (XPS), and related UHV techniques, thermal desorption mass-spectrometry, electrochemistry and optical spectroscopy [2-8,14,18-27]. Engstrom and Strasser used XPS to measure the changes in the oxygen to carbon ratio on GC electrode surfaces before and after electrochemical oxidation procedures which were shown to improve ET kinetics for some redox couples [58]. Cabaniss et. al. determined by XPS that on GC surfaces that had been prepared by polishing, approximately 25% of the total surface sites were oxides with the distribution being about 15% phenolic, 5% carbonyl and 5% carboxylate moieties. Upon electrochemical oxidation these values were substantially increased so that about 47% of the surface sites were in the form of oxides [2]. Other workers have reported the use of a variety of chemical derivitization techniques including the formation of XPS tags for surface carbonyl and phenolic groups, and fluorescence tags for surface carboxylates [1,14,60,61]. Kepley
and Bard reported the use of ellipsometry to monitor the rate of growth of the oxidized carbon film under different electrochemical oxidation conditions [62].

Vibrational spectroscopy, and specifically Raman spectroscopy, is an attractive technique for characterization of carbon surfaces because of an excellent ability to differentiate between different types of oxides. One should be able to distinguish between carbonyls and phenols for example, with much more certainty than is possible with techniques such as XPS. IR has been used successfully for the analysis of high surface area carbon surfaces but these materials are difficult to characterize electrochemically [43,63]. No reports of successful application of IR to the direct study of oxides on low surface area carbon exist in the literature. Factors which make Raman an attractive technique for the study of carbon electrodes include the ability to probe changes in the carbon near-surface microstructure through observation of changes in the graphite phonons, and the ability to monitor the electrode while immersed in aqueous solutions. Unfortunately, however, normal Raman has previously proven difficult or impossible to use for the direct analysis of surface oxides due to the inherently low polarizability of carbon oxygen bonds and lack of sufficient instrumental sensitivity. In order to successfully characterize electrochemically useful carbon surfaces with Raman spectroscopy, improvements in instrumentation and technique are necessary.
Research Objectives

The broad goal of this work is to investigate the chemical and structural changes that occur at the surface and near surface of carbon electrode materials following various treatment procedures. The investigation of these changes will be carried out using direct probes such as Raman spectroscopy, STM and XPS. The results of these probes will then be correlated, where possible, to observed ET kinetics. The work described will first involve the observation of the differences in how various pretreatment procedures which have been shown effective means to activate carbon electrodes affect the oxides which exist at the electrode surface. This will include examining the effects of polishing, fracturing, laser activation and electrochemical pretreatment (ECP) in the presence of various electrolytes. An attempt to correlate the results of the direct probes of surface structure to the indirect kinetic measurements will then be made for several redox couples that are believed to have a strong dependence on the chemical nature of the interface.

Chapter II will focus first on instrumental advances in Raman that were necessary to make the later analyses possible. Specifically, a novel optical design which dramatically improves the sample to sample reproducibility of the Raman signal will be described. Other interesting aspects of this optical geometry will also be discussed. Second, a procedure for correcting spectra for changes in the instrumental efficiency as a function of wavelength was developed and demonstrated. Both of these instrumental improvements are critical to the use of Raman as a quantitative
technique for surface analysis. Another application where Raman cross sections of molecules can be easily measured will also be discussed.

Chapters III and IV will deal with the development and application of a reactive probe molecule which has been developed for the analysis of oxides on carbon by RRS. Chapter III will discuss primarily the development and validation of the probe as well as detection limits. Some normal mode analyses for some model compounds as well as comparison to literature studies will then be used to assign some of the observed Raman features for the model compounds and also probe-carbon adduct so that some inferences may be drawn regarding the structure of the adduct at the carbon surface. Chapter IV will discuss applications of the reactive RRS probe to the study of various carbon electrode pretreatment procedures. The focus here will be to observe the changes in surface oxide density as a function of pretreatment procedure and to relate that information to observed ET kinetics for a series of redox couples thought to be catalyzed by the detected oxide functional groups.

Chapter V will discuss the correlation between Raman spectra of the near surface and scanning tunneling micrographs of the surface of carbon samples following treatment with increasing power density laser pulses. Microstructural changes as detected by Raman will be related to previous electrochemical observations.
CHAPTER II
RAMAN INSTRUMENTATION

Introduction

This chapter is concerned with instrumental improvements that were necessary for the implementation of Raman spectroscopy (RS) as a quantitative analytical technique. First, a novel optical geometry is described and evaluated. This optical geometry allows for the excellent reproducibility of sampling necessary for day to day quantitation under conditions where internal standards are not always convenient. Other advantages of this optical geometry such as increased path length will also be discussed. Second, a procedure for the measurement of the response function of a Raman spectrometer will be discussed. This procedure allows for the direct comparison of the efficiency of different spectrometers as a function of wavelength. More importantly however, one can correct acquired spectra for changes in the spectrometer efficiency with wavelength. Correction of this kind of instrumental attenuation of the observed signal is critical to the success of quantitative analysis based on comparison of relative Raman band intensities.

Raman spectroscopy, like fluorescence spectroscopy, is different from many other common optical spectroscopies in that the measured signal is collected from a
radiating sample. The Raman scattering molecule behaves like a point source which emits over $4\pi$ sr, though the intensity of the scattered light varies somewhat as one changes the angle of observation with respect to the excitation source. For the purposes of this discussion however, the Raman scattering intensity will be considered isotropic. Because the spectrometer is collecting light from a volume emitter, the Raman generated photons that are detected represent some fraction of the total signal that is determined by the area of the sample that is monitored, the solid angle over which the spectrometer collects light, the transmission efficiency of the spectrograph, and the quantum efficiency of the detector [40,84]. Figure 7 illustrates the spectrometer in a block format which shows the variables from equation 1.1 with their associated spectrometer components. Sampling from an isotropically radiating sample is fundamentally different from the sampling techniques generally used for IR and UV-visible spectroscopies so that double beam Raman instruments are very difficult or impossible to construct. Under conditions where sampling reproducibility is high and no components of the sample absorb significantly at the wavelength of the excitation laser, however, one should be able to make absolute, quantitative Raman measurements if the illumination volume and the spectrometer's ability to collect and detect signal are both known and reproducible. Issues of reproducibility can be addressed fairly easily with appropriate optical design and careful sample placement. Issues related to determining the parameters related to excitation of the sample and the spectrometer's ability to monitor the resulting signal are somewhat more complex in their nature.
Figure 7. Block diagram of spectrometer components.
This discussion will focus primarily on multichannel Raman spectrometers using single stage spectrographs and CCD detectors. The advantages of high quantum efficiency, low dark and readout noise, near infrared (NIR) sensitivity, and multichannel operation have made CCDs very attractive when compared to scanning PMT systems for RS [65-79]. Several instrumental issues associated with CCDs, however, demand attention in order that accurate spectral information may be obtained. First, the quantum efficiency (QE) curve of a CCD, illustrated along with a the QE curve of a typical PMT in figure 8, varies strongly with wavelength [40]. This variation can lead to significant perturbation of the observed relative intensities of Raman bands that are widely separated in frequency. Second, because the actual wavelength range which is spanned by a particular Raman spectrum depends on the wavelength of the laser used for excitation, the observed relative band intensities will appear very different for spectra of the same sample excited using different laser wavelengths (782nm versus 488nm excitation for example). In addition to changes in CCD quantum efficiency, attenuation of band intensities will occur because of changes in spectrometer transmission efficiency. These changes may be caused by chromatic aberrations in the focusing lenses, variation in the efficiency of the dispersion grating and variation in the transmission efficiency of laser band rejection (BR) filters [30,79]. This last effect can be particularly severe because some BR filters can have significant structure in their transmission efficiency curves which can lead to severe attenuation of bands which are coincident with regions of low filter transmission. Perturbed Raman spectra can be corrected for changes in spectrometer efficiency by
Figure 8. Typical quantum efficiency curves for charged coupled device (CCD) and photomultiplier tube (PMT).
the use of a standard emission source for which the photon output as a function of wavelength is known. Previous reports of such intensity calibration have described the use of fluorophores, such as quinine sulfonate, which have a known quantum yield as a function of wavelength [78]. Another common approach has been to use an uncalibrated tungsten bulb which is considered to have a simple black body emission output as the standard output source [30,87]. Both of these approaches suffer from shortcomings. The fluorophore is highly specific for a particular excitation wavelength and may undergo photodegradation with time. The approximation of a tungsten bulb as a simple black body emitter fails to take into account attenuation by intervening glass and plastics. An additional problem with the use of a bare tungsten bulb is that the light that enters the spectrometer is likely to be mostly collimated and therefore a poor representation of an actual Raman scatterer. The calibration source described here is a small, weak white source of known specific intensity which is placed at the Raman sampling position so as to accurately mimic the Raman experiment. Use of this standard source allows for removal of spectrometer induced spectral artifacts and also provides a convenient way for accurate evaluation of the relative performance of different Raman spectrometers.

Once the spectrometer performance has been carefully characterized, measurements can be made and compared on the basis of absolute intensity. This comparison allows for the ranking of different modes of different scattering molecules based on their relative scattering efficiency or Raman cross section (\(\beta\)). Such a ranking is useful for the creation of internal standards which may subsequently be
used for quantitative analytical methods and also as a secondary test of the performance of a particular spectrometer.

Theory

A detailed discussion of the theoretical expressions relating signal to spectrometer and sample variables will be helpful for further discussions. Much of the following treatment is based on a previous analysis [40]. Because of the large number of variables which characterize a Raman experiment, no single SNR expression can be viewed as universally applicable [39,40,69,77,78,80-86]. Therefore several different sampling geometries which are germane to the following discussion will be treated here. The detector noise will be considered zero in all cases, so that the only remaining noise source in the signal is shot noise from the sample, which may be either from analyte or background. For this discussion, background is defined as any laser derived light other than analyte Raman, and may include stray light, sample luminescence or solvent Raman. Further, this discussion assumes that the spectrometer is overfilled so that the image of the sampled region at the entrance slit of the spectrometer is larger than the entrance slit and also that the solid angle of the lens focusing onto the slit is greater than that of the spectrometer itself. This arrangement maximizes the signal by using all of the available slit or detector area and by using all of the collection angle of the spectrograph. The treatment will be further simplified by assuming that sample Raman scattering is isotropic and linear with laser power. This assumption is reasonable for 180°
geometry used for this work and many other common situations. Finally, it is assumed that the laser beam is homogeneous in its power density both across the beam and along the propagation axis. This assumption prevents the use of absorbing samples in this discussion and ignores the gaussian beam distribution.

When the spectrometer is divided into components as in figure 7, one can more easily construct expressions relating signal (S) and SNR to instrumental parameters. First, the sample has a specific intensity, \( L \), which has units photons s\(^{-1}\) cm\(^{-2}\) sr\(^{-1}\).

\[
L = P_D \beta_a D_a K
\]  

(2.1)

\( L \) is the total Raman scattering from the illuminated sample volume divided by the area associated with the scattering volume, and \( K \) is a constant which is determined by the sampling geometry. It should be emphasized that \( \beta_a \) is integrated with respect to wavelength over the Raman linewidth so that a Raman signal calculated using \( \beta_a \) represents the signal over the entire Raman linewidth.

Following the excitation of the sample, it is required that the Raman generated photons be collected and dispersed. The analyzer in figure 7 consists of optics which maps a two dimensional collection area, \( A_\text{D} \), onto the scattering volume. In most cases, \( A_\text{D} \) will be determined by the entrance slit of the spectrograph which may be magnified depending on the optical arrangement used. In cases where some other element of the instrument, such as the detector, limits the sampling area, \( A_\text{D} \) will be determined from the projected area of that element at the sample. It is common with the use of CCD detectors for this to be the case so that \( A_\text{D} \) is usually described by the
intersection of the CCD pixel area and the slit image. From the area defined by $A_D$, some solid angle, $\Omega$ of radiated light will be collected and transmitted into the spectrograph. The photon flux leaving the spectrograph, $\phi$ (photons s$^{-1}$) is given by:

$$\phi = L A_D T(\lambda) \Omega$$  \hspace{1cm} (2.2)

where $T(\lambda)$ is the transmission efficiency of the spectrograph expressed as a function of wavelength.

Once the Raman generated light has been collected and dispersed it must be detected. Limiting the discussion to a single resolution element, the Raman signal ($S$) in photoelectrons is:

$$S = \phi Q(\lambda) t$$  \hspace{1cm} (2.3)

where $Q(\lambda)$ is the quantum efficiency of the detector (photoelectrons photon$^{-1}$) expressed as a function of wavelength and $t$ is the measurement time (seconds).

Combination of equations 2.1-2.3 gives the expression for the expected signal from a Raman scatterer. Notice that Eq. 2.4 is the general case of Eq 1.1.

$$S = P_D \beta_D D_\Omega A_D T(\lambda) Q(\lambda) K t$$  \hspace{1cm} (2.4)

This expression is general and can be applied to a number of sampling geometries by modification of the constant $K$ depending on the geometric relationship between the illuminated volume and the scattering area. Some common sampling geometries will now be considered.
Sampling Geometries

As a first example let us consider the optical geometry shown in figure 9. In this case the excitation beam and the collection optics are oriented 90° to each other. It is assumed that the sample is optically transparent in the wavelength range of interest. Secondly, it is assumed that the length associated with \( A_n \) along the excitation axis, \( h \), is small enough that the laser focus can be considered a cylinder of diameter equal to 2\( r \). Under these conditions, \( L \) is the ratio of the total Raman scattering from the sampled volume to the area of the scattering cylinder:

\[
L = \frac{P_D \beta_a D_a \pi r^2 h}{2 \pi h} = \frac{P_D \beta_a D_a r}{2} \tag{2.5}
\]

so \( K = r / 2 \) and \( S \) is given by Eq. 2.4. An interesting case is that which arises if the focus of the excitation beam is made sufficiently sharp that the spectrometer is underfilled. As long as this condition holds, \( A_n \) equals 2\( rh \) and further reduction in the beam diameter will have no effect on \( S \) because changes in \( P_n \) are exactly compensated for by changes in \( A_n \).

The second optical arrangement to be considered is that illustrated in figure 10. In this 180° geometry the excitation beam cylinder and the cylinder associated with the collection optics are perfectly collinear. When applied to a surface, some modifications of the previous expressions are necessary because the surface number density \( D_s \) of scatterers is expressed in molecules cm\(^{-2} \). Therefore, for a two dimensional scattering region, i.e. molecules confined to a surface, \( K = 1 \) and the specific intensity of the scattering is:
Figure 9. Schematic representation of 90° Raman sampling geometry.
Figure 10. Schematic representation of 180° Raman sampling geometry.
\[ L = P_D D_S \beta_S \]  
(2.6)

so that for an overfilled arrangement:

\[ S = P_D \beta_s D_s \Omega A_D T(\lambda) Q(\lambda) t \]  
(2.7)

Notice that in the case where the spectrometer is underfilled, \( A_D \) is determined only by the size of the focal spot so that sharper focusing will have no effect on \( S \).

Another important sampling arrangement involving this optical geometry is that in which instead of a surface, the sample is a short path length cell of transparent scatterers. If the path length of the cell, \( h \), is less than the depth of field for the focusing/collection optics so that both the laser and the collection "beam" can be considered cylindrical, the cylinder of scatterers can be treated as if they were compressed into a two dimensional disk that is completely analogous to the surface case. This is most easily realized by the consideration of \( K \) for the case of observing a cylinder end-on:

\[ K = \frac{\pi r^2 h}{\pi r^2} = h \]  
(2.8)

Substitution of \( K = h \) into Eq. 2.4 with the appropriate values for this optical arrangement gives:

\[ S = P_D \beta_a D_a \Omega A_D T(\lambda) Q(\lambda) ht \]  
(2.9)

Functionally, \( D_a \) is the number density of scatterers contained within the scattering cylinder. Therefore, \( D_a h = D_S \) so that substitution of this identity into Eq. 2.9 yields
Eq. 2.7. If the depth of sample is greater than the spectrometer depth of field, the sampled volume can no longer be considered cylindrical, so that $D_a h \neq D_a$.

**Signal-to-Noise Ratio**

Because the dark and readout noise associated with modern liquid nitrogen cooled CCD detectors is very small, the dominant noise source which needs to be considered in SNR expressions is shot noise [30, 31, 40, 72, 76]. Inconsistencies in the laser power with time may be ignored because the multichannel nature of the CCD has the consequence that all resolution elements in the spectrum are being monitored simultaneously and for the entire exposure time. Thus, CCD Raman spectrometers generally can be treated as though the only noise source were the shot noise associated with analyte signal and background. For this treatment, all background scatter will be combined into a single term with its own number density, $D_0$ and cross section, $\beta_p$. If the signal is measured as the mean peak height above background and the noise is the square root of the total signal, sample and background, then Eq. 2.4 yields the following SNR expression:

$$SNR = \frac{\beta_s D_s}{(\beta_s D_s + \beta_p D_p)} (P_D \Omega A_D T(\lambda) Q(\lambda) K)^{1/2}$$  \quad (2.10)

Important observations related to Eq. 2.9 are that SNR is linear in $\beta_s D_s$ when operating in the background shot noise limit, and linear in $(\beta_s D_s)^{1/2}$ when in the signal shot noise limit.
The expressions developed thus far have dealt with the S and SNR observed in a Raman spectrum on a per-resolution element basis. When one takes into account the multichannel advantage inherent in all array detectors, including CCDs, the true SNR advantage of these devices becomes apparent. For an array detector of \( N_e \) channels, one can monitor each channel \( N_e \) times longer than a single channel instrument in the same total measurement time. So, in order to construct an analogous SNR expression for the multichannel case, \( SNR_{mc} \), one must replace \( t \) with \( N_e t \):

\[
SNR_{mc} = \frac{\beta_d D_a}{\left(\beta_d D_a + \beta_d D_b\right)} \left( P_D \Omega A_D T(\lambda) Q(\lambda) KN_e t \right)^{1/2}
\]

(2.11)

Thus for equivalent total observation time, the multichannel advantage gives rise to an \( N_e^{1/2} \) improvement in SNR provided that all else is equal (i.e., \( A_n, T, Q \) etc.). It is also important to note that this expression becomes Eq. 2.10 for the single channel case where \( N_e = 1 \). In both the single channel and multichannel case, \( t \) is the exposure time per resolution element.

A final useful modification of the preceding expressions involves the separation of instrumental variables from those associated with the sample and the laser in order to arrive with a measure of the efficiency of a spectrometer, \( E \). In terms of \( S \), the spectrometer efficiency, \( E \), is:
Because $E_s$ depends only on variables associated with a spectrometer's ability to collect, transmit and detect Raman generated light, it is a very useful parameter for the comparison of the efficiency of different spectrometers. Efficiency can also be expressed in terms of SNR:

$$E_{SNR} = \frac{SNR}{(P_D \theta_s D_s t)^{1/2}} = \left( \frac{\lambda A D T(\lambda) Q(\lambda) N_c K}{\lambda A D T(\lambda) Q(\lambda) N_c K} \right)^{1/2}$$

Use of a standard source has the potential to allow the measurement of the actual value of $E$ for different Raman spectrometers so that they may be compared directly.

Experimental

The four Raman spectrometers which are compared on the basis of efficiency are listed in Table 4. Spectrometer B, with various modifications as noted, is essentially the system that will be used throughout the remainder of the experiments described in this and subsequent chapters. Spectrometer A, the Spex 1403, was equipped with a model 1459 sample chamber which $f/1$ matches an $f/4$ elliptical collector mirror to an $f/8$ monochromator. Detection for spectrometer A was via a cooled PMT (RCA 31034A) with approximately 4 counts $s^{-1}$ of dark signal. Spectrometers B and C both employ ISA monochromators with entrance optics consisting of 120mm focal length, $f/4$ lenses. The Chromex Raman One has built in $f/4$ collection optics. For both spectrometer B and C, the CCD detectors were cooled.
Table 4. Spectrometer Configuration.

<table>
<thead>
<tr>
<th>Label</th>
<th>Collection/ spectrograph f/ (^a)</th>
<th>Spectrometer</th>
<th>Grating lines mm(^{-1}) and Blaze (dispersion cm(^{-1}) mm(^{-1}))</th>
<th>Detector</th>
<th>Relative E(_s)</th>
<th>600nm(^b)</th>
<th>800nm(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1/8</td>
<td>Spex 1403 Double Monochromator</td>
<td>1800/450nm (12.5)(^c)</td>
<td>RCA 3104A PMT</td>
<td>1.0</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>4/5.6</td>
<td>ISA HR 640 Single Spectrograph</td>
<td>150/500nm (148)(^c)</td>
<td>PM512 CCD 512 channels</td>
<td>1.67</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>4/5.6</td>
<td>ISA HR 640 Single Spectrograph</td>
<td>300/1000nm (76)(^d)</td>
<td>EEV05-10 CCD 1152 channels</td>
<td>0.53</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>4/4</td>
<td>Chromex Raman One Single Spectrograph</td>
<td>300/1000nm (187)(^d)</td>
<td>TEK 512 CB/AR 512 channels</td>
<td>3.14</td>
<td>4.73</td>
<td></td>
</tr>
</tbody>
</table>

a. First number is f/ of collection optics, second number is f/ of spectrometer.
b. Calculated for 1cm\(^{-1}\) resolution.
c. Dispersion calculated for 514.5nm
d. Dispersion calculated for 800nm
to -110°C during use. All CCD spectra are corrected for bias and gain (e- ADU⁻¹), but subtraction of dark signal was unnecessary for the short integration times used. Excitation for Raman spectra was provided by a Coherent 90-5 Ar⁺ laser or a Coherent Ti:sapphire laser pumped by a Coherent 90-5 Ar⁺ laser. In all cases laser output was filtered by an interference filter ("DF-10" series, Omega Optical, Brattleboro, VT). The standard irradiance source (Eppley Labs, Newport, RI) was calibrated by the manufacturer versus NIST standards at 31 wavelengths in the 250-2400nm range and was directed through a diffuser into a 200μm diameter optical fiber (C-Technologies, Verona, NJ). The output cone of the optical fiber was approximately f/1.8 which overfills Ω for all of the spectrometers except A.

All Raman shifts were calibrated versus known peak positions for naphthalene. All chemicals used in this analysis were reagent grade and were used as received.

Results

Figure 11 shows an illustration of a dispersive CCD Raman spectrometer using the in-line, combined excitation and collection optics. Though this optical arrangement is based on the relatively common 180° back-scatter geometry, the use of the same lens for both the focusing of the laser and for the collection of the inelastic scattering improves the ease of reproducible sample positioning considerably. Because both excitation and collection are performed by the same lens, one merely places the sample in the path of the laser beam and adjusts its distance from the lens until a maximum in the observed Raman intensity is found. With the more common
Figure 11. Diagram of Raman instrument using in-line, combined excitation and collection optics.
90° excitation-collection scheme, the laser beam and the collection optics must be independently manipulated so that their foci intersect exactly at some point on the sample.

Reproducibility

As a test of the sample-to-sample reproducibility of the in-line optics, a comparison of this sampling arrangement to that of fiber optic sampling was conducted. Fiber optics have gained wide acceptance as a sampling method for both Raman and fluorescence spectroscopies because of the advantages of ease of sample positioning and sample to sample reproducibility [31,76]. These advantages stem primarily from the fixed spatial relationship of the excitation fiber and the collection fibers. Fixing the excitation and collection events in space has the effect that one must merely bring the sample into detection range for the fiber optic probe (which usually means immersing the probe), and run the experiment. Assuming that all of the detection range is occupied by a transparent sample, the sample to sample reproducibility is extremely high. Functionally, the in-line optics has exactly the same advantages. Namely, the excitation and collection events have a fixed spatial relationship (because only one focusing/collection lens is used), and therefore all that is required is that a sample be brought into optimal detection range for data to be collected. Figure 12 shows schematically how these two sampling procedures compare.
Figure 12. Comparison of fiber optic and in-line optical sampling arrangements.
In order to evaluate the sample to sample reproducibility of the fiber optic sampling approach, a sample containing a 1:1 mole ratio of benzene and acetonitrile was repeatedly sampled. Between spectra, the probe was removed from the sample container (a 7 cm deep, 2 cm diameter cell) and then re-immersed. The spectrometer used for this analysis was system C from table 4 with fiber optic sampling hardware. Excitation was with 35 mW of 515 nm laser light measured at the sample and integration time was 1 s. Entrance slits were held at 50 μm. For each of 25 spectra that were acquired the area of the benzene 992 cm\(^{-1}\) band and the acetonitrile 2944 cm\(^{-1}\) bands were measured.

For comparison the system shown in figure 11 was used to repetitively sample an aqueous solution containing 0.10 M NaNO\(_3\) and 0.10 M Na\(_2\)SO\(_4\). In this case the spectrometer was spectrometer B from table 4 with some minor changes. The entrance lens was 40 mm diameter f/5 and the collection lens was 40 mm diameter f/2.5. The dispersion grating 600 lines mm\(^{-1}\) with a blaze angle optimized for 500 nm. Excitation was by 20 mW of 488 nm laser light focused to a 60 μm spot. The entrance slit was held at 49 μm. Each spectrum was integrated for 10 s and between spectra the sample was removed from its holder and then replaced prior to the next spectrum. 26 spectra were acquired and the integrated area of the NO\(_3^-\) band at 1050 cm\(^{-1}\) and the SO\(_4^{2-}\) band at 980 cm\(^{-1}\) were measured. The results are summarized along with those for the fiber optic sampling are summarized in table 5. Notice that the standard deviation in the measured peak areas in table 5 is less than 2% of the mean peak area in all cases.
Excellent sample-to-sample reproducibility such as that which has been demonstrated for these two Raman sampling techniques allows one to do quantitative analysis of a known material without the use of an internal standard. One can simply measure the signal associated with standard solution of the analyte and compare it to that obtained for the unknown. Assuming that the refractive index difference between the samples has little effect on the signal, one can determine the concentration of the unknown by a simple ratio:

\[
C_{\text{unk}} = \frac{S_{\text{unk}}C_{\text{std}}}{S_{\text{std}}}
\]  

(2.14)

Alternatively, if one knows the efficiency, \( E_\alpha \), of the spectrometer and the cross section of the scatterer, \( \beta_\alpha \), the concentration can be calculated directly from the signal using equation 2.4.

Table 5. Reproducibility comparison for two sampling methods

<table>
<thead>
<tr>
<th></th>
<th>Fiber Optic</th>
<th>In Line Optics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Benzene 992\text{cm}^{-1}</td>
<td>Acetonitrile 2944\text{cm}^{-1}</td>
</tr>
<tr>
<td>Mean Peak Area (e-)</td>
<td>8.22x10^4 (25)</td>
<td>6.57x10^4 (25)</td>
</tr>
<tr>
<td>Std. Deviation</td>
<td>6.55x10^3</td>
<td>7.96x10^3</td>
</tr>
<tr>
<td>Relative Std. Deviation</td>
<td>7.97x10^{-1}</td>
<td>0.0121</td>
</tr>
</tbody>
</table>
Path Length Effects

An interesting side effect of having the excitation beam and the collection "beam" collinear is that all of the available depth of focus associated with the focusing/collecting lens is available to be used by the spectrometer provided that the sample is deep enough. Depth of focus is defined to be the maximum distance away from the ideal focal plane which is possible without serious degradation of the image [88,89]. In figure 13 a ray trace for a spherical wave, A'B', converging on a point, F' is shown.

![Fig 13. Ray trace for a spherical lens.](image)

An Airy pattern will be formed at the plane intersecting F' and normal to the axis A'-C'. At point C', the central maximum will be less intense than at point F' because the waves do not all arrive in phase [88]. As long as the phase differences between waves arriving at C' is less than \( \pi /2 \), there will not be a significant deterioration of the image. If \( \delta \) is taken to be the depth of focus associated with a phase difference of \( \pi /2 \) when waves from A'B' arrive at C', then:
where \( n^* \) is the refractive index of the medium and \( \theta \) is the angle described by \( A'B'F' \) in figure 13. The importance of Eq. 2.15 to this discussion is that as the focal length of the lens \( (A'F') \) increases so does the depth of focus, \( \delta \).

As a practical test of the effect of depth of focus on the ability of a Raman spectrometer to collect signal, a variety of focusing/collecting lenses were tested in the spectrometer previously described in figure 11. Five different lenses were tested in position L1. All of the lenses had an effective diameter (\( \Psi \)) of 30mm. Focal lengths (f) included: \( f = 40\text{mm} \), \( f = 120\text{mm} \), \( f = 200\text{mm} \), \( f = 500\text{mm} \) and \( f = 1000\text{mm} \). In order to assess the effective depth of focus, a 1cm path length cell of toluene was positioned at varying distances from each lens and a spectrum was acquired at each distance. The area of the 1004cm\(^{-1}\) band of toluene was then determined for each spectrum obtained for each lens.

Figure 14 shows a plot of the observed signal intensity as a function of distance from the lens center for each of the lenses tested. Notice that as the focal length of the lens increases the peak Raman intensity of that lens at the focal distance decreases. This is because both \( \Omega \) and \( P_n \) are decreasing and the spectrometer is not able to collect from all of the increasing \( A_n \) because it is already overfilled. However, as was shown before, as the focal length of a lens increases (with \( \Psi \) being held constant), the depth of focus increases so that the length of the region where the beam can be considered cylindrical and effectively collected becomes longer. This is
Figure 14. Integrated toluene 1004 cm\(^{-1}\) peak area as a function of distance from lenses of varying focal length. Laser power was 40 mw (515 nm), integration time was 5 s, and entrance slit width was approximately 40 \(\mu\)m.
easily seen in Fig. 14 by the increase in the full width half max of the distribution of intensity as the focal lengths increases. Comparison of the total signal collected at all distances by the different lenses (table 6) reveals that all of the lenses collect nearly the same amount of total signal (within a factor of 2.5) so that if one were collecting

<table>
<thead>
<tr>
<th>Focal length of lens (mm)</th>
<th>Total signal collected at 1004 cm⁻¹ at all distances from lens (e⁻ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>4.13 x 10⁵</td>
</tr>
<tr>
<td>120</td>
<td>4.15 x 10⁵</td>
</tr>
<tr>
<td>200</td>
<td>2.96 x 10⁵</td>
</tr>
<tr>
<td>500</td>
<td>5.50 x 10⁵</td>
</tr>
<tr>
<td>1000</td>
<td>2.44 x 10⁵</td>
</tr>
</tbody>
</table>

from a transparent sample with depth that is at least twice the focal length of the longest lens, the effective collection efficiency would be approximately the same regardless of which lens was used.

If the sample is a truly two dimensional scatterer (i.e. a surface), there is no advantage to increasing the f/ of L1 beyond that which gives an A_D which just overfills the spectrograph. This is because losses in power density will no longer be compensated by gains in sampled area since the slit/detector image is limiting A_D. Additional losses occur if one increases the f/ of L1 beyond this limit because of a decrease in solid angle of collection, Ω, which cannot be compensated for by increased path length in the surface scattering case. The net result is that the f/ of L1
is dictated for a particular spectrometer by the maximum useable aperture (usually defined by BR filters) and the \( A_n \) imposed focal length limit.

**Spectrometer Efficiency**

In addition to the potential random errors related to sampling reproducibility, there exist potential pitfalls in quantitative Raman related to changing spectrometer response. Such variations in the instrumental response function are less of a problem in spectroscopies where the measured quantity is a difference in transmission, because it is relatively simple to construct a double beam instrument which removes instrumental effects by ratios. Because Raman (and also fluorescence) is a radiometric technique, the construction of a double beam instrument is considerably more challenging and is in general impractical. It is therefore desirable to develop a method for accurately measuring and subsequently removing the contribution of variable spectrometer response to observed spectra. Previous reports discuss the use of a continuum source, usually a tungsten filament, which is positioned so that its output may be recorded under conditions mimicking those of the Raman experiment \[30,87\]. If the white light output is considered to be constant as a function of wavelength, then the recorded white light spectrum is simply divided into the Raman spectrum to remove the spectrometer response function. A more accurate approach models the tungsten filament as a black body emitter whose output (photons s\(^{-1}\) cm\(^{-2}\) nm\(^{-1}\) sr\(^{-1}\)) is known or can be calculated from the filament temperature. This approach will still be less than ideal however unless the source is very small and placed exactly
at the position where Raman sampling occurs. This is because the photons from a tungsten filament place at "infinity" will be essentially collimated when they are sampled by the spectrometer so that the off-axis performance of the instrument will not be rigorously tested. An excellent calibration source would be a weak white source, comparable in size to the normal Raman scattering area with a known specific intensity (photons s⁻¹ cm⁻² sr⁻¹ nm⁻¹) which could be placed at the Raman sampling position. Such a source would be capable of testing all aspects of the spectrometer efficiency.

A near-point source has been constructed from a 200μm diameter optical fiber which transmits the output of a tungsten filament to the focal point of the collection optics of a Raman spectrometer; see figure 15. By determining the shape of the fiber output as a specific intensity function \( L_f(\lambda) \) (photons s⁻¹ cm⁻² sr⁻¹ nm⁻¹), the fiber becomes a secondary standard which mimics the size and radiometric output of a Raman sample, yet has known specific intensity. In order to determine the specific intensity of the fiber source, a standard source of known spectral irradiance \( I(\lambda) \) was used as a primary standard. A reference spectrum, \( (S_r(\lambda)) \) was collected by placing the primary standard 100cm away from the entrance slit of the spectrograph without any intervening optics. The manufacturer provided \( I(\lambda) \) curve is shown in figure 16. The fiber optic source, including secondary standard bulb, diffuser, and intervening fiber, was then placed so that the output end was ~1cm from the entrance slit and the spectrum of its output \( S_f(\lambda) \) was recorded. \( L_f(\lambda) \) was then calculated using equation 2.16:
Figure 15. Apparatus for generating white light emission from the end of an optical fiber.
Figure 16. Irradiance of standard source ($I(\lambda)$) and specific intensity $L_r(\lambda)$ of secondary fiber source. Points indicate manufacturers' values for irradiance; the $I(\lambda)$ line is a fifth-order polynomial fit to the points. $L_r(\lambda)$ was determined as described in the text.
where \( r_e \) is the radius of the fiber output cone 1 cm from the fiber end and \( r_F \) is the fiber radius. The spectrometer collection angle, \( \Omega \) occurs in Eq. 2.16 because it is less than the solid angle of the fiber output cone for all cases except spectrometer A. The factor \( r_e^2/r_F^2 \) corrects for the expansion of the fiber output cone radius in the 1cm separating the fiber end from the entrance slit and is equal to 772 in this case. The measured \( L_F(\lambda) \) for the secondary standard is also shown in figure 16. Differences in the shape of \( I(\lambda) \) and \( L_F(\lambda) \) are likely due to changes in the fiber and diffuser transmission. It must be emphasized that it is the shape of \( L_F(\lambda) \) which is most accurately determined by this procedure, and that the absolute magnitude of the function, though reproducible, may only be considered approximate.

In practice, the use of the white light fiber is much like acquiring a Raman spectrum. With sampling optics and filters in place, one places the fiber at the position where a Raman sample would normally be placed and the fiber then fine positioned for maximum signal from the detector. A white light spectrum is then obtained under identical conditions as those used to acquire the Raman spectra that are to be corrected. By analogy to Eq. 2.4, the signal from the fiber is:

\[
S_F = L_F \Omega T(\lambda) Q(\lambda) A_F \Delta \lambda
\]

where \( A_F \) is the intersection of the slit image at the sample spot and the fiber, taking any magnification of the slit image by the collection and entrance optics into account.
The term $\Delta \lambda$ is present in Eq. 2.17 to account for the fact that the source is white. Functionally, $\Delta \lambda$ is equal to the reciprocal linear dispersion of the spectrograph times the slit width (or pixel width, whichever is the resolution limiting element).

Rearrangement of Eq. 2.17 shows how $S_p$ can be used as a measure of a spectrometer's ability to collect, transmit and detect light.

$$\Omega T(\lambda) Q(\lambda) = \frac{S_F}{L_F \Delta \lambda A_F} \quad (2.18)$$

Recalling Eq. 2.12, the product $\Omega T(\lambda) Q(\lambda)$ is proportional to the spectrometer efficiency, $E_p$. In practice, the product $\Omega T(\lambda) Q(\lambda) A_D$ is determined by first measuring $S_p$ for a particular spectrometer configuration, then $\Omega T(\lambda) Q(\lambda)$ is calculated and multiplied by $A_D$ for a given resolution. Figure 17 shows the measured $\Omega T(\lambda) Q(\lambda) A_D$ function for the spectrometers listed in table 4. To normalize the comparisons, the bandpass used to determine $A_D$ was set arbitrarily to 1 cm$^{-1}$. For the multichannel systems, a 1 cm$^{-1}$ bandpass was not experimentally practical so the observed signal was multiplied by the ratio of the theoretical 1 cm$^{-1}$ $A_D$ to the experimental $A_D$. The comparison in figure 17 gives an accurate representation of the relative efficiency of each spectrometer on a per-resolution element basis; the multichannel advantage is not included.

It is obvious from Fig. 17 that the instrumental efficiency is not constant with wavelength. Figure 18 shows two raw white light spectra ($S_p$) collected using spectrometer C but in this case plotted as a Raman shift from two common laser excitation wavelengths. When excitation is at 515 nm (Ar$^+$ ion laser) the instrumental
Figure 17. Spectrometer response functions for the spectrometers listed in table 4. All curves have been adjusted to a theoretical bandpass of 1\text{cm}^{-1}.
Figure 18. Uncorrected white light spectra ($S_p$) collected using spectrometer C. The x-axis is plotted as Raman shift relative to 515nm and 784nm.
response is increasing sharply so that low frequency vibrations will be attenuated and higher frequency vibrations will appear enhanced in intensity. The "spectrum" plotted relative to 784nm (Ti:sapphire laser) shows just the opposite trend primarily because of rolloff in the detector quantum efficiency, Q. Figures 19 and 20 are illustrations of how variation in $\Omega T(\lambda)Q(\lambda)A_D$ can perturb the apparent relative intensities of bands within a the Raman spectra of methylene chloride and naphthalene and how white light correction can remove the instrumental effects. To correct a measured Raman spectrum for the attenuation of bands caused by nonlinear response, one must merely divide the raw spectrum by the instrumental response to the white light under identical conditions. In practice the, white fiber spectrum, ($S_d$), is collected under identical conditions as those used to collect the raw Raman spectrum, ($S_{obt}$), and a corrected spectrum ($S_{cor}$) is calculated by a computer program using Eq. 2.19.

$$S_{cor} = \frac{S_{obt} L_F}{S_F} \quad (2.19)$$

The ratio of the observed intensities is approximately five times greater with 515nm excitation than that observed for 784nm excitation over the entire frequency shift range in the corrected spectra. This result indicates that changes in the spectrometer efficiency have effectively been corrected, and that direct comparison of data collected under completely different excitation conditions may be achieved by correcting only for the $\propto^4$ variation in scattering efficiency. Notice that the 1382cm$^{-1}$ band in naphthalene which appears slightly more intense in the 515nm spectrum. This band is associated with the ring breathing mode of naphthalene and is likely to
Figure 19. Raman spectra of methylene chloride obtained using 515nm and 784nm excitation. Figure A is before intensity correction and figure B is after intensity correction as described in Eq. 2.19. For 515nm spectra, 50mw of laser power was used at the sample; integration was for 10s and the spectrometer slit was held at approximately 40μm. For the 784nm spectra, laser power was 40mW, integration time was 5s and slit width was 40μm.
Figure 20. Raman spectra of naphthalene obtained using 515nm and 784nm excitation. Figure A is before intensity correction and figure B is after intensity correction as described in Eq. 2.19. Spectral conditions are the same as in figure 19.
be pre-resonant when excited at 515nm. Because this change in relative intensity is
not spectrometer related, it is not "corrected" for by the white light procedure.

Relative Raman Cross-sections

If one scans the Raman literature, it quickly becomes clear that most authors
either report intensities in relative terms or without any intensity scale at all. Under
the conditions where sampling is very reproducible and spectrometer induced signal
variations can be corrected, however, the prospect of comparing Raman spectra based
on absolute intensity becomes a possibility. Previous sections in this chapter have
demonstrated that high degrees of reproducibility can be attained if one is very careful
in the design of collection and excitation optics. It has also been demonstrated that
spectrometer induced attenuation of intensities can be effectively corrected for by use
of a white light source of known spectral irradiance. Given the high degree of
control over spectrometer related variables associated with these techniques, one can
make accurate measurements regarding the relative scattering efficiency of various
samples.

Absolute Raman cross sections are rarely reported in the literature because
they are difficult to measure. Asher et. al. have reported both the measurement of
absolute differential Raman cross sections and of Raman excitation profiles for
benzene, tyrosine and various other molecules and ions [91-94]. A number of reports
of RR excitation profiles also exist in the literature from other groups [90, 95-98]. Because of the difficulties associated with measuring absolute Raman intensities
however, many of the cross section determinations that exist in the literature have been made relative to some internal standard of known cross section. The use of an internal standard for the accurate measurement of the relative scattering efficiency of a band in an unknown requires that the spectrometer effects on the relative band intensities be accurately compensated. Following the development of an excellent method for correction of these spectrometer effects, a number of relative Raman cross sections were measured.

Measurements were made using a method similar to that reported by Fung and Tang, where a series of five solutions containing varying mole ratios of standard and analyte were examined [99]. Raman spectra of each solution were collected using the inline optical arrangement described previously, and then each spectrum was corrected using the white light procedure reported earlier in this chapter. The relative scattering efficiency was then determined for each mode of interest by plotting the ratio of the integrated band intensities of the unknown to the standard versus the mole ratio. Because both the standard and the analyte are measured under identical conditions, the ratio of the corrected band intensities can be expressed:

\[
\frac{S_z}{S_a} = \frac{\beta_z D_z}{\beta_a D_a}
\]  \hspace{1cm} (2.20)

The plot of the ratio of band intensity ratio versus mole ratio should therefore be linear with an intercept of zero and a slope equal to the ratio of the Raman cross sections for the standard to that of the analyte, \( \beta_z/\beta_a \). Table 7 is a listing of 14 different analyte molecules for which the cross section has been measured for one or
Table 7. Relative Raman Cross Sections for Selected Molecular Vibrations.

<table>
<thead>
<tr>
<th>Molecule or Ion</th>
<th>Frequency (cm⁻¹)</th>
<th>Relative Cross Section¹ ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene, C₆H₆⁴</td>
<td>992</td>
<td>1.000</td>
</tr>
<tr>
<td>Isopropyl alcohol, C₃H₇OH</td>
<td>816, 940</td>
<td>0.244, 0.074</td>
</tr>
<tr>
<td>Acetate, C₂H₅O⁻</td>
<td>930</td>
<td>0.204</td>
</tr>
<tr>
<td>Acetonitrile, CH₃CN</td>
<td>2249, 2944</td>
<td>0.237, 0.412</td>
</tr>
<tr>
<td>Perchlorate, ClO₄⁻</td>
<td>936</td>
<td>1.073</td>
</tr>
<tr>
<td>Sulfate, SO₄²⁻</td>
<td>980</td>
<td>0.846</td>
</tr>
<tr>
<td>Carbon tetrachloride, CCl₄</td>
<td>459</td>
<td>1.057</td>
</tr>
<tr>
<td>Dioxane, C₄H₈O₂</td>
<td>836</td>
<td>0.244</td>
</tr>
<tr>
<td>Cyclohexane, C₆H₁₂</td>
<td>804</td>
<td>0.415</td>
</tr>
<tr>
<td>Toluene, C₆H₅CH₃</td>
<td>1004</td>
<td>0.851</td>
</tr>
<tr>
<td>Naphthalene, C₁₀H₈</td>
<td>1385</td>
<td>2.848</td>
</tr>
<tr>
<td>1,4-Bis(2-methylstyryl)-benzene</td>
<td>1598</td>
<td>245</td>
</tr>
<tr>
<td>β-Carotene⁴</td>
<td>1525</td>
<td>1.98x10⁴</td>
</tr>
<tr>
<td>2,4-dinitrophenyldrazine (DNPH) + p-Benzoquinone (pBQ)⁴</td>
<td>1140</td>
<td>1938</td>
</tr>
</tbody>
</table>

a. All measurements were made using 514.5nm excitation except DNPH + pBQ adduct which was made using 488.0nm excitation.

b. Spectral bandpass was 10cm⁻¹ in all cases except DNPH + pBQ for which it was ca. 4cm⁻¹.

c. β for the 992cm⁻¹ vibration of benzene is 2.86x10⁻²⁹ cm² molecule⁻¹ sr⁻¹ [100].

d. Solutions of resonant scatterers were made as dilute as possible to avoid significant attenuation of the excitation beam by sample absorption.
more bands relative to that of the 992cm\(^{-1}\) band of benzene. This band is of \(a_{1g}\)
symmetry and represents the symmetric stretch of the benzene ring. The cross
section of the 992cm\(^{-1}\) band has been reported to be \(2.86 \times 10^{28}\) when excited by the
514.5nm line of an Ar\(^+\) laser [95-98,100]. Several observations regarding table 6
merit discussion. First, it is important to note that cross sections relate to individual
vibrational modes so that a single molecule will exhibit a range of cross sections that
will be manifested as bands of different intensities within a Raman spectrum. Second,
\(\beta\) values must always be reported with reference to a specific excitation wavelength,
515nm in this case. This is because the observed cross section will vary with the
fourth power of the \textit{absolute} frequency of the scattered photon and also because
resonance effects will be strongly wavelength dependent. Third, for the analytes
which would be expected to be nonresonant or at least very weakly resonant, the
relative cross sections are typically not more than a factor of 10 larger or smaller than
that of the 992cm\(^{-1}\) band of benzene. Comparison of the 992cm\(^{-1}\) band with the
980cm\(^{-1}\) sulfate symmetric stretch of \(\text{SO}_4^{2-}\) for example, reveals that the cross sections
for these very different molecules differs only by approximately 20\%. However, if
one considers more conjugated molecules, for which electronic states will lie at lower
energies and resonance enhancement can occur, vibrations can have much larger
relative cross sections in the visible than those of benzene whose electronic states lie
far into the UV. \(\beta\)-carotene for example, which is an orange material and strongly
resonance enhanced at 515nm, exhibits a cross section, \(\beta_{1532\text{cm}^{-1}}\), that is approximately
\(2 \times 10^5\) times that of the benzene 992cm\(^{-1}\) band.
A similar approach to that outlined above was used to measure the relative scattering efficiency of glassy carbon. In this case it was clearly not possible to create a solution containing the analyte and an internal standard, so an external standard was necessary. The spectrometer was essentially spectrometer B from table 4 except that in this case the spectrometer was fitted with a grating having 600 lines/mm and a 500nm blaze angle. Optics consisted of a \( f = 200 \text{mm} \), \( f/5 \) lens focusing onto the entrance slit of the spectrograph and a \( f = 100 \text{mm} \), \( f/2.5 \) lens for excitation and collection. Band rejection was by a 38mm diameter Holographic Notch Plus filter (Kaiser Optical Systems) and entrance slits were held at 49\( \mu \text{m} \). To establish a standard by which the scattering efficiency of GC could be judged, a 1mm thick cell of pure benzene was sampled repetitively. The benzene sample was removed from and then replaced in the spectrometer sampling region prior to each spectrum. Under the above conditions and with 10mW of 488nm laser excitation, the 992\( \text{cm}^{-1} \) band of benzene (\( \beta = 3.58 \times 10^{30} \text{ cm}^2 \text{ molecule}^{-1} \text{ sr}^{-1} \) with 488nm excitation) gave a signal of \( 1.75 \times 10^4 \text{ e}^- \text{ s}^{-1} \pm 7 \times 10^3 \text{ (N=3)} \) [90]. The predicted signal using independently measured or calculated values of \( \Omega = 0.045 \text{ sr} \), \( A_n = 1.76 \times 10^{-4} \text{ cm}^2 \), \( TQ = 0.025 \), and \( D_e = 6.77 \times 10^{30} \text{ molecules cm}^{-2} \), was \( 2.34 \times 10^3 \text{ e}^- \text{ s}^{-1} \). The good agreement between the experimental and theoretical signals strongly implies that all of the important variables have been accounted for in equation 2.4. The high degree of reproducibility (0.4% relative std. deviation) should also be noted as important for quantitative analysis.
When freshly polished GC was repeatedly sampled under conditions that were identical to those used for the benzene sample discussed above, $S$ was $737 \pm 35 \text{ e} \cdot \text{s}^{-1}$ ($N=3$). Using the benzene signal as a standard, permits determination of the $\beta D_0$ product of GC as $4.66 \times 10^{-11} \text{ sr}^{-1}$. This value is integrated over both the band width of the $1360 \text{cm}^{-1}$ peak and the sampling depth (ca. $200 \text{Å}$) and is valid only at $488 \text{nm}$. It is important to restate that because in both the case of a $1 \text{mm}$ thick layer of benzene, and a $200 \text{Å}$ thick layer of GC the thickness of the sample are less than the depth of field of the optics, the use of equation 2.4 conceptually compresses the sampled "cylinder" into a two dimensional scattering surface.

Conclusions

This chapter has been concerned with demonstrating that with sufficient care, Raman spectroscopy can be used for the quantitative analysis of samples with or without the use of internal standards. A optical design which approaches fiber optic sampling for reproducibility was described and characterized. These in-line optics have an several important advantages over fiber optic sampling including the exclusion of optical fiber background which can be very large with solid samples, and excellent sampling efficiency for transparent liquids due to large depth of field. These depth of field effects were then described in some detail and a comparison of various excitation/collection lenses showed that the reduction in solid angle of collection that occurs as the $f/#$ increases was compensated for by increased depth of field.
The heart of this chapter involves a procedure for accurate determination of the shape of the response function for a Raman spectrometer. The correction of spectrometer induced attenuation of the observed intensity of Raman bands is critical for several reasons. First, the spectrometer efficiency is quite variable with wavelength so that relative intensities of widely separated bands will be significantly attenuated from their actual intensities by increasing or decreasing spectrometer efficiency. Second, because the efficiency function as a function of wavelength first increases then decreases as one moves from 400 to 1000 nm, the relative intensities that are observed in a given Raman spectrum will depend heavily on the excitation wavelength used. Measurement and subsequent mathematical removal of the spectrometer response function allows for accurate comparison of the relative intensities of Raman bands both within a single spectrum and in spectra collected under totally different conditions.

Finally, a list of some relative Raman cross sections which were measured by comparing the relative intensities of bands within intensity corrected spectra was given. These cross sections are useful as internal or external standards for quantitative Raman under conditions where spectrometer collection variables can be accurately measured or calculated. An example where repeated measurement of a benzene sample gave intensities very close to the predicted values shows that Raman intensities can be quantitatively reproduced and predicted. Comparison of the benzene values was used to measure an absolute scattering efficiency for glassy carbon which will be of use in research described in subsequent chapters.
CHAPTER III

Resonance Raman Detection of Carbonyl Groups on Carbon Electrode Surfaces

Following Dinitrophenylhydrazine Derivitization

Introduction

Carbon electrodes have been used extensively in both electroanalytical and electrosynthetic applications. Despite the wide use of carbon electrodes, however, the rich surface chemistry and specifically the chemical nature of oxides existing at carbon surfaces has been inadequately characterized. Characterization of the chemical identity and local environment of surface oxides on carbon is of interest for several reasons. First, standard electrode pretreatment procedures often involve either the direct electrochemical generation of surface oxides or mechanical treatments which are likely to induce some degree of surface oxidation [6,54-59]. Second, though creation of surface oxides may not be the primary activation mechanism for all redox couples, direct catalysis by specific surface oxide functionalities is believed to be important for electrochemical activation of some systems [17,59,60]. Inner sphere catalysis, redox mediation, proton transfer, and chemisorption have all been reported to involve oxygen containing functional groups on carbon electrodes [2,7,8,17]. It is
therefore desirable to develop techniques which may qualitatively and quantitatively identify certain specific surface oxide functional groups.

Glassy carbon (GC) and Highly Oriented Pyrolytic Graphite (HOPG) are two carbon electrode materials which have been studied extensively. GC is a commonly used material for electroanalytical purposes but is often found to exhibit slow electrochemical kinetics unless the electrode is pretreated using one of several procedures. The standard rate constant, $k^0$, is the electron transfer rate at equilibrium, and is often used to indicate electrochemical reactivity. Commonly used procedures which can lead to increased $k^0$s on GC include, but are not limited to polishing [6,7], laser activation [54,55], fracturing [101] and electrochemical pretreatment (ECP) [58,59]. Each of these pretreatments may result in improved kinetics for certain redox couples but rarely is one pretreatment procedure equally effective in all cases. This observation implies that different activation mechanisms are at work for different redox couples. HOPG is essentially "perfect", large microcrystalline graphite and serves as an excellent model for the study of the effect of microstructure on surface reactivity. Due to the low reactivity of the basal plane however, HOPG is a kinetically slow electrode material for electroanalytical purposes [11,15].

A variety of surface analytical techniques have been used to characterize surface oxides on carbon electrodes, including acid/base titrations, XPS and related UHV techniques, thermal desorption mass spectrometry, electrochemistry, and optical spectroscopy [1,5,19-22,24,25,27,43,63,102-110]. Derivitization with a fluorescence
tag to identify surface carboxylates was described recently [14], and XPS tags for
carbonyl and phenolic groups have been reported [61,62]. The results of these
methods depends strongly on the nature and history of the carbon material studied and
also on the pretreatment procedure employed. Though a substantial amount of data
has been collected, the nature of the oxidized carbon surface and how it changes
following various pretreatment procedures remains a matter of debate.

Vibrational spectroscopy is an attractive technique for characterizing of oxides
on carbon because both IR and Raman are able to differentiate between different kinds
of carbon-oxygen functional groups. In principle, is should be possible to distinguish
between carbonyl groups, phenols, carboxylates and ethers and also to infer structural
differences from one carbonyl site to another. The structural information available
using vibrational spectroscopy is generally much more structurally informative than
that available through XPS or fluorescence assuming good quality spectra are
available. Unfortunately, the only carbon surfaces for which good quality vibrational
spectra have been obtained are those of high surface area materials which are difficult
to characterize electrochemically [43]. The weakness of a surface selection rule for
IR absorption at carbon surfaces has precluded the acquisition of spectra of
monolayers on low surface area carbons [109]. No surface enhancement effect has
been reported for Raman on carbon surfaces and it is unlikely that one exists. This
fact coupled with the fact that carbon-oxygen functional groups are weak Raman
scatterers to begin with, has frustrated attempts to use Raman for direct observation
of surface oxides.
The research described in this chapter will show that 2,4-dinitrophenylhydrazine (DNPH) may be used as a reactive probe for surface carbonyl groups which can then be detected and analyzed by resonance Raman spectroscopy. Resonance Raman spectroscopy has significant advantages over previously used techniques for this analysis, including high sensitivity due to large resonance cross-section and a high degree of structural specificity with regard to the local chemical environment of the chromophoric group. DNPH is a standard test reagent for carbonyl groups, including aldehydes, ketones, and quinones. Each of these carbonyl groups is thought to be present to some degree on oxidized carbon surfaces with about 1-15% of all surface sites being carbonyl functionalities depending on surface preparation [2,61,62]. The reaction product of DNPH and carbonyl groups is an azo/hydrazone tautomeric structure that is typically a strong chromophore with an absorption maximum in the range of 350 - 500 nm [112-121]. The resonance enhancement allows detection of the DNPH-carbon adduct at sub-monolayer surface coverages. At these levels, normal Raman scattering from the unreacted oxides would be unobservable. In order to gain further knowledge about the relationship between observed spectral features and the structure of the surface bound species, a series of model molecules have been studied as graphite analogues. These analogue molecules were treated with DNPH and then spectroscopically analyzed in order to correlate spectral features with those observed on carbon. Figure 21 illustrates the formation of the DNPH-carbon adduct on an electrode surface.
Figure 21. Schematic representation of formation of adduct between 2,4-dinitrophenylhydrazine and carbon electrode surface.
Experimental

Materials

Glassy carbon electrodes (GC20s) were either purchased as a complete electrode (Bioanalytical Systems) or were constructed from 1mm thick GC20s plate (Tokai, Japan). GC was polished on Microcloth polishing cloth using successive 1.0, 0.3 and 0.05 μm alumina (Buehler). The dry polishing alumina was wet with NANOpure 18 MΩ water (Barnstead) and the electrode was rinsed and sonicated between polishing steps also with NANOpure. HOPG was a gift from Arthur Moore at Union Carbide Corp. HOPG surfaces were prepared by cleaving the basal plane using Scotch tape (3M).

2,4-Dintirophenylhydrazine was used as purchased (J. T. Baker) in a 10 mM solution with 1% HCl (J. T. Baker) in dry Ethanol (Quantum Chemical). Model molecules were all used as received and included; benzophenone (Fisher), p-benzoquinone (MCB), phenanthrenequinone (Aldrich), 1,2-naphthoquinone (Aldrich), 1,4-naphthoquinone (Aldrich), 2-hydroxy-1,4-naphthoquinone (Aldrich), 5,8-dihydroxy-1,4-naphthoquinone (Aldrich), coumarin (J. T. Baker), 9-flourenone (Aldrich), benzoic acid (Fisher) and phenol (Fisher).

Instrumentation

Electrochemical pretreatment was performed using a PAR 173 potentiostat. The potentiostat output was monitored using a home-built V to F converter and a pulse counter (Hewlet Packard) so that total charge passed during anodization could
be monitored. Oxidation of the carbon working electrode was done in an all glass
cell containing 1M H₂SO₄, a Pt auxiliary and Ag/AgCl (3M KCl) reference electrode
(BAS). The potential was stepped to 2.2V and held for 10s.

Raman experiments were conducted using a spectrometer like that shown in
figure 11. The spectrograph was a 640mm, f/5.6 single stage monochromator
(Instruments SA) containing a single grating with 600 lines/mm blazed at 500nm. A
PM512 CCD (Photometrics) was used for detection. The focusing/collection lens was
40 mm diameter, f/2.5 and the lens focusing onto the monochromator entrance slit
was also 40mm diameter but f/5. A 38 mm diameter, 488nm holographic band
rejection filter (Model HNPF-488-1.5, Kaiser Optical Systems, Ann Arbor MI) was
used in the collimated region. The entrance slit width was held at 49 μm for a
theoretical resolution of approximately 4 cm⁻¹. Excitation was carried out using the
488nm line of an Argon ion laser (Coherent Innova 70) with powers of approximately
10 mW at the sample focused to a 60 μm diameter, circular spot.

FTIR spectra were obtained using a Perkin Elmer Model 1600 FTIR
spectrometer. All spectra were the result of 4 scans and the resolution was 4cm⁻¹.

Procedures

Model adduct molecules were made by addition of 1x10⁻³ moles of the model
compound to 100 ml of dry ethanol containing 1x10⁻³ moles of DNPH and 1% HCl.
Figure 22 shows the reaction of DNPH with a generic carbonyl group. The reaction
product is capable of undergoing azo/hydrazone tautomerism under conditions where
Figure 22. Reaction between DNPH and carbonyl group to form azo/hydrazone tautomeric product.
negative charge can easily be accommodated. In the preparation of the model adducts described here, reactions occurred rapidly as evidenced by color change. Typically the reaction products were orange to red in color. If an insoluble precipitate was formed, the solution was filtered and both the filtrate and the supernatant liquid were examined spectroscopically. In order to "force" the azo form of the adduct, a fraction of each product was treated with 0.1M KOH in dry ethanol until a color change was observed. The resulting product was then examined spectroscopically.

Carbon samples were pretreated prior to reaction with DNPH. GC surfaces were polished, and in some cases then electrochemically pretreated (ECP'd) prior to reaction with DNPH. In the case of HOPG, fresh basal plane was exposed by cleaving and the surface was then either examined as is or ECP'd prior to analysis. The DNPH reaction protocol for the carbon samples involved immersing the carbon surface in a solution containing 10 mM DNPH in dry ethanol with 1% HCl. The DNPH solution was deoxygenated prior to use by bubbling Ar gas through it for 20 min. The solution with the carbon immersed, was then heated to its boiling point (about 75 °C). The heat was then turned off and the electrode was allowed to continue soaking in the solution with stirring for a total contact time of 2 hours. After the 2 hr. DNPH treatment, the electrode was removed from the solution and rinsed carefully with dry ethanol. Unless otherwise noted, the electrode was then soaked for 5 min in a solution containing 0.1M KOH in dry ethanol. Following this treatment the electrode was removed from the KOH solution, rinsed again with dry
ethanol, and carefully dried in a stream of argon gas. The electrode was then analyzed spectroscopically.

Results and Discussion:

The Raman spectra of the reagents and products of the reaction between DNPH and p-benzoquinone (pBQ) are shown in figure 23. Notice that the adduct has a Raman intensity that is greater than either of the reagents despite having a lower number density. The ratio of signal (in e\(^{-} \text{ s}^{-1}\)) to number density for the DNPH-pBQ adduct is approximately \(1 \times 10^{4}\) times that for neat pBQ indicating a much larger cross section for the adduct. After dilution to a concentration where negligible absorption of the laser beam occurred, the cross section of the 1140 cm\(^{-1}\) band of the deprotonated DNPH-pBQ adduct was measured relative to the 992 cm\(^{-1}\) band of benzene. The integrated 1140 cm\(^{-1}\) band intensity when excited at 488 nm was 1938 times that of the 992 cm\(^{-1}\) band of benzene which yields an absolute cross section for the deprotonated adduct of about \(7 \times 10^{-28} \text{ cm}^{2} \text{ molecule}^{-1} \text{ sr}^{-1}\). A similar determination for the deprotonated form of the adduct formed between DNPH and acetone resulted in a measured cross section of \(5.3 \times 10^{-28} \text{ cm}^{2} \text{ molecule}^{-1} \text{ sr}^{-1}\) for the 1140 cm\(^{-1}\) band.

There is a small but reproducible background signal in the Raman spectrum of polished GC which is equal to about \(2.8 \pm 0.5 \text{ e}^{-} \text{ s}^{-1}\) (\(N = 4\)) at 1140 cm\(^{-1}\) when excited with 10 mW of 488 nm laser light focused to a 60 \(\mu\)m spot. Because this background signal (\(\phi_{b}\)) and the GC signal (\(L_{Et}\)) are the dominant noise sources, the signal to noise expression which is pertinent here is:
Figure 23. Raman spectra of DNPH, p-benzoquinone (pBQ), DNPH-pBQ adduct in acidic solution and DNPH-pBQ adduct in basic solution. In all cases excitation is with ca. 10mW (488nm); spectral bandpass is approximately 4cm⁻¹.
Under the background conditions described above for GC, a Raman signal of about 0.3 e⁻ s⁻¹ should be detectable at a SNR = 3 with 300s of integration time. If one assumes that the cross section of the DNPH-pBQ adduct is representative of what can be expected for the adduct formed between DNPH and the carbon electrode, a monolayer of adduct (3x10¹⁴ molecules cm⁻²) should yield a signal of approximately 270 e⁻ s⁻¹ which leads to a predicted detection limit of substantially less than 1% of a monolayer.

Carbon electrodes have significant oxide density wherever a graphitic plane has an edge [40]. In the case of Highly Oriented Pyrolytic Graphite (HOPG), the graphite microcrystallites are quite large (up to 1µm) so the density of oxides for a region of basal plane surface is expected to be very low. This is significant because graphite edges are the active sites for both electron transfer and adsorption. Figure 24 shows the Raman spectra of HOPG in its native form and following various pretreatment procedures. Spectrum A is of basal plane HOPG following DNPH treatment. Notice that the treatment has no effect on the HOPG so that only the E₂g mode at ca. 1582 cm⁻¹ is observable. Spectrum B shows the same basal plane HOPG after being electrochemically oxidized. Spectrum C shows basal plane HOPG following ECP and treatment with DNPH. The Raman spectra in B and C clearly show the disruption of the graphite lattice through broadening of the 1582 cm⁻¹ band and the appearance of the "disorder" or D band at ca. 1360 cm⁻¹ (40). Spectrum C
Figure 24. HOPG Raman spectra. A) freshly cleaved basal plane after reaction with DNPH; B) basal plane following 10s ECP at 2.2V (Ag/AgCl) in 1M H$_2$SO$_4$; C) same as B plus DNPH treatment.
also reveals new bands which can be assigned to the azo/hydrazone adduct bound to
the surface at 1139 cm$^{-1}$ and 1332 cm$^{-1}$.

Glassy Carbon (GC) is a disordered graphitic material. GC's microcrystallites
are quite small (> 100 Å) so that it can be considered isotropic on scales greater than
about 1000 Å [40]. Because of its very high edge site density, GC is a much more
reactive surface both toward adsorption and electron transfer than HOPG. Figure 25
shows the Raman spectrum of various polished GC surfaces following different
surface treatment procedures. Spectrum A is of a polished GC electrode surface, the
ratio of the areas of the graphite bands at 1360 cm$^{-1}$ and 1580 cm$^{-1}$ is about 1.8 for
this surface. Spectrum B is of a similarly polished GC surface that has been reacted
with DNPH. Spectrum 25C is the resulting spectrum when figure 25A is subtracted
from 25B. A GC surface which gave no observable Raman signal for the DNPH
adduct was prepared by Ar$^+$ sputtering under UHV (< 10$^{-4}$ torr) conditions.
However, the Raman spectrum of the sputtered surface also revealed extensive
damage to the graphite lattice so the usefulness of this surface as an electrode is
questionable.

The presence of carbonyl groups on a polished surface has been previously
detected by XPS at levels of approximately 1-5% of total surface sites [2]. Equation
2.7 can be used to calculate the surface coverage of adduct molecules based on the
observed Raman signal. Assuming that the deprotonated DNPH-pBQ model cross-
section of 7x10$^{-26}$ cm$^2$ molecule$^{-1}$ sr$^{-1}$ is representative of that for the surface species,
Figure 25. Polished GC Raman spectra. A) freshly polished GC 20s; B) polished GC after reaction with DNPH; C) difference spectrum remaining after subtracting A from B.
the intensity of the band at 1141 cm\(^{-1}\) should indicate the surface coverage of adduct. Using the appropriate values for the sampling conditions relevant to spectrum 22B (\(S = 8 \times 10^3\) e\(^{-}\), \(P_{\text{in}} = 8.7 \times 10^{20}\) photons s\(^{-1}\) cm\(^{-2}\), \(A_{\text{in}} = 1.3 \times 10^{-3}\) cm\(^2\), \(TQ = 0.025\) e\(^{-}\) photon\(^{-1}\), \(\Omega = 0.044\) sr and \(t = 300\) s), the theoretical surface coverage, \(D_s = 3.1 \times 10^{13}\) molecules/cm\(^2\). A perfect (and flat) graphite plane would have \(4.5 \times 10^{13}\) graphite atoms per cm\(^2\) so the observed signal corresponds to about 0.7% of all carbon atoms on the polished GC surface having carbonyl groups available to react with DNPH.

Glassy carbon is clearly not a perfectly flat carbon surface, but its roughness is thought to arise from nodules and protrusions, not from porosity [40]. As long as the surface is bumpy but non porous, increases in surface area should be exactly compensated for by decreased power density so that calculated surface coverages remain valid.

Electrochemical pretreatment is known to increase the O/C ratio on carbon surfaces [1,7,5,24,25,27,102-107]. If some of the oxides formed are of the carbonyl type, ECP should also lead to a significant increase in the detectable adduct formed on a DNPH reacted GC surface. Figure 26 shows Raman spectra from the same piece of polished GC prior to oxidation (A), following 10s ECP at 2.2V vs Ag/AgCl in 1.0 M H\(_2\)SO\(_4\) (B), and following ECP and DNPH derivitization (C). The increase in signal from the carbon surface following ECP has been reported previously and likely arises from an increase in the sampling depth for the partially transparent oxide layer [11,110]. Kepley and Bard have reported the formation of a layer containing small graphitic carbon particles surrounded by an oxidized carbon film and it may be
Figure 26. Effect of electrochemical oxidation on polished GC 20s Raman spectra. A) freshly polished GC 20s; B) polished GC 20s after 10s ECP at 2.2V (Ag/AgCl) in 1M H₂SO₄; C) same as B plus DNPH treatment.
that these particles are responsible for the observed increase in carbon Raman signal
[63]. The Raman features associated with the DNPH-carbon adduct are much more
intense on the ECP'd surface in Fig. 26C than the polished surface in Fig. 26A.

Figure 27 compares the DNPH-carbon features observed on two ECP'd surfaces with
the carbon bands subtracted. The surface in 27A was soaked in a solution containing
0.1M HCl in ethanol for 5 min. following reaction of the electrochemically oxidized
surface with DNPH. Spectrum 27B shows a similarly prepared surface to that in
spectrum 27A except that in this case the ECP'd GC surface was soaked in a solution
of 0.1M KOH in ethanol following reaction with DNPH. The overall insensitivity of
the spectra to pH implies that no large changes are occurring in the structure of the
DNPH-carbon adduct. Comparison of the spectra in figure 27 shows that only minor
changes in the relative intensity of the group of bands in the 1500 - 1580 cm⁻¹ range
occur in response to the soak in acidic or basic ethanol. The changes which do occur
in the DNPH-carbon spectra are rather minor compared to those observed for all of
the model adducts. This insensitivity to environmental pH suggests that the DNPH
carbon adduct has one structure which is strongly favored.

In an effort to characterize the reactivity of various carbon-oxygen functional
groups toward DNPH and determine the resulting vibrational signature, an array of
model compounds with representative structures was examined. DNPH is a standard
test reagent for aldehydes and ketones and therefore should be quantitatively reactive
towards quinones and simple carbonyl groups. Some slow reaction of DNPH with
carboxylates and lactones may be possible through acyl hydrazide formation but
Figure 27. Effect of pH on DNPH-carbon adduct Raman spectra. A) soaked 5 min in 0.1M HCl/ethanol solution following DNPH treatment; B) soaked 5 min in 0.1M NaOH/ethanol solution following DNPH treatment. Spectra are shown on same intensity scale.
phenolic groups are expected to be unreactive. Spectral interpretation was assisted by comparison of observed features to results obtained by Zhao using a commercial molecular mechanics program Hyperchem (release 3, Autodesk, Inc.) and to literature assignments [112-122]. Computer calculations cannot be expected to yield accurate vibrational frequencies, but the results can be helpful in the assignment of normal modes to observed spectral features. The DNPH-pBQ structure was first optimized using the semi-empirical PM3 procedure, yielding the structures shown in figure 28. The hydrazone form, which is favored in acid, is protonated at the nitrogen adjacent to the dinitrophenyl ring so that hydrogen bonding occurs between the proton and the ortho NO₂ group. Both forms, protonated and deprotonated, of the DNPH-pBQ adduct are planar. The calculated bond length for the "hydrazone" C=N bond is 1.315 Å which is typical for a C-N double bond, while the calculated N-N bond length 1.371 Å, is quite long for a N-N double bond. In base, the DNPH-pBQ adduct is deprotonated to yield an anion with the negative charge delocalized over the dinitrophenyl ring and N-N linkage, implying extensive conjugation of the φ-N-N-C backbone. The calculated N-N bond length is decreased in base to 1.323 Å, and the dinitrophenyl-N bond distance decreases from 1.400 to 1.362 Å. These results indicate a delocalization of the negative charge following deprotonation with a shift from a localized, hydrazone structure in acid to a delocalized structure with partial double bonds along the φ-N-N-C backbone in base.

Figure 29 shows the IR and Raman spectra of the DNPH-pBQ derivative in both protonated and deprotonated form. Prominent features in the observed Raman
Figure 28. Optimized structures for adduct formed between 2,4-dinitrophenylhydrazine and p-benzoquinone. Numbers in parenthesis are the charge on an atom; numbers not in parentheses are bond lengths in Å.
Figure 29. FT-IR and Raman spectra of DNPH-pBQ adduct. FT-IR spectra of KBr pellets prepared using precipitate from acidic ethanol solution of adduct (A), and basic solution (B). Raman spectra are of solutions with solvent subtracted.
Figure 30. Calculated normal modes for the DNPH p-BQ adduct.
spectra in Fig. 29 have been attributed to the calculated normal modes in figure 30. These normal modes have been selected from the more than 70 possible as ones which are predicted to be strongly Raman active based on contributions from functional groups which are expected to have strongly allowed Raman vibrations. These modes were then correlated with the observed features based on comparison to FT-IR spectra and comparison with literature values for similar structures. Because of the extensive conjugation in the adduct, most of the calculated modes represent mixtures of vibrations which extend throughout the structure. The assignments that have been made are tentative this point and should be verified by isotopic substitution for confirmation. The Raman mode observed at 1139 cm\(^{-1}\) (\(\nu_{34}\)) is primarily N-N stretch, while that at 1328 cm\(^{-1}\) (\(\nu_{49}\)) is made up primarily of dinitrophenyl-N stretch. The 1599 cm\(^{-1}\) band (\(\nu_{67}\)) has the C=N hydrazone stretch as a primary contributor. IR and Raman spectra for the protonated forms of DNPH and several of the DNPH adducts are shown in figures 31 and 32. Some important support for the assignments made here can be derived from consideration of these spectra. Observe in Fig. 31B that the protonated form of the adduct formed by the reaction of DNPH with 1,4-naphthoquinone (14NQ) shows a very strong C=N stretch at 1598 cm\(^{-1}\) in the Raman spectrum and also a significant carbonyl stretch at 1648 cm\(^{-1}\) in the IR spectrum. This adduct is easily deprotonated in base, however, to form the delocalized anion in which only a very weak band is evident at 1600 cm\(^{-1}\) in the Raman spectrum. By contrast, the Raman spectra of the DNPH derivatives of 1,2-naphthoquinone (12NQ) and phenanthrenequinone (PHQ) in Fig. 32 show intense hydrazone bands at near
Figure 31. FT-IR and Raman spectra of protonated forms of A) DNPH; B) adduct formed between DNPH and 1,4-naphthoquinone (14NQ). DNPH-14NQ sample was precipitated from acidic ethanol solution.
Figure 32. FT-IR and Raman spectra of protonated forms of A) adducts formed between DNPH and 1,2-naphthoquinone (12NQ); B) DNPH and phenanthrenequinone (PQ). Both samples were precipitated from acidic ethanol solution.
1600 cm\(^{-1}\) in both forms. The hydrazone form of this structure should be stabilized by extensive internal hydrogen bonding in the protonated form. This hypothesis is supported by the observation that in the FTIR spectra of each of these structures, the stretching frequency of the \(\alpha\)-carbonyl has been reduced to about 1610-1620 cm\(^{-1}\).

Table 8 and table 9 summarize the Raman results for each of the model adducts. The protonated form of the adduct formed by reaction of 5,8-Dihydroxy-1,4-naphthoquinone with DNPH was too fluorescent to record a Raman spectrum with either 488 nm or 784 nm excitation. Notice that bands with frequencies in the range associated with \(\nu_{31}, \nu_{41}\) and \(\nu_{67}\) appear in most of the model compounds though the relative intensities vary widely. The DNPH adducts of a carboxylic acid (benzoic acid) and a lactone (coumarin) were substantially weaker scatterers than the other model compounds and did not exhibit bands in the 1330 cm\(^{-1}\) range. Phenol did not react with DNPH to form a resonant scatterer. Table 10 lists the observed IR and Raman band frequencies for the DNPH-pBQ derivative and compares them to the calculated frequencies from Hyperchem and to the observed bands on several carbon surfaces. Hyperchem often predicts vibrational frequencies that are about 10% higher than those that are experimentally observed, but the fact that the general trends between predicted frequencies and intensities and those observed in the IR spectra are similar lends further support to the assignments [115]. The frequencies of the bands observed in the IR and Raman do not always exactly agree because certain modes (e.g. 1327 cm\(^{-1}\)) are composed of a number of vibrations with similar frequencies but
### Table 8. Observed Raman Bands for DNPH-model Derivatives.

<table>
<thead>
<tr>
<th>Model Molecule</th>
<th>Conditions</th>
<th>Adduct Raman Bands (cm⁻¹)*</th>
<th>N-N $\nu_{31}$</th>
<th>$\phi$-N $\nu_{41}$</th>
<th>C=N $\nu_{67}$</th>
<th>Other Strong Raman Bands</th>
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<td>acidic</td>
<td>1335(s)</td>
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<td></td>
<td>1280, 1362, 1616</td>
<td></td>
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<tr>
<td></td>
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<td>1134(s) 1327(s)</td>
<td>1602(vs)</td>
<td></td>
<td>919, 1364, 1440, 1472</td>
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<tr>
<td><img src="image2" alt="Basic" /></td>
<td>acidic</td>
<td>1356(vs)</td>
<td></td>
<td></td>
<td>1275, 1314, 1583, 1620</td>
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</tr>
<tr>
<td></td>
<td>basic</td>
<td>1132(vs) 1338(s) 1603(s)</td>
<td></td>
<td></td>
<td>920, 1022, 1453, 1544</td>
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<tr>
<td><img src="image3" alt="Acidic" /></td>
<td>acidic</td>
<td>1151(w) 1312(s) 1607(s)</td>
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<td></td>
<td>984, 1197, 1347, 1553</td>
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</tr>
<tr>
<td></td>
<td>basic</td>
<td>1149(s) 1327(vs) 1607(s)</td>
<td></td>
<td></td>
<td>923, 969, 1029, 1557</td>
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<td>1130(w) 1337(m) 1598(s)</td>
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<td></td>
<td>921, 960, 1194, 1576</td>
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<td>1125(m) 1340(s) 1598(s)</td>
<td></td>
<td></td>
<td>964, 1049, 1225, 1500</td>
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</tbody>
</table>

* Final wash before spectroscopy was 0.1 M HCl in ethanol.

b. Final wash before spectroscopy was 0.1 M KOH in ethanol.

c. Subscripts on $\nu$ are Wilson numbers for modes shown in Figure 27.
<table>
<thead>
<tr>
<th>Model Molecule</th>
<th>Conditions</th>
<th>N-N ( \nu_{51} )</th>
<th>( \phi-N ) ( \nu_{59} )</th>
<th>C-N ( \nu_{57} )</th>
<th>Other Strong Raman Bands</th>
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<td></td>
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<td>1331(vs)</td>
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<tr>
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<td>1598(vs)</td>
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<td></td>
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<td>1600(w)</td>
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<td></td>
<td>basic</td>
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</tbody>
</table>

\(^a\) Final wash before spectroscopy was 0.1M HCl in ethanol.

\(^b\) Final wash before spectroscopy was 0.1M KOH in ethanol.

\(^c\) Subscripts on \( \nu \) are Wilson numbers for modes shown in Figure 8.
Table 10. Assignments of Observed and Calculated Vibrational Modes

<table>
<thead>
<tr>
<th></th>
<th>DNPH/p-Benzoquinone Adduct</th>
<th>GC/ECP</th>
<th>Polished GC</th>
<th>HOPG/ECP</th>
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<td>IR*</td>
<td>Hyperchem Calc.</td>
<td>Raman</td>
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<td>shldr, s</td>
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</table>

a. w: weak; m: medium; s: strong; vs: very strong; shldr: shoulder; b: broad
b. Wilson number for normal modes; several are illustrated in figure 8
c. Benzene ring deformation
different IR and Raman intensities. It was not possible to calculate mode frequencies for the DNPH-carbon adduct because of the complexity of the graphite matrix, so assignments were made by analogy to the DNPH-pBQ adduct. The correspondence between the major bands at approximately 1140, 1330 and 1600 cm\(^{-1}\) in the DNPH-carbon adducts and the model compounds implies that these bands are common to adducts formed with carbonyl groups in a variety of local environments but not for phenolic, carboxylate or lactone groups.

From Fig. 27 and table 10 it is clear that the DNPH-carbon surface adduct is less sensitive to pH changes than the model compounds. The fact that the DNPH-carbon structure remained essentially unchanged under both strongly acidic and strongly basic conditions implies that the adduct does not lose protons between pH 0 and 13. Under all conditions, the DNPH-carbon adduct more closely resembles the deprotonated form of the DNPH-pBQ adduct than the protonated form. One would expect that the graphite lattice would have great ability to accommodate a negative charge making the derivative a much stronger acid than any of the model compounds. It therefore seems likely that the DNPH-carbon adduct is deprotonated under all conditions considered leading to the structure in figure 30 with the anion delocalized in a similar fashion to that predicted for the DNPH-pBQ anion in base.

Conclusions

This chapter has shown that DNPH can be used as a reactive probe for carbonyl groups existing on the surface of carbon electrodes. The large resonance
Figure 33. Proposed structure of DNPH-carbon adduct.
enhanced Raman cross section of the bound DNPH-carbon adduct makes detection possible at surface coverages of > 1% of a monolayer. The observed Raman features of the DNPH-carbon adduct closely resemble those of the deprotonated DNPH-pBQ model and are in general quite similar to the deprotonated forms of all of the model compounds. From this observation, it is inferred that the surface species is very acidic and therefore exists primarily in the deprotonated in the pH of 0-13. When deprotonated, the structure is a highly delocalized anion that is intermediate between azo and hydrazone forms.

The next chapter in this thesis will describe the use of this technique to determine how various electrode pretreatment procedures affect the surface carbonyl density. The measured surface carbonyl density can then be related to observed kinetic behavior. The use of this derivitization technique has several important advantages over previously used techniques such as XPS, ellipsometry and electrochemistry. First, the DNPH reaction is chemically specific for carbonyl groups so that the importance of this particular functional group to the activation of certain redox couples can be probed independent of interference from other oxide groups. Second, the technique has very low detection limits due to strong resonance enhancement. This may be important since electrochemical kinetics are typically very sensitive to small changes in the chemical makeup of the electrode surface. Third, the technique does not require the exposure of the treated electrode to UHV conditions which may have unknown effects on the observed O/C ratio.
CHAPTER IV

Catalysis of Aquated Metal Ion Redox Reactions by Surface Carbonyl Groups

Introduction.

As discussed in Chap. I, many redox couples display slow electrochemical kinetics at carbon surfaces unless some pretreatment procedure is first applied to the electrode. Potential mechanisms for the activation of these redox couples include surface cleaning, increase in surface hydrophillicity, and introduction of surface groups for which specific interactions with the redox couple are possible. For many redox couples, such as Ru(NH$_3)_6^{3+/2+}$ and IrCl$_6^{3-/2-}$, the major requirement for activity appears to be that the carbon surface be clean and free of adsorbed impurities. For such couples, fast electrochemical kinetics are observed on freshly exposed, fractured GC surfaces and on polished surfaces which have been cleaned with high energy laser pulses [54, 101]. Fractured surfaces are thought to closely approximate native GC, and should be initially very low in if not totally free of adsorbed impurities and surface oxides. Laser activation (LA) of polished surfaces at low to moderate power densities (25 MW cm$^{-2}$) is thought to have the primary effect of removing polishing debris and exposing the underlying carbon matrix, though removal of some surface oxides is possible [9-12,54]. Some redox couples however, have been shown to be slow even on clean, freshly exposed carbon [17]. These systems seem to require
some modification of the carbon surface to facilitate electron transfer.

Electrochemical pretreatment of GC surfaces has been shown to increase the hydrophillicity of these surfaces, presumably by introduction of surface oxide groups [59]. Though increased hydrophillicity could itself lead to improved redox rates by allowing the active center to approach the surface more closely, previous studies seem to preclude this effect from being a major activation mechanism [123,124]. In the case of simple, outer-sphere electron transfer, surface cleaning is probably the major activation mechanism resulting from ECP. For certain other redox couples, however, the effectiveness of ECP procedures is thought to arise from the introduction of oxide sites which catalyze the electron transfer process through some close interaction with the redox center. Cabaniss et. al. suggested that proton coupled electron transfer involving phenolic groups on GC surfaces may be involved in the activation of catechol and ruthenium bipyridine [2]. Redox mediation via carbonyl groups has also been implicated as a rate increasing pathway for catechol at GC surfaces [7].

Recently, an inner sphere catalysis mechanism, shown in figure 34, for the activation of some aquated metal ions at GC surfaces has been proposed [17]. Inner sphere processes involve some strong interaction between the redox center and the electrode surface; often involving bond formation. In this recent study, Fe$^{2+/3+}$, V$^{3+/2}$ and Eu$^{3+/2}$ were all shown to have electron transfer rates which were very sensitive to mild amounts of surface oxidation. Beginning with a fractured GC surface, enhancements in the electron transfer rates of as much as a factor of 500 were observed following relatively mild oxidation, with the post-ECP rates being higher
Figure 34. Proposed surface catalysis site for aquated metal ions [17, 125]
than predicted for simple outer sphere processes. It was proposed that a catalytic site
resembling the ligand acetoacetanoate (acac), first proposed by Sherwood and
Koslowski [125], was formed by the ECP process and was responsible for the
increase in rate. Because ECP is generally considered to increase the total surface
density of oxide groups and these groups have often been included in the explanation
of enhanced redox rates at carbon electrodes, a method of direct determination of the
surface density of particular oxides and comparison to observed electron transfer
kinetics is of interest.

Cyclic voltammetry (CV) is a useful technique to measure changes in electron
transfer rates for on different surfaces. The potential separation between the peak
anodic ($E_{pa}$) and peak cathodic ($E_{pc}$) currents can be used to diagnose the degree of
irreversibility of a redox couple at a surface [126]. For an electrochemically
reversible redox couple, the peak separation, $\Delta E_p$, will be:

$$\Delta E_p = E_{pa} - E_{pc} = \frac{0.057 V}{n} \quad (4.1)$$

where $n$ is the number of electrons transferred. For such a reversible couple, $\Delta E_p$ is
independent of scan rate, $\nu$, and the magnitude of the anodic and cathodic currents
will scale with the square root of the scan rate. If a couple is irreversible, meaning
electron transfer is kinetically slow between the redox center and the working
electrode, $\Delta E_p$ will be greater than 0.057 V/n and will be dependent on scan rate. In
this case, the heterogeneous electron transfer rate constant, $k^0$, can be determined
from the observed $\Delta E_p$ by the method of Nicholson [127].
Thus far, chapters II and III have dealt primarily with the application of Raman spectroscopy to the quantitative and qualitative analysis of carbonyl groups on carbon electrode surfaces. With the use of DNPH derivitization, the surface coverages of carbonyl groups can be determined for carbon electrodes that have been pretreated using various methods. The goal of this chapter then is to relate the spectroscopically determined carbonyl site density following various pretreatment procedures to the observed heterogeneous electron transfer rates for Fe$^{+2/+3}$, V$^{+3/+2}$ and Eu$^{+3/+2}$. If the previously proposed model for an inner sphere catalysis mechanism involving an acac analogue is correct, it is expected that some relationship between carbonyl density and electrochemical rate should exist.

**Experimental.**

Electrochemical Pretreatment was performed on prefabricated GC-20 electrodes (BioAnalytical Systems) using the same instrumentation described in Chap. III. Solutions for ECP were prepared from reagent grade H$_2$SO$_4$ (Mallinckrodt), NaOH (Fisher), HNO$_3$ (Mallinckrodt) and NaNO$_3$ (Fisher) which were used as received. All solutions were made using NANOpure 18 MΩ water and were deoxygenated by bubbling argon through them for 20 min. prior to use. All ECP treatments were for 10 s at 2.2V (Ag/AgCl) unless otherwise noted. Polished GC surfaces were prepared as described in Chap. III. Laser activation of polished GC surfaces was accomplished in a similar method to that previously used [54, 101], by delivering a series of 9 ns pulses of 1064 nm light from an Nd:YAG laser to the
surface while submerged in deoxygenated water. The power density of the laser was measured to be 25 MW cm$^{-2}$.

DNPH derivitization of 10mm x 5mm x 1mm polished GC surfaces was performed using the same procedure described in Chap. III. All of the GC pieces used in the described analysis came from a single 10 cm x 10 cm x 1 mm plate (Tokai, Japan). Raman experiments were performed using the same instrument described in Chap. III and excitation was again carried out using 10 mW of 488nm laser light from an Ar$^+$ laser. All instrument settings were the same as those described in chapter III unless otherwise stated.

Electrochemical solutions were all prepared from NANOpure 18 MΩ water and all contained 0.2M HClO$_4$ supporting electrolyte. The metal ion solutions were prepared at 5mM concentration from: Fe(NH$_4$)$_2$(SO$_4$)$_2$•6H$_2$O (J. T. Baker), VCl$_3$ (Aldrich) and Eu(NO$_3$)$_3$•5H$_2$O (Aldrich). Each of these metal salts was reagent grade and was used as received without further purification. All solutions were degassed by bubbling Ar gas through them for 20 min. prior to use.

The electrochemical rate of the aquated metal ions on different surfaces was evaluated by cyclic voltammetry. All electrochemical measurements were made using the above mentioned prefabricated electrodes. Experiments were conducted using a conventional three electrode potentiostat (Advanced Idea Mechanics, Columbus, Ohio). All voltammetry was performed at scan rates of 0.2 V s$^{-1}$ using a Pt auxiliary and a 3 M KCl Ag/AgCl reference electrode. Rate constants were calculated using the method of Nicholson [127] assuming an $\alpha = 0.5$. The following diffusion
coefficients were obtained from the literature: $D_\text{Fe}^2$ for Fe$^{2+}$ (0.1M HClO$_4$) = 9x10$^{-6}$ cm$^2$ s$^{-1}$ [128,129], $D_\text{Eu}^3$ for Eu$^{3+}$ (ph 0.3, 1M NaClO$_4$, HClO$_4$) = 7.9x10$^{-4}$ cm$^2$ s$^{-1}$ [130], $D_\text{V}^3$ for V$^{3+}$ (1M HClO$_4$) = 5.2x10$^{-4}$ cm$^2$ s$^{-1}$ [131].

Because extensive ECP can lead to the formation of a thick, hydrated oxide film, observed currents can be complicated by contributions from adsorbed or preconcentrated electroactive species. In order to confirm that the observed currents were diffusion controlled, digital simulation of some of the experimentally obtained voltammograms was carried out. Results obtained with a commercial digital simulation program, DigiSim Version 1.0 (BioAnalytical Systems, W. Lafayette, IN) were compared to some of the experimental CVs.

X-ray Photoelectron Spectroscopy was performed on some surfaces to establish the relative change in surface oxide density and to compare the present results with literature values. Spectra were obtained using a V. G. Scientific X-Ray Photoelectron Spectrometer using the Kα X-radiation from a Mg anode (290 Watts). Data analysis was done using Peakfit peakfitting software (Jandel Scientific). Carbon samples were identical to those used in the ECP - Raman experiments.

Results and Discussion.

A variety of pretreatment procedures have been used to improve the electrochemical reversibility of different redox couples at GC electrodes. For the purposes of this study nine different pretreatment procedures, which are representative of some previously reported in the literature [4, 10, 53, 57, 132, 133], were
evaluated first for their relative tendency to form surface carbonyl groups as measured by derivitization with DNPH, and second, their enhancement for the rates of Fe$^{2+/3+}$, V$^{3+/2+}$ and Eu$^{3+/2+}$. The treatment procedures studied include: polishing on alumina, polishing plus LA (10 pulses, ca. 25 MW cm$^{-2}$, 1064 nm), fracturing, ECP in 1M H$_2$SO$_4$ (10s at 1.5 V, 10s at 2.2 V and 5 min. at 1.8 V), ECP in 1M NaOH (10s at 2.2 V), ECP in 1M NaNO$_3$ (10s at 2.2 V) and ECP in 1M HNO$_3$ (10s at 2.2 v).

Figures 35 and 36 show the resonance Raman spectra of the DNPH-carbon derivatives formed for each of these surfaces except for fractured, following subtraction of the carbon features. Satisfactory spectra of subtracted fractured surfaces were not obtained, though it was possible to measure the area of the 1140 cm$^{-1}$ band in the unsubtracted spectra for comparison purposes. An unsubtracted spectrum of a fractured GC surface that has been treated with DNPH is shown in figure 37. The basic features of each of these spectra are very similar but the signal intensities vary considerably. The polished surface, the polished and LA surface and surprisingly the ECP in NaOH surface all show similar reactivity towards the DNPH reagent, implying that they all have similar surface densities of carbonyl groups.

Each of these surfaces had similar line shapes for the carbon Raman bands as well. This observation implies that the additional treatments of LA and ECP in NaOH had little effect on the near-surface carbon microstructure beyond the damage originally done by the polishing procedure. Each of the other pretreatment procedures led to some increased reactivity of the surface towards DNPH as well as increased damage to the GC near-surface microstructure. ECP at 1.5 V in 1M H$_2$SO$_4$ led to a signal
Figure 35. Raman spectra of DNPH-carbon adducts obtained on different GC surfaces. Carbon Raman bands have been subtracted in all cases.
Figure 36. Raman spectra of DNPH-carbon adducts obtained on different GC surfaces. Carbon Raman bands have been subtracted in all cases.
Figure 37. Raman spectra of fractured GC 20s surfaces before (A) and after (B) DNPH treatment.
due to DNPH-carbon adduct that was roughly twice that observed for the polished surface while increasing the potential to 2.2V led to a total increase in signal of about 12 fold. Because the oxide layer formed in ECP is many atomic layers thick, it is difficult to calculate a meaningful surface density of carbonyl groups, so from this point on surfaces will be compared strictly on total signal from the DNPH-carbon derivative.

Electrochemical pretreatment in NaOH has been previously been shown to be effective in the activation of dopamine and ferrocyanide at carbon electrodes [132, 133], so it was curious that no discernable change from the polished surface was observable by Raman analysis of either the carbon bands themselves or those due to the DNPH adduct. In order to attempt to answer the question of whether ECP in NaOH causes any increase in the surface oxide density, XPS spectra of several pieces of polished GC following ECP in NaOH over half of their surface were studied. Figures 38 and 39 show the wide scan (0 to 1000 eV) spectra as well as high resolution scans of the O$_{1s}$ (525 - 545 eV) and C$_{1s}$ (275 - 295 eV) regions. Comparison of these spectra clearly shows that the oxygen to carbon ratio (O/C) has been increased for the region of the surface that was ECP'd in NaOH over that of the polished region. In studies on carbon fibers, Sherwood et. al. found that anodization in 0.5M KOH formed much less surface oxides than similar oxidation done in 2.7 and 0.22 M HNO$_3$ as well as in 0.5 M H$_2$SO$_4$ but that in all cases the O/C ratio increased following the procedure [23, 24, 125]. Additionally, they found that the major oxidation products of the oxidation treatments done in acid were usually carbonyls
Figure 38. XPS spectra of a polished GC 20 surface.
Figure 39. XPS spectra of a polished GC 20 surface with subsequent ECP for 10s at 2.2V in 1M NaOH.
and/or phenolic type groups, while in KOH the major products were phenolic and carboxylic/ester groups. Figure 40 shows the deconvoluted XPS spectra of the C1s regions of a polished surface and the same surface after ECP in NaOH. The spectra were fitted using the same binding energies for the various carbon oxygen functionalities given by Sherwood et. al. [125]. Measurement of relative peak areas revealed that phenolic (ca. 286.0 eV), carbonyl (ca. 286.5 eV) and carbonate (ca. 290.4 eV) groups each increased by about 12-15%. The intensity of the carboxy/ester peak at ca. 288.4 eV however increased by more than 300% following the ECP procedure. Therefore the XPS results obtained here are consistent with Sherwood’s results on carbon fibers and with the DNPH-Raman observation that ECP in NaOH causes little increase in surface carbonyl density over polished GC.

Another common practice in ECP procedures that has been reported in the literature is to follow the anodic oxidation of the surface with a brief reduction step [58, 59]. Some researchers have proposed that at least some of the current observed in the reduction step is due to the reduction of quinone species on the surface [7, 8, 134, 134]. In order to test this hypothesis, several different surfaces were compared. Following the ECP method of Engstrom [58, 59], polished surfaces were oxidized for 5 minutes at +1.8 V and then reduced for 1 min. at -1.0 V in 1M H2SO4. These surfaces gave an integrated Raman intensity for the 1140 cm⁻¹ band of 1.62x10⁴ ± 4.5x10⁴ e⁻ (N = 9) compared with 2.75x10⁴ ± 562x10⁴ e⁻ (N = 9) for surfaces treated only with the oxidation step. It therefore appears that some of the surface carbonyls have been reduced, although most remain available for reaction with
Figure 40. Deconvoluted XPS spectra of polished GC (top) and ECP in NaOH GC (bottom) surfaces. Contributing components are: I) graphitic (284.3 eV); II) phenolic (286.0 eV); III) carbonyl (286.5 eV); IV) carboxylate/ester (288.4 eV); V) carbonate (290.4 eV).
DNPH. The electrode which has been both oxidized and reduced still gives a Raman signal due to the DNPH adduct that is approximately 4 times greater than that observed for the original polished surface.

Each of the pretreatment procedures described in Figs. 35 and 36 was then applied to prefabricated GC electrodes and then used to measure the electrochemical rates of Fe$^{2+/3}$, V$^{3+/4}$ and Eu$^{3+/2}$. Figure 41 shows the CVs resulting for the ferrous/ferric couple at three differently prepared GC electrodes, including: polished, polished plus 10s ECP at 2.2 V in 1 M NaOH and polished plus 10s ECP at 2.2V in 1 M H$_2$SO$_4$. Because the ferrous/ferric couple is relatively fast on the polished surface ($k^0 = 4.7 \times 10^{-3} \pm 1.3 \times 10^{-4} (N = 5) \text{ cm s}^{-1}$), the observed rate changes are relatively small. However, inspection of the voltammograms clearly indicates that the surface which has been ECP'd in base has not been activated relative to the polished surface, and in fact the rate is actually slightly lower on this surface ($k^0 = 2.7 \times 10^{-3} \pm 1.1 \times 10^{-4} (N = 4) \text{ cm s}^{-1}$). By contrast, the surface prepared by ECP in 1 M H$_2$SO$_4$ shows a decrease in $\Delta E_p$ of about 37 mV over that of the polished surface. This change in peak separation corresponds to an increase in rate of about a factor of two ($k^0 = 1.06 \times 10^{-2} \pm 1.8 \times 10^{-3} (N = 6) \text{ cm s}^{-1}$) over that observed on the polished surface. To test that the observed Fe$^{2+/3}$ voltammetry was classical and that the calculated rates were reasonable, each of the CV's in figure 41 was digitally simulated. Results of the simulations are shown in figure 42. Agreement between the digital simulations and the experimental results was very good indicating that the experimentally observed currents are diffusion controlled and that contributions from
Figure 41. Cyclic voltammetry of 5mM Fe^{2+/3} on polished, ECP in NaOH, and ECP in H_2SO_4 surfaces. Supporting electrolyte is 0.2M HClO_4; \nu = 0.2 \text{ V s}^{-1}. 
Figure 42. Simulations of voltammetry in figure 41. Dashed lines are simulated voltammograms and solid lines are experimentally obtained data. Rate constants ($k^0$) and transfer coefficients ($\alpha$) were calculated using simulation program.
effects such as adsorption or preconcentration of analyte in the ECP film are negligible.

The first voltammetric scans for both V^{2+/3+} and Eu^{3+/2+} on GC surfaces prepared by 10s ECP at 2.2 V in 1M H_2SO_4 were obscured by a large reduction wave at about -0.5 V. The wave, shown in figure 43, has a shape that is indicative of an adsorbed species, is totally irreversible, and is only observed on the first negative scan following the ECP procedure. Alsmeyer reported oxygen reduction in 1 M HClO_4 at ca. -0.5 V on polished GC [136], so it seems reasonable that the feature observed here is adsorbed O_2 which was formed by the oxidation of water during the ECP process and became trapped in the hydrated ECP film. After the first negative scan, no trace of this adsorbed oxygen wave remained. Therefore, all the voltammetry of vanadium and europium presented here was collected on subsequent scans. On surfaces that were prepared by polishing, polishing plus LA, fracturing and ECP in NaOH, no oxygen reduction wave was observed so the first scan following treatment could be used.

Vanadium III, like iron, is a redox active metal which exists as a hexaquo species in perchloric acid solutions [137]. Figure 44 shows the CV's measured for V^{2+/3+} on surfaces prepared in an identical manner to those described for Fe^{2+/3+}. Vanadium is slower than iron on the polished surface with a peak separation of 208 ± 21 mV (N = 9). This polished rate of \( k^0 = 1.3 \times 10^{-3} \pm 3.5 \times 10^{-4} \text{ cm s}^{-1} \) increases only very slightly on the surface that has been ECP'd in NaOH to \( k^0 = 2.03 \times 10^{-3} \pm 3.1 \times 10^{-4} \) (N = 8) so that V^{2+/3+}, like Fe^{2+/3+}, does not appear to be activated by this
Figure 43. First and second negative going scan following ECP of GC electrode at 2.2V in 1M H₂SO₄. Solution contains only 0.2M HClO₄ supporting electrolyte. \( \nu = 0.2 \text{ V s}^{-1} \).
Figure 44. Cyclic voltammetry of 5mM $V^{2+/3}$ on polished, ECP in NaOH, and ECP in $H_2SO_4$ surfaces. Supporting electrolyte is 0.2M $HClO_4$; $\nu = 0.2$ V s$^{-1}$. 
surface pretreatment procedure. Upon ECP treatment in H₂SO₄ however, the rate for vanadium increased over that observed on the polished surface by more than a factor of six to $k^0 = 8.68 \times 10^{-3} \pm 2.8 \times 10^{-3} \ (N = 6)$. So far the trends for iron and vanadium seem to support the hypothesis that increased surface carbonyl density leads to an increase in observed electron transfer rates.

Eu⁺³/²⁺ is another redox couple which exists as an aquated complex in dilute HClO₄ [137]. Europium has been previously been reported to undergo inner-sphere catalysis by interaction with thiocyanate anions at mercury electrodes [138] and is suspected to be catalyzed by carbonyl groups on carbon [17]. The voltammetry for Eu⁺³/²⁺ recorded at three electrodes prepared in an identical fashion as those used for Fe⁺²/⁺³ and V⁺³/⁺² is shown in figure 45. Eu⁺³/²⁺ was the slowest of the three systems studied at the polished GC surface, $k^0 = 1.04 \times 10^{-3} \pm 3.2 \times 10^{-4} \ (N = 4) \ \text{cm s}^{-1}$, and has also been reported to be the slowest of these systems at fractured GC surfaces [123, 124]. Upon ECP treatment in NaOH however, the peak separation of Eu⁺³/²⁺ is decreased almost to the reversible limit, $\Delta E_p = 73 \pm 5 \ \text{mV} \ (N = 5)$. In fact, the rate on the ECP in base surface, $k^0 = 3.0 \times 10^{-2} \pm 9.5 \times 10^{-3} \ \text{cm s}^{-1}$ is nearly the same as that observed on the surface pretreated by ECP at 2.2 V in 1M H₂SO₄ ($k^0 = 3.2 \times 10^{-2} \pm 5.69 \times 10^{-3} \ (N = 4) \ \text{cm s}^{-1}$). The activation of europium by ECP in NaOH is quite different from the results obtained for Fe⁺²/⁺³ and V⁺³/⁺², implying that either europium is somehow activated to a greater degree by the same mechanism or that the activation mechanism is somehow different. Some possible explanations for these differences will be discussed later.
Figure 45. Cyclic voltammetry of 5mM Eu$^{2+/3+}$ on polished, ECP in NaOH, and ECP in H$_2$SO$_4$ surfaces. Supporting electrolyte is 0.2M HClO$_4$; $\nu = 0.2$ V s$^{-1}$. 

- Polished

- ECP 1 M NaOH, 10s, 2.2V (Ag/AgCl)

- ECP 1 M H$_2$SO$_4$, 10s, 2.2V (Ag/AgCl)
Tables 11 and 12 summarize the electrochemical results for Fe^{2+/3}, V^{3+/4} and Eu^{3+/2} obtained on all of the nine surfaces studied. Table 11 gives the raw Raman signal, in e^*, observed for each of the surfaces with the corresponding observed CV peak separations for each redox couple. Table 12 presents the same data as e^- s^-1 for the Raman data and as calculated rate constants (cm s^-1) for electron transfer. The data for each redox system from table 12 are plotted in figures 46-48. Figure 41 shows the data for Fe^{2+/3}, in which the electrochemical rate correlates well with the observed Raman intensity due to DNPH derivitized carbonyl groups on the electrode surface. A similar relationship between the observed electron transfer rate for iron and the solution concentration of chloride and other halides has been reported to exist on Pt and Au electrodes (139-141). In these cases, an inner sphere catalytic bridging mechanism has been proposed which leads to an increase in the observed rate of more than 100 in the presence of trace halide ions. The slowest rate reported for iron at a Pt electrode in solutions carefully purified of chloride was 4x10^-5 cm s^-1, which is about 30 times slower than the lowest rate observed on GC. The fact that these rates do not agree well may be an indication of the difficulty involved in preparing a truly "oxide free" GC surface; a conclusion that is supported by the fact that none of the tested surfaces showed zero reactivity towards DNPH. In the presence of catalytic chloride, Fe^{2+/3} rates on Pt have been reported to approach 1x10^-3 cm s^-1 (141), which is very similar to fastest rate reported here.

For V^{3+/2} and Eu^{3+/2}, the relationship between the observed rate constant and surface carbonyl groups is less obviously monotonic than in the case of iron. In
Table 11. Voltammetric peak separations on different surfaces.

<table>
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<th>DNPH $A_{[1141cm^{-1}}$</th>
<th>$\Delta E_p$ (mV)</th>
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<tr>
<td></td>
<td>$(e^-)$</td>
<td>Fe$^{+2/+3}$</td>
</tr>
<tr>
<td>Polished</td>
<td>4320 ± 512 (6)</td>
<td>133 ± 14 (5)</td>
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<tr>
<td>ECP 10s, 2.2V, 1M H$_2$SO$_4$</td>
<td>50800 ± 6656 (7)</td>
<td>96 ± 6 (5)</td>
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<tr>
<td>ECP 5min, 1.8V, 1M H$_2$SO$_4$</td>
<td>27456 ± 5616 (9)</td>
<td>107 ± 4 (6)</td>
</tr>
<tr>
<td>ECP 10s, 1.5V, 1M H$_2$SO$_4$</td>
<td>8400 ± 826 (6)</td>
<td>136 ± 7 (4)</td>
</tr>
<tr>
<td>ECP 10s, 2.2V, 1M NaOH</td>
<td>4389 ± 1011 (7)</td>
<td>172 ± 4 (4)</td>
</tr>
<tr>
<td>ECP 10s, 2.2V, 1M HNO$_3$</td>
<td>12112 ± 2467 (8)</td>
<td>142 ± 11 (4)</td>
</tr>
<tr>
<td>ECP 10s, 2.2V, 1M NaNO$_3$</td>
<td>13568 ± 2784 (6)</td>
<td>138 ± 9 (4)</td>
</tr>
<tr>
<td>Polished + LA 25 MW/cm$^2$</td>
<td>3232 ± 976 (6)</td>
<td>263* (2)</td>
</tr>
<tr>
<td>Fractured</td>
<td>5408 ± 1440 (6)</td>
<td>186 ± 19* (9)</td>
</tr>
</tbody>
</table>

a. Data taken from reference [123].
<table>
<thead>
<tr>
<th>Surface Treatment</th>
<th>DNPH $A_{110cm^{-1}} (e^s^{-1})$</th>
<th>$k^2 \times 10^4 (cm^s^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fe$^{+2+/+3}$</td>
</tr>
<tr>
<td>Polished + LA 25 MW/cm$^2$</td>
<td>10.8 ± 3.3 (6)</td>
<td>12$^*$ (2)</td>
</tr>
<tr>
<td>Polished</td>
<td>14.4 ± 1.7 (6)</td>
<td>47 ± 1.3 (5)</td>
</tr>
<tr>
<td>ECP 10s, 2.2V, 1M NaOH</td>
<td>14.6 ± 2.4 (7)</td>
<td>27 ± 1.1 (4)</td>
</tr>
<tr>
<td>Fractured</td>
<td>18.0 ± 4.8 (6)</td>
<td>23 ± 5.0$^*$ (8)</td>
</tr>
<tr>
<td>ECP 10s, 1.5V, 1M H$_2$SO$_4$</td>
<td>28.0 ± 2.8 (6)</td>
<td>42 ± 5.9 (4)</td>
</tr>
<tr>
<td>ECP 10s, 2.2V, 1M HNO$_3$</td>
<td>40.4 ± 8.2 (8)</td>
<td>40 ± 6.6 (4)</td>
</tr>
<tr>
<td>ECP 10s, 2.2V, 1M NaNO$_3$</td>
<td>45.2 ± 9.3 (6)</td>
<td>42 ± 7.2 (4)</td>
</tr>
<tr>
<td>ECP 5min, 1.8V, 1M H$_2$SO$_4$</td>
<td>91.5 ± 18.7 (9)</td>
<td>73 ± 5.4 (6)</td>
</tr>
<tr>
<td>ECP 10s, 2.2V, 1M H$_2$SO$_4$</td>
<td>169.3 ± 22.2 (7)</td>
<td>106 ± 18 (6)</td>
</tr>
</tbody>
</table>

a. Kinetic data taken from Allred-McDermott and Kneten-Cline
Figure 46. Relationship between electrochemical rate, $k^0$, for Fe$^{+2/+3}$ and density of surface carbonyl groups as determined by area of 1140 cm$^{-1}$ DNPH-carbon Raman band. Error bars indicate standard deviations in measurements.
Figure 47. Relationship between electrochemical rate, $k_0$, for $V^{3+/4+}$ and density of surface carbonyl groups as determined by area of 1140 cm$^{-1}$ DNPH-carbon Raman band. Error bars indicate standard deviations in measurements.
Figure 48. Relationship between electrochemical rate, $k^0$, for Eu$^{2+/3+}$ and density of surface carbonyl groups as determined by area of $1140\text{cm}^{-1}$ DNPH-carbon Raman band. Error bars indicate standard deviations in measurements.
all cases though, the surface with the highest Raman signal due to DNPH-carbon adduct (the surface ECP'd at 2.2 V in 1M H₂SO₄) also gave the highest observed electrochemical rate constant. In this study, europium proved to be much more sensitive to small degrees surface oxidation than either Fe²⁺/³⁺ or V³⁺/⁴⁺. Even at an oxidation potential of 1.5 V in 1M H₂SO₄, conditions for which very little current flowed during ECP, an increase in k⁰ of nearly an order of magnitude over the polished rate was observed for Eu³⁺/⁴⁺. Under all of the other ECP conditions used, the observed rate was approximately 3x10⁻¹ cm s⁻¹, regardless of the observed surface carbonyl density. It appears that Eu³⁺/⁴⁺ is different from Fe²⁺/³⁺ and V³⁺/⁴⁺ in the conditions that are necessary to achieve activation.

Other possible mechanisms that could lead to observed rate increases include double layer effects, adsorption or preconcentration of analyte in the ECP film and hydrophobic effects. Double layer effects would be expected to depend heavily on the relative position of the redox potential of the species to that of the point of zero charge (pzc) for the electrode. Jaworski measured the point of zero response (pzr, analogous to pzc) of polished GC to be 0.08 V and of oxidized GC (3 min. at 1.8 V in 0.1 M NaNO₃) to be at 0.24 V in 0.1 M NaNO₃ [142]. Though the pzr will vary with surface preparation and electrolyte, it is likely that under most conditions, it will lie inside the range of redox potentials (ca. +0.5 to -0.7 V) of the systems studied here. If double layer effects were responsible for much of the observed activation, one would expect that systems with standard potentials to one side of the pzr would respond oppositely than those on the other side. Because all of the systems showed
accelerated redox kinetics, double layer effects seem unlikely.

Previous semi-integration and digital simulation studies [123,124] as well as the simulations shown here also seem to rule out preconcentration or absorption effects as a primary mechanism of activation. In addition, because the ECP procedures studied here are relatively mild and are expected to form only a thin ECP film (< 100nm) [63], it is unlikely that large quantities of analyte could be preconcentrated. Hydrophobic effects have not been shown to be of great importance in the study of other outer sphere redox systems on GC or on HOPG and therefore seem unlikely here [124].

The fact that the observed rates track carbonyl coverage in concert with the fact that the rates following ECP exceed those predicted by Marcus theory for outer sphere electron transfer [124], leads to the proposed inner-sphere catalysis mechanism involving carbonyl groups. The differences in sensitivity of the different redox couples to the degree of surface carbonyl coverage may be related to differences in the ligand exchange kinetics for the different ions. For rapid electron transfer to occur via an inner sphere mechanism, the interaction between the metal center and the catalytic group should be fast. One measure of ligand exchange kinetics is the water exchange rate constants [137]. Table 12 gives water exchange rate constants for iron, vanadium and europium.
Table 13. Water exchange constants for some metal ions.

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>log $k_{ew}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{2+}$</td>
<td>6.64</td>
<td>143</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>2.20</td>
<td>143</td>
</tr>
<tr>
<td>V$^{2+}$</td>
<td>1.90</td>
<td>143</td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>2.69</td>
<td>143</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>7.8*</td>
<td>137</td>
</tr>
</tbody>
</table>

a. Adapted from Ref. 124  
b. Water exchange rate constant, with literature reference.  
c. Estimated from other lanthanide data.

The water exchange rate constant for Eu$^{3+}$ has not been measured but is estimated at $10^7$-$10^8$ by comparison to other lanthanides. The fact that Eu$^{3+}$ likely has the most rapid exchange kinetics may indicate why its redox rate is most affected by surface introduction of carbonyl groups. Fe$^{3+}$ and V$^{3+}$ both have much lower exchange constants and also show much less of a change in redox rates following mild surface oxidation.

Conclusions

The results presented in this chapter lead to several important conclusions regarding the surface modification that occurs with various activation procedures on GC surfaces and how those modifications affect the observed kinetics of redox couples that are thought to be sensitive to surface oxides. First, it is clear that the pretreatment procedures studied lead to different degrees of damage of the near-
surface GC lattice (as indicated by Raman band intensity and shape) and formation of surface carbonyl groups. Analysis by derivitization of the surface with DNPH and subsequent probing with resonant Raman shows that by merely changing the electrolyte present in the ECP solution, the total signal due to surface carbonyl groups can be increased by more than a factor of ten. It is also apparent that different ECP media can lead to the formation of different types of oxide functional groups. This observation may be particularly helpful in the design of new ECP procedures for the activation of other redox couples. New reactive probes specific for different surface functional groups would also add considerably to the ability to diagnose other specific interactions between redox centers and GC electrodes.

The results described in this chapter lend further support to the hypothesis that the redox reactions of the aquated metal ions; Fe$^{+2/+3}$, V$^{+2/+2}$ and Eu$^{+3/+2}$ are catalyzed surface carbonyl groups on GC electrodes. In all three cases, a positive correlation was observed between surface carbonyl coverages as determined by DNPH derivitization and subsequent Raman analysis, and the observed rate of electron transfer. Although the existence of an acetoacetanoate analogue on the oxidized surface as proposed by Sherwood and Kozlowski [125] cannot be specifically proven to be the active site using this analysis, it is clear that the activation mechanism for these aquated metal ions somehow involves carbonyl groups. Thus far we have not been successful in the preparation of an oxide free GC surface, but it is possible that such a surface would exhibit the very slow $k^0$ observed on Au and Pt in the absence of Cl$^-$. 
CHAPTER V

Laser Induced Microstructural Changes in Glassy Carbon Electrodes

Heterogeneous electron transfer reaction rates may be strongly influenced by the atomic scale surface composition of the electrode as well as its underlying physical and electronic structure. Chapters III and IV have illustrated how a chemical derivitization technique can be used to make possible the Raman spectroscopic analysis of surface bound oxides on glassy carbon. Because only the interfacial region of the electrode is available for oxide formation and subsequent derivitization, this Raman analysis probes a similar depth to that which will influence electrochemical rates. Another facet of the Raman analysis of GC electrodes that has been mentioned in previous chapters but not fully exploited, is the sensitivity of the Raman active phonons to changes in the microstructure of the GC. With excitation wavelengths in the 500nm range, the Raman probe depth for GC is approximately 300Å so that Raman is best categorized as a "near-surface" technique in this application [49]. Previous studies have shown Raman to be a valuable technique for the elucidation of the relationship between graphitic microstructure and electron transfer properties [9-13, 54, 101, 144].

Another technique which has been successfully exploited to study carbon electrode microstructure is Scanning Tunnelling Microscopy (STM) [145-152]. STM
is a true surface technique which is capable of giving atomic scale images which are a convolution of the surface topography and electronic structure. The analysis is carried out by bringing an atomically sharp needle (usually tungsten or a platinum-iridium alloy) to a distance of approximately one angstrom from a conductive surface. A bias voltage is applied between the tip and the surface so that electrons may tunnel between them. The observed tunnelling current is given by equation 5.1 [154]:

\[ j = \left( \frac{e^2}{\hbar} \right) \left( \frac{\kappa_0}{4 \pi^2 S} \right) (V_b) \exp \left( -2 \kappa_0 S \right) \]  

(5.1)

where \( j \) is the current density (A cm\(^{-2}\)), \( s \) is the effective tunneling distance (Å), \( e \) is the electron charge, \( \hbar \) is Planck's constant, \( V_b \) is the applied bias voltage and \( \kappa_0 \) is the decay constant of the wavefunctions in the tunneling barrier. The important point to notice concerning Eq. 5.1 is that the tunnelling current density is exponentially dependent on the distance between the tip and the substrate so that the resolution along the axis of the tip (z) is very high; typically ca. 0.1Å. Tunneling currents are typically on the nA scale, and tip-sample separations are usually 5-15 Å.

Previous chapters in this work have been concerned with the detection and quantification of specific functional groups on carbon electrode surfaces with the goal of relating these functional groups to the enhancement of electron transfer rates for certain redox couples. This chapter will examine some results pertaining to the microstructural effects of some electrode pretreatment procedures which have previously been considered non-oxidative. Specifically, the effects of high power laser treatments on the surface and near surface characteristics of both polished and
previously been considered non-oxidative. Specifically, the effects of high power laser treatments on the surface and near surface characteristics of both polished and fractured GC electrodes will be discussed. The results presented here will attempt to clarify some of the remaining questions regarding the activation mechanism of laser pretreatment procedures.

Laser activation (LA) for the pretreatment of carbon electrodes has been used effectively to improve rate constants of many redox couples at polished GC electrodes [10-12, 52, 53]. Typical procedures employed in this lab and others involve the in situ delivery of three 1064nm pulses of 9ns duration from a Nd:YAG laser at power densities of ca 25 MW cm\(^2\). Rates of as high as 0.8 cm s\(^{-1}\) for the Fe(CN)\(_6^{3/-4}\) redox couple have been reported on polished GC using this technique [12]. Techniques such as Raman spectroscopy, profilometry, scanning electron microscopy (SEM) and STM have all shown that the surface microstructural changes induced by LA at 25 MW cm\(^2\) are minimal [53, 123, 153, 155, 156]. Indirect probes such as measurement of capacitance (C\(^0\)) and adsorption also indicate that LA at 25 MW cm\(^2\) has little effect on surface structure. Rice and McCreery have performed theoretical calculations which indicate that at power densities (PD) of 25 MW cm\(^2\), the local heating caused by the pulse should be insufficient to induce surface melting [54]. At PDs in excess of ca. 30 MW cm\(^2\) however, the calculated surface temperatures were in excess of 4000 K, which is approximately the melting point of GC. These calculations are consistent with experiments where the effects of higher PD pulses have been evaluated. Bowling et. al. showed that at PDs of 40 MW
cm² or higher, significant damage occurred to the lattice of HOPG and that the edge sites created by this treatment could be correlated to activation of some redox couples [10,11]. Recently, McDermott, McDermott and McCreery reported that STM images of polished and polished and laser activated at 25 MW cm² (P/LA25) GC 20 surfaces showed similar surface morphology and roughness but that 70 MW cm² pulses produced a noticeable increase in surface roughness related to the formation of large "protrusions" along polishing scratches on the surface [153]. Fractured surfaces were also found to be quite rough, with the surface being covered with "nodules" having diameters of about 200nm. These nodules have been previously reported on fractured surfaces studied by SEM [155].

Some workers have reported changes to the surface structure of GC upon laser activation at low power densities. Poon et. al. measured a small (ca. 40%) reduction in oxides on P/LA24 surfaces by Scanning Auger spectrometry (SAM) when compared to the polished surface [53]. Also, Pontikos et. al. reported a change in the GC microstructure as measured by Raman spectroscopy for fractured surfaces as a function of increasing numbers of 25 MW cm² pulses [155,157]. In this study, the intensity ratio of the 1360 cm⁻¹ to 1580cm⁻¹ bands in the fractured GC 20s Raman spectrum were reported to increase from the initial fractured value of ca. 1.1 to a value similar to that observed for polished GC 20s (ca. 1.8). These changes were attributed to damaging of the native GC lattice, as displayed by the fractured surface, to the level exhibited by the polished surface. It is in part because of the uncertainty in the microstructural effects of LA that the current research was undertaken.
The results described here are the product of several studies on the tendency of high power density laser pulses to inflict microstructural and surface morphological changes on GC electrodes. Fractured GC surfaces were treated with laser pulses at a variety of PDs so that the degree of surface and near surface modification could be assessed. Raman spectroscopy was used to assess the near surface microstructural damage and STM was used to assess surface modification. Polished surfaces were examined for changes in the surface carbonyl density via the previously developed DNPH derivitization method.

Experimental.

All fractured GC surfaces were prepared from a single 10 cm long, 3 mm diameter GC 20s rod (Tokai, Japan). Approximately 2 mm long segments of the rod were fractured in air from the original rod by shearing with a pair of wire cutters. Though this method is somewhat different than that used for previously reported electrochemical experiments [12, 101, 158], it produced conveniently sized samples for Raman and STM analysis. For comparison, several samples were fractured while immersed in deoxygenated 18 MΩ water and no observable differences were noted by Raman or STM between these surfaces and those fractured in air. Laser activation was accomplished in a teflon electrochemical cell with a quartz window. The cell was filled with deoxygenated 18 MΩ water and then laser pulses were delivered to the GC piece from a Nd:YAG laser (Model 580-10, Quantell) operating at 1064 nm with a pulse duration of 9 ns. Average power density was measured using a Scientech 365...
thermal power meter by allowing the Nd:YAG beam to pass through an aperture of known area with a known pulse duration and frequency. Power densities have been estimated to be accurate within ± 20 percent. Varying numbers of pulses at different power densities were used and will be specified for each experiment. Polished surfaces were prepared from a 1mm thick GC 20s plate as described in Chapter III. Laser activation of the polished GC plates was performed under identical conditions as those used for the fractured surfaces.

Raman spectra of the fractured and fractured plus LA (F/LA) surfaces were acquired using 514.5nm excitation from an Ar* laser (Coherent). The spectrometer was similar to that described in chapter III except that for the experiments described here the ISA 640 monochromator used a 150 line/mm grating blazed at 500nm operated on the second diffraction order. Detection was by a PM 512 CCD array detector (Photometrics). Exclusion of the intense Rayleigh scattering from the spectra was accomplished using two 14mm diameter holographic band rejection filters (Kaiser Optical Systems). Laser powers were typically 200-250 mW at the sample and slit widths of 50μm were used giving a spectral band pass of ca. 8cm⁻¹. For the polished plus laser activation experiments the surfaces were examined under identical DNPH treatment conditions as used in Chaps. III and IV. This includes the use of 488nm excitation, so that direct comparison to the results presented in those chapters is possible.

STM experiments were carried out using a NanoScope II (Digital Instruments, Santa Barbara, CA). Images were obtained using 0.01" diameter Tungsten wire tips.
The W tips were electrochemically etched by immersing in 1.5M KOH to ~3mm and applying 30V rms versus a graphite rod until reaction ceased. All images were obtained under ambient conditions. Constant current mode was used for all images, meaning that as the tip was rastered across the surface, a feedback loop adjusted the tip to sample distance in order to maintain a constant tunnelling current. Fractured GC samples were mounted using silver paste to a conducting base through which a bias voltage was applied. Samples were sonicated in NANOpure water prior to laser treatment or prior to STM examination if no laser treatment was used.

Results and Discussion

Previous reports have drawn a correlation between the features observed in Raman spectra of various graphitic carbons and the degree of order in the material [10, 11, 13, 44]. Specifically, it has been found that for many graphitic carbons, ratio of the area of the Raman band at ca. 1360cm⁻¹, which is commonly called the disorder or "D" band, to the E₂g mode at ca. 1580cm⁻¹ is inversely proportional to the average microcrystallite size (often referred to as Lₐ) [44]. Additionally, Raman analyses of this kind have been successfully used to evaluate how the edge site density of a graphitic surface varies with different electrode pretreatment procedures [9-13, 101, 155]. These analyses have led to the conclusion that graphitic edges are an important contributor to electron transfer kinetics for many redox couples, probably because of disruptions in the electronic structure of the "perfect" graphite lattice. Because of this broad body of previous work, and the inherent sensitivity of
the Raman active graphite phonons to microcrystallite changes, Raman spectroscopy seemed a logical technique for assessing the microstructural effects of increasing laser pulse power densities.

Of most pressing electrochemical concern is the issue of whether LA at the relatively low PD of 25 MW cm$^{-2}$ induces microstructural, and therefore electronic changes in GC electrodes. Fractured surfaces were examined without LA, and following increasing numbers of 25, 70 and 100 MW cm$^{-2}$ Nd:YAG pulses. Figure 49 shows the GC Raman spectra of some of these surfaces. Figure 45A is the Raman spectrum of a native fractured GC surface and 45B is a surface that has been treated with twenty-five laser pulses at 25 MW cm$^{-2}$. For 8 different fractured surfaces, the ratio of the integrated areas of the ca. 1360 cm$^{-1}$ band to the ca. 1580 cm$^{-1}$ was 1.18 ± 0.05 ($N = 18$ spectra). Three different fractured surfaces were treated with twenty-five 25 MW cm$^{-2}$ pulses; the graphite Raman band ratio ($R_A$) for these spectra was $R_A = 1.18 ± 0.04$ ($N = 6$). Under these conditions, LA25 did not seem to affect the GC microstructure to the sample depth probed by the Raman experiment. Figure 45C is the Raman spectrum of a fractured surface following twenty-five 70 MW cm$^{-2}$ laser pulses. The Raman ratio for four different F/LA70 surfaces was measured to be: $R_A = 1.41 ± 0.11$ ($N = 11$). According to the relationship first proposed by Tuinstra and Koenig, this increase in the 1360 cm$^{-1}$ to 1580 cm$^{-1}$ ratio indicates a decrease in the graphitic microcrystallite size; or put another way, an increase in disorder in the GC. A similar increase in the Raman peak ratio was observed by Pontikos [155], though at much lower power densities (25 MW cm$^{-2}$).
Figure 49: Raman spectra of fractured GC surfaces following LA at various power densities. A) no LA; B) 25 x 25 MW cm$^{-2}$; C) 25 x 70 MW cm$^{-2}$; D) 20 x 100 MW cm$^{-2}$. 
is responsible for the changes observed here. Figure 45D is the Raman spectrum of a surface first fractured then exposed to twenty 100 MW cm\(^{-2}\) laser pulses. In this case the Raman peak ratio has been reduced to a level below that of the original fractured surface; \(R_A = 0.93 \pm 0.04\) (\(N = 4\)). This decrease in the Raman band ratio was somewhat unexpected, and may be interpreted in several different ways. First, one might use the relationship of Tuinstra and Koenig and conclude that there has been an increase in the average microcrystallite size and therefore the material is now some more ordered form of carbon. Calculations by Rice and McCreery indicate that, ignoring phase changes, under conditions where a GC surface is exposed to 100 MW cm\(^{-2}\) laser pulses in air, the transient surface temperature increase could approach 12900 K, and that in water this temperature increase would be even greater. Calculations by other workers which allow for phase changes, suggest that high laser power densities are unlikely to cause the temperature of the surface to greatly exceed 4000 K, but instead that melting of the carbon will proceed deeper into the sample as the power density increases [159,160]. Some sort of annealing process which leads a more ordered crystalline structure is consistent with the observed trends in \(R_A\). Conversely, some similarities exist between the Raman spectrum of the F/LA100 surface and that of the ECP’d surface shown in Chapter III, Fig. 23B. Specifically, the broadening of and filling of the "valley" between the carbon Raman bands is very similar to the trends observed for increasingly oxidized surfaces. Since it is difficult to imagine a mechanism by which ECP could increase microcrystalline order, it seems that the relationship of Tuinstra and Koenig may not be applicable here.
Perhaps the surfaces resulting from ECP and LA100 are no longer sufficiently
graphitic to be compared on this basis with other forms of graphitic carbon. This
issue will be dealt with in some more detail later in this chapter.

Fractured surfaces were examined by Raman spectroscopy under conditions
where the power density was held constant and the number of pulses delivered to the
electrode was increased. Figure 46 shows how $R_A$ varied as a function of the number
of pulses delivered at 25, 70 and 100 MW cm$^2$. In figure 46, it is shown that up to
100 pulses of 25 MW cm$^2$ 1064nm laser light had no apparent affect on the Raman
ratio of fractured surfaces. An additional data point not shown in figure 46 was for a
surface exposed to approximately 1200 25 MW cm$^2$ pulses by allowing the laser to
fire onto the electrode at 10Hz for approximately 2 minutes. This surface also
showed no apparent change in the Raman peak area ratio from the initial fractured
value ($R_A = 1.2$). Figure 46 also shows that after ca. 20 pulses, the Raman peak
ratio has changed considerably from the initial fractured value for both the 70 and the
100 MW cm$^2$ surfaces. Perhaps the local heating which is assumed to induce these
microstructural changes is confined to a region relatively close to the surface which
represents only a fraction of the Raman probe depth in the F/LA70 case. In this case,
annealing could occur very near the surface while below the first few atomic layers
the primary effect of the laser pulses might be shock damage. Because the observed
Raman spectrum is an average over approximately 300Å of sampling depth, the
resulting spectrum might not give a true representation of the surface effects of the
laser pulses.
Figure 50. Variation of 1360 cm⁻¹ to 1580 cm⁻¹ ratio with laser pulse power density and number of pulses delivered.
In order to probe the effects of the Nd:YAG laser on the first few atomic layers of the GC surfaces, STM images of the surfaces were examined. Figure 51A through C shows representative images obtained from fractured surfaces. Figure 51A has a scale of 100nm x 100nm shows several of the "nodules" which have been previously observed with SEM and STM [153, 155, 156]. It is important to notice that the z scale, represented by the gray-scale bar to the right of the 2D image, is much smaller than the xy scale. Figure 51B is a smaller (20nm x 20nm) scale scan of the top a nodule like those seen in Fig. 51A. The steps observed on the tops of the nodules in Fig 51A and 51B may represent the edges of overlapping graphitic domains, however no regular height of 3.48Å (d_{002} for GC as determined by XRD [49]) was observed. Figure 51C shows an atomic scale image of a fractured GC surface. Though some periodicity is evident, it is clear that the fractured GC surface displays no long range order. McDermott observed some degree of periodicity in 17 of 38 atomic scale images on fractured GC [156]. For 26 separate regions, an average periodicity of 2.9 ± 0.1 Å was observed. For the image in figure 51C, the periodicity in the regions appearing ordered is also approximately 3Å.

Figure 52 shows images obtained of surfaces which had been laser activated with twenty-five 25 MW cm² pulses. The scales in figure 52 are the same as those in figure 51 for comparison. Figure 48A is a 100nm x 100nm scan which shows the intersection of two nodules on the F/LA25 surface. At this level, no obvious differences between this surface and the fractured surface are evident. Figure 48B shows a 20nm x 20nm scan comparable to that in Fig. 52A. Comparison of the
Figure 51. STM images of fractured GC. A) 100nm x 100nm image of several nodules; B) 20nm x 20nm image of top of a nodule; C) 5nm x 5nm atomic scale image.
Figure 52. STM images of fractured plus LA25 GC. A) 100nm x 100nm image of several nodules; B) 20nm x 20nm image of top of a nodule; C) 5nm x 5nm atomic scale image; D) 5nm x 5nm side view.
Figure 53. STM images of fractured plus LA70 GC. A) 100nm x 100nm image of several nodules; B) 20nm x 20nm image of top of a nodule; C) 5nm x 5nm atomic scale image; D) 5nm x 5nm atomic scale image; E) 2nm x 2nm scale image. Periodicity in atomic scale images is ca 2.4Å.
Fig 53. (continued)
Fig 53. (continued)
fractured with the F/LA25 surfaces reveals that the z scale is roughly the same for these two surface, with the z scale for the F/LA25 surface approximately 10% smaller than that observed in the fractured image. There seem to be a larger number of small features on the F/LA25 surface than that on the fractured surface but it is unclear whether this is due to any laser induced surface modification or cleaning or if it is simply due to sample to sample variability. Figure 52C shows a 5nm x 5nm scale scan of a F/LA25 surface. On this scale this surface appears somewhat more ordered than what was observed for the fractured surface but again, it is unclear whether the differences result from laser induced modification. One possibility is that the removal of debris by the laser has led to more sharply defined features in the STM image of the F/LA25 surface. The steps in figure 52C were measured to be between 3 and 4 Å high so it seems possible that these represent overlapping edges of graphitic regions. Some faint periodicity is visible on flat regions in this image and was also observed on other images from similarly prepared surfaces. No long range order was observed however in 14 atomic scale images obtained from 3 separate surfaces.

The images obtained on fractured surfaces which were exposed to twenty-five 70 MW cm⁻² Nd:YAG pulses are shown in figure 53. One large nodule is prominent in the 100nm x 100nm scan shown in figure 53A. Comparison of this image with those in figures 51A and 52A reveals some apparent morphological changes in the F/LA70 image. The top of the nodule seems to be covered with rather large plate like structures, each of which appears quite flat at this resolution. This is quite different from the fractured and F/LA25 surfaces (51A and 52A) for which the tops
of the nodules appeared striated with relatively narrow ridges. Figure 53B shows a 20nm x 20nm image of a F/LA70 surface and again some clear differences exist between this image and those obtained from fractured and F/LA25 surfaces. The surface in Fig. 53B appears to be covered in rather large, smooth regions which are stacked on top of each other. Measurement of some of these steps revealed them to be approximately 3.5Å in height. Notice also that the overall z scale in this image is approximately half that of the images shown in figures 51B and 52B. Perhaps most striking however are figures 53C, 53D and 53E. In these atomic scale images of F/LA70 surfaces, a much higher degree of order is evident than has previously been observed on GC. In Fig. 53C, several large regions of order are clearly evident. Within these regions an average periodicity of 2.6 ± 0.1 Å was obtained for five separate measurements. Figure 53D shows a region of order which is at least 20 Å² in size. Six separate measurements in this large region of order gave an average periodicity of 2.38 ± 0.11 Å which is very similar to basal plane HOPG (ca. 2.46 Å). Toward the bottom of Fig. 53D there appears to be a step edge with a second ordered sheet below. The height of this step was measured to be ca. 4 Å which is considerably larger than the interlayer spacing of HOPG (d_002 = 3.354 Å [49]). Figure 53E is a 2nm x 2nm scan of one of the very ordered regions found on F/LA70 surfaces. In this image a periodicity of 2.5 - 2.6 Å was measured. Notice also the large apparent increase along the z axis near the apparent step edge, this increase in tunnelling current is similar to that observed by McDermott near HOPG defect sites. Apparently discontinuities in the graphitic lattice lead to significant
perturbation of the electronic structure of the carbon which result in increased tunnelling current. The images in Fig. 53 are profoundly different than any that have previously been observed on GC surfaces. Because of the high surface temperatures which are likely to occur immediately following the 70 MW cm\(^2\) laser pulse (at least 4000 K [54]), rapid surface annealing by the laser pulses seems plausible. Such annealing might result in the more ordered surfaces observed in Fig. 53. The increase in order observed in the F/LA70 STM images, however, seems to be inconsistent with the Raman results obtained on similarly treated fractured surfaces. It seems probable that this discrepancy is related to the large difference in probe depth between the two techniques. Raman will probe many atomic layers deeper than STM so that microstructural deformation caused by the rapid melting and cooling of surface layers could dominate the observed Raman spectrum. As was previously stated, it is also possible that the relationship proposed by Tuinstra and Koenig is limited in its applicability so that it may not be possible in this case to draw direct correlation between the graphitic Raman band area and the average microcrystallite size. Regardless of the absolute meaning of the band areas for these laser damaged materials, it is clear that both STM and Raman support the conclusion that LA at 25 MW cm\(^2\) causes little if any morphological changes to the GC surface. These results are consistent those previously obtained using SEM, STM, Raman, XPS, profilometry and capacitance measurements, and lend further support to the hypothesis that morphological changes are not required for activation [12, 17, 54]. At power densities 70 MW cm\(^2\) however, both Raman and STM measurements indicate severe
perturbation of the GC structure.

One surface structural change that has been reported to occur following LA at ca. 25 MW cm\(^{-2}\), is the reduction of total surface oxides as measured by SAM [53]. Poon and McCreery reported that the oxygen to carbon ratio of a polished GC 20 surface was reduced by ca. 38% following one 24 MW cm\(^{-2}\) 1064nm laser pulse. Another potentially important observation was made by Rice and McCreery [54] and also by McDermott [123] where it was found that LA at 70 MW cm\(^{-2}\) had the effect of partially activating polished GC surfaces for the ferrous/ferric couple. Because of the previously demonstrated relationship between surface carbonyl groups and redox kinetics the Fe\(^{2+}/^+\), it is of interest to determine how LA affects the surface density of carbonyl groups on GC. The DNPH analysis described in Chapters III and IV was applied to polished surfaces following exposure to 10 pulses of either 25 MW cm\(^{-2}\) or 70 MW cm\(^{-2}\). Figure 54 shows the Raman spectra of polished, polished and DNPH treated, P/LA25 and DNPH treated, and P/LA70 plus DNPH treated surfaces. Notice that the polished and P/LA25 surfaces appear to have similar reactivity towards DNPH whereas the P/LA70 surface shows much more intense DNPH adduct bands. Figure 55 shows the DNPH adduct bands which result from subtracting the untreated GC spectrum from the spectra shown in figure 54B - 54D. Though the spectral features are similar for all three surfaces, the total carbonyl density has been decreased by about 25% following LA at 25 MW cm\(^{-2}\) and increased by approximately a factor of three on the LA70 surface. Table 14 lists the observed intensities (300s integration) of the 1140cm\(^{-1}\) DNPH adduct band for the different
Figure 54. Raman spectra of polished GC surfaces following LA at various power densities and subsequent DNPH treatment. A) Polished only; B) polished plus DNPH; C) polished plus LA25 plus DNPH; D) polished plus LA70 plus DNPH.
Figure 55. Raman spectra of polished GC surfaces following LA at various power densities and subsequent DNPH treatment. Graphite Raman bands have been subtracted out. A) Polished plus DNPH; B) polished plus LA25 plus DNPH; C) polished plus LA70 plus DNPH.
The results given in table 13 agree well with the previous reports of the effects of LA at different PD's on surface oxides. Similar to the observations of Poon, a reduction in surface carbonyl group density is shown to occur following LA at 25 MW cm$^2$. Though this power density is not expected to be sufficiently high to induce surface melting, the pulses appear to be of sufficient power to caused removal of some of the surface oxides. It is possible that GC microparticles remain on the fractured surface and that these particles are removed by the LA procedure. If these particles exist, their high surface area to volume ratio would be likely to lead to a high overall oxide density. The results presented here regarding P/LA70 are also consistent with those presented by McDermott, in that the increase in surface carbonyl density observed via the DNPH technique is roughly equivalent to that observed for surfaces ECP'd in
NaNO₃ or HNO₃. It is not surprising then that LA at this power density lead to some degree of activation of the Fe⁺²⁺⁺⁺ redox couple [55,123].

Conclusions

The results of the work described in this chapter have several important implications for the field of carbon electrochemistry. First, this work lends strong support to the conclusion that 1064nm pulsed laser treatments at or below power densities of 25 MW cm⁻² induce no observable microstructural changes to GC electrodes. Any changes which do occur appear to be related primarily to cleaning of the electrode of surface bound species and debris. The findings of this research are consistent with previous studies done via profilometry, SEM and STM which have all shown no significant change in surface topography following 25 MW cm⁻² treatments. The report of LA at 25 MW cm⁻² causing an increase in the 1360cm⁻¹ to 1580cm⁻¹ ratio [155] seems to have been incorrect. As the changes in Raman peak area ratio are not large, it is possible that the recent improvements which have occurred in Raman hardware were necessary for accurate assessment of this effect. The previous report of microstructural changes at 25 MW cm⁻² was based on Raman spectra which were collected using a single channel instrument [155]. The resulting spectra had rather low signal to noise ratios and apparently were misinterpreted.

A second important result is that it is clear that there exists a threshold power density between 25 MW cm⁻² and 70 MW cm⁻² where microstructural changes are evident both by Raman spectroscopy and STM. It seems likely that these changes are
related to a large increase in the surface temperature following interaction with the laser pulse, and that the resulting microstructural modifications involve both annealing of the carbon to form a more ordered lattice and thermally induced shock waves which may lead to disordering of the lattice. It was proposed that the annealing effect would be more prevalent nearer to the surface of the GC, and that as one probed deeper into the sample, shock wave induced disorder would become more evident.

The final section of this chapter showed that LA can have an effect on the density of carbonyl groups present at a polished GC surface. A small (ca 25%) reduction in the surface carbonyl group density was observed following ten 25 MW cm$^2$ laser pulses. This result is consistent with previous observations where a 38% reduction in total surface oxides was observed by SAM following LA at 24 MW cm$^2$. DNPH analysis of a polished surface following LA at 70 MW cm$^2$ showed an increase in surface carbonyl density of approximately a factor of three. It is possible that as the GC cools from a molten state into a solid state that reaction with water to form carbonyl groups at edge sites is favorable. The observed increase in surface carbonyl groups following LA at 70 MW cm$^2$ is consistent with the observation that this power density was capable of causing partial activation of the Fe$^{2+}$/Fe$^{3+}$ redox couple at polished electrodes.
SUMMARY

The unifying theme of the work presented here is the characterization of carbon electrode surfaces with the intention of developing relationships between surface and near-surface microstructure and observed electrochemical reactivity. An array of different electrode pretreatment procedures which are known to affect electrochemical kinetics under different circumstances were applied to different carbon surfaces so that the resulting surface structural changes could be evaluated. Carbon surfaces were evaluated following pretreatment for changes in surface carbonyl groups, changes in near-surface microstructure and also for changes in atomic scale structure of the interfacial region of the electrode. For a variety of GC surfaces, a correlation was drawn between the density of particular surface functional groups and observed electrochemical reactivity.

In Chapter II, techniques were developed to improve the quantitative reliability of Raman spectroscopy so that quantitative surface analysis was possible. An optical geometry was developed and characterized which gives comparable levels of reproducibility and ease of sampling to fiber optic probes, while retaining great versatility and freedom from fiber background. The high reproducibility of this Raman sampling technique made quantitative analysis possible using either internal or external standards. To improve the convenience of such quantitative analyses, a large
number of Raman cross sections were measured and collected into a single reference
table. Development of a reproducible sampling technique which could be easily
applied to surfaces, and the establishment of cross section standards were both critical
developments necessary for the success of experiments described later in this work.

A chemically specific and quantitative derivitization technique involving
2,4-dinitrophenylhydrazine (DNPH) and utilizing the specificity and sensitivity of
resonance Raman was developed to probe the production of surface carbonyl groups
under various electrode preparation conditions. Several different carbon surfaces
including basal plane HOPG, polished GC and fractured GC were analyzed for their
native surface density of carbonyl groups. It was then demonstrated that one common
electrochemical pretreatment (ECP) procedure led to a large increase in the surface
density of carbonyl groups. To assess the structure of the DNPH-carbon adduct, a
number of model carbonyl containing molecules were reacted with DNPH and the
resulting model adducts analyzed by Raman under conditions like those used for the
DNPH-carbon adduct. By comparison, it was concluded that the DNPH-carbon
adduct exists in a delocalized form that is spectroscopically similar to the adduct
formed between DNPH and 1,4-naphthoquinone. The DNPH-carbon adduct was
found to be structurally insensitive to large changes in pH, implying that the
delocalized anion form of this structure is very stable.

The quantitative probe of surface carbonyl groups was then used to evaluate a
proposed catalytic mechanism involving an inner sphere reaction pathway for aquated
metal ions at oxidized carbon surfaces. Previous work by McDermott and Kneten
showed that surface oxides were necessary in order to observe fast electron transfer kinetics for a series of aquated metal ions at carbon electrodes [17, 123, 124]. A model catalytic site which included a carbonyl functionality was proposed based on previous XPS investigations [125]. To test the importance of carbonyl groups in the activation of these redox couples, a series of pretreatment procedures were evaluated via the DNPH derivitization technique to determine the relative increase in carbonyl groups. It was shown that for Fe$^{+2/+3}$, V$^{+3/+2}$ and Eu$^{+3/+2}$, there exists a positive correlation between surface carbonyl group density and electron transfer rates with higher rates being associated with faster rates. In the case of Fe$^{+2/+3}$, the relationship was shown to be linear.

Finally, the effects of laser treatments on carbon surfaces were evaluated for induced surface and near surface changes in the carbon. A combination of normal Raman spectroscopy, scanning tunneling microscopy (STM) and resonance Raman spectroscopy of the DNPH-carbon derivative, were used to show the effects of increasing power densities of 1064nm, Nd:YAG laser pulses on GC surfaces. Through these studies, it was concluded that laser activation (LA) at 25 MW cm$^{-2}$ has little effect on the surface or near-surface microstructure of fractured GC but may lead to a small decrease in the surface carbonyl group density on polished GC surfaces. It was found, however, that there exists a threshold power density between 25 and 70 MW cm$^{-2}$ where pronounced microstructural changes begin to occur. These changes were made evident on fractured surfaces by an increase in the graphite Raman band area ratio and also increase in the observed atomic scale ordering as
measured by STM. The STM images were particularly striking because the surface structure resembled ordered graphite more than GC implying that a surface annealing mechanism may be at work. Polished surfaces were observed to have an increased carbonyl group density following LA at 70 MW cm$^2$. 
This appendix will give the experimental details necessary to perform the intensity calibration described in chapter II. The intensity calibration procedure is used to correct raw Raman data for variations in instrumental efficiency with wavelength. First, a detailed description of how the intensity calibration is performed on a day to day basis will be given. Second, the computer program which was used to perform the calculations will be shown.

As described in chapter II, the standard by which the instrumental response function is determined is a fiber optic which delivers the output from a tungsten source to the focal spot of the spectrometer optics. This fiber optic source has a known specific intensity ($I_0$) which has been fitted to a sixth order polynomial for the computer program (INTCAL) given below. In practice, the white light spectrum, $S_p$, is collected under identical spectrometer settings as the Raman spectra, $S_{Raman}$, which are to be corrected. This involves positioning the fiber exactly at the focal point of the spectrometer so that maximum intensity from the source is observed at the detector. One then collects the "spectrum" of the standard white source for use in correction of Raman spectra. Use of the INTCAL program involves first calibrating both the Raman spectra and the white light spectrum so that they are expressed in frequency shift from the laser line. One then modifies the white light spectrum to include the
number of x,y data pairs (equal to the number of CCD pixels) in the first line of text, and the laser line wavelength in the second line of text. The INTCAL program reads the white light data file and constructs a specific intensity "spectrum" from the polynomial which approximates $L_p$ which has the same number of points as the spectra and covers the proper wavelength range. The intensity corrected Raman spectrum, $S_{corr}$ is calculated by multiplying each data point in $S_{obs}$ for the ratio of $L_p$ to $S_p$ according to:

$$S_{corr} = \left( \frac{S_{obs}}{S_p} \right) L_p$$  \hspace{1cm} A.1$$

This procedure has the effect of dividing out all changes in spectrometer efficiency as a function of wavelength. The benefits of such a procedure are described in detail in chapter II.

The computer program INTCAL was written by Prof. R. L. McCreery and Mark Fryling with additional development testing from Christopher J. Frank.
INTCAL

10 REM Conducts intensity calibration for spectral
20 REM data from CCD's, based on a spectrum of white light
30 REM from a calibrated source
40 REM Arrays are two dimensional, X and Y:
50 REM
60 REM SFI(1152,1): spectrum of calibrated white source
70 REM PHIF(I,1152): actual light flux from source
80 REM SSI(1152,1): raw spectrum from sample
90 REM PHIS(I,1152,1) corrected sample spectrum
100 REM
110 REM The procedure is as follows:
120 REM Read in SFI and laser wavelength
130 REM 2. Convert to absolute wavenumbers
140 REM 3. Construct PHIF from polynomial coefficients
150 REM based on absolute calibration vs. absolute wavenumbers
160 REM 4. Convert sample spectrum to wavenumbers
170 REM 5. Calculate corrected spectrum by:
180 REM PHIS = SS*PHIF/SF
190 REM 6. output corrected spectrum as Raman shifts
200 REM
210 REM Variables:
220 REM n% = number of spectral points
230 REM LLAMB = laser wavelength in nm
240 REM LWNUM = laser frequency in wavenumbers
250 REM
260 REM Files:
270 REM ICAL.DAT: calibration data as follows:
280 REM
290 REM N%
300 REM llamb!
310 REM SFI(X1) SF!(Y1)
320 REM SFI(X2) SF!(Y2)
330 REM ...
340 REM SFI(XN) SF!(YN)
350 REM
355 REM SOURCE.CAL: SOURCE POLYNOMIAL COEFFICIENTS
360 REM A6
370 REM A5
380 REM A4
390 REM ...
390 REM A0
410 REM SPEC.RMN: SAMPLE RAMAN DATA AS RAMAN SHIFT
420 REM
430 REM SPEC.CAL: OUTPUT DATA CALIBRATED FOR INTENSITY
440 REM
450 DIM SF!(1750,1)
460 DIM PHIF!(1750,1)
470 DIM SS!(1750,1)
480 DIM PHIS!(1750,1)
490 OPEN "ICAL.DAT" FOR INPUT AS 01
500 INPUT# 1,N%,LLAMBI!
510 LWNUMI=1/(LLAMBI!*0000001)
520 FOR L%=0 TO N%-1
530 INPUT#1, SF!(L%,0),SF!(L%,1)
540 NEXT L%
550 CLOSE #1
560 REM
570 REM READ IN POLYNOMIAL COEFFICIENTS
580 REM
590 OPEN "SOURCE.CAL" FOR INPUT AS 02
595 REM
600 INPUT #2,A5!
610 INPUT #2,A4!
620 INPUT #2,A3!
630 INPUT #2,A2!
640 INPUT #2,A1!
650 INPUT #2,A0!
660 REM
670 CLOSE#2
680 REM
690 REM CONVERT SF! TO ABSOLUTE WAVENUMBER AXIS
700 REM
710 FOR L%=0 TO N%-1
720 SF!(L%,0)=LWNUMI-SF!(L%,0)
730 NEXT L%
740 REM
750 REM CONSTRUCT STANDARD SOURCE OUTPUT FOR NEEDED WAVENUMBERS
760 REM
770 FOR L%=0 TO N%-1
780 PHIF!(L%,0)=SF!(L%,0)
790 XI=1E+07/SF!(L%,0)
791 REM
795 REM POLYNOMIAL COEFFICIENTS ARE FOR FIBER OUTPUT
796 REM PLOTTED VS. NANOMETERS
799 REM
800 PHIF(L%,1) = A0! + A1!*X! + A2!*X!^2 + A3!*X!^3 + A4!*X!^4 + A5!*X!^5 + A6!*X!^6
810 NEXT L%
820 REM
830 REM READ IN RAW SAMPLE SPECTRUM
840 REM,
850 OPEN "SPEC.RMN" FOR INPUT AS #3
860 FOR L% = 0 TO N%-1
870 INPUT#, SS!(L%,0), SS!(L%,1)
880 NEXT L%
890 CLOSE #3
900 REM
910 REM CALCULATE CORRECTED SPECTRUM AND OUTPUT
920 OPEN "SPEC.CAL" FOR OUTPUT AS #1
930 FOR L% = 0 TO N%-1
940 PHIS!(L%,0) = LNUM! - SF!(L%,0)
950 PHIS!(L%,1) = SS!(L%,1)*PHIF(L%,1)/SF!(L%,1)
960 PRINT#, USING "0000.00 -------##.####"; PHIS!(L%,0), PHIS!(L%,1)
970 NEXT L%
980 CLOSE #1
990 SYSTEM
1000 END
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