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SURFACE RAMAN SPECTROSCOPY: INSTRUMENTATION AND APPLICATION IN SURFACE AND CORROSION SCIENCES

DISSERTATION

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

by

Jun Zhao

* * * * *

The Ohio State University

1997

Dissertation Committee:
Professor R. L. McCreery, Advisor
Professor P. K. Dutta
Professor P. K. Gallagher

Approved by

Advisor
Department of Chemistry

R L McCreery
This thesis discusses both instrumentation developments and applications of Raman spectroscopy. In the second chapter of this dissertation, the application of Raman spectroscopy to the study of the migration and corrosion inhibition effect of chromate conversion coatings (CCC) on an aluminum aircraft alloy is discussed. This alloy, designated as AA-2024-T3, is very susceptible to corrosion, therefore it is treated with a chromate solution to form a thin film prior to use. The CCC film offers the alloy an outstanding corrosion resistance and self-healing properties. Combined with X-ray photoelectron spectroscopy (XPS) and electrochemical techniques typically exploited in corrosion science, Raman spectroscopy revealed that the self-healing process is based on the chromate release of the CCC film, and corrosion inhibition effect of the chromate adsorbed on the alloy. It is found that the released chromate works like a guided missile to passivate corrosion sites, and prevent pitting corrosion at very low bulk concentrations.

Chapter 3 deals with Raman spectroscopic instrumentation. By combining a Sagnac interferometer and a charge coupled device (CCD), a multichannel Fourier transform (MCFT) Raman spectrometer is developed, which offers the advantages of both multichannel technique and interferometry, and accomplishes the goal of a large sampling area and simultaneous data collection in a solid state device. The principle,
characterization, and possible applications of the multichannel Fourier transform Raman spectrometer are discussed.

In chapter 4, a method to determine surface molecular orientations is developed, using polarized Raman spectroscopy. This method expands the utility of a previously developed method, and enables the determination of adsorbate orientation of all planar molecules. Methylene blue (MB) adsorbed on highly ordered pyrolytic graphite (HOPG) is used as an example. It is found that the monolayer MB molecules all adsorb flat on HOPG surface.
Dedicated to my wife,

Rongkun
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VITA

November 25, 1968 .......................Born, Lixian, Hebei, China

1992 .................................................B. S. in Chemistry,
University of Science and Technology of China,
Hefei, Anhui, China

1992-1994........................................M. S. Chemical Physics. University Fellow, Graduate Research and Teaching Associate, Chemical Physics Program, The Ohio State University, Columbus, Ohio

1994-present.....................................Research Associate, Department of Chemistry, OSU

PUBLICATIONS

Research Publication


**FIELD OF STUDY**

Major Field: Chemistry
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CHAPTER 1

INTRODUCTION

This thesis deals with Raman spectroscopy on surfaces, particularly those involved in electrochemistry. Raman spectroscopy is the study of the spectral components of the light inelastically scattered by matter. As schematically shown in figure 1.1, when a monochromatic light strikes a material, the scattered light has several frequencies. Beside elastic scattering, the scattered light contains frequency components different from the incident light, which is named "Raman scattering" after its discoverer. Like IR spectroscopy, a Raman spectrum is characteristic of the scattering material and can be used to obtain compositional and structural information, hence Raman spectroscopy should be a very useful analytical technique. A very attractive feature of Raman spectroscopy is the easy sample preparation. Spectra of samples of any form and size can be obtained without going through complicated preparation procedure, such as those required by IR spectroscopy and many high-vacuum techniques. Water, which is troublesome for IR spectroscopy, is not a problem for Raman. Such features are uniquely suited for in-situ observation or in-line industrial quality control. Both the excitation light and the Raman scattered light are transmittable by silica based optical fibers, hence remote
monitoring is possible. Equipped with a microscope, high spatial resolution can be achieved. Even without a microscope, moderate resolution up to 20 μm can be obtained.

On the other hand, Raman scattering is a very weak effect, up to $10^{12}$ times weaker than the incident light. Raman spectroscopy on surfaces is particularly troublesome, due to the small amount of analytes available. For more than half a century, poor sensitivity has hindered Raman spectroscopy from developing into a major analytical technique, and Raman spectroscopy remained largely a laboratory research technique since the phenomenon was discovered in 1928.

The invention of lasers in 1960's is a major milestone in the development of Raman spectroscopy. Lasers are monochromatic, intense, coherent, and collimated, making them ideal as excitation sources. However, the invention of laser alone was not enough to bring the sensitivity to a practical level for routine analysis. The discovery of surface enhanced Raman scattering (SERS) aroused some excitement in the spectroscopic community. It was observed that up to a million fold increase in Raman scattering efficiency can be achieved when some compounds are adsorbed on silver surface. However, the mechanism of this enhancement is not clear, and the requirement of noble metals (silver, gold, copper) as substrates has restricted SERS to somewhat limited analytical use.

Resonance Raman spectroscopy (RRS) is another way of enhancing sensitivity. When the laser wavelength matches an electronic absorption band of a molecule, the Raman scattering can be greatly enhanced by way of electronic resonance. RRS does not
require adsorption on nobles metals, and when a suitable laser wavelength is available, it is a more practical way of increasing sensitivity than SERS.

A major development in the hardware occurred in the 1980s, when multichannel detectors replaced single-channel photo-multiplier tubes. Suddenly the whole spectrum can be obtained at once, without having to scan the monochromator step by step. This instantly reduced the acquisition time (or increased the sensitivity) by a factor of a thousand or so. Today almost all dispersive Raman spectrometers use charge coupled devices (CCD) as detectors, and the number of channels is typically 1024. Other advances include the utility of high efficiency interference and holographic filters, which allowed the construction of compact, single-stage spectrographs of high collection capability. This further improves the sensitivity by several fold.

With all these technical advancements, Raman spectroscopy has recently been experiencing a major renaissance. The number of commercial Raman spectrometer companies has increased from 3 to 10 since 1985, with an increase in sales of about a factor of 5. The sensitivity has reached such a level that fast, routine analysis is no longer a challenge. As soon as sensitivity is not a problem, Raman spectroscopy's other merits begin to stand out. As noted earlier, these include easy sampling, in-situ capability, compatibility with water, and good spatial resolution. These features are highly desirable for study of on-going events, and surface phenomena.

This thesis discusses both instrumentation developments and applications of Raman spectroscopy. In the second chapter of this dissertation, the application of Raman spectroscopy to the study of the migration and repassivation effect of chromate
conversion coatings (CCC) on an aluminum aircraft alloy will be discussed. This alloy, designated as AA-2024-T3, is very susceptible to corrosion, therefore is treated with a chromate solution to form a thin film prior to use. The CCC film offers the alloy an outstanding corrosion resistance. However, the mechanism is not clear. Because corrosion is a heterogeneous surface phenomenon, and it happens in aqueous environment, Raman spectroscopy is an attractive probe. Its merits are further enhanced by the fact that chromium compounds are colored, and hence are amenable to RRS. Very small amount of chromates can be detected in a very short time. Combined with X-ray photoelectron spectroscopy (XPS) and electrochemical techniques typically exploited in corrosion science, Raman spectroscopy can provide vital information on the mechanism of corrosion resistance of the CCC film.

The third chapter of this thesis deals with instrumentation. It is often observed when dealing with surface Raman spectroscopy, or even Raman on bulk samples but at high laser powers, that the Raman peak intensities change with time. This is caused by either photo or thermal degradation of the material exposed to the highly focused laser spot. Such is the case of the CCC film when a 514 nm excitation source was used. To reduce this problem, one needs to either decrease the laser intensity, or spread out the laser such that it is not so tightly focused. Either way, this ends up decreasing the sensitivity. The reason in the former case is obvious. In the latter case, it is because all dispersive spectrometers has a narrow entrance slit, typically 50 µm, and all Fourier transform spectrometers require a certain degree of beam collimation inside the interferometer, which limits the size of the detector and therefore the sampling area.
Spreading the laser beyond that size limit wastes the laser light. To get around this problem would require fundamental changes to the way light is collected by the spectrometer. Chapter three describes a new kind of Raman spectrometer that combines the advantages of both multichannel technique and interferometry, and accomplishes the goal of large sampling area. The principle, construction, software, operation instruction and characterization of the multichannel Fourier transform Raman spectrometer will be addressed in chapter 3.

In addition to compositional and structural information, Raman spectroscopy has more to offer. Both theoretical treatment and experimental observation have shown that Raman scattering is orientation sensitive. This has to do with the fact that both the excitation source, i.e. the laser, and the scattered light are spatially polarized. In addition, the molecules under study may be oriented to some extent. Nature offers abundance of examples, such as cell membranes, self assembled monolayers, and liquid crystals. In these cases and others, the interaction of polarized light with oriented molecules produces complicated Raman polarization, consequently, analyzing polarized Raman spectra may give clues about the molecular orientation. Such information is very important to studying molecular interactions, particularly at surfaces. In a previous thesis [1] and a publication[2], the author has shown that orientation of monolayers of highly symmetric metallophthalocynine molecules adsorbed on graphite can be probed, with polarized Raman spectroscopy. Unfortunately, not all molecules are as symmetric as metallophthalocynines, and for these less symmetric molecules, the method developed previously failed to yield useful information [1]. To expand the utility of this method to
these molecules, the previously devised experiment was slightly modified, and a simple theoretical explanation is given in chapter four, for all planar molecules. A molecule with the symmetry of the water molecule, namely methylene blue, was used as an example. Excellent results revealed orientation information that was not obtained before, and this completes the development of Raman polarization experiment for molecular orientation determination at surfaces.
Figure 1.1: Schematic representation of Raman scattering.
CHAPTER 2

THE SELF-HEALING ANTI-CORROSION MECHANISM OF CHROMATE CONVERSION COATING ON AA-2024-T3 ALLOY

2.1 INTRODUCTION

2.1.1 Background

Chromates have been used in the metal finishing industry for almost 100 years. The chromate ion is an excellent corrosion inhibitor for a range of metals including aluminum, zinc, steel, cadmium, and magnesium. It is used in chromate conversion coatings (CCC), as paint pigments, primers, and in sealing anodized and phosphate coatings. Chromate inhibitors are also used by the water treatment industry, mostly for recirculating waters (e.g. of cooling towers, rectifiers, and internal combustion engines).

Of particular interest to the aircraft industry is the corrosion protection of the high copper content aluminum alloy AA-2024, which is used to construct airplanes. The composition of this alloy is listed in table 2.1. The added copper gives the alloy strength, however, it also makes the alloy more susceptible to corrosion. To inhibit corrosion, the alloy is typically passivated with CCC prior to painting and adhesive bonding. On top of the CCC, the alloy may be further protected by coating with a layer of primer and then
paint, both of which may contain chromate inhibiting pigments. This has been widely practiced for several decades.

<table>
<thead>
<tr>
<th>%Cu</th>
<th>%Si</th>
<th>%Mn</th>
<th>%Mg</th>
<th>%Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4</td>
<td>0.5</td>
<td>0.6</td>
<td>1.5</td>
<td>balance</td>
</tr>
</tbody>
</table>

Table 2.1. Composition of AA-2024-T3 alloy [3].

It has been recognized over the past two decades that chromates are both highly toxic and carcinogenic[4, 5]. For example, oral digestion of chromate can cause kidney failure, liver damage, blood disorders and even death. Prolonged exposure of skin to chromates can cause rashes, blisters and ulcers. Chromates can also enter the body by inhalation, and may eventually cause lung cancer. Because of the high toxicity, chromates are now becoming regulated by government agencies. The use of chromates as corrosion inhibitors and the inevitable waste disposal problem is one of the major reasons the metal finishing industry is being targeted by US EPA as one of the most significant contributors to environmental pollution. Although improvement in handling and waste disposal procedures may to some extent reduce the problem, it is likely that more stringent regulations are yet to come, and the development of chromate replacements will become the only effective option both environmentally and commercially.

As one major consumer of chromate inhibitors, the aircraft industry has actively engaged in research for a chromate replacement for years. The early focus of development
was centered on the metal oxyanion analogues of chromates, such as molybdates, tungstates, vanadates, and permanganates. Many patents have been filed based on the use of these compounds, however none of the formulations proposed are as effective as chromates, particularly on aluminum alloys. For example, Bibber has developed a conversion coating based on the use of potassium permanganate, which is very effective in protecting aluminum alloys[6, 7]. Salt spray testing results indicated a significant level of corrosion protection on AA-2024 alloy, but still not as good as the CCC, and the procedure is much more complicated.

The US Air Force has been particularly interested in improved and environmentally friendly chromate replacements, due to a combination of regulation pressures, increased service life requirements of the fleet, and the cost of preventive maintenance. The failure of these early efforts has forced the industry to take a more careful look at chromates. The report of the Blue Ribbon Advisory Panel on Aircraft Coatings indicated that “developing a better understanding of the mechanisms of aluminum corrosion and chromate inhibition is a top priority and a prerequisite for the development of a successful replacement”[8]. For this reason, the Air Force has decided to invest in a research endeavor, put up together by an international, multidisciplinary consortium of researchers from academia, industry, and a national lab. It is expected that “a result of this program will be a comprehensive understanding of the role of chromate in the corrosion protection of Al alloys, which will provide the Air Force a basis for reasoned approach toward developing an effective, environmentally sound replacement for chromate”[8].
Raman spectroscopy is well suited to the investigation of CCC chemistry for a number of reasons. It can provide specific molecular information. Analysis of the line width and shape of Raman features can yield structural and phase information. Raman with 515 nm laser excitation is very sensitive to chromate and dichromate species. It does not require sample preparation, and is suitable to in-situ observation in aqueous solutions. Thus it is an excellent probe to study the behavior of the CCC film in a corrosive environment. Equipped with a microscope, it can provide spatial resolution as high as 1μm, thus is superior to many other techniques for study of localized corrosion.

2.1.2 Corrosion Economics

Corrosion is the destructive result of chemical reaction of a metal or metal alloy and its environment [9]. Most metals are extracted chemically from their natural forms, i.e. minerals. In opposition to the process of metal production, corrosion is a process during which metal is returned to its natural state, thus it should be prevented. Corrosion is the leading cause of degradation and destruction of automobiles, airplanes, power plants, chemical manufacturing and processing plants, concrete structures, and many others involving metal parts. The economic cost of corrosion is enormous. In the United States alone, an annual cost of $70 billion was estimated in 1976 [10], while an estimated cost of $126 billion was projected by the Department of Commerce in 1982 [11]. In addition to this direct cost, corrosion also takes a significant toll in many indirect costs, such as plant downtime, environmental pollution, and even human lives as results of fatal accidents.
Therefore corrosion is a very important subject for electrochemists, material scientists and engineers.

Corrosion is a complicated process, and the knowledge accumulated over the years about corrosion science and corrosion prevention is enormous. To familiarize the readers with the concepts mentioned in the experimental section, a brief review is given in this introduction, concerning a few subjects closely related to the methods used in this investigation.

2.1.3 Fundamentals of Corrosion Science

**Electrochemical Nature of Aqueous Corrosion** Nearly all metal corrosion involves charge transfer in aqueous solutions. The whole reaction can be divided into two parts, the metal dissolution, which is called the anodic reaction, and the reduction of oxidizing agents, which is called the cathodic reaction. Accompanying these two reactions are the electron transfer inside the metal and ionic charge transfer in the electrolyte. The anodic reaction can be uniformly written as

\[
M \rightarrow M^{n+} + ne^-
\]  

While the cathodic reaction is one of a few, and is either oxygen reduction,

\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]  

2.2a

and

\[
O_2 + 4H^- + 4e^- \rightarrow 2H_2O
\]  

2.2b

or, reduction of \( H^- \) or water,
\[ 2H^+ + 2e^- \rightarrow H_2 \tag{2.3a} \]

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2.3b} \]

or, in some rare cases the reduction of a dissolved oxidizer. The rate of these reactions are governed by fundamental electrochemical principles.

Consider the half cell reaction (2.1) in its reversible form. The potential at which M and \( M^{n^-} \) are at equilibrium has many names, including equilibrium potential, reversible potential, rest potential, null potential, and it is noted as \( E_n \) here. At any other potential \( E \), the reaction proceeds predominantly in one direction. The relationship between the rate of reaction, or the current density \( i \), and the driving force represented by the overpotential \( \eta = E - E_n \), can be described by the classical Butler-Volmer equation:

\[ i = i_0 \exp \left\{ \frac{\beta nF \eta}{RT} \right\} - i_0 \exp \left\{ -\frac{(1 - \beta) nF \eta}{RT} \right\} \tag{2.4} \]

Where \( i_0 \) is the exchange current, \( F \) is the Faraday constant, and \( \beta \approx 0.5 \) is a symmetry factor.

For a sufficiently large overpotential, (2.4) is reduced to

\[ i \approx i_o = i_0 \exp \left\{ \frac{\beta nF \eta}{RT} \right\} \tag{2.5} \]

for anodic polarization, and to

\[ i \approx i_c = i_0 \exp \left\{ -\frac{(1 - \beta) nF \eta}{RT} \right\} \tag{2.6} \]

for cathodic polarization.
Rearranging (2.5) and (2.6), one gets the Tafel equation

\[ \eta = b \log \frac{i}{i_0} \]

where \( \eta \) is either \( \eta_a = E - E_{n,a} \) for anodic polarization, or \( \eta_e = E_{n,e} - E \) for cathodic polarization, and \( b \) is either \( b_a = \frac{2.3RT}{\beta nF} \) for anodic polarization, or

\[ b_e = \frac{2.3RT}{(1 - \beta)nF} \] for cathodic polarization. \( b \) is 0.12 V for \( n = 1 \) and \( \beta = 0.5 \).

**Mixed Potential Theory of Metal Corrosion** The Tafel equation states that when far from equilibrium, the overpotential is linear with the logarithm of the current for any half cell reaction, with \( b \) as the slope. This relationship is schematically shown in figure 2.1 for the Zn\(^2+\)/Zn and H\(^+\)/H\(_2\) half cells. Now consider zinc electrode corroding in an acid solution. Mixed potential theory views such an action as two coupled electrochemical reactions, rather than one single chemical reaction. At open circuit, the charge conservation principle requires that oxidation current equal the reduction current. This occurs at the crossing of the two corresponding Tafel plots. In mixed potential theory, the oxidation current and the open circuit potential are called corrosion current \( i_{\text{corr}} \) and corrosion potential \( E_{\text{corr}} \), respectively.

**Polarization Curve** The electrochemical behavior of the corroding metal electrode near \( E_{\text{corr}} \) is very similar to a half cell reaction near its \( E_0 \). This can be derived from the two Tafel equations of both oxidation and reduction reactions. Continuing with the zinc/acid system as an example, assuming both reactions are far from equilibrium at \( E_{\text{corr}} \), such as the case shown in figure 2.1, then the metal oxidation (anodic) current is
\[ i_a = i_{0,M} \exp \left( \frac{E - E_{n,M}}{b'_M} \right) \]

and the reduction (cathodic) current is

\[ i_c = i_{0,H} \exp \left( \frac{E - E_{n,H}}{b'_H} \right) \]

where \( b' = b / 2.3 \). Using the definition of \( i_{\text{corr}} \) and \( E_{\text{corr}} \),

\[ i_{\text{corr}} = i_{0,H} \exp \left( \frac{E_{\text{corr}} - E_{n,H}}{b'_H} \right) = i_{0,M} \exp \left( \frac{E_{\text{corr}} - E_{n,M}}{b'_M} \right) \]

one can work out the current \( i \) at any potential \( E \):

\[ i = i_a - i_c = i_{\text{corr}} \exp \left( \frac{E - E_{\text{corr}}}{b'_M} \right) - i_{\text{corr}} \exp \left( \frac{E - E_{\text{corr}}}{b'_H} \right) \]

Equation (2.11) is very similar to the Butler-Volmer equation in (2.4). Just as one can determine \( i_0 \) by measuring \( i-E \) response, \( i_{\text{corr}} \) can be obtained by measuring the polarization curve. As shown in figure 2.1, this is simply the interception of the Zn/Zn\(^{2+}\) and the H\(_2\)/H\(^-\) Tafel extrapolations.

The above theory assume both anodic and cathodic reaction are activation controlled. In case the cathodic reaction is diffusion limited, as is often observed for oxygen reduction is neutral solutions, \( i_c \) reaches a constant, this is mathematically equivalent to setting \( b_H \), consequently \( b'_H \), to infinity.

**Polarization Resistance** Compared with conventional weight loss methods to assess corrosion rate, polarization curve measurement is much easier, and relatively nondestructive. However, well defined Tafel behavior usually requires the data to span at least a decade of linearity in the E-log(i) plot, which in turn require large polarization
potentials away from $E_{\text{corr}}$. This may be difficult to achieve, especially in solutions containing dilute oxidants, where concentration gradient may cause the system to depart from activation polarization. This makes the Tafel slope hard to determine. Very often, anodic polarization curves contain large hysteresis and are not reproducible. Such is the case of AA-2024-T3 alloy corroding in neutral salt solutions.

Polarization resistance method was developed to overcome this difficulty. This method exploits the linearity of the polarization curves near $E_{\text{corr}}$. At small $E-E_{\text{corr}}$, equation (2.11) becomes

$$i = i_{\text{corr}} \left( \frac{1}{b'_M} - \frac{1}{b'_H} \right) (E - E_{\text{corr}})$$

So $i$ and $E$ become linear. Polarization resistance $R_p$ is defined as and given by:

$$R_p = \frac{dE}{di} \bigg|_{E=E_{\text{corr}}} = \frac{b'_M b'_H}{2.3 i_{\text{corr}} (b'_M + b'_H)}$$

Rearranging (2.13) yields $i_{\text{corr}}$

$$i_{\text{corr}} = \frac{b'_M b'_H}{2.3 (b'_M + b'_H)} \cdot \frac{1}{R_p}$$

Thus the corrosion rate is inversely proportional to the polarization resistance $R_p$. One practical advantage of this method is that the proportional constant in (2.14a) does not change much with variations of the Tafel slopes, $b_M$ and $b_H$. Therefore, one can make assumptions with little error. For $b_M = b_H = 0.1 \text{ V}$, $i_{\text{corr}} = 0.022 \text{ V/R}_p$.

An extreme case is $b_H = \infty$, corresponding to the diffusion limited cathodic reaction. In this case,
For \( b_M = 0.1 \text{V} \), \( i_{\text{corr}} = 0.043 \text{V}/R_p \).

**Passivity** The Tafel equation indicates as the potential increases, so does the anodic current. This is not always the case. In some metals, such as iron, nickel, chromium, the corrosion rate actually decreases above some critical potential, \( E_{pp} \), by as much as six orders of magnitude. This high corrosion resistance above \( E_{pp} \), despite a high driving force for corrosion, is defined as passivity [9]. As schematically shown in figure 2.2, above \( E_{pp} \), the corrosion rate does not change significantly with potential, until the anodic polarization passes a certain point and enters the transpassive region, when the anodic current will suddenly increase again. The potential range within which the current does not change significantly is called the passive region. Passivity plays an important role in corrosion protection. It is the basis of anodic protection. By maintaining the potential within the passive region, the metal can be protected from corrosion.

Passivity is a result of the formation of a thin and protective, corrosion-produced surface film, which serves as a barrier to reduce the rate of the metal dissolution reaction. In addition to anodic polarization, passive films can also be formed naturally on many metal and alloys. For example, chromium is a commonly used alloying element which can foster such passive films, based on its reaction with oxygen to form \( \text{Cr}_2\text{O}_3 \). When >12% Cr is added to iron which may also contain a small amount of nickel, an alloy known as stainless steel is produced. The otherwise very reactive aluminum relies solely on passivity for its extensive utility. Because of its high reactivity, aluminum readily forms a thin and
dense, transparent oxide film upon exposure to air, which isolates the metal from its corrosive environment.

On the other hand, passivity is associated with localized corrosion. Because the passive film is very thin and fragile, it usually contain defects. If the generation of defects in a corrosive environment is not matched up by sufficient repairing, then corrosion will proceed in these spots, sometimes rather quickly.

2.1.4 Forms of Corrosion

Corrosion may manifest itself in many forms, depending on the nature of the metal and the environment. The most commonly observed is uniform corrosion, during which the metal surface is consumed evenly. Although uniform corrosion accounts for the greatest tonnage of metal consumed, it is more visible and predictable, therefore is the preferred form, if corrosion is inevitable. Other localized forms of corrosion may not consume much material, however, they are concentrated in smaller areas. Insidious and difficult to predict and control, they can penetrate deep into the metal with high speeds and cause sudden failure. Of particular importance to AA-2024-T3 are these localized forms. Most relevant to this chapter are galvanic corrosion and pitting corrosion.

**Galvanic Corrosion and Cathodic Protection** When two dissimilar metals are electrically connected in a corrosive electrolyte, one of them is preferentially corroded while the other is protected from corrosion. This is because when two electrode with two different $E_{corr}$ are coupled, a current will flow so as to bring the two electrodes to the same potential level. Thus, the potential of the metal with the higher $E_{corr}$ (the cathode) will be
reduced, and according to figure 2.1, its corrosion rate will drop; on the other hand, the potential of the metal with the lower $E_{corr}$ (the anode) will be raised, therefore its corrosion rate will increase. Due to the large Ohmic potential drop in commonly encountered electrolyte, this galvanic effect is often localized at the border of the two metals.

Galvanic effect is the basis of sacrificial anode cathodic protection. Thus sacrificial anodes made of active metals such as aluminum, zinc, and magnesium, are attached to sea-going ship hulls, off-shore oil-drilling platforms, and thousands of miles of buried pipelines to protect the main structure, usually made of carbon steels.

**Pitting Corrosion**  Pitting corrosion is another form of localized corrosion that depends on galvanic effect. It is also the main form of corrosion for AA-2024 in near neutral electrolyte, therefore deserves more discussion. Using aluminum as an example, the initiation of pits results from defects of the passive oxide film. As shown in figure 2.3a, local corrosion is developed only at these defects because the matrix is protected by the passive film. Corrosion at the defects consumes oxygen, and differential oxygen concentration sets up local electrochemical cells. Oxygen is depleted at the defects and hydrogen generation becomes the cathodic reaction, which has lower potentials, therefore the defects become tiny anodes, and their immediate surrounding matrix the cathodes. Metal dissolution at the anodes generate $\text{Al}^{3+}$, which hydrolyzes according to

$$\text{Al}^{3+} + 3H_2O \leftrightarrow \text{Al(OH)}_3 + 3H^+ \quad 2.15$$

and renders the anode acidic; oxygen reduction occurs according to reaction (2.2a) at the cathodes, and makes them basic. In the neutral region between the anodes and cathodes, the metal hydroxide precipitates out. Most local cells polarize and passivate rather quickly,
however, some may survive long enough to develop visible pits, and pitting corrosion enters a self-propagating stage.

In this propagation stage, shown in figure 2.3b, oxygen diffusion into the pits is further restricted by the presence of a corrosion product cap, the pH inside the pits may become so low that the metal starts to react with the acid via a pure chemical reaction:

\[
2Al + 6H^+ \rightarrow 2Al^{3+} + 3H_2 \uparrow
\]  

Adding to the electrochemical reaction (2.1), this further accelerates the growth of the pits. Thus pitting is an autocatalytic process. The electrical current is carried by electrons in the metal, and by Al\(^{3+}\), H\(^+\), OH\(^-\), as well as other ions, such as Cl\(^-\), in the solution. Cl\(^-\) can greatly accelerate pitting corrosion because of its high mobility and the high solubility of its salt AlCl\(_3\), which produces a highly acidic solution in the pits when hydrolyzed.

Polarization measurements performed on many passive alloys indicate pitting initiates above a critical pitting potential, \(E_{pit}\). Anodic polarization can induce pitting because it speeds up the metal dissolution reaction. The more noble \(E_{pit}\) is, the more resistant the alloy is to pitting corrosion. Therefore, it is desirable for any passive alloy to have an environment which provides an \(E_{cor}\) between \(E_{pp}\) and \(E_{pit}\). The situation is illustrated in figure 2.4. Chloride substantially decreases \(E_{pit}\) and should be avoided whenever possible[12].

Pitting corrosion is particularly important for the AA-2024-T3 alloy. The majority of the surface of this alloy is passive within a pH range of 4.5 to 8.5 [3], however, there are many tiny defects within the passive film. Intermetallic particles that are formed during and after heat treatment are believed to be a major source of defects. Most intermetallic
particles are small, typically a few μm in size. Figure 2.5a shows a few big such particles observed under a microscope. Most of these particles are rich in copper, such as Al₂Cu (the θ phase), and are noble relative to the matrix [13]. Thus galvanic cells are set up at phase boundaries, which promotes pitting. Figure 2.5b shows the preferential attack at the boundary of an intermetallic particle cluster after immersing in a NaCl solution for 20 hours. The intermetallic particles are left relatively intact. This situation probably represents the initiation stage of pitting on AA-2024-T3.

**Crevice Corrosion** Another localized attach is often found in crevices formed between a metal and another material, or within the metal itself. In atmosphere a crevice corrode faster than the exposed surface by retaining water. In solution, preferential corrosion inside a crevice proceeds in a similar fashion as pitting corrosion [3], i.e. through differential aeration in and out of the crevice and acidification inside the crevice.

### 2.1.5 Corrosion Prevention

**Coatings** In addition to cathodic protection and anodic protection (passivity) mentioned previously, metals can also be protected from corrosion by application of surface coatings and inhibitors. There are many types of coatings. Their primary function in corrosion control is to provide a physical barrier between the substrate and the corrosive environment. Metallic coatings may also act as sacrificial anodes to provide cathodic protection for the substrate. Examples are galvanized zinc coating on steel applied by hot zinc bath immersion, and tin coating electroplated on steel used for food and beverage containers. Organic coatings may also serve as a reservoir for chemical
inhibitors. Often a chemical conversion coating is applied prior to organic coatings to offer the substrate superior adherence. Chemical conversion coatings are a special kind of coating which are formed during a reaction between the metal and an applied chemical, either phosphoric acid or a chromate. Phosphate conversion coating is formed by a classic metal-acid reaction to form a metal phosphate salt precipitate on the surface[14]. Chromate conversion coating (CCC) is formed by the metal reducing chromate to chromium oxide while itself is oxidized. When treating copper rich aluminum alloys, fluoride F\(^-\) and ferricyanide [Fe(CN)\(_6\)]\(^{3-}\) salts are often added to enhance the performance.

**Inhibitors and Passivators** are chemical compounds which when added in small concentrations to a corrosive environment effectively reduce the corrosion rate of a metal in that environment [15]. The mechanisms of inhibition are complicated and vary from case to case. They can be loosely classified into two categories depending on whether they affect the cathodic reaction or the anodic reaction. Cathodic inhibitors function by forming surface deposits which impede the cathodic reaction, usually reduction of dissolved oxygen. For example, zinc and magnesium cationic inhibitors can form insoluble hydroxides or calcium can form carbonate at the cathodic sites which generate OH\(^-\) via reaction (2.2). Similarly, anodic inhibitors form deposits at anodic sites. Passivators, such as chromate and nitrite, are generally viewed as anodic inhibitors. They inhibit the anodic reaction by initiating high anodic current densities which exceed \(i_{crv}\) for passivation [16]. For this reason, passivators are viewed as dangerous inhibitors. If present in insufficient concentration and consequently not able to render passivity for the entire surface, they can
behave as active polarizers and encourage corrosion at localized areas [15]. This situation is depicted in figure 2.6.

2.1.6 Chromate Conversion Coatings on Aluminum Alloys

Chromate conversion coatings were first reported in 1915 when Bauer and Vogel suggested that dichromate could be used to form a corrosion resistive film on aluminum alloys [17]. Over time, a great deal of effort has been devoted to understanding the nature of the CCC film and its formation, using various modern analytical techniques, such as XPS [18, 19, 20, 21, 22], Auger electron spectroscopy [21, 22, 23], FTIR [24], secondary ion mass spectrometry (SIMS) [25], X-ray absorption fine structure (EXAFS) and X-ray near edge structure (XANES) [26]. The majority of these studies were performed on pure aluminum, and in this case, it is now well accepted that the main component of the CCC film is a gel-like hydrated chromium and aluminum oxides, formed by aluminum reduction of chromate [19, 20]. The reduction half cell reaction can be represented by

\[ \text{CrO}_4^{2-} + 3H^+ + 3e^- \rightarrow \text{CrOOH} + H_2O \]  

or, in the form of dichromate,

\[ \text{Cr}_2\text{O}_7^{2-} + 8H^+ + 6e^- \rightarrow 2\text{CrOOH} + 3H_2O \]

The oxidation reaction is

\[ \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \]  

\[ \text{Al}^{3+} \text{ is immediately precipitated out via [26, 27]} \]

\[ \text{Al}^{3+} + 2H_2O \rightarrow \text{AlOOH} + 3H^+ \]
or, in the presence of $F^-$, it may form a soluble compound via \[ 26 \]

$$AI^{3+} + 3F^- \rightarrow AlF_3$$

Depending on the extent of hydration, CrOOH and AlOOH may exist in various forms, with \( \text{Cr}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \) representing the completely dehydrated form, and \( \text{Cr(OH)}_3 \) and \( \text{Al(OH)}_3 \) the completely hydrated form, respectively. Reaction (2.20) is thought to be responsible for the acceleration offered by fluoride in CCC formation, and the lack of Al species on the surface of the CCC [28]. The mechanism by which ferricyanide accelerate CCC formation and its corrosion resistance is not known, although it is reported that it can form a complex compound \( \text{CrFe(CN)}_6 \) on the surface of the hydrated chromium oxide.

In contrast, very little attention has been given to the CCC film on the industrially important copper rich alloys. Hagan and Haas suggested that ferricyanide interacts with AA-2024-T3 by altering the activity of copper-rich intermetallic phases by forming complex compounds with \( \text{Cu}^- \) and \( \text{Cu}^{2+} \) [23, 27]. Most recently, Hughes et. al. studied the CCC formed following pretreatment of the alloy with industrial cleaning and degreasing pretreatment procedures, and reported the effect of aging in air on its corrosion resistance. A marked increase in $E_{\text{corr}}$ was observed after aging for longer than 44 hours [27].

In addition to chromium oxide and aluminum oxide, various amount of Cr(VI) species were observed on the surface of the CCC film by different authors [18, 19, 22, 23, 24, 25, 27, 29]. The content of Cr(VI) inside the film has been a difficult subject, since in XPS and AES, depth profiling is usually obtained by argon ion sputtering, which is found to induce the reduction of Cr(VI) to Cr(III)[30].
2.2 OBJECTIVE

This investigation is focused on the influence of the CCC film on the corrosion resistance of the AA-2024-T3 alloy, rather than the characterization of CCC film itself, in another words, why CCC is so effective in corrosion prevention. At the heart of the corrosion inhibition mechanism is the unique self-healing property of the CCC. That is to say, CCC not only offers corrosion protection for the alloys underneath, but is can also heal a region of exposed alloy where the CCC has been scratched out. This effect is vividly demonstrated by the ASTM standard scratch and salt spray testing method. A scratch on CCC treated alloy is supposedly free of chromate therefore should be susceptible to corrosion, however, testing results indicate it can withstand a very corrosive salt spray for a long time before a white corrosion product is developed. It is thought that this may be caused by the chromate released from the CCC coating which subsequently migrates to and repassivates the exposed alloy [20]. Although chromate has been observed in the CCC film, and its content decreases when the CCC treated sample was immersed in NaCl solution [26], the chromate release-migration-repassivation hypothesis has never been confirmed experimentally. Presumably this is due to the difficulty of study of ill defined scratches, and to the extremely small amount of chromate that the CCC could release into the solution. However, experiments done with dichromate on pure aluminum indicated a fairly high dichromate/chloride ratio is needed to prevent pitting corrosion [31].
Another mysterious issue is that the CCC treated AA-2024-T3 has a lower corrosion potential than the untreated alloy, contrary to the expected passivity which raises the corrosion potential. In view of this, a scratch could be cathodically protected by its surroundings in the presence of an electrolyte. This possibility has not been demonstrated experimentally.

It is our belief that these are key issues to be resolved before a reasonable approach to develop a chromate replacement can be established. Therefore, it is the objective of this chapter to offer a clear understanding of the self-healing process. Specifically, the following four questions will be addressed:

1. Does the CCC film release chromate species into a solution, and does the chromate migrate to the exposed alloy?

2. If so, does the migrated chromate repassivate the exposed alloy? How fast is the releasing process?

3. If repassivation does occur, in what manner does this happen?

4. What role if any does cathodic protection play in the self-healing process?

In order to answer these questions, a series of experiments were designed to study migration and cathodic protection separately. Macro and microphotography were used to show the effect of chromate migration. Measurements of the polarization curve and polarization resistance were employed to assess corrosion behavior. XPS and argon ion sputtering were utilized to examine elemental distribution, and finally, spatially resolved Raman spectroscopy was used to study chromate release, migration, localized corrosion and protection.
2.3 EXPERIMENTAL

2.3.1 Reagents and Sample Preparation

Alodine 1200S powder is a product of Parke Amchem, Henkel Corporation, it is a mixture of 50-60% CrO₃, 20-30% KBF₄, 10-15% K₃Fe(CN)₆, 5-10% K₂ZrF₅, and 5-10% NaF by weight[32]. K₂CrO₄, K₂Cr₂O₇, Cr₂O₃, HNO₃, NaCl, AlCl₃·6H₂O, KOH were reagent grade. All the water used in experiments was nanopure water (resistivity is 18.2 Ω-cm).

AA-2024-T3 coupons of 0.6 mm thick was punched into 1 cm² squares and 19 mm diameter discs. In order to perform electrochemical measurements, copper wires were attached to one side of the samples by a silver epoxy, obtained from SPI Supplies. The samples were then mounted into an epoxy resin (Epoxide), purchased from Buehler Limited. To prepare the resin, the hardener and the epoxy were mixed at a little over 1:5 ratio, typically between 1.05:5 and 1.15:5. Five minutes of stirring was applied to the mixture to assure a complete mixing, after which the resin was set aside to allow the bubbles to escape for 10 minutes. It was then poured into the plastic cup which held the alloy sample. Pressure was applied to the sample with the stirring stick in order to squeeze out the air which might be caught underneath the sample. This will assure the alloy surface is level with the resin surface. The cups were covered with a large glass dish to prevent dust. After 24 hours of curing at room temperature, the samples were taken out of the cups and polished.

To expose the alloy, the above prepared samples were polished in water on a Buehler Ecomet 3 variable speed grander-polisher, using 240, 400, 600, 800, and 1200...
grit sand paper successively. The rotating speed of the polisher was set at 300 cycles per
minute. The samples were held by hand. Even polishing over the entire alloy surface was
assessed by visual examination. The samples were then tested for good electrical
connection between the wires and the alloy by measuring the resistance between the wire
and the polished surface. A good connection between the copper wire and the alloy results
a resistance typically between 0.1Ω and 10Ω.

CCC solution was made by dissolving 1.51 g Alodine powder in 200 ml water, and
the pH was adjusted to 1.69 with HNO₃. For CCC treatment, the mounted alloy samples
were immersed in the room temperature Alodine solution for 60 seconds, immediately
rinsed afterwards, and then soaked for ca. 1.5 minutes in each of three portions of 80 ml
water. They were then dried and aged in air. The coated samples exhibit a golden color.

2.3.2 Raman Spectroscopy and Spectroscopic Imaging

Raman spectroscopy is uniquely suited to this investigation for a number of
reasons. Raman with 515 nm laser excitation is very sensitive to chromate and dichromate
species. It usually does not require sample preparation, and is suitable to in-situ
observation in aqueous solutions. Equipped with a microscope, it can provide spatial
resolution as high as 1μm, thus is superior to most other optical spectroscopy techniques
for pitting corrosion study. One problem associated with Raman microscopy is the high
energy density as a result of the tight focusing of the laser, which may cause photo-
degradation or heating of the sample, as is observed for the chromate conversion coating.
Very often, however, only moderate spatial resolution is needed. For example, in pitting
corrosion study, 20 μm resolution would be enough to study a fully developed pit, which is usually bigger than 30 μm. In this case, a Raman spectrometer working at a macro mode, equipped with a simple imaging system would be enough to offer the high sensitivity and required spatial resolution, yet reduce sample damage.

To achieve high sensitivity and moderate spatial resolution, a sensitive Raman spectrograph working at 515 nm excitation was combined with a focal plane video imaging system. As shown in figure 2.7, the imaging system consists of a TV monitor, a CCD video camera, an illuminating light source, and a swing mirror placed in the Raman collection light path. The Raman collection lens L1 is a conventional Canon camera lens (50 mm, f/1.4), and it also serves as the front lens of the focal plane imaging system. L3 on the CCD camera is an f=28~200 mm zoom camera lens (φ 72 mm), which provides a variable magnification. It was fixed at 200 mm focal length for a maximum magnification of 4. L2 and L3 were both focused at infinity which guarantees simultaneous focusing for both the Raman spectrometer and the imaging system. A 515 nm dielectric band rejection filter was placed between L3 and the CCD, to reduce laser light. When the swing mirror is set in the video position, the light is reflected toward the CCD video camera and an image of the sample is shown on the TV monitor. One can then move the three axis translation stage to select a desired spot to take a Raman spectrum. Then the mirror may be flipped out of the light path for Raman collection. The maximum spatial resolution of the imaging system is the pixel size of the CCD on the video module, divided by the magnification, or about 5 μm. The spot size of the laser at the focal point of L1, however, is what determines the spatial resolution of the Raman measurement, and it was about 20 μm.
2.3.3 Observation of Chromate Migration with Raman Spectroscopy and XPS

The following experiment was designed to observe the release and migration of chromate by the CCC film. A 1 mm diameter hole was drilled through a 19 mm diameter alloy disc in a 3 mm thick epoxy mounting. The sample was then coated with the CCC film. After 20 minutes of aging in air, the sample was placed on a Teflon support. The sample was then placed in a weighing bottle. 1 ml of 0.1 M NaCl was dropped onto the sample. The surface tension was enough to prevent the liquid from falling through the hole. The bottle was then placed on the sampling stage of the Raman spectrometer. The laser was focused on the hole so that only water but not the CCC film or the epoxy contributed to the spectrum. The sampling configuration is demonstrated in figure 2.8a. The concentration of chromate in the solution was thus monitored as a function of time. In between taking spectra, the bottle was covered with a lid to prevent evaporation of the liquid. 1 ml of 0.1 M NaCl was placed in the bottle to further conserve the moisture.

The concentration of chromate was calculated using the chromate peak intensity, with the ~1635 cm\(^{-1}\) water peak as an internal standard. A 100 ppm K\(_2\)CrO\(_4\) solution provided the concentration calibration. To see if the salt makes any difference, nanopure water was used instead of 0.1 M NaCl, and the experiment repeated. To assess the effect of aging on chromate release, another experiment was conducted for a sample aged 10 days in air after CCC treatment.

Chromate films formed on initially untreated alloy samples via migration were examined with both XPS and imaging Raman spectroscopy. In order to measure the
surface coverage and thickness of the chromate film formed on an untreated sample with XPS, a small piece (7 mm by 7 mm) was cut from a polished AA-2024 alloy, and placed on a CCC treated disc, about 1 ml of 0.1 M NaCl solution was dropped on the disc, and the small piece of alloy was completely covered by the solution, as demonstrated in figure 2.8b. The set up was placed in a weighing bottle to prevent water evaporation. After 20 hours, the top sample appeared unaltered. It was then taken out, rinsed with water, dried in air, and placed in the XPS vacuum chamber for analysis. An approximate depth profile was obtained by combining XPS with Ar⁺ sputtering. The sputtering removed ca. 3 to 6 nm material per minute.

The samples prepared for XPS experiment were also monitored with Raman spectroscopy during the migration process. It was noticed that on some samples tiny spots of white corrosion product could be seen on the edge of the samples, with the aid of the Raman imaging system. Raman spectra of this product were taken and are shown in figure 2.12, b.

For reference, XPS depth profiling of the CCC film itself was also performed after 10 days of aging in air.

2.3.4 The “Sandwich” Experiment: Migration and Repassivation by Chromate

Ideally, to study self-healing, one would like to examine a scratch on a CCC treated sample with conventional electrochemical methods. However, a scratch is ill defined, and would be very difficult if not impossible to isolate electrically from its CCC coated surroundings. In order to overcome this difficulty and perform electrochemical
measurements on an untreated sample affected with chromate migration, we took a rather extreme measure to separate the target from the source of chromate migration, namely to separate the untreated alloy from the CCC treated alloy during and after the migration experiment. Thus the following sandwich experiments were designed.

As shown in figure 2.9, a1, a Teflon O-ring was placed on top of an untreated 1 cm² square alloy sample, on top of which sat an CCC treated 19 mm disc, with both samples in epoxy mountings. The O-ring was large enough so that neither sample was in contact with it. The O-ring has a 25 mm outer diameter and a 1.8 mm thickness, thus the volume between the two samples was approximately 0.6 ml. This space was filled with 0.1 M NaCl, and the two samples were bound together by a rubber band with enough pressure to keep the O-ring and the liquid from moving around. The set up was then placed inside a beaker. To prevent the solution from evaporating, 1 ml 0.1 M NaCl was put inside the beaker, which was then sealed with parafilm. This configuration was used to assess the effect of the presence of a conversion coated sample on the corrosion of the untreated sample. Furthermore, the wires leading to the two electrodes were not connected. Thus the setting provided for mass transport but eliminated the electrical contact between the two electrodes, so that migration and cathodic protection can be studied separately.

To assess the influence of atmosphere, another sandwich experiment without the O-ring was set up, schematically shown in figure 2.9, b1. The O-ring was replaced with a Teflon holder, which provided the same separation between the two samples, but kept the solution exposed to air. About 0.6 ml of 0.1 M NaCl solution was placed in this space,
kept in contact with both alloy samples by surface tension. The perimeter of the solution was in direct contact with the air, but the alloy samples were not.

Since a scratch is in electrical contact with the alloy underneath the CCC film, a more realistic setting would require electrical contact between the wires leading to the two AA-2024 electrodes. This was achieved by simply connecting the wires together, as shown in figure 2.9, a2 and b2, or by connecting both electrodes to a zero resistance ammeter (ZRA), which can monitor the galvanic current flow at the same time. The ZRA was set up simply by connecting both the reference and auxiliary electrodes of a PGP 201 Potentiostat/Galvanostat to the CCC treated sample, and the working electrode to the untreated sample. The current was monitored by setting the potential difference to zero.

To provide a control experiment, the top CCC treated sample was replaced by another 19 mm diameter electrode but without CCC treatment, such as shown in figure 2.9, a3 and b3. Thus altogether eight combinations were possible with the sandwich experiment, namely with or without air contact, with or without electrical connection, and with or without CCC treatment to the top electrode. Assuming electrical contact has no effect on the case where the top piece was not CCC treated, only six configurations were left, all of which were shown in figure 2.9.

A number of sandwich experiments were set up for each one of the six configurations, and each experiment was terminated after a different length of time, up to 96 hours. The untreated electrode was then rinsed with water, without drying, and their corrosion behavior was studied with linear polarization resistance experiments and
potentiodynamic polarization experiments in 0.1 M NaCl. They were also examined visually under a microscope, and by Raman spectroscopy.

All the above six settings involved ionic contact. In order to study cathodic protection alone, without possible protection by migrated chromate, another experiment was set up according to figure 2.10. A polished 1 cm² alloy electrode was placed inside a 100 ml beaker, which was put inside a glass dish, 170 mm diameter, × 90 mm high. Five CCC treated electrodes of 19 mm diameter were placed inside the dish but outside the beaker, and they were welded together to a copper wire placed outside the dish. The beaker and the dish were then filled with 2 liters of 0.1 M NaCl, which was just enough for the solutions in and outside the beaker to be in contact. It is assumed the amount of chromate released from the CCC film is small and the concentration of it in the large amount of solution is insignificant, and lack of convection further prevents migration of it to the untreated electrode. A piece of glass covered the dish to prevent evaporation, and a hole was cut in the center of the glass to give access to an SCE reference electrode. A galvanic corrosion experiment was thus set up with a Gamry potentiostat, which monitored both the current and the potential of the galvanic couple over a period of 20 hours. The IR drop of potential in the electrolyte was estimated from the conductivity of the solution and the monitored current. After completion of the experiment, the center electrode was examined visually and under a microscope, also by Raman spectroscopy and electrochemical measurement.
2.3.5 Polarization Resistance and Potentiodynamic Polarization Analysis

Linear polarization resistance and potentiodynamic polarization analysis were performed on a PGP 201 Potentiostat/Galvanostat. Polarization resistance $R_p$ was measured as the inverse of the slope of a cyclic voltammogram (CV). The CV was started at the open circuit potential (OCP), scanning toward the anodic (positive) direction first. The amplitude of the cycle was 20 to 30 mV toward both the anodic and cathodic directions. The scan rate was set at 50 mV/min.

For most polarization curve experiments, only the anodic region was measured. The experiment started at the OCP, scanning at 100 mV/min, until the current density reached 100 $\mu$A/cm$^2$, then after 10 seconds of waiting period, the potential was scanned backward, until 0.1 $\mu$A/cm$^2$ was reached.

One difficulty encountered in measuring the pitting potential of these samples is that crevice corrosion occurred occasionally at the edges where the alloy meets the epoxy mounting, as shown in the photographs (figures 2.18, 2.19, and 2.20). Covering these edges with black wax can reduce crevice corrosion, however, because of the extremely small amount of chromate that migrated during the experiments, this method was not adopted since black wax might alter the outcome. With crevice corrosion happening, one might doubt the credibility of any pitting potential measurement. Nevertheless, we used the potential at which the current density reached 100 $\mu$A/cm$^2$ as the breakdown potential, $E_{bark}$. This potential was defined as the pitting potential by Kendig, etc.[33]. For the samples that did not show widespread pitting corrosion, it is reasonable to assume that the
real pitting potential is higher than the measured $E_{\text{corr}}$. For the samples in which corrosion spread evenly across the surface, $E_{\text{corr}}$ is probably very close to $E_{\text{p}}$.

2.4 RESULTS AND DISCUSSION

2.4.1 Aging Has a Significant Effect on Chromate Release of the CCC Film

Cr(VI) can be present in solution as both chromate $\text{CrO}_4^{2-}$ and dichromate $\text{Cr}_2\text{O}_7^{2-}$, the balance of which is affected by the pH as well as the total chromate concentration[34].

$$2\text{CrO}_4^{2-} + 2H^+ \leftrightarrow \text{Cr}_2\text{O}_7^{2-} + H_2O, \quad \log \left[ \frac{[\text{CrO}_4^{2-}]}{[\text{Cr}_2\text{O}_7^{2-}]} \right] = -14.59 + 2pH \quad 2.21$$

A typical Raman spectrum of the CCC film is shown in figure 2.11a. For comparison, the spectra of Alodine solution, 8.6 mM K$_2$CrO$_4$, 4.2 mM K$_2$Cr$_2$O$_4$, and Cr$_2$O$_3$ paste are shown in figure 2.11b, c, d and e, respectively. The CCC film Raman peak is broad and asymmetric, centered at 860 cm$^{-1}$, and FWHM is 83 cm$^{-1}$. This is between the main peaks of $\text{CrO}_4^{2-}$ and $\text{Cr}_2\text{O}_7^{2-}$, but closer to $\text{CrO}_4^{2-}$. While Cr(VI) in Alodine solution itself is predominantly in the $\text{Cr}_2\text{O}_7^{2-}$ form due to the low pH, it is probably present in the film as an amorphous mixture of chromate and dichromate. Simply mixing 8.6 mM K$_2$CrO$_4$ and 4.2 mM K$_2$Cr$_2$O$_4$ at 1:1 volume ratio could not reproduce the CCC film spectrum. Cr(III) can not be observed, presumably because of the low Raman cross section of Cr$_2$O$_3$.

The chromate released by the film can be in the form of either chromate or dichromate. Both were observed in the in-situ Raman observation. This might be due to the very low concentration of this material, which subjects the balance in equation 1 to small pH variations caused by CO$_2$ in the air. The pH of the solution measured after the
release experiment varied from run to run, and was between 4.5 and 6.2. This range also covers the pH of the solutions after the sandwich experiments a1, a2, b1 and b2. The chromate release by the CCC film is a very slow process. For a sample aged for 20 minutes, the concentration reached ca. 40 ppm in terms of CrO₄²⁻ after 72 hours of immersing in 1 ml solution. The release rate for the first two days was roughly 0.2 × 10⁻⁶ g CrO₄²⁻/hour-cm². A Raman spectrum of this 40 ppm CrO₄²⁻ solution is shown in figure 2.12a. For the sample aged in air for 10 days, the release rate dropped to about 0.07 ×10⁻⁶ g CrO₄²⁻/hour-cm². The concentration of chromate in the solution after 3 days of experiment was roughly 10 ppm. Figure 2.13 shows the Cr(VI) concentration curve. The release rate is apparently affected by the chromate concentration in the solution. The yellow color of the CCC film aged for 10 days disappears after 48 hours, if the sample is placed in 80 ml of 0.1 M NaCl; However, it only showed minor degradation in 1 ml of solution, and did not show much color degradation when placed in 80 ml of solution containing 9 ppm CrO₄²⁻. Therefore an equilibrium may be reached around this concentration for the samples aged in air for 10 days.

The release rate was fairly reproducible from run to run. In another experiment, CCC coated samples (17 mm x 17 mm squares) were aged in air for 20 hours, and chromate release was examined in 0.5 ml 0.1 M NaCl and 0.5 ml 0.05 M Na₂SO₄. After 9 hours, a Cr₂O₇²⁻ peak started to appear in the solution spectrum, and the concentration was 23 ppm in terms of CrO₄²⁻ in 0.1 M NaCl (assuming Cr₂O₇²⁻ is converted to CrO₄²⁻), and 24 ppm in 0.05 M Na₂SO₄. After 23 hours, 40 ppm in 0.1 M NaCl, and 35 ppm in 0.05 M Na₂SO₄. After taking into consideration of the reduced volume of the electrolyte,
the release rate was $0.3 \times 10^{-6} \text{ g CrO}_4^{2-}/\text{hour-cm}^2$ in 0.1 M NaCl, and $0.26 \times 10^{-6} \text{ g CrO}_4^{2-}/\text{hour-cm}^2$ in 0.05 M Na$_2$SO$_4$, comparable to the $0.2 \times 10^{-6} \text{ g CrO}_4^{2-}/\text{hour-cm}^2$ obtained on the sample aged for 20 minutes.

2.4.2 XPS Results

The sample prepared according to figure 2.8b for XPS after the migration experiment was still shiny and did not show any sign of corrosion. The XPS survey spectra are shown in figure 2.14. The top layer showed the presence of chromium and fluorine, in addition to aluminum and oxygen. The surface coverage of chromium varied from sample to sample, and it was between 1% and 5.3%, much lower than the 12% obtained on the CCC film. These values are to be used with caution, however, because of the finite sampling depth of XPS. If the surface was completely covered with a chromate monolayer, but the XPS sampling depth was much deeper than the thickness of the chromate monolayer, then the calculated coverage would be much lower than the real value. High resolution spectra in figure 2.15 indicate that the majority of the chromium was in Cr (VI) state, and aluminum was Al(III). After 3 minutes of sputtering, which removed the top 10-20 nm material, metallic Al and Cu and CuO emerged, and Cr(VI) and F disappeared. Instead, a small peak at centered at 574.5 eV appeared, attributable to metallic Cr. The origin of the small amount of Cr is difficult to assess. It is unlikely that aluminum can reduce chromate during the migration experiment. It is probably the result of Cr(VI) reduction by the Ar$^-$ bombardment during the depth profile experiment. After another 6 minutes of sputtering, copper was relatively enriched over aluminum, possibly
due to preferential removal of Al by corrosion. Both metals were mainly present in the metallic form, with small amounts of CuO and Al(III). After another 9 minutes of sputtering, the abundance of copper started to decrease, indicating the base alloy is being reached. From these results, one can conclude that the chromate is adsorbed on the very top layer of the oxide film, with a chromate film thickness of no more than 10 nm.

These results are in contrast to those obtained on the CCC film, shown in figure 2.16 and 2.17. The top layer of the CCC film showed large amounts of C, N, Cr, O, and smaller amounts of Al, Fe, and F. The distribution and depth profile of these elements were similar to that reported by Hughes et. al.[27] on pretreated AA-2024-T3 alloy. Of importance is the continued presence of a large amount of Cr throughout the depth of the CCC film. Again, chemical state analysis of Cr after ion bombardment is to be viewed with caution.

<table>
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<th>Sputter time</th>
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<th>%C</th>
<th>%N</th>
<th>%O</th>
<th>%Cr</th>
<th>%F</th>
<th>%Fe</th>
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<td>26</td>
<td>12</td>
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Table 2.2. Depth profile of the CCC.
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<th>%O</th>
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<th>%F</th>
<th>%Fe</th>
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<td>0</td>
<td>3.9</td>
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</tbody>
</table>

Table 2.3. Depth profile of elements of the initially untreated sample after 20 hours of migration experiment, according to figure 2.8b.

2.4.3 The Sandwich Experiments

Both macro and micro-photographs of the samples clearly showed the effect of chromate migration on the corrosion of the polished alloy. The macro photographs were taken with a Minolta Camera with a 50 mm Sigma macro lens at 1:1 magnification, and they were shown in figure 2.18 and 2.19. For comparison, the photos of a polished alloy sample, a sample submersed in 0.1 M NaCl for 96 hours, a sample following 20 hours of "cathodic protection" depicted in figure 2.10, and a sample submersed in 15 ppm K$_2$CrO$_4$ with 0.1 M NaCl for 120 hours, are also shown, in figure 2.20a, b, c-20, and d respectively. Representative microphotographs are shown in figure 2.21 at 5X and figure 2.22 at 50X.

In the cases where the solution had contact with the air, the control sample b3 corroded badly. Visible white corrosion product was present, and pits were present under a microscope, even after only six hours. The corrosion product accumulated with time,
pits became larger, deeper and more densely populated, and some of them became interconnected as corrosion continued. At 72 hours, the sample was completely covered with white corrosion product. At 50X, it became evident that not only had the sample been pitting, but it had also suffered from general corrosion, since the polishing marks had completely disappeared, much like the picture shown in figure 2.22, a3-72.

In contrast, however, the corrosion rate of sample b1 was significantly reduced. No visible white corrosion product was present even after 96 hours. Under the microscope, most of the sample appeared unaltered. At 50X, the polishing marks were still clearly visible after 96 hours. Although at 5X, there were some sparsely located pits, one can see at 50X they are often clusters of small and shallow pits, like the one shown in figure 2.22, a1-96, rather than single large and deep pits, and very few of them were covered with a cloudy corrosion product. The depth of the pits can be compared with those found in b3 and a3 samples, by polishing with 1200 grit sand paper. Deep pits leave many black dots on a shiny matrix after relatively hard polishing, and this is the case with the b3 and a3 samples. Shallow pits will completely disappear and leave a good looking shiny surface, even after slight polishing, and this is the case with the a1, a2, b1, and b2 samples.

In the cases where the solution was sealed up by the O-ring, namely a1, a2 and a3, the results were similar to the cases b1, b2, and b3 respectively. Photographs showed that corrosion was the worst in the case a3. After 48 hours, the sample was already covered completely with corrosion product. At 72 hour, the sample was corroded beyond recognition. Even the epoxy mounting was covered with white corrosion product. The
liquid had vanished when the sample was taken out, presumably because the liquid was forced out by the hydrogen gas generated by corrosion.

2.4.4 Polarization Resistance, Corrosion Potential, and Breakdown Potential

The electrochemical behavior is consistent with the visual appearance of the samples after the sandwich experiment. As shown in figure 2.23, $R_p$ of the b3 samples remained low, regardless of the surface conditions. They ranged from $8 \times 10^3$ to $40 \times 10^3 \ \Omega \cdot \text{cm}^2$. This is about the same as a freshly polished alloy sample, and about two orders of magnitude lower than the CCC treated alloy. Typical cyclic voltammograms of the sample b2-72 and a CCC treated alloy are shown in figure 2.29. As shown in figure 2.24, Corrosion potential ($E_{\text{corr}}$) and breakdown potential ($E_{\text{brk}}$) for the b3 samples were largely unchanged by corrosion, and they were around -550 mV and -480 mV vs. SCE, respectively. The narrow separation between $E_{\text{corr}}$ and $E_{\text{brk}}$ was consistent with the fast pitting of these samples and continuous growth of the corrosion product.

On the other hand, $R_p$ of the b1 and b2 samples were two orders of magnitude higher than the samples of b3, and they were about $10^6 \ \Omega \cdot \text{cm}^2$. These are also shown in figure 2.23. As shown in figure 2.24, a significant drop of $E_{\text{corr}}$ was observed for all the samples in b1 and b2 relative to b3. $E_{\text{corr}}$ ranged from -610 mV to -700 mV. On the other hand, $E_{\text{brk}}$ was increased relative to b3, from around -480 mV to as high as -412 mV. Thus from b3 to b1 and b2, the separation of $E_{\text{corr}}$ and $E_{\text{brk}}$ increased from ca. 70 mV to ca. 200 mV on average. This is in good agreement with the high corrosion resistance of samples b1 and b2.
The galvanic current measured in b2 over a period of 24 hours showed interesting results. As shown in figure 2.25, b2, the current was initially high, up to 0.6 μA/cm², but after about an hour, it decreased to below 0.2 μA/cm². This is consistent with the fact that migration of chromate increases R_p and decreased E_corr of the initially untreated sample. Then, at about 14 hours, the current became reversed, indicating the E_corr of the bottom sample had decreased to below that of the top CCC treated sample.

The near zero galvanic coupling as judged from the small galvanic current between the top and bottom samples in b2 explains the lack of difference between the results of b1 and b2, both visually and electrochemically. The R_p, E_corr and E_break of the samples in b2 are also shown in figures 2.23 and 2.24. Despite some sample to sample variations, these electrochemical parameters for b2 are similar to those of b1.

In the cases where the solution was sealed up by the O-ring, namely a1, a2 and a3, the results were similar to the cases b1, b2, and b3 respectively. The R_p is shown in figure 2.26, E_corr and E_break in figure 2.27, and the galvanic current measured in a2 is shown in figure 2.25, a2. Comparing a1 and a2 with a3, the trends were found similar to the case in b. From a3 to a1 and a2, R_p were also increased by about two orders of magnitude, and (E_break-E_corr) were increased by 80 mV to 250 mV.

By comparing a1 and b1 to a3 and b3, it is clear that AA-2024-T3 can indeed be passivated by the chromate migration from the CCC film nearby. On the other hand, the result of the galvanic corrosion experiment in figure 2.10 indicated that “cathodic protection” did not work. As shown in by the photograph c-20 in figure 2.20, after 20 hours, the alloy corroded as much as it did in the a3 and b3 sandwich experiments, in spite
of the relatively large "cathodic protection" current, which was around 2 \( \mu \text{A/cm}^2 \). The sample was covered with white corrosion product, and severe pitting was observed under the microscope. The current and potential of the galvanic couple was shown in figure 2.28. The three spikes were caused by intentional agitation of the working electrode.

<table>
<thead>
<tr>
<th></th>
<th>( a1 )</th>
<th>( b1 )</th>
<th>( a2 )</th>
<th>( b2 )</th>
<th>( a3 )</th>
<th>( b3 )</th>
<th>9 ppm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{\text{corr}} ) (mV)</td>
<td>-574</td>
<td>-660</td>
<td>-666</td>
<td>-620</td>
<td>-550</td>
<td>-550</td>
<td>-716</td>
</tr>
<tr>
<td>( E_{\text{brk}} ) (mV)</td>
<td>-388</td>
<td>-423</td>
<td>-397</td>
<td>-447</td>
<td>-461</td>
<td>-481</td>
<td>-388</td>
</tr>
<tr>
<td>( E_{\text{brk}} - E_{\text{corr}} ) (mV)</td>
<td>186</td>
<td>237</td>
<td>269</td>
<td>173</td>
<td>89</td>
<td>69</td>
<td>328</td>
</tr>
<tr>
<td>( R_p ) (k( \Omega \cdot \text{cm}^2 ))</td>
<td>2,900</td>
<td>1,600</td>
<td>960</td>
<td>1,900</td>
<td>7.7</td>
<td>7.9</td>
<td>450</td>
</tr>
</tbody>
</table>

* 9 ppm represents the initially untreated sample immersed in 0.1 M NaCl / 9 ppm (0.077 mM) \( \text{CrO}_4^{2-} \). Electrochemical measurements were also conducted in the same solution, instead of 0.1 M NaCl alone. See section 2.4.5.

Table 2.4. Electrochemical parameters of the initially untreated samples after the sandwich experiments. Values are obtained by averaging three measurements conducted in 0.1 M NaCl after 2, 3, and 4 days of sandwich experiments.

### 2.4.5 Passivation of AA-2024-T3 in 9 ppm \( \text{CrO}_4^{2-} / 0.1 \text{ M NaCl} \)

XPS indicated that along with chromate, fluorine also migrates. To determine if chromate alone is enough to cause passivation, polished alloy samples were immersed in
80 ml of a solution containing 0.077 mM K$_2$CrO$_4$, or 9 ppm in terms of CrO$_4^{2-}$, with 0.1 M NaCl for up to 120 hours. HCl was added to adjust the pH to 5.2 to match the pH measured in the sandwich experiments. E$_{corr}$, E$_{ Berk }$, and R$_p$ were measured in this solution from time to time, and are shown in figure 2.30, and figure 2.31. The trend was similar to that obtained in 0.1 M NaCl following the sandwich experiments. E$_{corr}$ decreased while E$_{Berk}$ increased, causing their difference to increase, therefore increasing the sample’s resistance to pitting corrosion. At 2 hour, the E$_{corr}$ was not stable and fluctuated $\pm$ 50 mV around -650 mV, R$_p$ was difficult to measure but was estimated to be $0.25 \times 10^6$ $\Omega \cdot$cm$^2$. At 18 hour, E$_{corr}$ was stabilized at 670 $\pm$ 5 mV, and R$_p$ was $0.30 \times 10^6$ $\Omega \cdot$cm$^2$. No corrosion product was visually observable. Under a microscope, the majority of the sample surface appeared unaltered, except that there were many tiny and shallow pits around a few $\mu$m in size. After 120 hours, most part of the sample appeared the same except for some crevice corrosion on the edges. A few large pits around 50 $\mu$m were observed under the microscope.

2.4.6 Potentiodynamic Polarization Analysis

Polarization curves of the samples immersed in 0.077 mM (15 ppm) K$_2$CrO$_4$/0.1 M NaCl at pH 5.2 for 45 hours and the samples immersed in 0.1 M NaCl alone for two hours were obtained using potentiodynamic method. The electrolyte was 0.1 M NaCl open to laboratory atmosphere, without additional aeration or deaeration. Typical polarization curves are shown in figure 2.32. Corrosion rate can be obtained by extrapolating of linear region of the cathodic curves to the corrosion potential.
There is a sharp contrast between the two polarization curves. The bare alloy cathodic curve shows a typical diffusion controlled oxygen reduction region between the corrosion potential -550 mV and -1040 mV vs. SCE, and then hydrogen evolution began to dominate the reduction current below -1040 mV, at which point a large amount of bubbles were seen evolving from the sample during the experiment. The corrosion rate obtained from the polarization curve was 3.2 μA/cm², this agreed well with the 5.6 μA/cm² calculated from equation (2.14b), using the $R_p$ measured from the polarization resistance experiment. The anodic branch showed no passivation behavior, indicating the sample was actively corroding. It appears that the alloy was corroding at the oxygen diffusion limit.

On the other hand, the sample treated with 15 ppm K$_2$CrO$_4$ showed a drastic reduction of corrosion rate. A passive region was evident between the corrosion potential -675 mV and the pitting potential -530 mV. The cathodic branch showed no diffusion controlled behavior, and the reduction current was between one and three orders of magnitude lower than the corresponding values of the bare alloy. The corrosion rate obtained from this polarization curve was $6.5 \times 10^3$ μA/cm², also agreed well with the value $4.4 \times 10^3$ μA/cm² calculated with equation (2.14a). Its $R_p$ was 5X10⁶ Ωcm².

Comparing these results, and referring to the XPS results, it is apparent that adsorption of even a minute amount of chromate greatly affects both anodic and cathodic reactions of the alloy in the applied conditions. The adsorbed chromate inhibits oxygen reduction, and reduces its exchange current density. This in turn reduces the corrosion
potential of the alloy to below $E_{\text{pt}}$, and brings the alloy into the passive region. As a result, the metal dissolution rate is drastically reduced.

### 2.4.7 Raman Spectroscopic Imaging

Chromate was observed with Raman spectroscopy on the samples of a1, a2, b1, b2, and the sample immersed in the 15 ppm $\text{K}_2\text{CrO}_4$, however only in the sparsely located pits. Due to the limitation of the spatial resolution of the Raman imaging system, only pits bigger than 10 $\mu$m were examined. As shown in figure 2.33, two kinds of pits observed under the imaging system showed distinctive features. Those that are covered with corrosion product appeared white and had a large chromate Raman signal (figure 2.33a), while those not covered with corrosion product appeared dark and showed a very small chromate Raman signal (figure 2.33b). Away from the pits, however, no chromate was observable with Raman spectroscopy (2.33c). All these spectra were obtained by averaging twenty 1-second exposures to increase SNR.

In order to show the spatial distribution of chromate, a Raman line scan was performed across a pit. 19 spectra were collected across a distance of 0.54 mm over a white pit, with 0.5 second exposure time for each spectrum. The sample moved at a speed of about 40 $\mu$m/second. The image and the spectra are shown in figure 2.34 and 2.35, respectively. Interestingly, the chromate peak was shifted to a lower wave number, 839 cm$^{-1}$, compared to 852 cm$^{-1}$ observed in figure 2.33a. This is because there was a sharp peak at 839 cm$^{-1}$ atop the broad asymmetric peak at 852 cm$^{-1}$, and this sharp peak is less stable under laser irradiation than the peak at 852 cm$^{-1}$. When the sample moved at 40
μm/second and the exposure time was only 0.5 second, this sharp peak was detectable; however, when the sample was not moving and was exposed for 20 seconds, the sharp peak disappeared, supposedly because the material yielding the sharp peak had degraded by the laser. Thus it seems there are at least two chromate species in the pits. The sharp peak at 839 cm\(^{-1}\) represents a species which easily degrades under the laser, and the peak represented by figure 2.33a comes from another species which is relatively stable under the laser irradiation.

The chromate peak of figure 2.33a was similar to that observed for the CCC film (figure 2.11a), except it appeared narrower (50–55 cm\(^{-1}\) FWHM), more asymmetric, and the position was shifted toward lower frequency by some 7 to 20 cm\(^{-1}\). If the narrower peak width can be used as an indicator for less amorphous structure, one can argue that the CCC film is formed in a very rapid and far-from-equilibrium way, while the product in the pits is formed very slowly and in a near-equilibrium environment. The shift may be caused by the pH variation, which affects the balance between Cr\(_4O_4^{2-}\) and Cr\(_2O_7^{2-}\). The chromate has a peak at 848 cm\(^{-1}\) and the dichromate peak is centered at 901 cm\(^{-1}\). In the CCC treatment, the pH was 1.69, and Cr(VI) was predominantly in the dichromate form; in the migration experiments, the pH was measured to be between 5.0 and 6.3, thus the Raman spectrum in the release experiment showed the presence of Cr\(_4O_4^{2-}\). Therefore the shift in Raman peak position can be regarded as a result of the pH variation of the solution from which the Cr(VI) was drawn.

The fact that chromate was only observed in the pits is consistent with the low Cr coverage measured with XPS. Cr coverage in the pits is probably much higher than the
measured value, however, XPS gives only an averaged result, and it fails to show the large variation of chromate distribution around the pits. A reasonable picture might show a thin but uniform coverage of chromate layer on the surface, with the thickness several times less than the XPS sampling depth, and large amounts of chromate accumulated within pits. Raman is not sensitive enough to probe the uniformly covered chromate for our conditions.

The concentration of chromate in pits may play a major role in the overall mechanism of repassivation. Several mechanisms may contribute to chromate concentration in pits. Firstly, since the progress of pitting releases Al$^{3+}$, chromate and dichromate anions may move into the pits along with Cl$^-$ to balance the charge. Secondly, the corrosion product Al$^{3+}$ may form an insoluble precipitate with chromate. Thirdly, the corrosion product Al(OH)$_3$ may adsorb chromate. Once chromate is adsorbed, the negative charge it carries will repel negative chloride ions away from the alloy.

CrO$_4^{2-}$ alone is not enough to precipitate Al$^{3+}$, for example, when 1 ml of 180 ppm (0.93 mM) K$_2$CrO$_4$ was added to 50 ml of 0.2 M AlCl$_3$, no precipitate was observed. However, when KOH was then added until the pH reached 5, a white precipitate was formed. After filtration and rinsing, the precipitate appeared yellow. The Raman spectrum of this wet product is shown in figure 2.12c. Comparing with figure 2.12b, it appeared to be the same as the corrosion product in the in-situ migration observation.

The formation of this precipitate can be explained by either chromate absorption by Al(OH)$_3$, or by a more complicated reaction involving OH$^-$, such as

$$xAl^{3+} + yCrO_4^{2-} + zCr_2O_7^{2-} + (3x - 2y - 2z)OH^- = Al_x(CrO_4)_y(Cr_2O_7)_z(OH)_{3x-2y-2z} \downarrow$$
Whether it is this reaction or simple adsorption or a combination of both, the product must be extremely insoluble, within the pH range of its environment, since a large amount of this product can precipitate out from a very dilute solution of chromate.

Thus, the self-healing of the alloy can be explained by the mechanism shown in figure 2.37. After the CCC film is scratched off, a passive film forms and covers the scratch. In solution, chromate is released from the surrounding CCC film, and is adsorbed on the alloy surface. The adsorbed chromate inhibit oxygen reduction, and prevents pits from forming in the first place. In case a pit is formed in the scratch, such as shown in figure 2.37, Al(OH)$_3$ is formed in and around the pit. Al(OH)$_3$ attracts more chromate from the solution to form a precipitate. Even though the chromate may be very dilute in the bulk solution, it may become relatively concentrated around the pit during precipitation. One can hypothesize from this point that the chromate would functions in several ways to stop pit growth. First, its negative charge may repel chloride ions and slow down pit growth. Second, it inhibits oxygen reduction around the pit, and this breaks the pitting corrosion electrochemical cycle. Third, it may become even more concentrated inside the pit, and react with the fresh alloy surface to form a passive film, which in turn stops the growth of the pit. After the pit growth is completely stopped, Al(OH)$_3$ along with the absorbed chromate may either stay or slowly dissolve into the solution and relocate elsewhere, this would explain why the pits not covered with corrosion product had very little chromate inside.
Thus, chromate is acting like a smart missile, guided toward any defect that is generating corrosion product, and repairs it. This is probably the reason why chromate is so effective in prevent pitting corrosion of the AA-2024-T3 alloy.

2.4.8 “Cathodic Protection” Does Not Work

It is not clear how effective the galvanic coupling arrangements in c, a2, and b2 were to assess cathodic protection, since the area ratio was only 14 in c and 2.8 in a2 and b2, while a narrow scratch may have a very large area ratio, and thus may be better protected. However, the reversed current observed in a2 and b2 indicates cathodic protection is unlikely to be responsible for the self-healing property over a long run. First, although $E_{corr}$ of a CCC treated alloy sample is initially negative relative to the bare alloy, it increases with time while the sample is immersed in solution. As shown in figure 2.36, a long time potential measurement in 0.1 M NaCl indicated $E_{corr}$ for the CCC treated sample showed a very negative initial potential of -780 mV; after one hour, the potential increased to -650 mV; after 18 hours, it seemed to be stabilized around -625 mV, which is positive relative to the $E_{corr}$ of bare alloy after the sandwich experiments as well as after immersing in the 9 ppm CrO$_4^{2-}$ solution. Second, the effect of chromate migration-repassivation on the scratch should be considered. As represented in the results of the sandwich experiments a2 and b2, although the $R_p$ of a fresh scratch may be low, while the scratch becomes passivated by chromate migration, its $R_p$ will rise and its potential will drop, so the galvanic current will decrease substantially, and may eventually be reversed. Therefore, we conclude that galvanic coupling is unlikely to play a major role in a natural
self-healing process. If the CCC film is covered with nonconductive primer or paint, cathodic coupling may be completely prohibited in the first place.

2.5 CONCLUSION

The chromate conversion coating on the AA-2024-T3 alloy does release chromate in an aqueous environment. The release rate is very slow, and depends on the age of the CCC film. The chromate can migrate to an exposed area of the alloy, and adsorb on the bare alloy surface. The adsorbed chromate inhibits oxygen reduction, lowers the corrosion potential down to the passive region, and prevents pitting corrosion. This may be solely responsible for the self-healing property of the CCC treated alloy. After being repassivated, the alloy’s corrosion potential drops, and its pitting potential rises, and its polarization resistance increases by about two orders of magnitude, and its corrosion rate decreases by the same factor. The repassivation is associated with formation of insoluble chromate species at places where corrosion products are formed, such as pits. The nature of the chromate species at these sites is similar to the chromate in the CCC film itself, and its Raman spectrum is nearly identical to a precipitate formed by mixing chromate, hydroxide and aluminum ions.
Figure 2.1: Demonstration of mixed potential theory.
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Figure 2.3: Schematic of pitting corrosion. Top: initiation stage. Bottom: propagation stage.
Figure 2.4: Pitting potential and pitting prevention by an passivator. $E_{pp}$: protective potential. $E_{pit}$: pitting potential. $E_{corr}$: corrosion potential.
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Figure 2.10: Experiment configuration for the galvanic corrosion experiment.
Figure 2.11: Raman spectra of: (a) CCC film, (b) Alodine solution, (c) 8.6 mM \( \text{K}_2\text{Cr}_4\text{O}_7 \), (d) 4.2 mM \( \text{K}_2\text{Cr}_2\text{O}_7 \), and (e) \( \text{Cr}_2\text{O}_3 \) paste. Conditions: 515 nm laser, 20 mW on sample. Exposure time: 10 seconds for (a) and (b), and 1 second for (c), (d), and (e).
Figure 2.12: Raman spectra. (a) the solution after 72 hours of chromate release and migration experiment of a sample aged for 20 minutes, average of twenty 3-second exposures. (b) the corrosion product observed in-situ during the release and migration experiment of the XPS setup, 1 second exposure. (c) the precipitate of chromate reacting with AlCl₃ and KOH, 1 second exposure. Conditions: 515 nm laser, 20 mW on sample.
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Figure 2.18: Photographs of the samples after the sandwich experiments “a1” through “a3”. The letters before the dash line “-“ represent the experiment configuration, and the numbers following the dash line represent the length of the experiment.
Figure 2.18
Figure 2.19: Photographs of the samples after the sandwich experiments “b1”, through “b3”. The letters before the dash line “-” represent the experiment configuration, and the numbers following the dash line represent the length of the experiment.
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Figure 2.20
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Figure 2.22: Microphotographs at “50X” magnification.
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Figure 2.24: Corrosion potential and breakdown potential of the samples after the sandwich experiments of b1, b2, and b3.
Figure 2.25: Galvanic current measured during the first 20 hours of the sandwich experiments of: (a) a2, and (b) b2, showing the effect of reversed current.
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Figure 2.32: Polarization curves measured in 0.1 M NaCl. Solid line is a bare alloy sample immersed in 0.1 M NaCl alone for two hours. Dashed line is an alloy sample after immersing in 15 ppm K$_2$CrO$_4$/0.1 M NaCl for 45 hours.
Figure 2.33: Raman spectra on different sites of an initially untreated sample after 48 hours of sandwich experiment a1. (a) on a white pit. (b) on a dark pit. (c) away from any pit. Conditions: 515 nm laser, 20 mW on sample, averaged over twenty 1-second exposures.
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Figure 2.35: Raman spectra across the pit. Condition: 515 nm laser, 20 mW on sample, 0.5 second exposure for each spectrum, sample moving at about 40 μm/sec.
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Figure 2.37: Propose self-healing mechanism of CCC film on AA-2024-T3 alloy. Top: chromate migrates from the CCC film to a scratch, mostly to pits in the scratch, and oxygen reduction is prohibited. Bottom: pit growth is stopped and the pit is passivated.
CHAPTER 3
MULTICHANNEL FOURIER TRANSFORM
RAMAN SPECTROSCOPY

3.1 INTRODUCTION

This chapter deals with Raman instrumentation. The rapid development of Raman instrumentation in the past ten years has progressed along two paths: spectrometers based on Michelson interferometers (FT-Raman)[35, 36, 37, 38, 39] and dispersive spectrometers with charge coupled device (CCD) detectors [40, 41, 42, 43, 44, 45]. The two developments have resulted in a rapid growth of applications of Raman spectroscopy in chemical analysis, as well as in fundamental research. This classification is based on the way wavelength is analyzed by the spectrometer. In the past, wavelength was analyzed with light dispersing optical prisms, but currently, gratings have largely replaced prisms and become the essential elements of dispersive spectrometers. Shown in figure 3.1a is a classic Czerny-Turner spectrograph upon which most modern dispersive Raman spectrometer designs are based. It consists of an entrance slit, a collimating mirror, a grating, and a focusing mirror. In early scanning spectrometers, an exit slit is placed at the focal point of the focusing mirror, where a single channel detector (i.e. a photo multiplier tube) is located. The whole spectrum is collected by rotating the grating step by step. In a multichannel spectrometer, a multichannel detector, typically a CCD, is placed at the focal...
plane of the focusing mirror, and the whole spectrum can be collected simultaneously. For an equal sampling time, an improved signal to noise ratio (SNR) over a single channel system results from the multichannel advantage.

FT-Raman spectroscopy was first introduced in 1986 [36, 37, 38, 39, 46, 47]. It stimulated rapid growth in Raman applications, due mainly to the reduced fluorescence interference of many samples excited by near infrared lasers. Commercial FT Raman spectrometers are all based on the Michelson interferometer, a schematic of which is shown in figure 3.1b. A beam-splitter splits the light beam into two halves, both of which are reflected by the beam-splitter and a mirror, and recombined after the beam-splitter. By fixing one mirror and scanning the other back and forth, sinusoidal interference patterns of different frequencies are generated for light of different wavelengths. The interfering beams are focused by a mirror or a lens onto a single detector, and a Fourier transform of the recorded interferogram yields a frequency domain spectrum comparable to that obtained on a dispersive instrument. Because all wavelengths are monitored at all times, an improved SNR over a single channel dispersive system results from a multiplex advantage.

Both dispersive and FT spectrometers have their advantages and disadvantages. FT Raman benefits from advantages inherent to interferometry: high collection efficiency due to the absence of slits, excellent wavelength precision, easily variable resolution and spectral coverage, and an active history of hardware and software development for FTIR applications. Unfortunately, FT-Raman as currently implemented has restrictions on the signal to noise ratio (SNR) which are fundamental. Detectors for the 1-2 μm wavelengths
of interest are noisy, so the SNR is limited by detector noise rather than signal shot noise. Even with a perfect (i.e. noiseless) detector, FT-Raman would suffer from noise redistribution because the shot noise from all wavelengths monitored by the detector would be detected simultaneously and distributed over the entire spectrum.

The absence of the entrance slit in a FT system is often misinterpreted. It does not mean the sampling area can be infinitely large. As shown in figure 3.1b, the Michelson interferometer requires the light beam be collimated to some extent. Uncollimated light will result in a larger spot at the detector position with decreased contrast of the interferogram, which reduces the signal to noise ratio (SNR). Hence a limiting aperture is often placed at the focal plane of the collimating lens/mirror. This sets an upper limit to the sampling area.

Dispersive Raman spectrometers with low noise multichannel CCD detectors avoid the limitation imposed by detector noise, and maintain the multichannel advantage of array detectors [40, 41, 42, 43, 44]. The sensitivity of silicon based CCD's extends to 1.1 μm, permitting laser operation at ca 800 nm, thus avoiding much of the fluorescence associated with visible excitation. Although dispersive CCD Raman spectrometers can yield much higher SNR than FT-Raman or scanning systems, they have some inherent limitations. The small CCD pixel width (typically 25 μm) requires a small entrance slit and corresponding small collection efficiency, and increasing efficiency by increasing slit width degrades resolution. For this reason, the excitation laser is usually tightly focused to a spot size similar to the CCD pixel size, as result, radiation damage to thermally or photochemically labile samples is a problem at higher laser power densities. In addition,
dispersive systems cannot easily vary spectral coverage, and always face a resolution vs. spectral coverage trade off. With a finite number of pixels along the wavelength axis, one must sacrifice resolution to cover a wider spectral range. The wavelength precision of a dispersive system is not generally as good as an interferometer, due to backlash and thermal drift of mechanical components and alignment.

For a large number of Raman samples, the spectroscopist would like to combine the precision and throughput of FT-Raman with the low noise and multichannel characteristics of CCDs. For surface Raman in particular, the reduced laser power density derived from the large sampling size of FT-Raman, and a quiet detector such as a CCD, if combined, might yield an instrument with less sample damage and high SNR. This concept has been experimented with in other fields of spectroscopy. For example, Sweedler and Denton reported such a device for emission spectroscopy [48,49], and one report of a related device used for Raman scattering has appeared [50]. Although a variety of optical arrangements have been reported [51,52], they share the common approach of generating an interferogram across the face of an array detector for simultaneous data collection. Historically, three configurations which produce an interferogram in space rather than in time have been described in the literature. One is based on a Michelson interferometer with a tilted rather than a moving mirror [53]. The second type utilizes a Savart plate interferometer and two polarization filters [50, 54], and the third a “common path” or “Sagnac” interferometer [48, 51, 55]. All three types are solid state and have no moving parts. Simultaneous recording of the interferograms in space has been achieved using photographic film [56], photodiode arrays [51] and CCDs [48, 50]. Of the three
configurations, the Sagnac type has attracted the most attention, possibly due to its superior mechanical stability compared with the Michelson type, and its more straightforward data processing as compared to the Savart plate type. A triangle Sagnac interferometer is shown in figure 3.2. There is no moving mirror, but a path length difference between the two beams leaving the beam-splitter generates the interferogram. As noted by Okamoto, et al.[51], the entrance aperture size does not affect resolution, leading to potentially high throughput. Fourier transformation of the interferogram leads to an intensity vs wavenumber plot, which is easily presented as a Raman spectrum.

Takahashi, et al., dubbed the combination of an interferometer and CCD “multichannel Fourier transform spectroscopy” or MCFT [50].

This chapter explores the suitability of the common path interferometer for Raman spectroscopy, with particular attention to wavelength precision, SNR, resolution, and practical advantages. Although the Sagnac interferometer has been analyzed before [48, 49, 50, 51, 52], a detailed analysis concerning the principle and optimum optical design is not available in the literature, and some reports in the literature contained errors. Such an analysis is necessary to understand the special properties of MCFT, and to make future improvements. Section 3.2 provides this analysis, followed with an initial assessment of efficiency, sensitivity, resolution, reproducibility, and stability of the first generation MCFT Raman spectrometer constructed in this lab. These results give directions toward which performance should be improved. Then, in section 3.3, the second generation MCFT Raman spectrometer and its performance are described, and its suitability to surface Raman study is discussed. Through detailed theoretical treatments, a software-
noise-correction procedure to improve SNR and an optical heterodyning technique to improve the resolution are developed.

3.2 MCFT RAMAN: THE FIRST GENERATION

3.2.1 Theory

The triangle Sagnac interferometer is a very simple device consisting of a beam-splitter, two mirrors, and a focusing lens, all at fixed positions. A schematic drawing is shown in figure 3.2. A diverging or converging light beam entering the interferometer is split into two identical halves, which travel in a common path but at reversed directions between the beam splitter and the mirrors. After leaving the beam splitter, the two light cones pass through the focusing lens, and form two circular beams which overlap with each other at the focal plane of the lens. The spatially distributed interferogram thus formed is collected by a CCD detector simultaneously, a Fourier transform of which yields a frequency domain spectrum.

The Sagnac interferometer functions as a source doubling mechanism. As shown in figure 3.2, two identical images IM1 and IM2 are formed by the beam splitter BS and the two mirrors M1 and M2. For optimum performance, the optical axis of the interferometer and that of the FT lens are superimposed. It can be proved mathematically that, when the two mirror planes both form 22.5 degree angles with the beam splitter plane, the line connecting the two images is perpendicular to this optical axis (the proof is trivial but lengthy, and purely mathematical, so is not given here). In this configuration, the distance
\( \alpha \) between the two images is related to the displacement of the mirror M2, referred to as \( l \) [48], by

\[
\alpha = \sqrt{2l} \tag{3.1}
\]

The path length difference at angle \( \theta \) relative to the optical axis of the FT lens is

\[
\Delta = \alpha \sin \theta \tag{3.2}
\]

Let \( E_i \) denote the electric field created by the \( i \)'th image, \( i = 1, 2 \), then at any time \( t \),

\[
E_1(\theta) = e \cos(\omega t + \varphi)
\]

\[
E_2(\theta) = e \cos \left( \omega t + \varphi + \frac{2\pi \alpha \sin \theta}{\lambda} \right) \tag{3.3}
\]

When interference occurs, the total intensity is

\[
I(\theta) = \left( E_1 + E_2 \right)^2 = e^2 \left\{ 1 + \cos \left( \frac{2\pi \alpha \sin \theta}{\lambda} \right) \right\} \tag{3.4a}
\]

Thus the centerburst of the interferogram is located at \( \theta = 0 \), where intensities of all wavelengths simply add up. Since \( I(\theta) \) is an even function of \( \theta \), the interferogram is symmetric around the centerburst. The implication is that one only needs to collect half of the interferogram, and the other half can be "fabricated" using a simple data reflection program (see appendix A).

At small angle \( \sin \theta \approx \theta \), equation (3.4a) reduces to

\[
I(\theta) = e^2 \left\{ 1 + \cos \left( \frac{2\pi \alpha \theta}{\lambda} \right) \right\} \tag{3.4b}
\]

If the focal length of the FT lens is \( F \), and the pixel width of the CCD is \( d \), then the pixel number is related to \( \theta \) by the following equation

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\[
\theta \approx \tan \theta = \frac{xd}{F} 
\]  

(3.5)

Substituting into (3.4b) yields

\[
I(x) = e^{\pm \left\{ 1 + \cos(2\pi \frac{\alpha d}{\lambda F} x) \right\}}
\]  

(3.6)

Therefore the intensity vs. the CCD pixel number is a sinusoidal function, whose frequency is given by

\[
f = \frac{\alpha d}{F} \sigma
\]  

(3.7)

where the wave number \( \sigma \) has replaced the inverse of the wavelength \( \lambda \). A direct implication of equation (3.7) is that the frequency after Fourier transformation will be linear with the wave number.

The maximum path length difference at a given \( \alpha \) is generated at \( x = N \), where \( N \) is the total pixel number of the CCD:

\[
\Delta_{\text{max}} = \alpha \theta_{\text{max}} = \frac{\alpha N d}{F}
\]  

(3.8)

Following basic Fourier transform theory, the instrumental line width (ILW) is simply the inverse of \( \Delta_{\text{max}} \), multiplied by an apodization factor. For triangular apodization [63], it is:

\[
\Delta \sigma = \frac{18F}{\alpha N d}
\]  

(3.9)

Equation (3.9) suggests ILW can be reduced by increasing \( \alpha \) as a consequence of increasing \( l \). However, there is an upper limit for which this can be done. According to equation (3.7), the maximum \( \alpha \) is determined by the Nyquist frequency:
Combining this with equation (3.7) yields

\[ \alpha_{\text{max}} = \frac{F}{2d\sigma} \]  

Plug this into (3.9), one gets

\[ \Delta\sigma_{\text{min}} = \frac{2 \times 1.8}{N} \sigma \]  

Therefore equation (3.12) sets an ultimate limit up to which the resolution can be improved by increasing \( l \).

For a spectrum containing multiple lines, the minimum ILW is determined by the Nyquist wave number \( \sigma_{\text{max}} \), below which no folding-over occurs. Of course this corresponds to the Nyquist frequency \( f = 0.5 \). From (3.7), it is

\[ \sigma_{\text{max}} = \frac{F}{2d\alpha} \]  

For Stokes Raman, this maximum wave number is usually set slightly higher than the laser wave number. For a laser wavelength of 830 nm, \( \sigma_{\text{max}} \) can be set as low as 12,048 cm\(^{-1}\).

With an \( N=1024 \) channel CCD, equation (3.12) gives \( \Delta\sigma_{\text{min}} = 42 \) cm\(^{-1}\). Furthermore, if the pixel width is 25 \( \mu \)m, and \( F \) is 470 mm, from equation (3.13), this 42 cm\(^{-1}\) resolution will be obtained at \( \alpha = 7.8 \) mm and \( l = 5.5 \) mm. At this setting, the higher wave number anti-Stokes lines would be folded over and give false peaks, thus they should be filtered out prior to the CCD.
Throughout the above analysis, the size of the light source was never mentioned, and in fact, does not matter. Equation (3.4) shows the interferogram is only a function of the angle. Thus light rays coming from a different point source but entering the interferometer at the same angle will be focused by the FT lens to the same point on the CCD, and the intensities will add up. No limit to the position of the point sources is set, as long as the rays are within the aperture of the interferometer and the FT lens. This means the sampling area can be much larger than a dispersive system where a slit must be present, or a conventional FT system where an limiting aperture is used to assure beam collimation inside the interferometer.

The light gathering capability of a spectrometer depends on its etendue, which is the product of sampling area A and collection solid angle Ω. The sampling area can be very large, as discussed. The solid angle is approximately inversely proportional to the square of the \( f \)-number, a more convenient measure of a spectrometer. The \( f \)-number of the Sagnac interferometer is \( F \) divided by the length of the CCD. For a 25.6 mm long CCD with \( F = 470 \) mm, this is \( f/18 \). Although this is relatively a high \( f \)-number, the actual \( f \)-number of the spectrometer can be significantly reduced using magnifying input optics (see figure 3.3), and the large sampling area of the interferometer leaves one enough room to do this. The actual \( f \)-number of the spectrometer is simply the \( f \)-number of the interferometer divided by the magnification of the input optics. The etendue remains constant, but Ω is increased (and the sampling area decreased) by magnification.

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3.2.2 Experimental

The optical apparatus is shown schematically in figure 3.3. The 830 nm light coming from a Ti:sapphire laser was focused onto the sample by lens L1 (FL=50 mm). The scattered light was collimated by lens L2 (FL=50 mm), and then focused by lens L3 (FL=320 mm) to form a magnified image of the sample at the entrance aperture. The aperture was 11 mm in diameter. A 3 mm thick CdTe absorption filter was placed before the aperture to eliminate wavelengths below 850 nm [57]. A CCD detector (EEV 15-11, deep depletion, 1024 channels, 25 μm pixel width) was placed at the focal plane of a Fourier lens L4 (FL=470 mm, f/8) to generate sharp fringes. The fringe spacing was controlled by adjusting the position and angle of M2. The interferometer is f/18, and the magnification of the input optics is 6.4, this gives an overall f/3 spectrometer.

Specification of other optical elements and instrument alignment instructions will be given in appendix B. In this section, Fourier transform with triangle apodization was performed with Hyperplot software. All spectra displayed are in magnitude mode.

The dispersive spectrometer used for comparison was an ISA 640 spectrograph and EEV CCD 05-10 (1152 channel) detector with f/5.5 collection. The laser illuminated the sample at 90° relative to the collection axis, with the beam parallel to the slit image. The beam diameter was varied as described below, by defocusing the laser with a lens placed on a translation stage.
3.2.3 Results and Discussion

Several performance criteria of the first generation MCFT Raman spectrometer will be addressed, including resolution, sampling area, sensitivity, and stability.

**Resolution** Figure 3.4, trace a, is the raw interferogram for naphthalene illuminated by 135 mW of 832 nm laser light. The CCD was positioned to monitor the centerburst and half of the symmetric interferogram. The decrease in amplitude and DC level away from the centerburst is apparently due to the uneven angular distribution of scattered and collected intensity. Fourier transformation with no preprocessing yields the upper trace of figure 3.5. The spectrum covers the entire Raman shift range from about -100 cm\(^{-1}\) on the anti-Stokes side (determined by the Nyquist limit) to the DC frequency component at ca. 13,000 cm\(^{-1}\) on the Stokes side. In this case, the laser, anti-Stokes Raman, and Stokes Raman up to about 350 cm\(^{-1}\) are absorbed by the CdTe filter, and Raman shifts above about 2400 cm\(^{-1}\) are beyond the red cut-off of the CCD quantum efficiency curve. The spectrum of figure 3.5a is an expansion of the upper trace in figure 3.5 over the useful range of 300-1800 cm\(^{-1}\), still without any preprocessing. The interferogram of figure 3.4b was obtained from 3.4a by removal of low frequency components and zero filling to a total of 2000 points. Figure 3.5b is the FT of 3.4b, showing increased data density but no improvement in resolution. Figure 3.4c shows an interferogram obtained from 4b by the “data reflection algorithm (DRA)” which doubles the number of points by reflection about the centerburst [58]. This effectively increases the maximum path length difference \(\Delta m\) and the number of the CCD channels, \(N\), therefore decreases the instrumental line width, \(\Delta\sigma_{\min}\) (see equation 3.12). Its FT (figure 3.5c)
shows a FWHM for the 764 cm\(^{-1}\) band of naphthalene of 27 cm\(^{-1}\). A dispersive Raman spectrum of naphthalene with the same laser power and integration time is shown in figure 3.5d; the FWHM for the same band is 6.4 cm\(^{-1}\).

The MCFT spectra exhibit significantly poorer resolution than the dispersive spectrum, due to the limitations imposed by equation (3.12). \(\sigma_{\text{max}}\) for the conditions of figures 3.4 and 3.5 was 14500 cm\(^{-1}\), yielding a minimum \(\Delta\sigma\) of 51 cm\(^{-1}\) for the 1024 channel detector employed, or 26 cm\(^{-1}\) after DRA. Increasing \(N\) is limited by available CCD's. Mathematical manipulation may yield some improvement in resolution [59, 60], as well as geometric modification which exploit the two dimensional nature of CCD's [49, 50]. However, it is unlikely that MCFT Raman techniques will outperform most dispersive or Michelson systems with respect to resolution.

\textit{Etendue}  
The MCFT has a much larger aperture (> 10 mm) which is limited by the size of the beam-splitter and the mirrors. A related advantage is the independence of MCFT response on laser spot size for a given laser power. A slit based instrument can only collect from a region whose image is as wide as the slit, often 25-50 \(\mu\text{m}\) for CCD systems. Figure 3.6 shows the effect of laser beam focus at the sample for a dispersive system with a 50 \(\mu\text{m}\) slit image. Compared to the signal strength with a tight beam focus (~ 60 \(\mu\text{m}\)), the signal decreases by 90% when the beam diameter is increased to 1.3 mm. For the MCFT spectrometer of figure 3.3, the 11 mm aperture can accept light from a 1.5 mm beam diameter at the sample, due to the magnification of the collection optics L2 and L3. At f/3 and sampling size of 1.3 mm, the etendue of the MCFT spectrometer is 70 times larger than that of the f/5.5 dispersive spectrometer with a 50 \(\mu\text{m}\) X 1.3 mm slit. If a
50 μm diameter spot is used in the latter, this difference would be 2,300 times. Thus the MCFT has a large light gathering capability compared with a dispersive system. Therefore, when the beam diameter is increased from 60 μm to about 1.3 mm, the signal decreases by only about 10% (figure 3.6) for the MCFT spectrometer. A 1.3 mm diameter beam is essentially unfocussed, and has a power density at the sample only 0.2% as large as the focused, 60 μm beam. The advantage to thermolabile or photochemically unstable materials is obvious, and results from the much larger MCFT aperture (at the sample) of 1.3 mm compared to 50 μm for a typical slit image.

**Stability** Since the band positions in the MCFT experiment are determined by rigid optical components and the CCD pixel spacing, frequency precision would be expected to be excellent. Furthermore, the absence of moving parts and the absence of a requirement for precise alignment of laser and slit should yield good intensity precision. Figure 3.7a is an overlay of 20 MCFT spectra of benzene obtained over an 8 hour period. Zero frequency jitter was observed for these spectra, but it should be noted that the resolution of the current MCFT system would detect only relatively large frequency shifts of >10 cm\(^{-1}\). Subtraction of spectra obtained 5 hours apart yielded no observable residuals (figure 3.7b), indicating the absence of observable frequency or intensity shifts. The standard deviation of the 992 cm\(^{-1}\) peak intensity for benzene was 1.4% for the 20 spectra, but most of this deviation resulted from a liquid nitrogen fill after the 15th spectrum. The standard deviation of 992 cm\(^{-1}\) peak intensity for the first 15 spectra (covering 4 hours) was 0.7%. A background spectrum obtained under the same conditions, but in the absence of benzene, is shown in Figure 3.7c. The small features
observed are presumably due to periodic variations in pixel sensitivity or dark signal and to background shot noise. Notice that the baseline in the benzene spectra is very reproducible and definitely nonrandom. It might be due to the apodization.

**Sensitivity** in terms of signal strength comparison between dispersive and MCFT instruments cannot be made directly, since the MCFT produces a modulated intensity over all of the CCD pixels, while a dispersive instrument places all of the intensity of a particular band on a few pixels only. It is appropriate, however, to compare signal/noise ratio (SNR) for the two methods for comparable measurement conditions. Figure 3.8 shows spectra of a weakly scattering solution (0.2 M K$_2$SO$_4$ in water) obtained with MCFT and dispersive instruments operating with the same laser power at 832 nm, and the same integration time. This case is an example where the SNR is determined by both analyte and background shot noise. For the dispersive system (figure 3.8b) the SNR determined as the ratio of SO$_4^{2-}$ peak height to the standard deviation of the baseline is 37. The SNR based on the ratio of peak height to the standard deviation of the peak height is 34. For the MCFT system (figure 3.8a), the SNR's determined by the same two relationships are 51 and 39, respectively. Figure 3.9 shows spectra of glassy carbon obtained with dispersive and MCFT instruments. The SNR based on the ratio of the 1315 cm$^{-1}$ peak height to the standard deviation of the baseline is 118 for the dispersive system, and 103 for MCFT. These examples establish that the MCFT technique can have comparable SNR for weak scattering from a clear solution and an opaque solid.

One should not be confused by the *etendue* comparison and SNR comparison. Although the MCFT has a much larger *etendue* than the dispersive system, and hence can
accommodate much higher laser powers without raising the power density, a higher SNR will not be obtained unless this capability is utilized, by raising the power.

3.2.4 Instrumental Improvements

The MCFT Raman spectrometer demonstrated superior stability, simplicity, accuracy, and throughput compared to a multichannel dispersive Raman spectrometer, and had comparable sensitivity. However, as noted earlier, the MCFT spectra exhibit significantly poorer resolution than the dispersive spectra. Improving resolution should be the priority in instrument development, and this should be done without sacrificing SNR. This issue is addressed in the second generation of MCFT Raman spectrometer, described in section 3.3.

3.3 MCFT RAMAN: NOISE ANALYSIS AND RESOLUTION IMPROVEMENT

This section reports significant instrumental improvements on MCFT Raman, plus several important theoretical considerations and performance evaluations. These efforts address three specific issues: theoretical limits on signal/noise ratio (SNR) and resolution, improvements in instrumental design directed toward noise reduction, and the use of an optical heterodyne technique for improving resolution.

3.3.1 Theory

**SNR Characteristics of MCFT** Before discussing the MCFT further, a good understanding of the signal and noise characteristics of the dispersive/CCD and
conventional FT Raman is necessary. SNR analysis of both dispersive/CCD [44] and FT-Raman spectrometers [35, 61, 62] have been described in detail, and in both cases depend on several experimental conditions, including laser power density, sample area (or volume) monitored by the spectrometer ($A_D$), detector quantum efficiency ($Q$), and contributions from detector dark or readout noise. Considered here is a sample illuminated by a uniform laser beam which overfills the spectrometer, and generates Raman scattering with a specific intensity of $L$ (photons s$^{-1}$ cm$^{-2}$ sr$^{-1}$) at a specific resolution element, $i$. For the case of a dispersive/CCD system, the signal, $S_n$, is

$$S_n = L_i A_D Q T t$$  \hspace{1cm} (3.14)

Where, $L_i$ is the specific intensity in the particular spectral resolution element, $T$ and $Q_i$ are spectrometer transmission and quantum efficiency, $\Omega$ is the collection solid angle at the sample, and $A_D \Omega$ is the etendue [40, 44, 47]. $t$ is the total measurement time, equal to the CCD integration time in this case. Now, the noise has several possible sources. For a good CCD detector, which has very little dark or readout noise, only the shot (quantum) noise is significant. This noise arises from the statistical characteristics of photons, and fundamentally limits SNR. For a measurement of a large number of photons of a certain mean value, the standard distribution (i.e., noise) of the measurement is the square root of the mean. Therefore, the SNR for a dispersive/CCD system is

$$SNR_{i,disp/m} = S_n^{1/2} = (L_i A_D \Omega Q T t)^{1/2}$$  \hspace{1cm} (3.15)

where the subscript "m" means multichannel. This formula is fundamental to all photon counting detectors. No more improvement on the SNR can be achieved beyond this limitation, due to the random, quantum nature of photons. Varying the gain of the
detector, or any post measurement magnification will change the signal and the noise by the same factor, therefore their ratio will remain the same.

Since measurement time \( t \) for each resolution element is \( N \) (where \( N = \text{number of resolution elements} \) times as large as the single channel measurement time for a scanning spectrometer, a **multichannel advantage** of \( N \) results, meaning that the SNR for the dispersive/CCD system is \( N \) times as large as that for a scanning single channel system with the same \( L, A, \Omega, Q, T \) and total measurement time \( t \).

Now consider the signal and noise of a conventional FT system. Assume \( L, A, \Omega, Q, T \) and total measurement time are the same as the dispersive/CCD (the 50% transmission loss from the beam splitter is included in \( T \)). In addition, assume the spectrum contains only one peak, at resolution element \( i \). Before Fourier transform, the total signal \( S \), integrated over the entire interferogram would be the same as \( S_{\text{div/m}} \), and its standard deviation will be its square root. After Fourier transform, it can be proved mathematically, that the signal in the frequency domain will remain the same \( S \), and that the noise at any resolution element, including \( i \), will be approximately the square root of the total signal, in this case, \( S \) (the proof is beyond the scope of this thesis, but interested readers are referred to Marshall's book[63]). Therefore, for a single-line spectrum, SNR of an FT system is the same as that of a dispersive multichannel system, and is \( N \) times better than a dispersive/single channel system. This is called the **multiplex advantage** (Fellget's advantage), and it is derived from the fact that in collecting an interferogram the same wavelength is monitored all the time. However, unlike a dispersive system where the noise is localized to the specific resolution element, an FT system redistributes the noise in any
resolution element to the entire frequency domain spectrum. This has a profound effect on the noise characteristics of all Fourier transform based techniques, and its influence will become clear as we progress to a more complicated spectrum.

Now, consider a spectrum having multiple peaks. In the interferogram, each resolution element contributes $S_i$ to the total signal, and consequently, the total noise becomes

$$\text{NOISE} = \left( \sum_{i=1}^{N_x} S_i \right)^{1/2} = \left( A_D \Omega T \sum_{i=1}^{N_x} L_i Q_i \right)^{1/2} \quad (3.16)$$

After FT, this will be the noise level for all resolution elements. Therefore, at any resolution element $i$ with a signal $S_i$, the SNR will become

$$\text{SNR}_{i,\text{FT}} = \frac{S_i}{\left( \sum_{i=1}^{N_x} S_i \right)^{1/2}} = \frac{L_i Q_i}{\left( \sum_{i=1}^{N_x} L_i Q_i \right)^{1/2}} \left( A_D \Omega T \right)^{1/2} \quad (3.17a)$$

Equation (3.17a) provides a direct SNR comparison between an FT system and a dispersive multichannel system. By comparing (3.17a) and (3.15) for the shot noise limit, it is clear that an FT system is always noisier than a dispersive/CCD system, assuming all else is equal. For a spectrum containing $M$ equally intense lines, (3.17a) becomes

$$\text{SNR}_{i,\text{FT}} = \frac{1}{M^{1/2}} \left( A_D \Omega T L_i Q_i \right)^{1/2} = \frac{1}{M^{1/2}} \text{SNR}_{i,\text{disp/m}} \quad (3.17b)$$

When $M=N_R$, the number of resolution elements, the SNR becomes equal to a dispersive/single channel system, and the multiplex advantage completely vanishes. This reduction of SNR is often inappropriately called the "multiplex (or Fellget's) disadvantage", when in fact multiplex is still an advantage, but its effect on SNR is
weakened. This SNR reduction can be partially compensated by the larger $A_0\Omega$ of the Michelson interferometer used in conventional FT-Raman, compared to a dispersive spectrometer.

To summarize, in a dispersive system, the signal and the noise are both localized to their specific resolution element, while in a FT system, the noise is distributed evenly over the entire spectrum. This has an interesting impact on the appearance of the spectra. In a dispersive spectrum, the noise accompanies the signal; where there is no signal, there is no noise; where there is a large signal, there is a lot of noise. In a FT spectrum, the noise level is the same over the entire spectrum, thus, the baseline appears relatively noisier, even though the SNR might be the same as, or even higher than, a corresponding dispersive spectrum. Therefore one can not compare the quality of a dispersive spectrum with that of a FT spectrum, if the SNR is based on the signal strength and the noise level at the baseline, for both methods.

Due to the much longer wavelength laser typically employed for FT-Raman, detectors for conventional FT-Raman spectrometers often have a large amounts of dark noise, and often this is the predominant noise source in a Raman spectrum. This noise will further worsen the SNR for a FT system. Assume the dark count rate is $\phi_d$ (electrons per unit time), then equation (3.18) applies:

$$SNR_{i,FT} = \frac{S_i}{\left(\phi_d t + \sum_{i=1}^{N_A} S_i\right)^{1/2}} = \frac{A_D\Omega TL_i Q_i}{\left(\phi_d + A_D\Omega T \sum_{i=1}^{N_A} L_i Q_i\right)^{1/2}}$$

(3.18)

In case of a dark count rate much larger than the sum of the signal, (3.18) reduces to
Equations (3.17a,b) and (3.19) are the two extreme special cases of equation (3.18).

Now it is time to consider MCFT Raman. MCFT is both multiplex and multichannel, in that many channels are monitored simultaneously, but each channel has contributions from all wavelengths, all the time. The MCFT design spreads the light from a given Raman feature over many CCD pixels, thus reducing the SNR compared to a dispersive system which puts all the light onto one (or a few) pixels. Mathematically, the MCFT interferogram is the same as that obtained with a Michelson interferometer and a shot noise limited detector, with the Michelson scan time equal to the integration time of the MCFT CCD. By this analogy, $SNR_{MCFT}$ has the same SNR behavior as FT-Raman, provided both operate in the shot noise limit.

$$SNR_{MCFT} = \frac{S_i}{\left(\sum S_i\right)^{1/2}} \cdot \frac{L_i Q_i}{\left(\sum L_i Q_i\right)^{1/2}} (A_0 \Omega T)^{1/2}$$  \hspace{1cm} (3.20)$$

Therefore, we expect $SNR_{MCFT}$ to equal $SNR_{FT}$ and $SNR_{DIS}$ for a single spectral line in the shot noise limit, assuming all else is equal. But $SNR_{FT}$ and $SNR_{MCFT}$ will decrease as the spectrum becomes more complex. It is also important to note that $(A_0 \Omega Q T)$ can be much larger for FT and MCFT spectrometers compared with dispersive, and this feature will be exploited later. In addition, the MCFT will be immune to source flicker noise, while a Michelson interferometer SNR will degrade if the laser fluctuates on a time scale comparable to the sampling interval.
**CCD Nonuniformity Correction**  
MCFT has an additional "noise" source not present in FT-Raman, from variations in angular distribution of the light and pixel gain across the CCD. This is a result of using multichannel detectors. In the perspective of the interferogram, this variation in MCFT is identical to the flicker noise in conventional FT. Fourier transformation of these variations yields fixed pattern noise, or to be more accurate, false peaks (since they are not entirely random). This issue has been addressed previously [48], but the approach to reduce the fixed pattern noise required cumbersome mirror adjustment and some loss in resolution. In the following, we will examine how this noise is introduced to the frequency domain spectrum, and how to reduce it.

When considering uneven angular distribution of the light, equation (3.3) needs to be rewritten

\[
E_i(\theta) = e_i(\theta) \cos(\omega t + \varphi) \\
E_2(\theta) = e_2(\theta) \cos(\omega t + \varphi + \frac{2\pi \alpha \sin \theta}{\lambda}) 
\]

(3.21)

Substituting variable angle \( \theta \) with CCD pixel \( x \), the light intensity inserted by the two images separately are

\[
I_i(x) = \langle E_i^2 \rangle = \frac{1}{2} e_i^2(x) \quad i = 1, 2 
\]

(3.22)

When interference occurs, the total intensity is

\[
I(x) = \langle (E_1 + E_2)^2 \rangle = [I_1(x) + I_2(x)] + 2\sqrt{I_1(x)I_2(x)} \cos(2\pi \frac{\alpha d}{\lambda F} x) 
\]

(3.23)

The detected signal, \( S(x) \), however, is the product of the light intensity and quantum efficiency \( Q \) of the individual pixels. Thus,
\[ S_i(x) = I_i(x)Q(x), \quad i = 1, 2 \quad (3.24) \]

and

\[ S(x) = I(x)Q(x) = \left[ S_1(x) + S_2(x) \right] + 2\sqrt{S_1(x)S_2(x)} \cos(2\pi \frac{\alpha d}{\lambda F} x) \quad (3.25) \]

The above equation indicates that the interferogram is complicated by the angular distribution of light intensity such as that arises from sample texture, and by the quantum efficiency variation of the CCD pixels. If \( S_i(x) \) and \( S_2(x) \) varies slowly with \( x \), then FT of the first term will introduce low frequency peaks which are well separated from Raman signal and therefore avoidable. However, the FT of second term will cause this noise to be convoluted into the Raman signal region thus worsen the spectral appearance. Equation (3.25) also points out a way to solve this problem. Suppose \( S_1(x) \) and \( S_2(x) \) can be collected separately, then one can subtract \( [S_1(x) + S_2(x)] \) out of \( S(x) \), and then divide the result by \( 2\sqrt{S_1(x)S_2(x)} \), the corrected interferogram \( S_C \) will be a true sinusoidal wave and bear the form

\[ S_C(x) = \frac{S(x) - [S_1(x) + S_2(x)]}{2\sqrt{S_1(x)S_2(x)}} = \cos(2\pi \frac{\alpha d}{\lambda F} x) \quad (3.26) \]

One approach is to block one of the split input beams, to prevent interference, and record the CCD output. The resulting plot of CCD output vs. pixel number contains the response nonuniformities from pixel gain variation and angular distribution variation. A similar trace can be recorded with the opposite beam blocked, and the corrected interferogram may be reconstructed via equation (3.26). We will show below that this procedure reduces the fixed pattern noise by 40%.
A more practical method involves only software manipulation. Suppose $S_1(x)$ and $S_2(x)$ are the same and are equal to one half of $S_{DC}(x)$, which is not an unreasonable assumption (since the two half beams are supposed to be identical), then equation (3.25) becomes:

$$S(x) = S_{DC}(x) + S_{DC}(x) \cos\left(2\pi \frac{\alpha d}{\lambda F} x\right)$$ \hspace{1cm} (3.27)

If the frequency domain spectrum of $S_{DC}(x)$ does not overlap with the Raman region, then $S_{DC}(x)$ can be obtained from the interferogram without separately collecting $S_1$ and $S_2$. By transforming the raw interferogram $S(x)$, zeroing the Raman frequency region, then inverting, the CCD response without Raman information (but containing nonuniformities), i.e. $S_{DC}(x)$, is reconstructed. In effect, the interferometer and CCD response are being corrected using light which is not modulated at Raman frequencies. Then, $S_C(x)$ is

$$S_C(x) = \frac{S(x) - S_{DC}(x)}{S_{DC}(x)} = \cos\left(2\pi \frac{\alpha d}{\lambda F} x\right)$$ \hspace{1cm} (3.28)

In case the spectrum contain more then one peaks, the above theory needs to be modified, but, as shown in appendix C, the methodology still applies. Note that this will not work if nonuniformities have oscillations similar to the Raman features.

**Vertical Focusing of the Interferogram and Multitrack Monitoring** To enhance the signal, a cylindrical lens can be used for lens 14, with its cylindrical axis oriented vertically. Since the light beam is collimated before this lens, it will still be collimated in the vertical direction after this lens, and therefore it will be focused at the focal plane of lens 19. This way, the circular interferogram will be compressed into a thin
horizontal strip, and signal loss will be minimum. Since the interferograms are narrow strips, multitrack monitoring becomes possible. If an array of light-carrying optical fibers is placed vertically at the sample position, thin strips of interferograms will appear on the CCD for each fiber, at different heights. By selecting a sampling area on the CCD for each interferogram, simultaneous multitrack monitoring of several fibers can be achieved. Because lens 14 is placed before the interferometer, its optical quality is not critical. Alternatively, a cylindrical lens can be placed between the CCD and the interferometer, with its cylindrical axis oriented horizontally, but to maintain the interference pattern, the required optical quality of this cylindrical lens will be unrealistically high.

**Resolution Improvement by an Optical Heterodyne**  

As noted in section 3.2.3, the resolution of the MCFT Raman spectrometer needs to be improved to compete with existing spectrometers. According to equation (3.12), there are only two ways to decrease $ILW$, either increase the CCD channels, or increase the laser wavelength. Increasing the laser wavelength has an adverse effect on the sensitivity, determined by both the CCD response and the $v^4$ law of Raman scattering. For this reason, 784 nm laser excitation will be used in the second generation of MCFT Raman. The resolution will be improved by using a 2,000 channel detector. For a 784 nm laser excitation and a 2,000 channel detector, $\sigma_{\text{max}} = 12,755 \text{ cm}^{-1}$, $N = 2,000$, and equation (3.12) gives $\Delta \sigma_{\text{min}} = 23 \text{ cm}^{-1}$. If the center burst is located at channel number $x = 1700$, then by using the DRA technique, $N$ can be effectively increased to 3400, and the theoretical $ILW$ will be reduced to 13.5 cm$^{-1}$. 

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Reducing ILW beyond the limit posed by equation (3.12) requires aliasing of the laser peak, and some or all the Raman features. This method has been tried before [64], but it quickly diminishes the SNR due to the reduced modulation depth of the interferogram, and hence is not feasible for Raman spectroscopy. Tilting the CCD can reduce aliasing [50], but it does not change the fact that the pixel is wider than the interference fringe and hence it also worsens the SNR. Several optical heterodyning configurations have been proposed to reduce the apparent frequency of spectroscopic features. Dohi et. al. used reflective gratings [65], Okamoto et. al. used a dispersing optical parallel to create variable path different for difference wavelengths [52], and Barnes et. al. used a Moiré fringe technique [55]. The configuration we are proposing here is also based on Moiré fringes, but the concept is much simpler and straight forward. It preserves both the frequency linearity and the large sample size capability of MCFT while improving its resolution.

The most straight forward way of heterodyning is to project a sinusoidal interferogram on the CCD to create a beat frequency. As shown in figure 3.10, this may be achieved by putting an imaging lens 14 in front of the beam splitter, and a holographic transmission grating at the object plane of this lens. The ratio of focal lengths of the FT lens 18 and lens 14 determines the ratio of the spatial frequency of the beating wave \( f_0 \) to that of the grating \( f_G \).

\[
\frac{f_0}{f_G} = \frac{F_{14}}{F_{18}}
\]  

(3.29)  

If the original interferogram \( S \) and the beating wave \( S_0 \) are written as the follows:
\[ S(x) = \sum_{j=1}^{N/2} S_j \left[ 1 + \cos(2\pi f_j x) \right] \quad x = 1 \text{ to } N \quad (3.30) \]

\[ S_0(x) = S_0 \left[ 1 + \cos(2\pi f_0 x) \right] \quad (3.31) \]

then multiplication yields

\[
S(x) \cdot S_0(x) = S_0 \sum_{j=1}^{N/2} S_j \left[ 1 + \cos 2\pi f_0 x + \cos 2\pi f_j x + \frac{1}{2} \cos 2\pi (f_j + f_0) x + \frac{1}{2} \cos 2\pi (f_j - f_0) x \right] \quad (3.32)
\]

In the last term the original spatial frequency \(f_j\) is heterodyned to \((f_j - f_0)\). The heterodyned Nyquist spatial frequency 0.5 now corresponds to unheterodyned spatial frequency \(0.5 + f_0\), and if the mirror 17 is readjusted so that this corresponds to the laser frequency, then \(l\) and \(\alpha\) are increased by a factor of \((1 + 2f_0)\), and following equation (3.12), ILW is decreased by the same factor, such that

\[
\Delta \sigma_{H_{\text{min}}} = \frac{3.6}{N(1 + 2f_0)} \sigma_L \quad (3.33)
\]

Due to the presence of the other terms in the bracket of equation 13, \(f_0\) must be carefully chosen to avoid frequency overlapping of different terms in the FT'ed spectrum. Even if this can be done, these terms still contribute a great deal of noise to the Raman spectrum. Fortunately, the design allows these terms to be eliminated and the heterodyned spectrum to be isolated on the CCD. This can be achieved when \(f_0\) is high enough such that the images formed by the \(0^{th}\) order and \(1^{st}\) order diffraction can be well separated in space. As demonstrated in figure 3.10, one can physically block the \(+1^{st}\) order diffraction of the clockwise traveling beam and the \(0^{th}\) and \(-1^{st}\) order diffraction of the counter
clockwise traveling beam, such that only the $0^{th}$ order of one beam and the $+1^{st}$ order of the other remain to interfere. The result is a pure heterodyned interferogram on the CCD.

### 3.3.2 Experimental

An optical layout of the second generation MCFT Raman spectrometer is shown in figure 3.11. The triangle Sagnac interferometer consists of a cubic beam splitter 15 and two mirrors, 16 and 17, all in fixed positions. A converging light beam enters the interferometer from the collection optics and is split into two halves by the beam splitter. The interferogram is imaged onto 19, a CCD detector (Spex Spectrum One Standard) by a Fourier transform lens 18. The CCD chip has 2,000 x 800 pixels and each pixel is 15 μm × 15 μm. The CCD temperature was maintained at -130°C, and the vertical pixels were binned to yield 2,000 superpixels. The interferogram was transferred to a PC computer in SpectraMax/GRAMS environment, and analyzed with GRAMS and Hyperplot commercial software. Component specifications are listed in appendix B.

The 784 nm light source 1 was a Ti:sapphire laser pumped by an Ar ion laser. A shutter 2 was used to control the exposure time. The laser was pre-filtered using a band pass interference filter 3 to reject plasma lines. It was reflected by a mini-prism 5, and focused by a lens 6 (FL=78 mm) onto the sample. An optional lens 4 can be placed before the prism to vary the laser spot size at the sample position. The scattered light was collimated by the same lens 6. The 784 nm and shorter wavelength components in the scattered light were filtered out by the two-stage filtering optics, namely, 785 nm interference long pass filter 8 (1" diameter), lens 9 (Nikon 50 mm, f/1.4) iris 10, lens 11...
(Nikon 50mm, f/1.4) and another long pass filter. After filtering, the collimated light was then focused by a lens into the interferometer. Lens was positioned such that the two virtual images IM1 and IM2 were formed between the two mirrors (see figure 3.2). By using a cylindrical lens (Melles Griot Precision Plano-Cylindrical), focal length = 240 mm for , the interferogram was focused to a horizontal stripe on the CCD and an improvement in sensitivity was achieved. The overall collection efficiency of the spectrometer was about f/5.2. In order to use the data reflection algorithm (DRA) or phase correction to enhance resolution without sacrificing sensitivity, the cylindrical lens was moved off axis by about 20 mm, so the center burst was shifted to one side of the CCD.

Optical heterodyning was performed using a 80 line/mm Ronchi transmission grating (Edmund Scientific) placed at the focal plane of lens 14, which was replaced with a high quality enlarging lens (Rodenstock, FL=240mm, f/5.6). It was essential to align the Ronchi grating lines parallel to the CCD vertical axis. The grating position was adjusted along the optical axis to generate maximum modulation depth at the CCD for a single line source. For the conditions used here, \( \Delta \sigma_\text{H} \) (resolution after heterodyne) equals 10.3 cm\(^{-1}\) for \( f_\nu = 0.613 \) (N = 2000), and 6 cm\(^{-1}\) when DRA and phase correction are applied (N is effectively increased to 3400).

The performance of the MCFT Raman spectrometer was compared to a multichannel dispersive Raman spectrometer, consisting of a Chromex 250IS f/4 spectrograph (600 l/mm, 50 mm slit), with an EEV 15-11 deep-depletion CCD in a Photometrics 270 housing. The observed ILW was about 6 cm\(^{-1}\) for an atomic emission
line from a neon bulb. The 1024 channel deep depletion CCD is more sensitive at the working Raman wavelengths than the Spex spectrum One CCD used for MCFT. A diode laser (SDL 8530) operating at 785 nm provided the Raman excitation for the dispersive spectrometer.

3.3.3 Results and Discussion

**Fixed Pattern Noise Reduction**

Before comparing SNR performance of various designs, the nonuniformity correction for MCFT should be discussed. The clockwise and then the counter-clockwise traveling beam was stopped separately and $S_1$ and $S_2$ were taken with the same integration time and number of accumulations. Figure 3.12a shows the raw interferogram of a HeNe laser line (632.8 nm). 3.12b and c are the CCD output when either the clockwise beam (3.12b) or counter clockwise (3.12c) beams are blocked in the interferometer. These patterns represent the system response in the absence of intentional interference, and contain contributions from pixel gain variation, sample texture, and variations in interferometer transmission. 3.12d is the interferogram reconstructed from 3.12a-c according to equation (3.26), demonstrating an observable decrease in noise. The software noise correction (SNC) procedure is illustrated in spectra 3.12e, f and i. Figure 3.12e is the raw interferogram from 3.12a after software removal of spatial frequencies above 0.3 ($\sigma = 4500$ cm$^{-1}$), which are those containing the Raman spectrum. 3.12f is the interferogram reconstructed in software from 3.12a and 3.12e via equation (3.28). The effect of these procedures on SNR is shown in spectra 3.13a, b, and c, which are FT's of the raw and reconstructed interferograms with the vertical scale.
magnified to show noise. The relative standard deviation of the Raman shift region of 500-1500 cm\(^{-1}\) has been reduced by a factor of 2 after SNC. Furthermore, the software procedure (3.12a, e, f, and i) requires no beam blocking or user intervention. The SNC procedure is used for all subsequent MCFT spectra unless noted otherwise.

The effect of SNC on a more complex spectrum is illustrated in figure 3.14 and 3.15, which were obtained with a neon bulb at the Raman sample position. The raw interferogram (figure 3.14a) shows a varying DC level due to the more efficient light collection at the center of the interferometer axis. The reconstructed interferogram after SNC is figure 3.14b. The FT of figure 3.14a is shown in 3.15a, following 8X zero filling and phase correction within GRAMS "Icompute.ab" routine. 3.15b is the FT of 3.14b, with both SNC and data reflection, and 3.15e is a dispersive/CCD spectrum for comparison. Note that the SNC procedure removes negative peak artifacts, and yields a FWHM of 14 cm\(^{-1}\) for the neon atomic emission lines. The theoretical FWHM for \(N=3,400\) and \(\sigma_{\text{max}}\) of 12,755 cm\(^{-1}\) is 13.5 cm\(^{-1}\), based on equation (3.12). Thus the unheterodyned MCFT spectrometer is demonstrating close to the limiting resolution for the conditions employed.

The SNR for the dispersive system is defined as the ratio of the peak area to the standard deviation of the peak area (i.e. the inverse of the relative standard deviation of the peak area). This is quite different from the ratio of peak height to the baseline standard deviation, which results in an erroneously high estimate of SNR for dispersive systems (since the baseline may contain little or no shot noise). For dispersive spectra, the peak area was measured 50 times to determine its mean and standard deviation. For
MCFT and FT-Raman, noise is spread equally over the spectrum, so the peak height has the same standard deviation as the baseline. These effects are illustrated in table 3.1, which lists SNR values for several samples and conditions. Figure 3.16 compares spectra of a strong scatterer (naphthalene) with relatively few Raman features. For similar laser power and measurement time, the MCFT and dispersive spectra yield similar SNR values. Although the MCFT spectrum has more baseline noise, the SNR’s measured correctly are comparable. Observed SNR values for several samples and conditions are shown in table 3.1. After adjustments for laser power and measurement time, the SNR for MCFT is generally lower than that for the dispersive system, as has been predicted in section 3.2.3. Of course, these comparisons depend on a variety of experimental conditions, including collection optics, resolution, power density, etc.

**Multitrack Monitoring** Utilization of a cylindrical lens for lens 14 enables the MCFT spectrometer to operate in “multitrack” mode, like some dispersive/CCD systems, in which several samples can be monitored simultaneously. A line of fibers carrying Raman light can be positioned vertically at the sample position in figure 3.11, and imaged onto the CCD. An interferogram will result from each fiber, and can be processed to yield a spectrum. Figure 3.17 shows an example, when six optical fibers monitored a neon bulb. Since the cylindrical lens (lens 4) compresses the interference pattern vertically on the CCD.

**Exploiting the Large Sampling Area** A second advantage of MCFT is the high $A_{0} \Omega$ product, which can be used to reduce laser power density or sample a large area, or both. Figure 3.18 shows MCFT and dispersive spectra of cobalt phthalocyanine.
<table>
<thead>
<tr>
<th>Sample</th>
<th>MCFT</th>
<th>Dispersive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene, 764 cm⁻¹</td>
<td>89 (n = 40)ᵃ</td>
<td>140 (n = 50)ᵃ</td>
</tr>
<tr>
<td></td>
<td>80 (n = 40)ᵇ</td>
<td>81ᵇ</td>
</tr>
<tr>
<td></td>
<td>100ᶜ</td>
<td>380ᵈ</td>
</tr>
<tr>
<td></td>
<td>(30 mW, 5 seconds, 785mm)</td>
<td>(120 mW, 1 second, 785mm)</td>
</tr>
<tr>
<td>Glassy Carbon, 1315 cm⁻¹</td>
<td>103⁶ (830 mm, 180 mW, 2 min)</td>
<td>108ᵇ (785 mm, 50 mW, 1 minute, n = 20)</td>
</tr>
<tr>
<td>0.2 M K₂SO₄, 980 cm⁻¹</td>
<td>39ᵇ (830 mm, 135 mW, 1 minute, n = 20)</td>
<td>88ˢ (784 mm, 50 mW, 1 minute, n = 20)</td>
</tr>
</tbody>
</table>

a. Mean peak area divided by standard deviation (sd) of peak area, n = number of runs used to determine standard deviation.

b. Mean peak height/standard deviation of peak height.

c. Mean peak height/standard deviation of baseline

d. Assessment of SNR as mean peak height over the standard deviation of the baseline can seriously overestimate the SNR for dispersive systems.

Table 3.1. SNR values for several samples measured on the MCFT and dispersive/CCD Raman spectrometers.
The laser was focused for the dispersive case, in order to image the laser spot (~50 μm) onto the entrance slit (also 50 μm), and the sample was degraded. An unfocussed beam covering ~1 mm yielded a useful spectrum with MCFT with no observable sample damage. The large AOQ of MCFT is also useful for a sample contained in an integrating sphere. The MCFT system can monitor a relatively large hole in a sphere, thus collecting a fairly large fraction of multiply reflected light. Figure 3.19 shows a factor of 13 increased in signal for a liquid sample placed in a 1.5 cm diameter sphere, compared to one in a 1 cm quartz cuvet.

**Frequency Stability** A third MCFT advantage is the inherent frequency stability of FT instruments. Since the entire interferogram is analyzed to determine the frequency, there is no concern about errors in grating position. The spectrum depicted in Figure 3.15b was acquired 26 times over a period of 12 days, yielding standard deviations of peak frequencies of 0.44 and 0.27 cm\(^{-1}\) for peaks at 11,771.13 and 11,936.58 cm\(^{-1}\). One month later, the same neon lines were located at 11,770.9 and 11,936.8 cm\(^{-1}\), well within the range observed over twelve days. Since the laser line may also appear on the MCFT spectrum, the precision of Raman shift could be even better when internally referenced to the laser frequency.

**Spectral Coverage** One of the advantages of all FT technique is the full spectral coverage, independent of spectral resolution. In the case of MCFT Raman, the coverage starts from the edge of the long pass filter, up until the wavelength where the CCD sensitivity dies out. The edge of the long pass filter is at ca. 100 cm\(^{-1}\) Raman shift relative to the 784 nm excitation, and the quantum efficiency of the CCD used in this spectrometer
diminishes at about 1 \mu m, thus for 784 nm excitation, the spectral coverage is from 100 to 2700 cm\(^{-1}\). For comparison, the dispersive spectrometer of 3.3 cm\(^{-1}\) resolution covers from 200 to 2000 cm\(^{-1}\). The spectra of an acetonitrile/toluene mixture taken from the two spectrometers are shown in figure 3.20. The low sensitivity at Raman shifts higher than 2400 cm\(^{-1}\) for MCFT is caused by the CCD response, and will improve upon further CCD sensitivity enhancement in the NIR region.

**Optical Heterodyne to Improve Resolution**

The optical heterodyne technique described in the theory section was implemented experimentally by placing a 80 line/mm Ronchi grating as shown in Figure 3.11. If no adjustment is made to the position of M2, the normal and heterodyned spectra of figure 3.21a and b result. Note the fundamental HeNe line, at 15,803 cm\(^{-1}\) absolute cm\(^{-1}\) plus the difference frequency at 1356 absolute cm\(^{-1}\). In addition, the aliased sum frequency appears at 6076 cm\(^{-1}\). If M2 is displaced further to improve resolution, aliasing becomes more severe and it becomes difficult to separate the sum, difference, and fundamental frequencies. Fortunately, this can be solved by placing masks as shown in figure 3.10. First, only the 0 and +1 diffraction orders from the Ronchi grating are allowed to enter the interferometer. Second, a mask between M1 and M2 limits the interference to that between the zeroth order light (counter clockwise) and +1 order (clockwise). The result is that only the difference frequency is projected onto the CCD and detected, as shown in figure 3.21c. Figure 3.22b is an expansion of the difference frequency region for a sample of Tylenol (4-acetamidophenol) following calibration against a Raman shift standard [66] and 3.22a is an unheterodyned MCFT spectrum. The line width for the 1168 cm\(^{-1}\) line of Tylenol has
decreased from 15.5 to 8 cm\(^{-1}\) when the optical heterodyne was employed. Table 3.2 summarizes the theoretical and observed line widths for several MCFT configurations.

<table>
<thead>
<tr>
<th>Unheterodyned</th>
<th>Predicted</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FWHM, cm(^{-1})</td>
<td>FWHM, cm(^{-1})</td>
</tr>
<tr>
<td>N=1024, no DRA</td>
<td>43(^b)</td>
<td>48 (naphthalene, 830 nm laser)</td>
</tr>
<tr>
<td>N=1024, DRA</td>
<td>24(^b)</td>
<td>27 (naphthalene, 830 nm laser)</td>
</tr>
<tr>
<td>N=2000, no DRA</td>
<td>24</td>
<td>24 (neon)(^c)</td>
</tr>
<tr>
<td>N=2000, DRA &amp; Phase Corrected</td>
<td>14</td>
<td>14 (neon)</td>
</tr>
<tr>
<td>N=2000, DRA and Phase Corrected</td>
<td>14</td>
<td>15.5 (Tylenol)(^c)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heterodyned</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N=2000, no DRA</td>
<td>11</td>
<td>11.1 (Tylenol)</td>
</tr>
<tr>
<td>N=2000, DRA &amp; Phase Corrected</td>
<td>6</td>
<td>8 (Tylenol)</td>
</tr>
</tbody>
</table>

a. N is the number of CCD pixels along the axis of the interferogram.

b. The predicted values listed here include the factor 1.8 caused by triangle apodization during Fourier transform.

c. Naphthalene (764 cm\(^{-1}\)) and tylenol (1168 cm\(^{-1}\)) values are from Raman spectra, neon values are from direct monitoring of neon bulb (absolute wavenumber = 11937 and 11771 cm\(^{-1}\)).

Table 3.2. Resolution improvement of MCFT.
Recall that in all MCFT cases, line widths do not vary when the input aperture is increased.

In the configuration yielding the spectra of figure 3.22b, the heterodyne technique causes a significant loss of signal and SNR, due mainly to the Ronchi grating. A square wave transmission grating generates many diffraction orders, but only one (+1) was analyzed to produce the spectrum 3.22a. The Ronchi grating diffracted about 3% of a laser beam into the +1 order when measured with a power meter. An ideal sinusoidal grating would theoretically diffract 50% of the incident light into the +1 order, so significant improvement in efficiency should be possible with a custom grating. In the best case, a heterodyned spectrum should have $1/\sqrt{2}$ the SNR of the nonheterodyned case, since a maximum of half of the light from the heterodyne grating is analyzed.

**Spectral Transferability** Finally, it is worthwhile to consider how MCFT spectra can be compared to existing dispersive spectra for purposes of compound identification, library searching, etc. The spectral response correction discussed elsewhere [45, 67] corrects the relative peak intensities for CCD response variation with wavelength, filter transmission, etc., so corrected MCFT spectra should have relative intensities comparable to those obtained with other spectrometers using 785 nm lasers. Of course, there will still be peak height variations between instruments operating with different instrumental linewidths. A test of the similarity of MCFT and dispersive spectra is provided by searching a 300 spectrum dispersive library for a match to an MCFT spectrum, with all spectra corrected for instrument response. As shown in figure 3.23, the first “hit” from the library search correctly matched the MCFT “unknown”, despite the
difference in MCFT instrumental line width (14 cm⁻¹) and the line width used to collect the library (6 cm⁻¹).

3.3.4 Conclusions

The MCFT approach to obtaining Raman spectra differs from dispersive Raman and FT-Raman (with a Michelson interferometer) in both fundamental and pragmatic ways. The fundamental benefits of MCFT Raman derive from the combination of a low noise multichannel detector with a spatial interferometer. The high throughput, wavelength accuracy, and stability of an interferometer are achieved, without sacrificing the low noise or multichannel advantage of modern CCDs. This fundamental difference between MCFT and either dispersive Raman or FT-Raman leads to several useful advantages. First, the entire Stokes Raman shift range is available to the interferometer, with the upper limit in Raman shift being determined by detector sensitivity. Second, the transformed frequency is linear with the real frequency of the light, thus wavelength calibration can be more accurate than dispersive systems. Third, interferometry with no moving parts yields excellent wavelength precision and stability, with minimum alignment required. The lack of moving parts and simple optical layout make the MCFT spectrometer relatively rugged and possibly inexpensive if offered commercially. Fourth, the large entrance aperture (and corresponding A Ω product) is usually under-filled, making the intensity much less sensitive to laser focus and position, and signal strength is weakly dependent on beam focal size and associated power density. Much lower power densities may be employed when sample damage is a concern. Fifth, the MCFT has
comparable SNR to a dispersive system, while still providing many of the advantages of FT-Raman.

Accompanying the benefits of MCFT are some drawbacks, some of which are common to other multiplex techniques. The Rayleigh line must be adequately filtered to avoid contributing shot noise across the interferogram. The dynamic range will generally be reduced compared to that of a dispersive system due to noise redistribution, possibly leading to difficulty observing minor components or peaks. As noted earlier, the spectral resolution is limited by the number of CCD channels, N. Although the heterodyne technique reduces the instrumental line width to a value similar to many natural Raman line widths, MCFT resolution will rarely equal or exceed those of typical dispersive and FT-Raman spectrometers.

As discussed in some detail, the SNR for MCFT will generally lie between that of FT-Raman and a dispersive/CCD system, for comparable laser power, measurement time, and sampling optics. $\text{SNR}_{\text{MCFT}}$ will be comparable to $\text{SNR}_{\text{FT}}$ if both systems operate in the shot noise limit. Since FT-Raman system often have high detector noise, $\text{SNR}_{\text{FT}}$ will often be less than $\text{SNR}_{\text{MCFT}}$ due to contributions from detector noise. In many practical situations (particularly with high background) $\text{SNR}_{\text{DIS}}$ will significantly exceed $\text{SNR}_{\text{MCFT}}$.

Although originally intended for surface analysis, the MCFT Raman spectrometer is generally not suited for analyzing low quantities of materials adsorbed on low surface area substrates, due to its inferior SNR characteristics compared with dispersive/multichannel systems (the same rule should apply to conventional FT Raman). For example, the chromate conversion coating film on AA-2024-T3, which was
successfully studied with the dispersive Raman spectrometer in chapter 2, did not yield any useful spectra on the MCFT spectrometer, when 200 mW 784 nm laser and 50 seconds integration was used. The resonance effect of chromate at 515 nm wavelength and the \( \nu^4 \) rule are likely the major sources of signal enhancement for the dispersive system, while no such resonance effect is evident for chromate at 784 nm. In addition, MCFT Raman is not suited to study weak signals on high backgrounds (such as fluorescence), due to noise redistribution. However it might be useful to study nonfluorescent thin films. An indication of surface sensitivity is provided by the glassy carbon spectrum in figure 3.9b, which sampled only \(-200\) Å thick of carbon.

Assuming high resolution is not a requirement, possible applications where MCFT Raman should be useful include those requiring precision and stability and those requiring a low laser power density. The combination of rigid optics without a slit and the inherent precision of interferometric frequency measurement leads to excellent reproducibility of both Raman shift and intensity.
Figure 3.1: Schematic of (a) Czerny-Turner monochromator, and (b) Michelson interferometer.
Figure 3.2: Principle of the triangle Sagnac interferometer. BS, beam splitter; M1 and M2, mirrors; IM1 and IM2, the two virtual images of the source (their actual position are between the two mirrors, but they are shown here for convenience); α, the space between the two images; l, displacement of M2. "0" position on the CCD represents the centerburst of the interferogram.
Figure 3.3: Optical diagram of the common path multichannel Fourier transform interferometer. BS is a cube beam splitter, L4 is a 470 mm focal length Fourier lens. L1 (FL=50 mm), and L2 (FL=320 mm) improve the collection of the interferometer (about f/10) to about f/3.
Figure 3.4: Interferogram of a naphthalene pellet. (a) raw interferogram from a 1024 channel detector, 135 mW laser power at sample, integrated for 5 seconds. (b) the interferogram from (a) after removal of low frequency components and zero filling to yield 2000 points. (c) after removal of the points left of the centerburst and reflection of the right half of the interferogram from (b).
Figure 3.5: Upper trace: raw FT of interferogram in figure 3.4a, plotted over entire Raman shift range. (a) Expansion of upper trace over 300-1800 cm\(^{-1}\) range. (b) FT of figure 3.4b. (c) FT of figure 3.4c. (d) Raman spectrum of naphthalene taken with dispersive system, with the same laser power and integration time as the MCFT system (135 mW, 5 seconds).
Figure 3.6: Laser spot size dependence of the benzene 992 cm$^{-1}$ band. "O", the MCFT system, and "+", the dispersive system with a 50 μm wide slit. Arrow indicates beam diameter where the MCFT aperture was exceeded.
Figure 3.7: Stability test of the MCFT system. (a) an overlay of 20 MCFT spectra of benzene obtained over an 8 hour period, 135 mW laser power at the sample, 10 second integration for each spectrum. (b) subtraction of two benzene spectra obtained 5 hours apart. (c) a background spectrum taken from an empty curvette. (d) a dispersive spectrum with same laser power and integration time.
Figure 3.8: Raman spectrum of a 0.2 M K$_2$SO$_4$ solution taken with the MCFT system (a) and the dispersive system (b). Experimental conditions are the same for both systems: 90 degree collection geometry, 135 mW laser power at sample, and 60 second integration time.
Figure 3.9: Raman spectra of glassy carbon. (a) raw interferogram. (b) FT of the raw interferogram zero filled to 2000 data points. (c) a spectrum taken with the dispersive system with back-scattering geometry. Experimental conditions for both systems: 180 mW laser power at sample, 120 second integration time.
Figure 3.10: Optical heterodyning illustrated in diffraction. S indicates optical stops used to eliminate unwanted heterodyned frequency components.
Figure 3.11: Optical layout of the second generation MCFT Raman spectrometer.
Figure 3.12: Noise correction procedure to improve SNR in unheterodyned MCFT. (a) Raw interferogram of the HeNe laser. (b) Clockwise traveling beam. (c) Counter clockwise traveling beam. (d) Noise removed interferogram following equation (3.26). (e) $S_{DC}$ obtained via inverse FFT after deleting the frequency domain features above 0.3. (f) the interferogram after SNC via equation (3.28).
Figure 3.12
Figure 3.13: Noise correction procedure to improve SNR in unheterodyned MCFT. (a) magnitude mode FFT of the raw interferogram 3.12a. (b) FFT of 3.12d. (c) FFT of 3.12f.
Figure 3.14: Effect of SNC procedure on peak shape, and resolution test without heterodyning. (a) Raw interferogram of neon bulb. (b) Interferogram after SNC via equation (3.28).
Figure 3.15: Effect of SNC procedure on peak shape, and resolution test without heterodyning. (a) phase corrected absorption mode FFT of 3.14a after 8x zero filling. (b) same as C, but from SNC interferogram 3.14b. (c) spectrum taken with the dispersive system.
Figure 3.16: (a) Naphthalene Raman spectrum taken with MCFT, 784 nm laser, 200 mW, 1 second integration time. (b) Spectrum taken with the dispersive spectrometer with a red enhanced CCD, 784 nm laser, 130 mW, 1 second integration.
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CHAPTER 4
POLARIZED RAMAN SPECTROSCOPY TO DETERMINE SURFACE MOLECULAR ORIENTATION

4.1 INTRODUCTION

The study of adsorbate orientation is an important subject of surface science. It is found that when molecules are adsorbed on a substrate, they often undergo a systematic reorientation to form a self-assembled structure. This kind of order is a direct result of adsorbate-substrate and/or adsorbate-adsorbate interaction. To put it in a wider context, molecular orientation is a special case of order/disorder. The second law of thermodynamics dictates that an isolated system can only develop toward the direction of entropy increase, which is the direction of disorder. For a system to remain ordered, a sufficiently strong force must be involved to overcome random thermal motion (interestingly this rule applies to human society as well). For example, the existence of a molecule itself is a case of order/disorder conflict. For the atoms to come together to form a perfectly ordered molecular structure, they must form strong enough chemical bonds. In this case, the random thermal motions of individual atoms are converted to harmonic molecular vibrations. If the temperature increases, the molecular vibrations will become more and more violent, until the chemical bonds are no longer strong enough to hold them
together, then the molecule will dissociate and the system returns to a disordered state. In general, whether a system is ordered or not depends upon the strength of its internal bonds relative to the thermal energy of its components. In a solution, the molecules are randomly oriented, because the interactions between them are not strong enough compared with their thermal energy. At the other extreme, the interactions between the molecules in a crystal are so strong that they develop a perfectly oriented three-dimensional network. As the orientations of the molecules change from random to ordered, the properties of the matter will also change. Liquid crystals that are used for display elements, for example, change their optical properties through a molecular orientation transition.

Interfacial phenomena are often orientation specific. For a molecule to adsorb onto a substrate from a solution, it must form a bond with the substrate surface to overcome its random motion. The bond may be either a chemical one or just a physical attraction. Chemical bonds, of course are highly oriented. Physisorption, if strong enough, will also exhibit discriminative orientation effect, if the adsorbate molecule is not spherically symmetric. Unfortunately, surface phenomena are generally difficult to study due to the minute amount of adsorbates available, and there have not been many techniques developed to probe surface molecular orientations.

In a Master’s Thesis, the author developed a method to determine adsorbate molecular orientation on highly ordered pyrolytic graphite (HOPG), using polarized Raman spectroscopy [1]. It was found that the depolarization ratios of many Raman bands of a highly symmetric molecule, cobalt phthalocyanine (CoPc), change depending upon whether it is adsorbed on HOPG or a less ordered form of graphite, glassy carbon.
Through a detailed theoretical analysis, this change in depolarization ratio was attributed to the partial orientation of CoPc molecule on HOPG, and it was concluded that the adsorbed planar CoPc molecules all lie flat on the HOPG basal plane.

However, not all molecules are as symmetric as the phthalocyanines. When the same technique was applied to another electrochemically interesting molecule[68], methylene blue (MB) of $C_{zz}$ symmetry, no significant difference between depolarization ratios of MB adsorbed on HOPG and GC was observed. Theoretical analysis indicated this could be due to the reduced symmetry or to the lack of preferential orientation of the molecule. It was impossible to decided exactly which was the real cause, and the experimental results remained inconclusive.

In a later publication, more metallophthalocynine molecules were found to behave the same way as CoPc[2]. More importantly, another experimental configuration was developed, which enabled the determination of orientations of all planar molecules adsorbed on graphite. By sampling the adsorbate/substrate edgewise, it was found that all in-plane vibrational bands became totally polarized, when the planar molecules were flat on the basal plane. This permits the study of other less symmetric molecules. Theoretical calculation showed this behavior is common to all planar molecules, regardless of the molecular symmetry and the vibrational modes. For example, Liu used this method and determined the molecular orientation and the order of the chemical bonding of two chemisorbed molecules, dinitrophenylhydrazine and nitroazobenzene [69].

Based on this prediction and the new findings, the MB/HOPG system was reconsidered. More importantly, this study will serve as an example for all low-symmetry
planar molecules, physisorbed and chemisorbed alike. The theoretical analysis extends the applicability of this methodology even further, possibly to molecules without any symmetry, provided the vibrational mode used for study is known.

4.2 THEORY

Raman scattering intensity is known to depend on the polarization of both the excitation light and the collected light. The source of this dependence can be traced to each individual molecule of any given orientation. Consider the Raman scattering for a specific vibrational mode, in a molecular fixed coordination system, (xyz). To the first order approximation, the scattered radiation can be written as

\[
\begin{pmatrix}
\mu_x \\
\mu_y \\
\mu_z
\end{pmatrix} =
\begin{pmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{pmatrix}
\begin{pmatrix}
\varepsilon_x \\
\varepsilon_y \\
\varepsilon_z
\end{pmatrix}
\] (4.1)

where \( \varepsilon_x, \varepsilon_y, \varepsilon_z \) are the components of external electric field, induced electric dipole, and the polarizability tensor derived from the specific vibration, respectively. Under normal conditions, the derived polarizability matrix is symmetric, therefore a coordinate system can be found in which only its diagonal elements are nonzero. Thus,

\[
\begin{pmatrix}
\mu_x \\
\mu_y \\
\mu_z
\end{pmatrix} =
\begin{pmatrix}
\alpha_x & 0 & 0 \\
0 & \alpha_y & 0 \\
0 & 0 & \alpha_z
\end{pmatrix}
\begin{pmatrix}
\varepsilon_x \\
\varepsilon_y \\
\varepsilon_z
\end{pmatrix}
\] (4.2)

According to group theory, molecular vibrations can be classified into different modes by their symmetry. In general, a totally symmetric mode preserves the molecular symmetry, and the sum of the diagonal elements of its derived polarizability matrix
$(\alpha_1 + \alpha_2 + \alpha_3)$ is nonzero. A nontotally symmetric mode distorts the molecular symmetry and the corresponding sum is zero.

Now consider the Raman collection geometry in figure 4.1. Lower case $x,y,z$ refer to molecular fixed coordinate system, while upper case $X,Y,Z$ refer to the laboratory fixed coordinated system. A laser beam polarized in $Y$ direction with an electric field amplitude of $E_Y$ was brought on to the sample along the $-Z$ direction, and the scattered light is collected in the $Z$ direction (back-scattering).

In the laboratory fixed coordinate system, the intensities of the scattered light in terms of polarization are directly derived from equation (4.1):

\[
I_{rr} = \frac{2\pi^3 v^4}{c^3} \mu_r^2 = \frac{2\pi^3 v^4}{c^3} \alpha_{rr}^2 E_y^2 \quad \text{(4.3a)}
\]

\[
I_{xt} = \frac{2\pi^3 v^4}{c^3} \mu_x^2 = \frac{2\pi^3 v^4}{c^3} \alpha_{xt}^2 E_y^2 \quad \text{(4.3b)}
\]

and the depolarization ratio, defined as the ratio of the intensity of the component perpendicular to the excitation polarization $Y$ to that parallel to it, is

\[
\rho \equiv \frac{I_{xt}}{I_{rr}} = \frac{\alpha_{xt}^2}{\alpha_{rr}^2} \quad \text{(4.4)}
\]

Equations (4.3) and (4.4) are appropriate for a single molecule; to obtain the expression for a solution whose molecules are randomly oriented with respect to the laboratory fixed coordinate system, (4.3a) and (4.3b) should be multiplied by the number of molecules and the terms $\alpha_{rr}^2$ should be averaged over all orientations of the principal axes with respect to the fixed $X$, $Y$, $Z$ axes. The general transformation for $\alpha_{rr}^2$ are:
\[ \alpha_{FF} = \sum_{i=1}^{3} \alpha_i \Phi_{F_i} \Phi_{F_i} \]  
\[ (4.5) \]

So the averages required in (4.3a,b) and (4.4) are:

\[ \bar{\alpha}_{FF}^2 = (\sum_{i=1}^{3} \alpha_i \Phi_{F_i} \Phi_{F_i})^2 \]  
\[ (4.6) \]

and the depolarization ratio for a randomly oriented system was found to be

\[ \rho = \frac{3 \beta^2}{45 \alpha^2 + 4 \beta^2} \]  
\[ (4.7) \]

where

\[ \alpha = \frac{1}{3} (\alpha_1 - \alpha_2 - \alpha_3) \]  
\[ (4.8a) \]

\[ \beta^2 = \frac{1}{2} \left[ (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2 + (\alpha_1 - \alpha_2)^2 \right] \]  
\[ (4.8b) \]

Thus \( \rho = 0.75 \) for nontotally symmetric vibrations (\( \alpha^2 = 0 \)), and \( \rho < 0.75 \) for totally symmetric vibrations (\( \alpha^2 > 0 \)). The equations (4.1) through (4.8) can be found in Wilson's book[70]( with minor modifications).

In deriving a formula similar to (4.7) for a uniaxially oriented system, in which the molecular fixed \( z \) axis defined in group theory is parallel to the laboratory fixed \( Z \) axis, as shown in figure 4.1, it was found that for all vibrations confined in the \( x-y \) plane [1],

\[ \rho = \frac{\alpha_{xy}^2}{\alpha_{yy}^2} = \frac{\beta^2}{4 \alpha^2 + \beta^2} \]  
\[ (4.9) \]

where \( \alpha \) and \( \beta \) are defined as:
Thus, for adsorbed CoPc lying flat on the HOPG basal plane which is within the X-Y plane, the depolarization ratio is

\[ \rho = 0, \text{ for } \alpha_{xx} + \alpha_{yy} \text{ modes (totally symmetric), because } \beta = 0, \alpha \neq 0 \]

\[ \rho = 1, \text{ for } \alpha_{xx} - \alpha_{yy}, \text{ and } \alpha_{xy} + \alpha_{yx} \text{ modes (nontotally symmetric), because } \alpha = 0, \beta \neq 0 \]

These drastically different ratios for different modes were indeed observed experimentally.

For the MB molecule oriented flat on the basal plane, the predicted depolarization ratios are no longer clear cut. This is because MB is of C_2v symmetry, and its in-plane vibrations are one of two types: \( \alpha_{xx} \) and \( \alpha_{yy} \). Thus either \( \alpha_1 \neq 0 \) and \( \alpha_2 = \alpha_3 = 0 \) (e.g. those modes stretching along x axis), or \( \alpha_2 \neq 0 \) and \( \alpha_1 = \alpha_3 = 0 \) (e.g. those modes stretching along y axis). In either case,

\[ \rho = \frac{\beta^2}{4\alpha^2 + \beta^2} = \frac{1}{3} \]

While in the case of random orientation, the ratio is also

\[ \rho = \frac{3\beta^2}{45\alpha^2 + 4\beta^2} = \frac{1}{3} \]

Therefore, theoretically the uniaxially oriented system would behave the same as the randomly oriented system, and information of molecular orientation can no longer be drawn from polarization analysis. This is exactly the problem!
So how do we extract orientation information? The answer lies within a simple sample orientation change. Suppose the HOPG sample is rotated 90 degrees, so that the basal plane is perpendicular to the $X$ axis, as shown in figure 4.2, then, if the MB molecule lies flat on the basal plane of HOPG, all the in-plane vibrations of MB will be confined in the $Y-Z$ plane, and the induced electric fields will be confined in the same plane as well. In this case, the Raman scattered light will contain only $I_{YY}$, and no $I_{XY}$ component, in the back-scattering configuration. Of course, the depolarization ratios will be zero, for all in-plane vibrations. This has been confirmed experimentally on the CoPc/HOPG system[2].

If, however, as depicted in the lower part of figure 4.2, the basal plane does not orient the MB molecules, and the molecular $z$ axis is free to rotate within the $X-Y$ plane, then the depolarization ratios will again be 1/3 [2]. Therefore, examining MB/HOPG edgewise should yield definitive results about the MB orientation on graphite.

4.3 EXPERIMENTAL

Methylene blue was dissolved in nanopure water to form a 0.1 mM solution. HOPG was “ZYA” grade, and was a gift from Union Carbide. It was cut into ca 1x1x0.05 cm pieces. Polycrystalline (“spectroscopic”) graphite rods (type U-5) were purchased from Carbone of America, Ultra Carbon Division, and were cut into small discs. Fresh HOPG basal plane can be easily obtained by peeling off the surface layers with a piece of scotch tape. HOPG edges were obtained by fracturing a 10 mm×10 mm×0.5 mm HOPG piece; the broken piece was then sonicated in water to remove the debris. The above carbon samples were immersed in the MB solution for 2 minutes, followed by rinsing in 3
washes of 5 ml of pure water for 1 minute each. The carbon samples were then dried and their Raman spectra obtained in air. All spectra were frequency calibrated using naphthalene and acetonitrile as standards, yielding ±2 cm⁻¹ accuracy. Peak position and area were measured by peak fitting.

The optics for the polarization measurement are the same as that employed in the MPc studies [2], except a polarization scrambler was used instead of a second polarizer, to correct the instrument response while maintaining sensitivity. As illustrated in figure 4.3, the Ti:sapphire laser used in chapter 3 was tuned to 691 nm and was used as the laser source. The laser was passed through a 691 nm dielectric band pass filter (Omega-691DF10-9227), reflected by a small prism, and then focused onto the sample by lens 1 (40 mm diameter, 120 mm FL). The scattered light was collected by the same lens, and sent through a dielectric band rejection filter (Omega-702 REFLP-9228) to remove the reflection and the Rayleigh scattering components. The light beam was then focused by lens 2 (120 mm FL ) onto the entrance slit of a single stage spectrograph (Instruments SA, HR640). The dispersed light was detected by an 1152×298 element CCD cooled to -110°C.

It was noted that the polarization scrambler is not a perfect one at the wavelength used. Using an unpolarized light source (an optical fiber carrying light from a desk lamp) as a standard, a slight difference was found between the transmittance of the parallel and perpendicular components. This difference varies with wavelength like an interference pattern. Although it did not contribute a significant error to the depolarization ratio measurement, it was still corrected using the unpolarized light source.
4.4 RESULTS AND DISCUSSION

MB is known to form a monolayer on graphite [68]. Although its Raman spectrum can not be obtained in the solution phase at 691 nm excitation due to high fluorescence background, a good spectrum can be obtained when it is adsorbed on graphite, due to the resonance effect at the used excitation wavelength and the excellent fluorescence quenching of the substrate[68].

The polycrystalline graphite consists of randomly oriented tiny graphite crystals. Although each crystal is a perfectly ordered substrate on the scale of the Raman sampling size employed in this work, the substrate as a whole had a disordered surface. Thus, the MB molecule adsorbed on this substrate can be considered randomly oriented.

Before analyzing data, the instrumental response to polarization was measured using an optical fiber carrying light from a desk lamp. The polarizer was rotated to the Y and X directions and the white light spectra $//_{\text{white}}$ and $\perp_{\text{white}}$ were recorded. If the system behaves perfectly, their intensity ratio should be 1 for all wavelengths. However, a small periodic variation was observed, as shown in figure 4.4. Although this contributes only 6% error at maximum, the following polarized Raman spectra were all corrected by dividing the $// (I_{YY})$ components by $//_{\text{white}}$ and the $\perp (I_{XY})$ components by $\perp_{\text{white}}$.

The polarized Raman spectra of MB on ultra carbon and on HOPG basal plane are shown in figure 4.5, and the measured depolarization ratios are listed in table 4.1. Due to the poor SNR on HOPG basal plane, only a few strong bands were measured. However, it is evident from the figures that MB depolarization ratios did not show any significant
changes upon changing the substrate from the rough surface of ultra carbon to the flat HOPG basal plane. The graphite $E_{2g}$ mode at 1581 cm$^{-1}$ showed a $\rho$ value of close to 1.0, confirming the HOPG basal plane orientation was indeed within the X-Y plane.

When the HOPG substrate was rotated 90 degrees so that the basal plane became parallel to the Y-Z plane, however, drastic changes were observed, as shown in figure 4.6. Including the graphite $E_{2g}$ mode, depolarization ratios of all Raman bands approached zero, just as predicted in the theory. Therefore, the conclusion is: MB does adsorb flat on the HOPG basal plane, and all the Raman modes observed are in-plane vibrations. The lack of difference between MB/HOPG basal and MB/ultra carbon is not because MB is not oriented on HOPG basal plane, rather it is because of the low symmetry of the MB molecule.

At this point we can reexamine the depolarization ratios of MB on HOPG basal plane and on ultra carbon. These values were not all exactly equal to the predicted, 1/3. The only way this can happen is by mixing the $\alpha_{xx}$ and $\alpha_{yy}$ modes. For example, if we assume a vibrational mode has a mixed derived polarizability $\alpha_{xx}=\alpha_1$ and $\alpha_{yy}=\alpha_2=m\alpha_1$, where the parameter $m$ represents the extent of mixing, then we can actually calculate $m$ according to equations (4.9) and (4.10). In general,

$$\rho = \frac{\beta^2}{4\alpha^2 + \beta^2} = \frac{(1-m)^2}{2(1+m)^2 + (1-m)^2}$$

Solving for $m$, one has

$$m \text{ (or } 1/m) = \frac{-(1+\rho) + \sqrt{8\rho(1-\rho)}}{3\rho - 1} \quad (4.11)$$

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Table 4.1. Depolarization ratios of selected Raman bands of MB at 691 nm excitation.

<table>
<thead>
<tr>
<th>Band (cm⁻¹)</th>
<th>on Ultra Carbon</th>
<th>on HOPG Basal</th>
<th>on HOPG Edge</th>
</tr>
</thead>
<tbody>
<tr>
<td>448</td>
<td>0.45</td>
<td>0.45</td>
<td>0.022</td>
</tr>
<tr>
<td>498</td>
<td>0.46</td>
<td>0.45</td>
<td>0.018</td>
</tr>
<tr>
<td>592</td>
<td>0.47</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>667</td>
<td>0.46</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>768</td>
<td>0.43</td>
<td></td>
<td>0.048</td>
</tr>
<tr>
<td>858</td>
<td>0.52</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>948</td>
<td>0.25</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>1038</td>
<td>0.50</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>1152</td>
<td>0.34</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>1181</td>
<td>0.40</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>1218</td>
<td>0.30</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>1301</td>
<td>0.44</td>
<td></td>
<td>0.056</td>
</tr>
<tr>
<td>1326</td>
<td>0.50</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>1396</td>
<td>0.44</td>
<td></td>
<td>0.031</td>
</tr>
<tr>
<td>1436</td>
<td>0.34</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>1471</td>
<td>0.45</td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>1552⁺</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1581ᵇ</td>
<td>0.69</td>
<td>1.06</td>
<td>0.085</td>
</tr>
<tr>
<td>1620</td>
<td>0.46</td>
<td>0.34</td>
<td>0.035</td>
</tr>
</tbody>
</table>

a, oxygen band.

b, graphite E₂g band.
$|m| < 1$ represents the mode whose major polarizability contribution is in $x$ direction, while $|m| > 1$ represents those in $y$ direction. Positive $m$ represents in-phase $x$ and $y$ direction vibrations, while negative $m$ represents out-of-phase $x$ and $y$ direction vibrations. The $m$-$\rho$ relationship for the $|m| < 1$ branch is plotted in figure 4.7. From this figure, the shape of the two-dimensional derived polarizability ellipse is revealed. For example, at $m=1$, the ellipse is a circle, and $\rho=0$. This corresponds to the $\alpha_{xx}+\alpha_{yy}$ modes of molecules whose $z$ axis is an $n>2$ fold rotational axis. At $m=0$, the ellipse shrinks to a line, and $\rho = 1/3$. This corresponds to the $\alpha_{xx}$ and $\alpha_{xy}$ modes of molecules not having $n>2$ fold rotational axis. At $m=-1$, the ellipse is an “anti-circle”, meaning $\alpha_{xx}$ and $\alpha_{yy}$ have the same amplitude, but opposite signs. This corresponds to the $\alpha_{xx}-\alpha_{yy}$, and $\alpha_{xy}+\alpha_{yx}$ modes, of molecules whose $z$ axis is an $n>2$ fold rotational axis. For MB/HOPG basal, the measured values of $\rho$ for most bands were higher than $1/3$, therefore the $x$ and $y$ direction contributions to a vibrational mode are out of phase. For the strongest band at 448 cm$^{-1}$, $\rho=0.45$, corresponding to $m=-0.12$, so the mixing is not severe. A schematic of typical vibrations of this kind is shown in figure 4.8.

It is of additional value to solve the $m$-$\rho$ relationship for the randomly oriented system. Assume $\alpha_3 = 0$ (this is a reasonable assumption for in-plane vibrations of big planar molecules), and $\alpha_2 = m\alpha_1$, equations (4.7) and (4.8) give:

$$ m \ (or \ 1/m) = \frac{-(1+2\rho)+\sqrt{(8\rho-1)(3-4\rho)}}{6\rho-2} \quad (4.12) $$
The corresponding $m-p$ curve is also plotted in figure 4.7, in dashed line. Thus, in the case of random orientation, the maximum value for $p$ is 0.75, and this occurs only at $m=-1$. The minimum value for $p$ is 0.125, and it occurs at $m=1$. The two $m-p$ curves cross at $p = 1/3$ and $m=0$.

As noted earlier, equation (4.12) applies only to vibrations whose $\alpha_3 = 0$. For small planar molecules, this may not be a good assumption. The benzene breathing mode, for example, has $\alpha_1 = \alpha_2 > \alpha_3 > 0$, therefore its $p$ can be less than 0.125 [2]. Although the vibration itself is strictly confined in the $x-y$ plane, as the ring and the electron cloud expand, the electron cloud also expands in the $z$ direction, making $\alpha_3 > 0$.

Finally, we can expand the utility of equations (4.11) and (4.12) beyond planar molecules. Because the only requirement for (4.12) is $\alpha_3 = 0$, and for (4.11) it is $\alpha_3 = 0$ and $(z=3)/Z$ (meaning $\alpha_1$ and $\alpha_2$ are in the X-Y plane), both equations apply to nonplanar molecules as well, as long as the particular vibrational mode satisfy the required conditions.

4.5 CONCLUSION

Methylene Blue molecules when adsorbed on graphite lie flat on the basal plane of the substrate. All the Raman modes observed at 691 nm excitation are in-plane totally symmetric vibrations. Most of the modes involve slightly mixed $x$ and $y$ direction vibrations.

For any planar molecule, if the molecular planes of all molecules are confined to the same spatial plane, and if the same plane also contains the Raman collection axis and
the excitation polarization in a back scattering configuration (figure 4.2 top), then, the depolarization ratio for all in-plane vibrations will be close to zero. This can be used to obtain orientation information.

Finally, for a particular vibration of any molecule, if the induced polarizability is confined to a molecular fixed plane, then, if this molecular fixed planes for all the molecules are confined in the same space fixed plane, and if the same plane also contains the Raman collection axis and the excitation polarization in a back scattering configuration, then, the depolarization ratio for this particular vibration will be zero.
Figure 4.1: Schematic representation of the perpendicular and parallel components for back-scattering geometry. HOPG basal plane is perpendicular to space fixed Z axis. The gray pentagons indicate the Methylene Blue molecular plane.
Figure 4.2: Schematic representation of the perpendicular and parallel components for back-scattering geometry. HOPG basal plane is perpendicular to space fixed X axis. Upper case, z//X, lower case, z⊥Z.
Figure 4.3: Optics for back-scattering polarization measurement in the laboratory fixed coordinate system, X-Y-Z.
Figure 4.4: Small polarization dependence of instrument response induced by the scrambler.
Figure 4.5: Polarized Raman spectra of MB on polycrystalline graphite in the upper case, and on HOPG basal plane with $z//Z$ in the lower case.
Figure 4.6: Polarized Raman spectra of MB on HOPG, with z//X.
Figure 4.7: Computed relationship between the depolarization ratio $\rho$, and the polarizability mixing indicator, $m$, for two molecular orientations: solid line, $z//Z$; dashed line, random. Condition: $\alpha_3=0$. 
Methylene Blue Cation

Point Group: $C_{2v}$

\[ \alpha_1 \gg -\alpha_2 > 0, \alpha_3 = 0 \]

\[ \alpha_2 \gg -\alpha_1 > 0, \alpha_3 = 0 \]

Figure 4.8: Schematic of typical MB in-plane vibrations according to the derived polarizability components.
LIST OF REFERENCES


8. G. Frankel, “Mechanism of Al Alloy Corrosion and the Role of Chromate Inhibitors”


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41. A. Campion, S. Perry, Laser Focus World, August 1990, p. 113.


66. 4-acetamidophenol, ASTM standard E 1848.

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APPENDIX A

DATA REFLECTION PROGRAM

The data reflection program is run with a batch program “APODRA.BAT” stored
in the n: drive. First, rename the data file to “xx” so its name does not have an extension,
then type “apodra xx”. The batch program first calls hyperplot stored in c:\hyperplt to
perform software noise correction (SNC) on “xx” and store the result in a temporary data
file “tempapo.dat”. After SNC, the “tempapo.dat” is automatically imported into a
gwbasic program, “dra2.bas”, which is also stored in the n: drive. The only input needed
from the operator is the centerburst position, and its value must be 0.5 multiplied by an
positive integral. “dra2.bas” performs the data reflection around the centerburst to
generate a symmetric double sided interferogram, and store it in a data file
“xxapodra.dat”.

***************APODRA.BAT***********
copy %1 temp.dat
copy start.tem c:\hyperplt\start.mac
call hyp
del c:start.mac
n:
gwbasic dra2.bas
copy tempdra.dat %1 apodra.dat
del tempapo.dat
del temp.dat
del tempdra.dat

********** START.TEM**********

2
#cursor
$numeric

Disk read, plot

n;temp.dat

3 store
D) X,Y --> A

Fourier xform

Calculate fft

Apodization

range

.27

.5

Inverse FFT
E) \( X, Y \rightarrow B \)

pRevious menu

Y math functions

process arrays

J) \( Y \rightarrow A - B \)

H) \( Y \rightarrow Y/B \)

3 store

C) \( X, Y \rightarrow \text{disk} \)

n:tempapo.dat

2

&EXIT

y

******DRA2.BAS******

100 DIM X(2000), Y(2000)

200 OPEN "TEMPAPO.DAT" FOR INPUT AS #1

300 INPUT "CENTERBURTS="; C

310 IF C>1000 GOTO 715

400 FOR I=1 TO 2000

500 INPUT #1, X(I), Y(I)

600 NEXT I
700  COLSE #1
710  GOT 760
715  C=2001-C
720  FOR I=1 TO 2000
730  INPUT #1, X(I), Y(2001-I)
740  NEXT I
750  CLOSE #1
760  IF INT(C)=C, GOTO 1300
780  CADJ=INT(C)+1-C
790  INTC=INT(C)
800  OPEN “TEMPDRA.DAT” FOR OUTPUT AS #2
900  FOR I=-2000-(INTC-INTC) TO -2001+INTC
1000  WRITE #2, I+I-CADJ, 0
1100  CLOSE #2
1110  SYSTEM
1200  END
1300  CADJ=0
1310  INTC=INT(C)-1
1320  GOTO 800
APPENDIX B

THE SECOND GENERATION MCFT RAMAN
SPECTROMETER: OPERATION INSTRUCTIONS

A1.1 Spectrometer Components and Specifications

1. Laser source: Ti:sapphire laser pumped by an Ar ion laser.
2. Shutter. 1” aperture.
3. 784 nm Band Pass interference filter. φ1”.
4. Optional lens on translation stage. Plano-convex. FL=200 mm.
5. Mini-prism.
6. Lens, FL=78 mm. φ2”
7. Sample on translation stage
8. 785 nm interference long pass filter. φ1”
9. Nikon camera lens, 50 mm, f/1.4
10. Iris, >2 mm variable opening
11. Nikon camera lens, 50mm, f/1.4
12. 785 nm interference long pass filter. φ1”
13. Grating for optical heterodyne, 80 line/mm.
14. Lens. Melles Griot Precision Plano-Cylindrical, FL= 240 mm; or Rodenstock enlarging lens, FL =240mm, f/5.6

15. Beam splitter, 40 mm cube, λ/20

16. Front reflection aluminum coated mirror, φ2", λ/20

17. Front reflection aluminum coated mirror, φ2", λ/20

18. Fourier lens. FL = 470 mm, f/7.7

19. Detector: Spex Spectrum One Standard CCD, 2,000×800 pixels and each pixel is 15 μm × 15 μm. Operation temperature: -130° C

A1.2 Instrument Installation and Alignment

The MCFT Raman spectrometer is very easy to install and align. The Sagnac interferometer including the two mirrors, the beam splitter, and the FT lens are bolted onto an aluminum base plate, which is fastened onto an optical table. The interferometer has an aluminum cover, which has three openings: the entrance facing the entrance optics, the exit facing the CCD, and an opening (with a cover lid) for fine tuning the vertical and horizontal tilting of mirror 17. The CCD and the entrance optics also stand on the optical table. An extendible aluminum tube connecting the CCD and the interferometer housing prevents room light from entering the CCD. Vibration isolation for the optical table is not required. A small HeNe laser is required for alignment.

The spectrometer can be set up for either on-axis (axis 1 and axis 2 overlap), or off-axis (axis 1 and axis 2 are parallel but do not overlap) configuration. Off axis is preferred for better resolution.

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On-axis Configuration

A. Align the Sagnac interferometer to zero path length difference

1. Fasten the base plate onto the optical table. The dimensions of the plate should be approximately parallel to the optical table. Mount the beam splitter and the two mirrors onto the base plate.

2. Direct the laser beam onto a mirror, which is bolted on to a translation stage. Adjust the height of the laser beam to the same level as the center of the beam splitter. Adjust the mirror to obtain a reflection beam parallel to any row of the holes of the optical table. Move the translation stage until the laser beam hit the center of the beam splitter.

3. Place a pin hole on the beam path, immediately after the mirror. close down the aperture until the beam barely passes. This beam is the axis 1, as shown in figure 3.11.

4. Tune the BS, until the beam reflected from the front surface overlaps the incoming beam.

5. Tune mirror 17 so it is parallel to the BS, You will obtain a reflected beam parallel to axis 1.

6. Tune mirror 16 to form a 22.5° angle with the BS. Look at the beam reflected by mirror 16 and then reflected back by mirror 17. When these two beams overlap, a 22.5° angle is formed.

7. Tune mirror 17 to form a 22.5° angle with the BS, and to obtain the zero-path-length-difference position of the interferometer. You will know this when the
clockwise and the counter clockwise traveling beams overlap. Note the position of mirror 17.

8. Place a viewing screen at the focal plane of lens 19 (the CCD position). Note the position of the beam on the screen. Install the FT lens 18. It should be located relatively close to the BS. Adjust its height and angle if necessary so that its optical axis overlaps the beam. The position of the beam on the screen is the centerburst of the interferogram.

B. Align the entrance optics

1. Install lens 6. Use the front and back surface reflection from the lens to help align its optical axes to overlap axis 1. The beam at the detector position should stay unchanged after lens 6 is aligned.

2. Find the focal point of lens 6 by placing a piece of half-transparent white paper at the sample position. Move the sample along the laser path, until a collimated beam is obtained after lens 6. Now the paper is at the focal point of lens 6. Take a note.

3. Remove the paper. Install lens 9, align it so its optical axis overlaps axis 1.

4. Replace the paper at the focal point of lens 6. Install lens 9.

5. Install iris 10 at the focal point of lens 9, where the beam is focused.

6. Remove the paper. Install lens 11, align it so its optical axis overlaps axis 1. Then, replace the paper at the focal point of lens 6, and move lens 11 along the beam path until the beam after lens 11 is collimated. This way Lens 11 and lens 9 will have a common focal point at the iris 10.
7. Remove the paper, and install lens 14, align it so its optical axis overlaps axis 1. At this point, the interferometer and the entrance optics are set up for on axis configuration. Replace the paper sample, an interferogram will appear on the viewing screen. Depending on whether cylindrical or spherical lens is used for lens 14, the interferogram will appear as either a thin strip, or a circular shape. Slightly adjust the vertical and horizontal tilting of mirror 17 to view the interferogram. When the vertical tilting is appropriately adjusted, the fringes should be vertical. The horizontal tilting of mirror 17 can affect the fringe density. When the horizontal tilting is appropriately adjusted, there should be no fringe, because the path length is zero at this stage.

C. Install and align the CCD

1. Slowly pull mirror 17 away from the BS until the fringes on the viewing screen are basely distinguishable. Bolt it down to the base plate. Adjust the vertical tilting to make the fringes as vertical as possible to the eye.

2. Temporarily place the shutter 2 on the beam path, in front of the paper sample.

3. Fill the CCD with liquid nitrogen, wait till it cools down to the operation temperature (this can be done prior to the above steps to save time). Replace the viewing screen with the CCD at the focal plane of lens 19. The CCD should be placed in the center of the beam. Cover the interferometer with the aluminum cover case. Install the tube connecting the CCD with the interferometer housing.

4. On the computer, click the CCD initialization icon “hwinit”, follow the directions to initialize the CCD. Close the “hwinit” window when done.

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5. Click the “SpectraMax” icon to enter the data collection program.

6. Set the area width to 2,000 pixels and the height to 800 pixels. Get into the continuous collection mode, select an appropriate exposure time. Start collecting data while moving the CCD back and forth, along the beam path, until maximum interferogram modulation depth is obtained.

7. Fine tune vertical tilting of mirror 17, and CCD position, to maximize modulation depth. It should be close to 100%.

8. Stop data collection, and bolt down the CCD.

D. Final Alignment of the interferometer to desired resolution

1. Remove the interferometer housing cover. Move mirror 17 to a predetermined distance relative to its zero path length position, for a desired resolution, calculated using equations (3.12), (3.13), and (3.1). Bolt it down to the base.

2. Entering the continuous data collection mode. Tune the vertical tilting of mirror 17 to obtain maximum interferogram modulation depth.

E. Install the laser

1. Turn on the Ti:Sapphire laser.

2. Install long pass filter 12.

3. Install long pass filter 8.

4. Install the shutter 2, the band pass filter 3, lens 4, and the mini prism 5. The height of the mini prism should be adjusted till it stays just below the 1” aperture determined by the long pass filters, so that it does not block the light path.
5. Tune the tilting of the mini prism, so that the Ti:Sapphire laser beam overlaps the HeNe laser beam at the paper sample.

6. Turn off the HeNe laser.

At this point, the MCFT Raman spectrometer is completely configured for Raman experiment, and Raman spectrum of any sample can be obtained by performing Fourier transform on the collected interferogram, within the Grams environment.

**Off-axis Configuration**

1. Follow the On-axis set up steps A1 through B7

2. Move lens 14 and the entire interferometer laterally toward the CCD direction, until the beam center is shifted to a desired distance relative to the centerburst of the interferogram, so that the centerburst appears at the desired pixel off the center of the CCD, if the CCD is place at the center of the beam. Fine adjust the position of the interferometer base plate so the beam is located in the center of the BS exiting face.

3. Follow steps C1 through E5.

**Optical Heterodyne**

As shown in figure 3.11, optical heterodyne was performed using a 80 line/mm Ronchi transmission grating (Edmund Scientific) placed at the front focal plane of lens 14. Use the enlarging lens for lens 14. It was essential to align the Ronchi grating lines parallel to the CCD vertical axis. The grating position was adjusted along the optical axis to generate maximum modulation depth at the CCD.

1. Remove filters 8 and 12. Illuminate the paper sample with the 784 nm laser.
2. Install grating 13 so its fringes are vertical.

3. Block the unwanted diffraction orders, as indicated in figure 3.10.

4. Enter continuous data collection mode, move the grating back and forth along the beam path, to maximize interferogram modulation depth.

5. Rotate the fringe tilting angle in the grating plane, to maximize modulation depth.

6. Reiterate steps 4 and 5, until maximum modulation depth is obtained.

7. Replace filter 12 and 8.

A1.3. Software and Data Processing

The computer is a 486 upgraded with a Pentium mother board with 32 Mb Ram. The operation system is Windows 95. The raw data is collected in “SpectraMax” and processed with a custom designed Grams Array Basic program “mcfrmn.ab”. “mcfrmn.ab” processes a raw interferogram into a frequency calibrated Raman spectrum.

After the raw interferogram is acquired, go to “Arithmetic” menu, select “do program”, then from the list, select “mcfrmn.ab”. The program performs three functions. First, it reconstructs the nonuniformity corrected interferogram according to the software noise correction equation (3.28). Then, it performs a fast Fourier transform. Finally, the Fourier transformed spectrum is frequency calibrated using a diode adjust function by calling either “adiodead.ab” for automatic calibration using existing coefficients, or “diodeadj.ab” for inputting new calibration coefficients. “adiodead.ab” is a customized version of “diodeadj.ab”.
```

`mcft` implements math processing on MCFT interferograms

`free`

`create new trace equal to #s`

`oldslot=getsfile()`

`first=getffp()`

`last=getflp()`

`points=npts(#s)`

`newspc mcft(points)`

`oldslot=oldslot+1`

`setffp first,last`

`#s=#oldslot`

`filter #s,0,1,.5,0,1,0`

"dccurve" is original #s, after 50% fourier smooth

`savespc "mcft"`

`noshow`

`openspc "mcft",subfile`

"subtract the smoothed from the original interferogram, then divide"

"by the smoothed one"

`#s=#s-subfile`

`#s=#s*inverse(subfile)`

"set the first three and last three points to zero, as they are"
at the edge of the interferogram and are usually bad

#s(#0)=0
#s(#1)=0
#s(#2)=0

lp=points-1

nl=points-2

nl2=points-3

#s(#lp)=0
#s(#nl)=0
#s(#nl2)=0

setytype 1

' compute FFT, 4 specifies triangular apodization, 8x zero fill
compute #s,4

' truncate high frequencies (above the detector response) and display

#s=#s(1000,2000)
savespc "mcft"
a..toscale

' request calibration options

dialogbeg "Calibration to Raman shift"
dialogloc 0,0
dialogtxt 0,0,0,"Use existing parameters or create new ones?"
dialogtxt 0,0,0,""
dialogask choice,4,1100,1200,"Existing New None"

dialogend 9

1100  doprogram "adiodead.ab"

goto 1300

1200  doprogram "diodeadj.ab"

1300  end
APPENDIX C
NONUNIFORMITY CORRECTION OF
MULTIPLE LINE SPECTRUM

The nonuniformity correction described in section 3.3.1 becomes more complicated when multiple wavelengths are added together. Both \( I \) and \( Q \) will be functions of \( x \) as well as \( \lambda \). Thus (3.24) becomes

\[
S_i(x) = \sum_{\lambda} I_i(\lambda, x)Q(\lambda, x), \quad i = 1, 2
\]

(C.1)

and

\[
S(x) = [S_1(x) + S_2(x)] + \sum_{\lambda} 2\sqrt{I_1(\lambda, x)I_2(\lambda, x)}Q(\lambda, x)\cos\frac{2\pi\alpha d}{\lambda F} x
\]

(C.2)

Now it is only possible to correct the noise due to the DC component, namely the first term in the equation (C.2). The difficulty rises from the fact that the second term can no longer be expressed as a function of \( S_1 \) and \( S_2 \) any more. However, if it is possible to separate the two factors \( \lambda \) and \( x \), such that

\[
I_i(\lambda, x) = I_i(\lambda) \cdot \delta I_i(x) \quad i = 1, 2
\]

\[
Q(\lambda, x) = Q(\lambda) \cdot \delta Q(x)
\]

(C.3)

then the second term becomes
\[ 2\left\{ \sum_{\lambda} \sqrt{I_1(\lambda)I_2(\lambda)Q(\lambda)} \cos \frac{2\pi d}{\lambda F} \delta(x) \right\} \sqrt{\delta I_1(x)\delta I_2(x) \cdot \delta Q(x)} \] (C.4)

and the geometric average of \( S_1 \) and \( S_2 \) is:
\[ \sqrt{S_1(x)S_2(x)} = \sqrt{\sum_{\lambda} [I_1(\lambda)Q(\lambda)] \sum_{\lambda} [I_2(\lambda)Q(\lambda)] \cdot \sqrt{\delta I_1(x)\delta I_2(x) \cdot \delta Q(x)}} \] (C.5)

Now, divide the second term by \( 2\sqrt{S_1(x)S_2(x)} \), the result is
\[ \frac{\sum_{\lambda} \sqrt{I_2(\lambda)I_2(\lambda)Q(\lambda)} \cdot Q(\lambda)}{\sqrt{\sum_{\lambda} [I_1(\lambda)Q(\lambda)] \cdot \sum_{\lambda} [I_2(\lambda)Q(\lambda)] \cdot \cos \frac{2\pi d}{\lambda F} \delta(x)}} \] (C.6)

This way, the angular nonuniformity of the light distribution and the quantum efficiency can still be corrected.