Vibrational Spectroscopic Investigations of Sulfate Behavior at
Environmental Interfaces

DISsertation

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By

Aaron Michael Jubb, B.A.

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The Ohio State University

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Dissertation Committee:

Professor Heather C. Allen, Advisor

Professor Prabir K. Dutta

Professor Terry L. Gustafson

Professor Steven K. Lower
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Abstract

Chemical interactions that occur at the interface between two bulk isotropic media are vital to understand as these interactions dictate many fundamentally important phenomena influencing life on Earth as we know it. This dissertation presents investigations focused on elucidating behavior for the simple inorganic anion sulfate at a variety of environmentally relevant interfacial regimes, primarily mineral/solution interfaces. Sulfate is a ubiquitous anion in the environment that plays a key role in various physical and chemical phenomena. With perspective toward atmospheric chemistry, sulfate is a large component of aqueous acidic aerosols and has been shown to influence the reactivity and growth of these aerosols. Sulfate coatings have also been linked to the retardation of ice nucleation by mineral dust aerosols. Sulfate is also highly relevant to geochemical systems where it can inhibit, or encourage, aqueous contaminant uptake onto soil adsorption sites. This may lead to added complications when attempting to predict the spatial and temporal transport of aqueous contaminants within the environment.

Work presented in this dissertation utilizes two different vibrational spectroscopic methods to probe sulfate behavior at the interfaces of interest. Chapter 2 presents studies harnessing vibrational sum frequency generation spectroscopy, an inherently interface specific spectroscopic technique, to investigate sulfate at the vapor/solution and the buried fluorite/solution interfaces. Results for the vapor/solution interface indicate that
protonated sulfate, bisulfate (HSO$_4^-$), features perturbed hydration compared to bulk solvated bisulfate. The presence of sodium (Na$^+$) and magnesium (Mg$^{2+}$) cations are found to disrupt bisulfate hydration to a greater extent within vapor/solution interfaces. The highly disruptive nature of Mg$^{2+}$ is attributed to its strongly solvated nature. The adsorption of sulfate to a mineral, fluorite, surface is observed in Chapter 2, as well. This adsorption is found to proceed with a bidentate inner-sphere structure preferred. The surface free energy of adsorption is calculated from the vibrational sum frequency results with a simple Langmuir adsorption model and is found to be $\Delta G_{ads}^o = -31 \pm 3$ kJ/mole.

Chapter 3 presents a procedure to generate and characterize thin films of three iron oxide polymorphs: hematite, maghemite, and magnetite. It was necessary to develop this procedure as accessing buried interfaces with optical spectroscopic techniques requires the transmission of the probe light through one of the interfacial media, generally the solid mineral phase. Due to the highly absorptive nature of colored oxide minerals, such as iron oxides, transmission of the probe light to the interface of interest is not possible when using a bulk sample. This obstacle is overcome through the use of thin films allowing for the study of sulfate at iron oxide/solution interfaces.

Chapter 4 presents results using total internal reflection Raman spectroscopy to investigate sulfate behavior at silica/solution and hematite/solution interfaces. Total internal reflection Raman is an interface selective spectroscopy which generally probes only the first 100 nm of an interface. These results indicate that sulfate forms ternary adsorption structures as a function of cation identity at silica/solution interfaces. For
buried hematite/solution interfaces sulfate is suggested to adsorb primarily in a bidentate inner-sphere manner at hematite/solution interfaces, in direct contrast to literature results.
Dedication

To my friends and family for their support; and to the better things in life: bikes, rocks, and science.
Acknowledgments

I first and foremost acknowledge my advisor, Dr. Heather C. Allen, for her patient guidance the past six years through my education. Her scientific integrity and insight are qualities that I hope to emulate in my future pursuits. I also acknowledge my parents for their endless love and encouragement to pursue interests to my, and not others, satisfaction. The kind and generous support from my fellow Allen Lab group members, past and present, during my tenure in the Allen lab has helped me greatly. Dr. Man Xu, Dr. Cheng Tang, and Dr. Xiangke Chen are acknowledged for thoughtful perspectives offered on my research. Special thanks are due to Dr. Chris Beekman, Christine Lemon, and Wei Hua for enlightening scientific discussions that bettered my understanding of the physical phenomena under study. Finally the love and patience I have received from my partner, Anna O. Levin, has allowed me to maintain perspective and realize that sometimes there is more to life than an interesting result.
Vita

January 17, 1984 ............................................ Born – Fort Hood, Texas, USA

June 2002 ...................................................... Lancaster Public High School – Lancaster, Ohio, USA

June 2006 .......................................................... B.A. Chemistry, Lawrence University – Appleton, Wisconsin, USA

September 2006 – June 2009 ......................... Graduate Teaching Associate, Department of Chemistry and Biochemistry, The Ohio State University – Columbus, Ohio, USA

June 2009 – Present ......................................... Graduate Research Associate, Department of Chemistry and Biochemistry, The Ohio State University – Columbus, Ohio, USA

Publications


• Jubb, A.M.; and Allen, H.C. “Vibrational Spectroscopic Characterization of Hematite, Maghemite, and Magnetite Thin Films Produced by Vapor Deposition”. 


**Fields of Study**

Major Field: Chemistry
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>PVD</td>
<td>physical vapor deposition</td>
</tr>
<tr>
<td>XRD</td>
<td>x-ray diffraction</td>
</tr>
<tr>
<td>DTGS</td>
<td>deuterated triglycine sulfate</td>
</tr>
<tr>
<td>LO</td>
<td>longitudinal optical</td>
</tr>
<tr>
<td>TO</td>
<td>transverse optical</td>
</tr>
<tr>
<td>cm(^{-1})</td>
<td>wavenumber</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>HWHM</td>
<td>half width at half maximum</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TIR</td>
<td>total internal reflection</td>
</tr>
<tr>
<td>VSFG</td>
<td>vibrational sum frequency generation</td>
</tr>
<tr>
<td>PS-SFG</td>
<td>phase-sensitive sum frequency generation</td>
</tr>
<tr>
<td>SHG</td>
<td>second harmonic generation</td>
</tr>
<tr>
<td>OPG</td>
<td>optical parametric generator</td>
</tr>
<tr>
<td>DFG</td>
<td>difference frequency generation</td>
</tr>
<tr>
<td>S/N</td>
<td>signal-to-noise</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>EMCCD</td>
<td>electron multiplying charge coupled device</td>
</tr>
<tr>
<td>ps</td>
<td>picosecond</td>
</tr>
<tr>
<td>s</td>
<td>second</td>
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<td>min</td>
<td>minute</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
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<tr>
<td>nm</td>
<td>nanometer</td>
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<tr>
<td>µm</td>
<td>micrometer</td>
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<tr>
<td>mm</td>
<td>millimeter</td>
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<tr>
<td>Hz</td>
<td>per second</td>
</tr>
<tr>
<td>µJ</td>
<td>microjoule</td>
</tr>
<tr>
<td>MΩ</td>
<td>megaohm</td>
</tr>
<tr>
<td>m</td>
<td>moles solute per kilogram solvent</td>
</tr>
<tr>
<td>x</td>
<td>mole fraction</td>
</tr>
<tr>
<td>SDS</td>
<td>sodium dodecyl sulfate</td>
</tr>
<tr>
<td>PP</td>
<td>peristaltic pump</td>
</tr>
<tr>
<td>V</td>
<td>valve</td>
</tr>
<tr>
<td>ATR</td>
<td>attenuated total reflection</td>
</tr>
<tr>
<td>pzc</td>
<td>point of zero charge</td>
</tr>
<tr>
<td>MSA</td>
<td>methanesulfonic acid</td>
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Chapter 1. Introduction

1.1. Motivation

Work presented in this dissertation is focused on elucidating the interfacial behavior for the simple, inorganic anion sulfate (SO$_4^{2-}$) at a variety of environmentally relevant vapor/solution and mineral/solution interfaces. By observing the normal modes of vibration exhibited by sulfate at these interfacial regimes it is possible to infer both the molecular environment experienced by sulfate anions within the interface and to judge the anion’s response to this environment. The primary instruments used in this work are vibrational sum frequency generation (VSFG) spectroscopy, an inherently interface-specific nonlinear optical technique, and total internal reflection (TIR) Raman spectroscopy, which generally only probes the first ~100 nm of an interface. Utilizing VSFG, sulfate behavior is first examined as a function of cation identity at vapor/solution interfaces before being applied to study sulfate adsorption characteristics at a model mineral/solution interface. Following this TIR-Raman spectroscopy is used to investigate sulfate behavior at a variety of oxide-mineral/solution interfaces, generally inaccessible with a VSFG approach, which feature different surface charge densities.

Sulfate behavior within environmental interfaces is vital to understand due to the global pervasiveness of the sulfate anion. This ubiquity contributes to the wide and varied physical and chemical phenomena in which sulfate takes part. Sulfate’s environmental prevalence arises as it is the third most abundant ionic component of seawater by weight,\textsuperscript{1}
as well as the large atmospheric release of sulfur containing compounds including \( \text{SO}_2(g) \)
from biofuel burning and volcanic eruptions\(^2,3\) and organosulfur compounds, i.e. dimethyl sulfide, from algal metabolic processes among many others.\(^4-6\) In the atmosphere sulfur containing compounds, such as \( \text{SO}_2(g) \), can undergo direct oxidation, primarily by reaction with OH radicals, to sulfate or may be taken up into aqueous aerosols where further oxidation may occur.\(^2,3\) In terrestrial ground water systems sulfate’s presence is primarily due to sulfur containing rock weathering and as such is a major component of acid mine drainage.\(^7,8\) This has resulted in sulfate being widely used as a tracer to judge pollution discharge from commercial mining operations into impacted ground and surface waters.\(^9\)

With perspective toward understanding atmospheric phenomena, sulfate is a key player in determining the physical and chemical behavior exhibited by aerosols. Aerosols refer to suspended particulate matter within the atmosphere and may consist of liquid, solid, or mixed phases. A thorough understanding of sulfate impact on aerosol behavior and reactivity is necessary as the consequences which aerosols have for very important atmospheric processes such as the climate forcing effects on Earth’s albedo are poorly understood today.\(^10\) With regards to aqueous aerosols, all interactions that the aerosol engages in directly involve crossing the vapor/aerosol-solution interface. Due to this, vapor/solution interfaces are critical to understand in order to predict aqueous aerosol behavior. Reactions at the vapor/aerosol-solution interface which have been linked to aerosol sulfate content include: the uptake of water,\(^2\) production of secondary organic aerosol precursors,\(^11,12\) and catalytic production of halogen radical species etc.\(^13,14\)
Sulfate also impacts many phenomena that mineral dust aerosols take part in. Sulfate coatings on mineral dust aerosols have been linked to qualities such as ice formation ability,\textsuperscript{15–17} water uptake, and general reactivity\textsuperscript{18} exhibited by these aerosols. In one specific example, the ice nucleating properties of various mineral dust aerosols, which directly relates to the ice content of cirrus and mixed-phase clouds, has been shown to be retarded by sulfate coatings recently.\textsuperscript{16} The ice content of such clouds is a large source of uncertainty in global climate change models. Sulfate coated mineral aerosols have also been shown to uptake water more efficiently directly effecting the scattering properties of these aerosols as well as their general reactivity toward atmospheric gas phase chemicals.\textsuperscript{18}

Beyond contributing to an understanding of atmospheric phenomena that sulfate influences, the work presented in this dissertation is greatly motivated by a desire to understand geochemical processes involving anion behavior within mineral/solution systems. Geochemical mineral/solution systems are very analogous to aerosol mineral/solution interfaces in their basic composition, even if the chemistries that occur for these systems are likely to differ drastically, facilitating an apt comparison for study. Mineral/solution interfacial systems are vital to understand as interactions between aqueous chemical species and solid phase minerals greatly influence the mobility and fate for these chemical species.\textsuperscript{19} In the context of aqueous inorganic pollutants, an understanding of the parameters governing adsorption, such as structure and energetics, for ions onto solid surfaces is vital in order to predict successfully the extent of contaminant movement through ground water.\textsuperscript{19–22}
While sulfate is not considered a primary ground water pollutant by the United States Environmental Protection Agency (EPA), it shares many similar characteristics, i.e. structure, valency, solubility, etc., with EPA primary inorganic water pollutants such as selenate (SeO$_4^{2-}$) and chromate (CrO$_4^{2-}$). These similarities enable the investigation of anion adsorption behavior at mineral/solution interfaces without the disadvantages of toxicity and waste disposal associated with directly studying inorganic pollutants. Also, due to sulfate’s environmental ubiquity within geochemical systems such as acid mine drainage, it can act as a competitor for adsorption sites on mineral surfaces with aqueous pollutants. In this way sulfate may act to inhibit negatively charged pollutant adsorption onto minerals or, in the case of positively charged aqueous cations (Pb$^{2+}$, Co$^{2+}$, Cd$^{2+}$, etc.), encourage contaminant adsorption through ternary mineral-anion-cation complex formation. Thus, a thorough understanding of sulfate adsorption behavior at mineral/solution interfaces may facilitate better modeling for the spatial and temporal transport of aqueous inorganic contaminants within the environment.

While many of the impacts that sulfate has on atmospheric and geochemical phenomena are clear, a molecular level understanding of these processes is generally lacking. In this dissertation we contribute to this understanding by probing sulfate behavior within environmentally relevant interfaces via interface-specific or interface-selective vibrational spectroscopies. This work is compared to sulfate behavior in bulk solution illustrating the unique chemistries that ions exhibit at interfaces in contrast to the bulk. These results clearly demonstrate the requirement for interface-sensitive techniques when seeking to elucidate inherently interfacial processes such as adsorption.
1.2. Dissertation Highlights

Chapter 2 begins by discussing the theory and instrumentation necessary for the application of the VSFG spectroscopic technique. A VSFG approach is utilized in Section 2.2 to study sulfate and bisulfate (HSO$_4^-$) behavior at vapor/solution interfaces as a function of cation identity (Na$^+$ or Mg$^{2+}$). No results were found for sulfate behavior due to the low VSFG signal arising from sulfate molecules possessing $T_d$ symmetry. For bisulfate, my results show that Na$^+$ and Mg$^{2+}$ both perturb the interfacial hydration of bisulfate compared to observations from a sulfuric acid solution. Mg$^{2+}$ is found to be highly disruptive to the hydration of interfacial bisulfate due to its large preference for solvation. These results are compared and contrasted to the results for bulk solution bisulfate behavior probed with conventional Raman spectroscopy. The trends observed for bulk solution bisulfate behavior are found to follow those observed for vapor/solution interfaces, but to a lesser degree.

Section 2.3 begins study on mineral/solution interfaces, where VSFG is applied to study sulfate adsorption at the fluorite/solution interface. Sulfate is found to adsorb in a bidentate inner-sphere structure onto the fluorite surface at pH 7 and 298 K. Two different VSFG polarization schemes, SSP and PPP, reveal that there is a distribution of sulfate adsorption structures with varying geometries but the same symmetry class. A Langmuir adsorption analysis is applied to the VSFG results to determine the free energy of sulfate adsorption at fluorite surfaces. The free energy of adsorption is found to be -31 ± 3 kJ/mole, which is in excellent agreement with literature values for reversible ion adsorption onto a mineral surface.$^{22}$
Chapter 3 details a procedure for the synthesis and characterization of thin films of three iron oxide polymorphs, hematite, maghemite, and magnetite, free of chemical precursors. These films are used later for the study of sulfate adsorption at the iron oxide/solution interface as presented in Chapter 4. It was necessary to develop this approach for iron oxide thin film synthesis as other available methodologies did not allow for a straight-forward thin film synthesis free of chemical precursors with controllable thickness and phase. The thin films are synthesized in a two-step procedure including the thermal evaporation of elemental iron onto the substrate of choice followed by thermal annealing in air to the desired iron oxide phase. Raman microscopy and Fourier transform infrared spectroscopy are used to characterize the thin film phase and overall degree of crystallinity via a phonon confinement analysis. It was found for films of all three iron oxide polymorphs that thinner films generally exhibited a greater degree of crystallinity compared to thick films.

Chapter 4 discusses the application of TIR-Raman to the study of sulfate adsorption at buried mineral/solution interfaces. Section 4.2 details the theory governing the TIR-Raman method as well as the development of the necessary TIR-Raman instrumentation. Section 4.3 focuses on applying a TIR-Raman approach to study sulfate behavior near silica/solution interfaces and the role that cation identity has on ternary complex formation at an oxide mineral surface. Finally Section 4.4 presents sulfate interactions at hematite/solution interfaces as a function of pH, cation identity, and water content. Results are compared and contrasted to literature studies on sulfate adsorption to hematite surfaces studied with attenuated total reflection infrared (ATR-IR) spectroscopy. The findings presented in this section suggest that sulfate forms bidentate inner-sphere
adsorption complexes within seconds after removal of the solution phase, contrary to ATR-IR results. Challenges and areas of improvement in adopting a TIR-Raman approach to study ion behavior at mineral/solution interfaces are presented and discussed.

In closing, Chapter 5 gives a summary of the work presented in this dissertation. Here the significance of my results is highlighted and a future outlook for each area of study covered by this dissertation is included.
Chapter 2. Vibrational Sum Frequency Generation Studies of Interfacial Sulfate Behavior

2.1. Vibrational Sum Frequency Generation Theory and Instrumentation


2.1.1. Theory

VSFG spectroscopy is a nonlinear optical spectroscopy based on the detection of coherent light generated by the second-order induced polarization of molecules subjected to incident high intensity electric fields, such as an incident laser beam.\(^{25}\) Conventional VSFG intensity is proportional to the square modulus of the effective second-order nonlinear susceptibility \(|\chi_{\text{eff}}^{(2)}|^2\) multiplied by the intensities of two input beams, which are generally a beam with visible wavelength and a beam with infrared wavelength.\(^{25–28}\)

\[
I_{\text{SFG}} \propto |\chi_{\text{eff}}^{(2)}|^2 I_{\text{vis}} I_{\text{IR}} \propto |\chi_{\text{eff, NR}}^{(2)}| + \sum_{\nu} |\chi_{\text{eff, }\nu}^{(2)}|^2 I_{\text{vis}} I_{\text{IR}} \tag{2.1.1}
\]
Here $I_{SFG}$, $I_{vis}$, and $I_{IR}$ are the intensities of the output sum frequency beam, the visible excitation beam, and the infrared excitation beam, respectively, and $\chi_{\text{eff}, \text{NR}}^{(2)}$ and $\chi_{\text{eff}, \text{R}}^{(2)}$ refer to the effective nonresonant and resonant components of the second-order nonlinear susceptibility. The $\chi_{\text{eff}}^{(2)}$ probed depends on the VSFG experimental setup (i.e., input beam geometry and polarization); most experiments utilize the four most-common beam polarizations: ssp, sps, pss, and ppp. In this notation the first letter corresponds to the output VSFG beam, the second letter corresponds to the input visible beam, and the last letter corresponds to the input infrared beam, with the ssp combination being the most widely utilized. Here s-polarized light signifies that the electric field vector of the respective beam is perpendicular to the plane of incidence, while p-polarized light has its electric field vector parallel to the plane of incidence. For these polarization combinations, the relationship between $\chi_{\text{eff}}^{(2)}$ and the actual nonlinear susceptibility, $\chi^{(2)}_{ijk}$, is given by Equations 2.12 – 2.15.

\[
\chi_{\text{eff}, \text{ssp}}^{(2)} = L_{yy} (\omega_{\text{SFG}}) L_{yy} (\omega_{\text{vis}}) L_{zz} (\omega_{\text{IR}}) \sin(\theta_{\text{IR}}) \chi_{yyz}^{(2)}
\]

\[
\chi_{\text{eff}, \text{sps}}^{(2)} = L_{yy} (\omega_{\text{SFG}}) L_{zz} (\omega_{\text{vis}}) L_{yy} (\omega_{\text{IR}}) \sin(\theta_{\text{vis}}) \chi_{yy}^{(2)}
\]

\[
\chi_{\text{eff}, \text{pss}}^{(2)} = L_{zz} (\omega_{\text{SFG}}) L_{yy} (\omega_{\text{vis}}) L_{yy} (\omega_{\text{IR}}) \sin(\theta_{\text{SFG}}) \chi_{zyy}^{(2)}
\]
\[ \chi_{\text{eff},ipp}^{(2)} = -L_{xx}(\omega_{\text{VSFG}})L_{zz}(\omega_{\text{vis}})L_{xx}(\omega_{\text{IR}}) \cos(\theta_{\text{VSFG}}) \cos(\theta_{\text{vis}}) \sin(\theta_{\text{IR}}) \chi_{xxz} 
- L_{xx}(\omega_{\text{VSFG}})L_{zz}(\omega_{\text{vis}})L_{xx}(\omega_{\text{IR}}) \cos(\theta_{\text{VSFG}}) \sin(\theta_{\text{vis}}) \cos(\theta_{\text{IR}}) \chi_{xxz} 
+ L_{zz}(\omega_{\text{VSFG}})L_{xx}(\omega_{\text{vis}})L_{xx}(\omega_{\text{IR}}) \sin(\theta_{\text{VSFG}}) \cos(\theta_{\text{vis}}) \cos(\theta_{\text{IR}}) \chi_{xxz} 
+ L_{zz}(\omega_{\text{VSFG}})L_{zz}(\omega_{\text{vis}})L_{xx}(\omega_{\text{IR}}) \sin(\theta_{\text{VSFG}}) \sin(\theta_{\text{vis}}) \sin(\theta_{\text{IR}}) \chi_{zzz} \]  

(2.1.5)

In Equations 2.1.2 – 2.1.5 \( L_{ii} \) is the nonlinear Fresnel factor associated with \( \omega_i \), and \( \theta_i \) is the input or output angle versus the surface normal for the associated beam.\(^{28,29}\) The nonlinear Fresnel factors are given by Equations 2.1.6 – 2.1.8.\(^{28-30}\)

\[ L_{xx}(\omega_i) = \frac{2\eta_i(\omega_i) \cos \gamma_i}{\eta_i(\omega_i) \cos \gamma_i + \eta_z(\omega_i) \cos \theta_i} \]  

(2.1.6)

\[ L_{yy}(\omega_i) = \frac{2\eta_i(\omega_i) \cos \theta_i}{\eta_i(\omega_i) \cos \theta_i + \eta_z(\omega_i) \cos \gamma_i} \]  

(2.1.7)

\[ L_{zz}(\omega_i) = \frac{2\eta_z(\omega_i) \cos \theta_i}{\eta_i(\omega_i) \cos \gamma_i + \eta_z(\omega_i) \cos \theta_i \left( \frac{\eta_i(\omega_i)}{\eta^*(\omega_i)} \right)^2} \]  

(2.1.8)

Here \( \eta_i \) is the refractive index of the first medium that the incident visible and infrared beams pass through to the interface, \( \eta_2 \) is the refractive index of the second interfacial medium, \( \eta^* \) is the refractive index of the interface, and \( \gamma_i \) is the angle for the transmitted sum frequency beam into the \( \eta_2 \) medium. By correcting for the nonlinear Fresnel coefficients, it is possible to remove spectral contributions arising from experimental geometry,\(^{30}\) as recently demonstrated by Feng et al. for the water spectra at the vapor/liquid interface with spectra originating from many research groups.\(^{31}\)
The resonant component of the Fresnel factor corrected second-order nonlinear susceptibility is related to the number density, \( N \), of VSFG active oscillators and the molecular hyperpolarizability, \( \beta_\nu \), through the orientationally averaged Euler angle transformation, \( \langle \mu_{IJK;lmn} \rangle \), between the laboratory coordinates (\( IJK \)) and the molecular coordinates (\( lmn \)):

\[
\chi^{(2)}_{IJK} = N \sum_{lmn} \langle \mu_{IJK;lmn} \rangle \beta_{lmn},
\]

(2.1.9)

The molecular hyperpolarizability term, \( \beta_\nu \), is proportional to the Raman polarizability tensor for the transition moment \( \langle g \! | \alpha_{\ell \nu} \! | v \rangle \) and the infrared transition moment \( \langle v \! | \mu_n \! | g \rangle \). This gives rise to the VSFG selection rule that a vibrational mode must be both Raman and infrared active for VSFG to be allowed.

\[
\beta_{lmn} = \frac{\langle g \! | \alpha_{\ell \nu} \! | v \rangle \langle v \! | \mu_n \! | g \rangle}{\omega_{IR} - \omega_v + i\Gamma_v},
\]

(2.1.10)

\[
\chi^{(2)}_{\nu,\text{eff}} \propto \frac{A_\nu}{\omega_{IR} - \omega_v + i\Gamma_v}.
\]

(2.1.11)

Generally, however, \( \chi^{(2)}_{\nu,\text{eff}} \) is what is presented in the majority of published VSFG studies. Equation 2.1.11 reveals the Lorentzian lineshape character of the collected VSFG
signal, where $A_\nu$ is the VSFG transition moment strength, $\omega_\nu$ is the frequency of the VSFG active vibration, $\omega_{\text{IR}}$ is the frequency of the incident infrared laser beam, and $\Gamma_\nu$ is the line width of the VSFG transition. It is clear from Equation 2.1.1 that during the collection of a conventional VSFG spectrum, the sign of the second-order nonlinear susceptibility is lost. This renders the direct collection of the orientation (phase) of the sum frequency transition dipole moment impossible. Ji et al.\textsuperscript{32} have recently developed a generally applicable technique to measure directly the imaginary component (Equation 2.1.12) of the second-order nonlinear susceptibility, termed heterodyne-detected phase-sensitive sum frequency generation (PS-SFG), and it is being rapidly adopted by a few researchers within the surface spectroscopy field:\textsuperscript{33–36}

$$\text{Im}\chi^{(2)}_\nu = -\sum_\nu \frac{A_\nu \Gamma_\nu}{(\omega_{\text{IR}} - \omega_\nu)^2 + \Gamma^2_\nu}.$$ (2.1.12)

While PS-SFG generally yields more information on interfacial molecule organization, due to the detection of the net molecular dipole moment direction, than conventional VSFG; all VSFG spectra in this dissertation were collected using conventional VSFG due to the greatly enhanced experimental difficulties in adopting a PS-SFG approach.

### 2.1.2. Instrumentation

All VSFG spectra shown were acquired using a 20 Hz scanning VSFG system (EKSPLA), Figure 2.1. The VSFG experiments were carried out using a fixed frequency visible beam at 532.1 nm and a tunable frequency infrared beam which was scanned over
the desired infrared frequency range during the course of a spectral acquisition. The 532.1 nm beam is generated by doubling the frequency (second harmonic) of 10% of the 1064 nm fundamental output from an Nd:YAG laser (25 ps pulse duration and 20 Hz repetition rate) (EKSPLA, PL2143A/20/SS). The visible energy produced in this manner is \( \leq 500 \, \mu \text{J/pulse} \). To produce the tunable infrared beam a portion (90\%) of the fundamental output is directed to an optical parametric generator (OPG) (EKSPLA, PG401/DFG2-16P) where a signal/idler beam pair is produced. The idler beam is sent to a difference frequency generation (DFG) stage where, using either a AgGaS\(_2\) (produces 2.3-10.0 \( \mu \text{m} \) light) or a GaSe (produces 8-12 \( \mu \text{m} \) light) crystal, the infrared beam is generated via the difference frequency mixing of the idler beam with a portion of the 1064 nm fundamental from the Nd:YAG (split in Harmonics Unit). The visible and infrared beams are then overlapped spatially and temporally at the sample stage and the generated sum frequency beam is collected in the reflection geometry. Temporal overlap is controlled via a CaF\(_2\) retro-reflector 90° prism mounted on a micrometer in the visible branch of the VSFG spectrometer, Figure 2.1. The 532.1 nm light is focused 40 mm after the sample stage by using a plano-convex lens (700 mm focal length). The infrared beam is focused at the sample stage using a ZnSe lens (50 mm focal length).

For the mineral/solution interface study, Section 2.3, all VSFG spectra shown were collected using an experimental geometry, Figure 2.2, where both the visible and infrared input beams are transmitted to the fluorite/solution interface through an equilateral fluorite prism mounted on a custom-made Teflon flow cell. In the vapor/solution study, Section 2.2, the VSFG spectra were acquired using the experimental geometry noted in Figure 2.3. For the fluorite/solution study, Section 2.3,
the incident angles for the visible and infrared input beams were 70° and 65°, respectively, relative to the surface-normal of the fluorite/Na₂SO₄ interface. Here the visible beam angle versus the surface-normal is large enough to achieve the total internal reflection condition which has been shown to yield drastically higher signal-to-noise (S/N) ratios for VSFG spectra. In the vapor/solution study detailed in Section 2.2, the visible and infrared beams were incident on the sample interface with an input angle of 60° and 55°, respectively, relative to the surface-normal of the sample solution.

The input energies of the visible and infrared beams during a typical VSFG spectral acquisition were generally ~300 µJ/pulse and 50-100 µJ/pulse, respectively. The generated sum frequency light was collected using a cooled electron multiplying charge coupled device (EMCCD) camera (Andor Technology, Newton, DU97ON-BV). All mineral/solution VSFG spectra shown were collected with 5 s of acquisition at each data point with an electron multiplying gain of 100 applied to the EMCCD. All vapor/solution VSFG spectra shown are collected with 30 s of acquisition at each data point with an electron multiplying gain of 150 applied to the EMCCD. The ability to adopt total internal reflection geometry in the fluorite/solution study enables shorter acquisition times per frequency step and less electron multiplying gain relative to the vapor/solution study. The only polarization combinations used for the VSFG studies were SSP and PPP.

All collected VSFG spectra have been normalized versus the input 532.1 nm and infrared beam intensities, simultaneously detected with the VSFG spectra with dedicated photodiodes. The fluorite/solution VSFG spectra are also normalized against the transmission curve for fluorite. All presented VSFG spectra are the average of 3-4 spectra. All VSFG spectra have been calibrated against the VSFG spectrum of the SO₃.
symmetric stretching peak at 1070 cm\(^{-1}\) of a sodium dodecyl sulfate (SDS) monolayer on neat water collected at the beginning and end of each day. This was necessary to account for deviations in the infrared frequency generated in the OPG/DFG process.\(^{38}\)

For the fluorite/solution VSFG experiments the Na\(_2\)SO\(_4\) solutions were purged with house N\(_2\) to remove dissolved CO\(_2\) until the pH of the solution was 7 before use. The Na\(_2\)SO\(_4\) solutions were then pumped to the fluorite/Na\(_2\)SO\(_4\) interface via a peristaltic pump (MasterFlex L/S, Cole-Parmer), Figure 2.2. The solutions were allowed to equilibrate with the fluorite surface for at least 10 min before the VSFG spectra were collected. The pH of each solution was checked (Ag/AgCl glass electrode, Accumet AB15, Fisher Scientific) before and after each VSFG spectrum was collected to ensure that the pH did not change during the course of the experiment. The pH meter was calibrated following the procedure of Wiesner et al. for high ionic strength solutions.\(^{39}\) Between experimental runs the flow cell was flushed with N\(_2\)-purged nanopure water (18.3 M\(\Omega\)) until the adsorbed sulfate signal was no longer detectable to ensure the reversibility of the adsorption process. In the vapor/solution study the experimental set-up consisted of preparing solutions which were then placed in copiously cleaned Pyrex petri dishes on the x-y-z sample stage prior to the collection of the VSFG spectra, Figure 2.3. All VSFG spectra have been fit using a modified Lorentzian function, Equation 2.1.13, without accounting for the non-linear Fresnel coefficients.\(^{40}\)

\[
I_{\text{VSFG}} = B_{\text{NR}} e^{i\phi} + \left( \sum_{\nu} \frac{A_{\nu}}{\omega_{\text{IR}} - \omega_{\nu} + i\Gamma_{\nu}} \right)^2.
\] (2.1.13)
Here $B_{NR}$ is the amplitude and $\phi$ is the phase of the non-resonant component of $\chi^{(2)}$.

While a modified Lorentzian profile is the typical function used to fit VSFG spectra, except for the broad O-H stretch continuum in VSFG spectra of water, attempts were also made to fit the VSFG spectra presented in this dissertation with a modified Voigt function (see Reference 40; Appendix A). The use of a modified Voigt function adequately fit the spectra presented in this dissertation, however, the Voigt fits exhibited almost entirely Lorentzian character and so the more straight-forward Lorentzian profile was chosen as the preferred fitting function.
Figure 2.1. 20 Hz scanning Vibrational Sum Frequency Generation spectrometer.
Figure 2.2. Experimental geometry and flow-cell schematic for VSFG experiments of fluorite/solution interfaces.
Figure 2.3. Experimental geometry used for VSFG experiments of vapor/solution interfaces.
2.2. Bisulfate Dehydration at Air/Solution Interfaces


2.2.1. Introduction

The structure and reactivity of simple inorganic ions at vapor/solution interfaces has been an intense area of study the last decade following the pioneering work of Jungwirth and Tobias who challenged the long held belief that ions are depleted from vapor/solution interfaces based on surface tension measurements. Ion behavior at vapor/solution interfaces has important implications for atmospheric aerosols as the interface between the gas phase atmosphere and the liquid phase aerosol plays host to reactions which control the growth and uptake of the aerosol. Aerosol reactivity and growth are vital to understand as the climate forcing effects of aerosols on Earth’s total albedo is poorly understood today.

Sulfate (SO₄²⁻) is a major ionic component of tropospheric aerosols, which may exist as SO₄²⁻, bisulfate (HSO₄⁻), or molecular sulfuric acid (H₂SO₄) depending on solution pH. High aerosol SO₄²⁻ content is mainly due to SO₂(g) uptake and subsequent oxidation within the solution phase of aqueous aerosols. Sulfate species (SO₄²⁻, HSO₄⁻, H₂SO₄, and organosulfates) are also very prevalent in marine aerosols due to sulfate being the third most abundant ionic species in seawater by weight and the large
atmospheric release of sulfur compounds from algal metabolic processes.\textsuperscript{1–3,5,23,56} Aerosol sulfate content is directly related to the growth potential of the associated aerosol due to sulfate ion’s large propensity for hydration.\textsuperscript{43,57–59} Sulfate content and acidity of aqueous aerosols has also been linked to important atmospheric processes such as catalytic production of chlorine radical and secondary organic aerosol formation.\textsuperscript{11–14}

Despite the relative importance in understanding interfacial processes to explain the physical and chemical phenomena that aqueous aerosols partake in, the vapor/solution interface remains very difficult to probe experimentally. The application of optical nonlinear spectroscopies such as second harmonic generation (SHG) and vibrational sum frequency generation (VSFG) spectroscopies, which are inherently interface specific, along with accompanying theoretical studies, have provided insight into the underlying driving forces for many interfacial processes.\textsuperscript{22,41–44,47,48,60–71} Generally these studies have focused on the elucidation of interfacial water structure as a probe of the molecular environment at the vapor/solution interface.\textsuperscript{41,42,46,48–50,60,61,66,67,70–77} However, there have been several recent studies demonstrating the suitability of SHG and VSFG to interrogate directly interfacial ions.\textsuperscript{62,63,65,78–81}

In a recent series of papers, Morita and coworkers have revealed the power of combining the VSFG method with theoretical modeling to probe acid dissociation within the vapor/solution interface for a series of H$_2$SO$_4$ solutions with perspective toward tropospheric acidic aerosols.\textsuperscript{62,80,81} These studies investigate both the interfacial water structure and the sulfate species’ vibrational modes at vapor/solution interfaces. Their findings indicate that the first acid dissociation of H$_2$SO$_4$ (Eq. 2.2.1) in vapor/solution interfaces is bulk-like for both concentrated and dilute solutions but that the second acid
dissociation (Eq. 2.2.2) is suppressed for high concentrations, $[\text{H}_2\text{SO}_4] > 0.2$ mole fraction (x), within the interface.$^{62,80,81}$

$$\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \Leftrightarrow \text{HSO}_4^- + \text{H}_3\text{O}^+ \quad \text{pK}_{a1} << 0 \quad (2.2.1)$$

$$\text{HSO}_4^- + \text{H}_2\text{O} \Leftrightarrow \text{SO}_4^{2-} + \text{H}_3\text{O}^+ \quad \text{pK}_{a2} = 2 \quad (2.2.2)$$

This conclusion is arrived at by modeling three scenarios for the interface: $K_{a1}$ and $K_{a2}$ both bulk like, $K_{a2}$ suppressed, or both $K_{a1}$ and $K_{a2}$ suppressed, and comparing the model results to experimental VSFG spectra in both the S-O and O-H stretching regions. While these studies provide critical insight into the behavior of sulfate species at vapor/solution interfaces, they do not address the role that cation identity may play for the interfacial behavior of sulfate species, such as $\text{HSO}_4^-$. Here we report on the effect that cation (Na$^+$ or Mg$^{2+}$) identity has on $\text{HSO}_4^-$ anions within vapor/solution interfaces probed via conventional VSFG spectroscopy. $\text{H}_2\text{SO}_4$ solutions were studied as a comparison to the findings of Morita and co-workers$^{62,80,81}$ as well as providing a basis from which to judge cation effects on bisulfate’s molecular environment. Na$^+$ and Mg$^{2+}$ cations were chosen as they represent the most prevalent cation species within seawater by weight and thus should be the most prevalent cations in marine aqueous aerosols.$^{1,23}$ Our VSFG findings show that both Na$^+$ and Mg$^{2+}$ cations perturb the hydration of interfacial $\text{HSO}_4^-$, analogous to a dehydration effect, with the Mg$^{2+}$ ions exhibiting a larger influence than Na$^+$. These VSFG findings
are compared to bulk solution studies on HSO₄⁻ behavior completed using conventional Raman and infrared spectroscopies.

### 2.2.2. Experimental Materials and Methods

All VSFG spectra shown in this section were collected with the procedure detailed in Section 2.1. All Raman spectra were collected using 200 mW output from a 785 nm continuous wave diode laser (Process Instruments, ECL-785-300-SH) coupled to a fiber optic probe (InPhotonics, RPS785/12-5) equipped with a 7 mm focal lens. The fiber optic probe was also used to collect the generated Raman Stokes-scatter in the 0° direction before the collected signal was sent to a monochromator (Princeton, Pixis 400) equipped with a thermo-electrically cooled CCD (Princeton, Acton LS785), calibrated versus the output of a Hg lamp and the Raman spectrum of crystalline naphthalene (Sigma Aldrich, > 99% pure), for detection. The Raman spectra are the sum of a 30 s acquisition. The infrared spectra shown were all taken using a home-built attenuated total reflection (ATR) apparatus equipped with a 45° cut ZnSe element to achieve total internal reflection of the infrared beam. This apparatus was mounted in a conventional bench-top Fourier transform (FT) infrared spectrometer (Spectrum 100, Perkin-Elmer). The infrared spectra shown are the average of 100 scans normalized against a background spectrum of pH 1 water (0.1 M HCl) for the salt solutions and the bare ATR element spectrum for the H₂SO₄ solutions.

All salt solutions were prepared by mixing the appropriate amount of salt, Na₂SO₄ (99+% pure, Acros Organics, crystalline, anhydrous) or MgSO₄ (>99.5% pure, Fisher, powder, anhydrous), with nanopure water (18.3 MΩ, NanoPure, Barnstead/Thermolyne).
For pH 1 salt solutions the salt solution was prepared and then brought to the appropriate pH using concentrated HCl (37% wt., Fisher, trace metal grade). The presence of Cl⁻ in the solutions is not predicted to substantially affect our results. H₂SO₄ solutions were prepared by mixing concentrated H₂SO₄ (Fisher, Certified ACS Plus) with nanopure water to the desired concentration. SDS solutions were prepared using solid SDS powder (99+% pure, A.C.S. reagent grade, Sigma-Aldrich) and nanopure water.

2.2.3. Results and Discussion

Figure 2.4 presents three VSFG spectra showing the SO₃ symmetric stretching mode (vₜₚ-SO₃) of interfacial HSO₄⁻ anions for a 0.4 x H₂SO₄ solution (Figure 2.4a) and pH 1 solutions of 0.033 x Na₂SO₄ (Figure 2.4b) and 0.035 x MgSO₄ (Figure 2.4c). For the salt solutions, as the solution pH drops below 2, the protonation of SO₄²⁻ becomes favorable (Eq. 2.2.2) and HSO₄⁻ is formed in solution. The 0.4 x H₂SO₄ VSFG spectrum is in good agreement with published literature results from Miyamae et al.⁸⁰ A concentration of 0.4 x H₂SO₄ was chosen as, at this concentration, the predominant ionic species in sulfuric acid solutions is HSO₄⁻ maximizing the VSFG signal arising from interfacial HSO₄⁻ anions.⁸⁰ Approximately 0.03 x was chosen as the representative salt solution concentration, analogous to ~2 M, as this concentration approaches the aqueous solubility limit of Na₂SO₄ and VSFG intensity was much weaker for more dilute salt concentrations tested.²³ As high salt concentrations can be found in aqueous tropospheric aerosols the concentration regime of 0.03 x seems to be a reasonable one to use for this study.²³,⁷²,⁸²,⁸³ The vₜₚ-SO₃ VSFG signal intensity for both Na₂SO₄ (Figure 2.4b) and MgSO₄ (Figure 2.4c) solutions at pH 1 is comparable to the 0.4 x H₂SO₄ solution results,
Figure 2.4a. While the $\nu_{SS}$-SO$_3$ VSFG signal intensity is comparable between all solutions tested, the $\nu_{SS}$-SO$_3$ peak frequency varies between solutions. The Na$_2$SO$_4$ and MgSO$_4$ solutions exhibit blue-shifted components for the $\nu_{SS}$-SO$_3$ peak relative to the $\nu_{SS}$-SO$_3$ peak position of the 0.4 x H$_2$SO$_4$ solution indicating perturbation to the HSO$_4^-$ interfacial environment.

For Na$_2$SO$_4$ and MgSO$_4$ both neutral, pH 7, and acidic, pH 1, solutions were tested using VSFG. It was not possible to resolve any spectral features in the S-O stretching region from 980-1170 cm$^{-1}$ for the neutral solutions, Figures 2.5 and 2.6. The absence of any VSFG signal for the neutral salt solutions does not indicate an absence of SO$_4^{2-}$ within the vapor/solution interface for these solutions. The lack of any appreciable SO$_4^{2-}$ signal for the pH 7 salt solutions is most likely due to a confluence of two factors including the preference of SO$_4^{2-}$ to reside near the bottom of the vapor/solution interface and the low molecular hyperpolarizability of tetrahedral SO$_4^{2-}$ molecular vibrations (Eq. 2.1.10).$^{43,45,62,73,74,80,81}$ Regardless, these factors render the direct interrogation of SO$_4^{2-}$ vibrational modes within the vapor/solution interface infeasible using a VSFG spectroscopic approach. In contrast, the HSO$_4^-$ vibrational modes are strongly Raman and infrared active and HSO$_4^-$ has been shown to have increased surface preference versus SO$_4^{2-}$, most likely due to its decreased valency.$^{62,81}$ The HSO$_4^-$ anion possesses $C_s$ symmetry but effectively behaves with $C_{3v}$ symmetry which has been demonstrated in many Raman, infrared, and theoretical studies.$^{84-89}$ The effective $C_{3v}$ symmetry of HSO$_4^-$ results in the strong molecular hyperpolarizability for the $\nu_{SS}$-SO$_3$ mode, as this mode is both strongly Raman and IR active, enabling the direct interrogation of HSO$_4^-$ anions within vapor/solution interfaces.
It is clear from Figure 2.4 that the presence of either Na\(^+\) or Mg\(^{2+}\) cations within the vapor/solution interfaces tested results in a blue shift for the observed HSO\(_4^-\) \(v_{SS-SO_3}\) peak frequency. The spectra in Figure 2.4 have all been fit using Equation 2.1.13 where the solid black lines correspond to the total fit and the dashed red lines are the corresponding Lorentzian peak components. Both the H\(_2\)SO\(_4\) and MgSO\(_4\) solutions are best fit with one Lorentzian component, centered at 1050 cm\(^{-1}\) and 1069 cm\(^{-1}\), respectively. The Na\(_2\)SO\(_4\) solution features a bimodal distribution with two Lorentzian component peaks centered at 1048 cm\(^{-1}\) and 1067 cm\(^{-1}\) suggesting that there are two distinct populations of HSO\(_4^-\) at vapor/solution interfaces for pH 1 Na\(_2\)SO\(_4\) solutions. The VSFG fitting results for all solutions have been summarized in Table 2.1.

These VSFG results, Figure 2.4, can be interpreted by considering the effects that cation-anion interaction can have on anion vibrational modes. One type of cation-anion interaction is the formation of solution ion pairs. Ion pair formation within salt solutions has been the subject of intense experimental and theoretical study for decades as the speciation of ionic solutions has large implications for many areas of physical and biological science.\(^{57,59,72,78,79,82,83,87,88,90–113}\) Vibrational spectroscopic techniques such as Raman and infrared have been successfully applied to study ion pairing effects between SO\(_4^{2-}\) and Na\(^+\) or Mg\(^{2+}\) in bulk solution by a number of groups.\(^{59,82,91–95,104,108–112}\) It is generally accepted that both Na\(^+\) and Mg\(^{2+}\) form ion pairs with SO\(_4^{2-}\) in bulk solution\(^ {104,110}\) following the stepwise association mechanism first proposed by Eigen and Tamm.\(^ {90}\)

Ion pairing involving SO\(_4^{2-}\) manifests in Raman spectra as a small shoulder on the blue side of the \(v_{SS-SO_4^{2-}}\) peak centered at 980 cm\(^{-1}\); with increased temperature or
decreasing water content this small shoulder grows into a distinct peak centered at 993 cm$^{-1}$. The $v_{SS}$-$SO_4^{2-}$ blue shift observed for ion pairs involving $SO_4^{2-}$ is most likely due to the symmetry lowering experienced by the $SO_4^{2-}$ tetrahedron on ion pair formation. This relationship between symmetry lowering and a blue shift for the $v_{SS}$-$SO_4^{2-}$ peak frequency is also observed in Raman spectra of solid sulfate salts. However, an observed blue shift for anion vibrational modes, as observed for bulk aqueous $SO_4^{2-}$ ion pair complexes, does not always indicate ion pair formation. For example, with ion pair formation involving nitrate (NO$_3^-$) anions a distinct red shift for the NO$_3^-$ symmetric stretching vibrational mode is observed with Raman spectroscopy. While there are fewer studies investigating the ion pair formation with aqueous HSO$_4^-$ compared to $SO_4^{2-}$, a distinct red shift for the $v_{SS}$-$SO_3$ peak of HSO$_4^-$ has also been observed with ion pair formation by Fung and Tang$^{96}$ using Raman spectroscopy in a study of supersaturated droplets of (NH$_4$)HSO$_4$, NaHSO$_4$, and KHSO$_4$. This trend is similar to the red shift observed for ion pairs involving nitrate in the NO$_3^-$ symmetric stretch vibrations.

From the results of Fung and Tang$^{96}$ it becomes necessary to consider effects that cation interactions may have on interfacial HSO$_4^-$ other than ion pair formation in order to rationalize the observed $v_{SS}$-$SO_3$ peak blue shifts for the two salt solutions. By considering effects of hydration on HSO$_4^-$ $v_{SS}$-$SO_3$ peak frequency clear interpretation of the VSFG results presented in Figure 2.4 is possible. Hydrogen bonding between waters of solvation and the aqueous HSO$_4^-$ anion effectively lengthen the S=O bonds of HSO$_4^-$ by abstracting electron density from the bond.$^{89}$ When these solvating hydrogen bonds are weakened this abstraction is reduced and the S=O bond is strengthened resulting in a
blue shift of the ν_{SS-SO}_3 peak frequency; this effect has been directly observed by Walrafen et al. for H_2SO_4 solutions with increased temperature. Dehydrating effects have also been invoked to explain blue shifts for NO_3⁻ vibrational mode frequency in studies of NO_3⁻ speciation within aqueous solutions as well as the symmetric P-O stretching mode of phosphate headgroup moieties with film compression for Langmuir monolayers of the phospholipid dipalmitoylphosphatidylcholine.

Considering the VSFG results in Figure 2.4 it can be surmised that the presence of Na⁺ and Mg^{2+} within the vapor/solution interface perturbs interfacial HSO_4⁻ hydration. This results in the observed blue shift of the VSFG ν_{SS-SO}_3 peak frequency for the salt solutions. There is no evidence of ion pair formation between HSO_4⁻ and Na⁺ or Mg^{2+} as this is predicted to result in a red shift for the ν_{SS-SO}_3 peak. That the presence of cations within the vapor/solution would affect the hydration of interfacial HSO_4⁻ is an intuitive result with the relatively high concentration of ions in the solutions tested. However, that Mg^{2+} would perturb HSO_4⁻ hydration to a greater degree than Na⁺ is non-intuitive considering the relative surface preference and higher number density (~2x) of Na⁺ compared to Mg^{2+}. This result can be interpreted from the high affinity for solvating water that Mg^{2+} exhibits compared to Na⁺ due to the high charge density of the Mg^{2+} ion. Mg^{2+} affinity for solvating water makes it highly disruptive to the hydrogen bonding of other interfacial ion solvation spheres.

Due to the strong solvation properties of Mg^{2+}, bisulfate anion hydration is highly perturbed by the presence of Mg^{2+} within the interface. This results in the observed blue shift for the ν_{SS-SO}_3 peak of 19 cm⁻¹ versus the peak position for H_2SO_4. In contrast, Na⁺ only affects a sub-population of the bisulfate distribution within the interface, most likely
due to the generally weak hydration properties of Na$^+$, resulting in the bimodal distribution observed for the $\nu_{SS}$-SO$_3$ peak in Figure 2.4b. It is also observed in Figure 2.4b that the bandwidth of the lower frequency peak component is approximately half that of the higher frequency peak component. The origin of this decreased bandwidth is unclear; but the result of interference effects arising from the near-by higher frequency component can be neglected as the origin for this spectral feature as fitting the two peak components with opposite phases did not affect the bandwidth of the lower frequency peak component. The excitation lifetimes for the $\nu_{SS}$-SO$_3$ modes of unperturbed and perturbed HSO$_4^-$ may vary and this could be the source of the observed bandwidth discrepancies, however, the VSFG instrumentation used in this study is not able to resolve dynamics effects. Indeed, there are currently no studies reported in the literature where VSFG has been utilized to directly study ion-mode vibrational dynamics.

Recent cluster studies by Yacovitch et al. on bisulfate which indicate that the $\nu_{SS}$-SO$_3$ peak frequency of HSO$_4^-$ is not sensitive to hydration should be considered. Yacovitch et al. examined aqueous HSO$_4^-$ clusters with up to $n = 16$ water molecules and found that the $\nu_{SS}$-SO$_3$ peak frequency was constant at 1049 cm$^{-1}$ for all cluster sizes. While this frequency is in excellent agreement with our VSFG results for a 0.4 x H$_2$SO$_4$ solution (Figure 2.4a) it is substantially higher than the value of $\sim$1035 cm$^{-1}$ observed for bulk aqueous HSO$_4^-$ solutions with infrared spectroscopy, both in the current study and elsewhere. The consistency for the $\nu_{SS}$-SO$_3$ peak frequency with increasing cluster size observed by Yacovitch et al. may reflect the interfacial nature, which is inherently disruptive to hydrogen bonding, even for the largest clusters tested ($n = 16$).
The response of HSO$_4^-$ to the presence of cations in bulk solutions exhibits similar trends to those observed for vapor/solution interfaces, but to a lesser degree. Shown in Figures 2.7 through 2.9 are bulk solution Raman and infrared spectra for a H$_2$SO$_4$ solution, and pH 1 solutions of Na$_2$SO$_4$ and MgSO$_4$, respectively. It is clear from Figure 2.7, corresponding to bulk solution spectra from a 0.4 x H$_2$SO$_4$ solution, that Raman spectra originating from solutions where both HSO$_4^-$ and SO$_4^{2-}$ exist are generally much easier to unambiguously interpret compared to infrared spectra of the same solution. This is due to the strong infrared activity of broad, overlapping asymmetric stretching vibrations from SO$_4^{2-}$ and HSO$_4^-$ anions. Thus, while the infrared spectra for all solutions tested are shown for completeness only the Raman spectra are considered when discussing cation effects on bulk HSO$_4^-$ solution behavior.

Figures 2.8 and 2.9 are the Raman and infrared spectra for pH 1 0.009, 0.017, and ~0.034 x solutions of Na$_2$SO$_4$ and MgSO$_4$, respectively. These spectra exhibit both SO$_4^{2-}$ and HSO$_4^-$ signatures, but the SO$_4^{2-}$ signatures dominate the spectra. This is because, at pH 1, the solution concentration of HSO$_4^-$ is only ~0.0017 x (0.1 molar) due to the limiting amount of H$^+$ present in solution. This result reinforces the idea that HSO$_4^-$ exhibits surface preference since HSO$_4^-$ features are clearly observable in the salt solution VSFG spectra, Figure 2.4, even for this concentration of HSO$_4^-$. Examining the $\nu_{SS}$-SO$_3$ region in the Raman spectra for the two bulk salt solution series, Figure 2.10, it is evident that the pH 1 Na$_2$SO$_4$ solutions exhibit greater $\nu_{SS}$-SO$_3$ intensity than the pH 1 MgSO$_4$ spectra. This phenomenon was first observed in 1972 by Daly et al. and was interpreted as an indication of increased ion association within MgSO$_4$ solutions versus Na$_2$SO$_4$ solutions.$^{94}$ The increased ion pair formation between Mg$^{2+}$ and SO$_4^{2-}$ seems to inhibit
effectively the protonation of $\text{SO}_4^{2-}$ to $\text{HSO}_4^-$ in solution. While this is an interesting result it does not affect the interpretation of our results and, as such, will not be discussed further.

By fitting the bulk solution Raman spectra (Figures 2.7 – 2.9) it is possible to examine the impact that increased solution concentration and cation identity have on $\nu_{\text{SS}-\text{SO}_3}$ peak frequency for bulk $\text{HSO}_4^-$ solutions. The Raman fitting results for the $\nu_{\text{SS}-\text{SO}_3}$ peak are summarized in Table 2.2 and a representative fit for one of the Raman spectra of bulk solutions is shown in Figure 2.11. Figure 2.12 plots the $\nu_{\text{SS}-\text{SO}_3}$ peak frequency with one standard deviation indicated by error bars for the bulk solution Raman spectra as well as the VSFG results versus the respective solution concentration. It is clear that $\nu_{\text{SS}-\text{SO}_3}$ peak frequency increases in bulk solution with increased solution concentration and with cation identity as $\text{H}^+ < \text{Na}^+ < \text{Mg}^{2+}$. Interestingly the degree of blue shift observed for the $\nu_{\text{SS}-\text{SO}_3}$ peak frequency between the bulk solution and interface results is very similar to the observed degree of blue shift in the presence of $\text{Na}^+$ or $\text{Mg}^{2+}$ ions within the data sets. Thus, $\text{HSO}_4^-$ ions at vapor/salt-solution interfaces should exhibit the highest $\nu_{\text{SS}-\text{SO}_3}$ peak frequency and indeed this is observed in our VSFG results for pH1 $\text{Na}_2\text{SO}_4$ and $\text{MgSO}_4$ solutions. These results suggest that the presence of cations within bulk solution is just as disruptive to $\text{HSO}_4^-$ hydration as is residing within a vapor/solution interface free of cations, which is an inherently dehydrating environment relative to the bulk.
2.2.4. Conclusions

The behavior of $\text{HSO}_4^-$ at vapor/solution interfaces for $\text{H}_2\text{SO}_4$, $\text{Na}_2\text{SO}_4$, and $\text{MgSO}_4$ solutions was examined as a function of cation identity via VSFG spectroscopy. The $v_{\text{SS-SO}_3}$ vibrational mode of the $\text{HSO}_4^-$ anion provides an excellent probe of the molecular environment experienced by $\text{HSO}_4^-$ within vapor/solution interfaces. The presence of $\text{Na}^+$ and $\text{Mg}^{2+}$ are found to perturb the hydration of $\text{HSO}_4^-$ anions resulting in an observed blue shift for the $v_{\text{SS-SO}_3}$ peak frequency. $\text{Mg}^{2+}$ is found to perturb the entire population of interfacial $\text{HSO}_4^-$ due to its strong solvation properties while $\text{Na}^+$ is less disruptive resulting in a bimodal distribution for the $v_{\text{SS-SO}_3}$ peak in the VSFG spectrum. These results are rationalized by considering the effect that dehydration, or hydrogen bond disruption, has on the $\text{HSO}_4^-$ $v_{\text{SS-SO}_3}$ mode, which is to shorten the S=O bond length resulting in a higher frequency of vibration. No ion pair formation is detected between interfacial $\text{HSO}_4^-$ anions and $\text{Na}^+$ or $\text{Mg}^{2+}$ cations. The bulk solution results from Raman spectroscopy reflect similar trends as the interface but with the observed $v_{\text{SS-SO}_3}$ peak frequency blue shifting to a lesser degree than what is observed with VSFG for interfacial $\text{HSO}_4^-$ ions. Infrared spectroscopic results do not offer any clear indication of bulk bisulfate behavior due to the $\text{HSO}_4^-$ $v_{\text{SS-SO}_3}$ mode being obscured by the broad, strong $\text{SO}_4^{2-}$ asymmetric stretching modes in the infrared spectra.

These results may have implications for tropospheric aqueous sulfate containing aerosols. In acidic aerosols, which may feature $\text{Na}^+$ or $\text{Mg}^{2+}$ cations along with $\text{HSO}_4^-$ anions within the aerosol vapor/liquid interface, results indicate that the $\text{HSO}_4^-$ anions will feel some degree of cation induced disruption to their hydration structure. This perturbation to $\text{HSO}_4^-$ hydration may retard the acid dissociation of $\text{HSO}_4^-$ beyond what is
predicted for H$_2$SO$_4$ solutions at vapor/solution interfaces.$^{62,80,81}$ By perturbing interfacial HSO$_4^-$ dissociation to H$^+$, known to prefer the topmost layer of vapor/solution interfaces,$^{64}$ and SO$_4^{2-}$, which will preferentially segregate to the interior of the aerosol,$^{73,74}$ cations residing in the vapor/solution interface may inhibit important acid catalyzed aerosol processes such as secondary organic aerosol formation.
Figure 2.4. SSP VSFG spectra from A) 0.4 x H\textsubscript{2}SO\textsubscript{4}, B) pH 1 0.033 x Na\textsubscript{2}SO\textsubscript{4}, and C) pH 1 0.035 x MgSO\textsubscript{4} solutions. Data (markers), fits to modified Lorentzian profile (solid black traces), Lorentzian peak components (dashed red traces) are shown.
Figure 2.5. SSP VSFG spectra of pH 1 (red squares) and pH 7 (black circles) 0.033 x Na$_2$SO$_4$ solutions.
Figure 2.6. SSP VSFG spectra of pH 1 (blue triangles) and pH 7 (black circles) 0.035 x MgSO₄ solutions.
Figure 2.7. Infrared (A) and Raman (B) spectra from a 0.4 x H₂SO₄ solution. Data (infrared – green solid lines, Raman – blue solid lines) and Lorentzian peak components of Raman fit (red solid lines) are shown. Spectral assignments, indicated by dashed vertical lines, are given for the Raman spectrum (B) but not included for infrared spectrum (A) due to overlapping peaks in infrared spectrum.
Figure 2.8. Infrared (A) and Raman (B) spectra from a pH 1 Na$_2$SO$_4$ solution series. Legend applies to both spectra sets. Spectral assignments given for both infrared (A) and Raman (B) spectra, indicated with dashed vertical lines. Weak $\nu_{SS-SO_3}$ peak at ~1050 cm$^{-1}$ in infrared spectra (A) is difficult to distinguish due to the broad, strongly absorbing $\nu_{AS-SO_4}^{2-}$ peak of sulfate at ~1100 cm$^{-1}$. 
Figure 2.9. Infrared (A) and Raman (B) spectra from a pH 1 MgSO\textsubscript{4} solution series. Legend applies to both spectra sets. Spectral assignments given for both infrared (A) and Raman (B) spectra, indicated with dashed vertical lines. \( \nu_{\text{SS- SO}_3} \) peak at \( \sim 1050 \text{ cm}^{-1} \) in (A) and (B) is more difficult to distinguish compared to Na\textsubscript{2}SO\textsubscript{4} results (Figure 2.8).
Figure 2.10. Raman spectra zoom in on the $\nu_{\text{SS-}}$-$\text{SO}_3^-$ peak region for pH 1 $\text{Na}_2\text{SO}_4$ (A) and $\text{MgSO}_4$ (B) solution series. Data (markers) and Lorentzian fits to data (solid lines) shown. Legend applies to spectra in both (A) and (B) where ~0.034 x solutions (blue triangles), 0.017 x (red squares), and 0.009 x (black circles) are indicated. Spectral assignments are given, indicated with dashed vertical lines. Spectra are offset for clarity.
Figure 2.11. Fit of representative Raman spectra (B) with fit residuals (A) and Lorentzian peak components (C). Data (pink triangles) from 0.0033 x Na$_2$SO$_4$ solution, fit (black line), fit residuals (red dots), and Lorentzian peak components (red lines) labeled 0-2 shown.
Figure 2.12. Peak frequency for the $v_{\text{SS}}$-SO$_3$ mode versus solution concentration in mole fraction for the VSFG (solid markers) and Raman (open markers) results. The H$_2$SO$_4$ solution results (black circles), Na$_2$SO$_4$ solution results (red squares), and MgSO$_4$ solution results (blue triangles) are shown. Error bars indicate one standard deviation from $v_{\text{SS}}$-SO$_3$ spectral fits.
Table 2.1. Curve-Fitting Results for VSFG Spectra of Bisulfate at Vapor/Solution Interfaces.

<table>
<thead>
<tr>
<th></th>
<th>Non-Resonant Terms</th>
<th>Peak 1</th>
<th>Peak 2</th>
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<tr>
<td></td>
<td>Concentration</td>
<td>$B$</td>
<td>$\phi$</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>0.4 x</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>0.033 x</td>
<td>0.05</td>
<td>0.03</td>
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<tr>
<td>MgSO$_4$</td>
<td>0.035 x</td>
<td>0.02</td>
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Table 2.2. Raman Spectra Fitting Results for $\nu_{\text{SS-SO}_3}$ Peak with One Standard Deviation.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentration</th>
<th>$\omega$ (cm$^{-1}$)</th>
<th>$I$ (counts)</th>
<th>FWHM (cm$^{-1}$)</th>
<th>Area x 10$^5$</th>
<th>Area x 10$^7$</th>
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<tbody>
<tr>
<td>H$_2$SO$_4$</td>
<td>0.4</td>
<td>1036 ± 0</td>
<td>3.7 (± 0.05)</td>
<td>51 ± 1</td>
<td>3.0 (± 0.07)</td>
<td></td>
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<tr>
<td>Na$_2$SO$_4$</td>
<td>0.009</td>
<td>1053 ± 1</td>
<td>711 ± 47</td>
<td>27 ± 3</td>
<td>29906 ± 2643</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.017</td>
<td>1053 ± 2</td>
<td>880 ± 137</td>
<td>19 ± 5</td>
<td>26152 ± 6697</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.033</td>
<td>1054 ± 2</td>
<td>1020 ± 215</td>
<td>20 ± 8</td>
<td>32705 ± 11947</td>
<td></td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>0.009</td>
<td>1052 ± 2</td>
<td>475 ± 79</td>
<td>18 ± 5</td>
<td>13181 ± 3741</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.017</td>
<td>1055 ± 3</td>
<td>427 ± 127</td>
<td>19 ± 10</td>
<td>12806 ± 6307</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.035</td>
<td>1059 ± 6</td>
<td>402 ± 250</td>
<td>19 ± 22</td>
<td>12175 ± 12768</td>
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</table>
2.3. Sulfate Adsorption at Buried Fluorite/Solution Interfaces


2.3.1. Introduction

Interactions that occur between charged mineral surfaces and aqueous ions play a large role in geochemical and atmospheric phenomena such as the uptake and retention of environmental contaminants by soils\textsuperscript{19} as well as the reaction and growth of mineral dust aerosols.\textsuperscript{2,16,18} These interactions also have industrial implications for processes such as mineral ore flotation.\textsuperscript{118,119} Despite the importance of surface interactions occurring at or near mineral/solution interfaces, characterization of the interfacial chemistry for such systems remains difficult. Analytical methods used to study mineral – ion interactions at buried mineral/solution interfaces typically involve batch and column experiments\textsuperscript{120,121}, vibrational spectroscopic techniques such as infrared and Raman spectroscopies\textsuperscript{122–129}, ultra-high vacuum techniques\textsuperscript{130,131}, and x-ray absorption spectroscopies.\textsuperscript{132–134} These experimental studies have been complemented by theoretical work which have helped elucidate many long standing questions with regards to adsorption structure and thermodynamics.\textsuperscript{20,21,135,136}

Sulfate adsorption onto mineral surfaces, predominantly oxide minerals, from aqueous solution has been reported widely within the literature utilizing a variety of
analytical methods. Much of this work has focused on applying infrared and Raman spectroscopies to distinguish sulfate adsorption structure. Vibrational spectroscopic techniques are appealing as these methods can be carried out at standard temperatures and pressures, are capable of in situ measurements during flow or exposure experiments, and are generally non-destructive of the sample. Sulfate (SO$_4^{2-}$) is a simple, inorganic anion whose behavior is important to understand as it is ubiquitous in the environment being the third most prevalent ionic chemical species in seawater by weight. It is also the end oxidation product of sulfur containing chemical species and has been linked to the growth of tropospheric aqueous aerosols. From a geochemical perspective, sulfate adsorption to mineral surfaces is important as it can compete with less environmentally benign aqueous anions such as selenate (SeO$_4^{2-}$), selenite (SeO$_3^{2-}$), chromate (CrO$_4^{2-}$), etc. for adsorption sites within contaminated soils increasing the mobility of these toxic compounds.

In this section the direct observation of sulfate adsorption at buried mineral/solution interfaces is reported as revealed by the adsorbed anion’s vibrational stretching modes probed with VSFG spectroscopy. Previous to this, Morita and coworkers have demonstrated the power of VSFG to interrogate directly bisulfate ion vibrational modes at vapor/solution interfaces. I have investigated the interaction and subsequent adsorption of the sulfate anion at the charged fluorite (CaF$_2$)/Na$_2$SO$_4$ solution interface at pH 7 and 298 K in the presence of a 1 molal (m) NaCl background electrolyte for a range of Na$_2$SO$_4$ solution concentrations. The VSFG results are compared to conventional infrared and Raman spectroscopic results for bulk aqueous Na$_2$SO$_4$ solution and solid Na$_2$SO$_4$. A discussion of the sulfate adsorption structure and surface free energy
of adsorption at the fluorite surface determined from the VSFG results follows. These findings may help provide physical insight to various geochemical and atmospheric phenomena such as the comparatively large disordering effect that aqueous sulfate has on water’s hydrogen bond network near charged mineral surfaces\textsuperscript{140} as well as the retardation of mineral dust aerosol ice nucleation by sulfate coatings.\textsuperscript{15,16,18,141}

Fluorite was chosen as the mineral substrate due to its importance as an industrial mineral being the main source for production of hydrofluoric acid by reaction with sulfuric acid.\textsuperscript{142} Fluorite also has many experimentally necessary qualities for VSFG studies of ion interactions at mineral/solution interfaces. These qualities include a large transmission range in the visible and infrared frequency ranges as well as a small aqueous solubility ($1.6 \times 10^{-3}$ g / 100 g H$_2$O at 25 °C).\textsuperscript{23} The ideal surface terminations of fluorite in contact with water was determined by Wu et al.\textsuperscript{118} via a thermodynamic equilibrium model and have been summarized in a later publication by Schrödle et al. for a range of pH values.\textsuperscript{143} At a pH value of 7 the ideal fluorite surface terminations should be two calcium centers coordinated to either water or fluoride. While the reported isoelectric point of fluorite has a broad range, an approximate working value of 8 is assumed here following the findings of Wu et al. and Schrödle et al.\textsuperscript{118,143} Hence it can be surmised that for pH values less than 8 the fluorite surface should feature a net positive charge. These qualities make fluorite an ideal model to study the adsorption behavior of sulfate from aqueous solution onto charged mineral surfaces.

The strength of vibrational spectroscopic techniques to study ion behavior at mineral/solution interfaces \textit{in situ} was first demonstrated in 1997 by Hug\textsuperscript{128} who utilized an attenuated total reflection (ATR) element coated with colloidal hematite particles to
study sulfate adsorption on the hematite particle surface via infrared spectroscopy. While Hug’s insights into using an ATR-infrared approach to study mineral – ion systems have been widely adopted,\textsuperscript{122,125,127,129,137,139} an inherent weakness of linear spectroscopic techniques is their lack of interfacial specificity. This may result in the collected spectra containing information from bulk solvated ions as well as the adsorbed chemical species of interest.

More recently nonlinear spectroscopic techniques such as VSFG have been applied to study buried mineral/solution interfaces, predominantly with perspective toward elucidating interfacial water structure near charged mineral surfaces.\textsuperscript{15,140,144–152} Taking advantage of third-order susceptibility ($\chi^{(3)}$) effects from water near charged mineral interfaces, several research groups have also indirectly probed aqueous ion behavior at buried mineral/solution interfaces via VSFG and second harmonic generation (SHG) spectroscopies.\textsuperscript{22,147,148,153} However, the application of nonlinear spectroscopic techniques to study directly adsorption at charged mineral/solution interfaces has seen limited adoption.\textsuperscript{6,143,153–158} VSFG reports of this nature are generally lacking due to increased experimental difficulties associated with accessing buried interfaces and producing input infrared frequencies at the low frequencies required to directly probe the ion vibrational modes of interest. While the increased experimental difficulties of the VSFG technique put it at a disadvantage for studying buried interfaces when compared to the relatively more straightforward ATR-infrared and Raman techniques, it has a large advantage in that it is inherently interface-specific.\textsuperscript{26} This specificity makes it possible to resolve spectral features associated with the adsorbed species of interest from non-
adsorbed interfacial chemical species residing within the electric double layer near the mineral surface.

### 2.3.2. Experimental Materials and Methods

All VSFG spectra shown in this section were collected following the procedure discussed in Section 2.1. The Raman experiments were carried out using a 532.1 nm continuous-wave diode-pumped Nd:YVO$_4$ laser (Millennium II, Spectra-Physics) with a parallel (p) input beam polarization and a power of 100 mW. All experiments were carried out with 30 s acquisition time with the collected Raman signal sent to a monochromator (SpectraPro 500i, Princeton Instruments) equipped with a 1200 groove/mm grating and detected on a liquid N$_2$-cooled deep-depletion CCD (1340/400-EB, Roper Scientific). The infrared spectra were collected utilizing a home-built ATR apparatus using a ZnSe element to achieve total internal reflection of the infrared beam. This apparatus was mounted in a conventional bench-top FTIR instrument (Spectrum 100, Perkin-Elmer). The infrared spectra shown are the average of 400 scans normalized against a background spectrum of neat water (Figure 2.13a) or of the bare ZnSe element (Figure 2.13b).

Molality ($m$), which is defined here as moles of solute per kg of water, is used as the concentration unit for the Na$_2$SO$_4$ solutions prepared. Solutions of Na$_2$SO$_4$ of various molality were prepared by mixing solid Na$_2$SO$_4$ (99+% pure, Acros Organics, crystalline, anhydrous), annealed at 600 °C for 4 h to remove organic impurities, and nanopure water (18.3 MΩ, NanoPure, Barnstead/Thermolyne) to the desired concentration with an appropriate amount of solid NaCl ($\geq$99.5% pure, Sigma-Aldrich), also annealed at 600 °C.
for 4 h, to bring the background electrolyte concentration to approximately 1 m NaCl. The equilateral fluorite prism (25x25x25 mm, flatness ±10 min, 40/20 surface finish) was purchased from ISP Optics Inc. and was cleaned by sonication in dry methanol (reagent grade, Sigma-Aldrich) followed by copious rinsing with nanopure water before use. The SDS solution used for calibration of the VSFG spectra was prepared from solid SDS powder (99+% pure, A.C.S. reagent grade, Sigma-Aldrich) and nanopure water.

2.3.3. Results and Discussion

The infrared and Raman spectra of a 1 m Na₂SO₄ solution in the S-O stretching region from 950-1250 cm⁻¹ are shown in Figure 2.13a. Both spectra exhibit the expected sulfate vibrational mode peaks with the Raman spectrum featuring a strong peak at 980 cm⁻¹ corresponding to the symmetric stretch (ν₉₈₀-SO₄²⁻) of solvated sulfate and a weak, broad feature centered at ~1100 cm⁻¹ assigned to the triply degenerate asymmetric stretching (ν₃₀₆-SO₄²⁻) modes of sulfate.⁵⁷,¹⁰⁴,¹²⁸ The infrared spectrum in Figure 2.13a exhibits a very strong peak centered at 1090 cm⁻¹, assigned to the degenerate ν₃₀₆-SO₄²⁻ modes of solvated sulfate, consistent with literature.¹²⁸ From the spectra shown in Figure 2.13a little to no VSFG activity is predicted for the fully solvated or “free” sulfate vibrational modes as neither ν₉₈₀-SO₄²⁻ or ν₃₀₆-SO₄²⁻ are both strongly Raman and infrared active, indicating weak hyperpolarizabilities for these vibrational modes (Eq. 2.1.10) when sulfate possesses T₉₈₀ symmetry.²⁶ However, upon inner-sphere adsorption it is expected that the sulfate anion symmetry will lower from T₉₈₀ resulting in both ν₉₈₀-SO₄²⁻ and ν₃₀₆-SO₄²⁻ becoming Raman and infrared active and as such VSFG active as well.¹²⁸
This symmetry lowering is the basis for the determination of sulfate adsorption structure at mineral surfaces via ATR-FTIR. For $T_d$ symmetry the triple degeneracy of $\nu_{\text{AS-SO}_4^{2-}}$ results in one broad strong peak observed in the infrared spectrum, Figure 2.13a. Upon inner-sphere adsorption, the sulfate symmetry will lower to $C_{3v}$ or $C_{2v}$ resulting in two or three distinct frequencies observed for the $\nu_{\text{AS-SO}_4^{2-}}$ modes, respectively. As shown in Figure 2.13b, three peaks are observed for the $\nu_{\text{AS-SO}_4^{2-}}$ modes in both the Raman and infrared spectra of solid Na$_2$SO$_4$ illustrating the symmetry lowering effects of coordination for the sulfate S-O stretching modes. Also apparent is the blue shift of the $\nu_{\text{SS-SO}_4^{2-}}$ mode from 980 cm$^{-1}$ to 993 cm$^{-1}$, along with $\nu_{\text{SS-SO}_4^{2-}}$ becoming infrared active consistent with a $C_{2v}$ or lower symmetry for the sulfate anion. From Figure 2.13b it may be surmised that upon inner-sphere adsorption to the fluorite surface the sulfate anion’s stretching vibrations should become VSFG active as adsorption will lower the sulfate anion symmetry such that $\nu_{\text{SS-SO}_4^{2-}}$ and $\nu_{\text{AS-SO}_4^{2-}}$ will become Raman and infrared active. Based upon the number and frequency of these modes the adsorption structure for sulfate at the fluorite surface can then be inferred.

Shown in Figure 2.14 are the VSFG results for sulfate adsorption at the fluorite surface from Na$_2$SO$_4$ solutions ranging in concentration from 0.1 mm to 100 mm in the presence of a 1 m NaCl background electrolyte at pH 7 and 298 K. The background electrolyte is necessary to ensure that the total ionic strength of the solution does not change significantly with an increase in Na$_2$SO$_4$ concentration as this will affect the effective charge of the fluorite surface. Two separate polarization combinations (ssp and ppp) were used to probe sulfate adsorption at the fluorite surface (Figure 2.14a, b).
The markers in Figure 2.14 correspond to the data while the solid lines represent the best fits to the data using Equation 2.1.13 and the fitting results are presented in Table 2.3. A representative fit to both a ssp and ppp VSFG spectra are shown in Figure 2.15.

In Figures 2.14a and 2.14b sulfate adsorption becomes discernible for the lowest concentration solution tested, 0.1 m, with two weak peaks centered at ~1115 cm\(^{-1}\) and ~1160 cm\(^{-1}\) for the ssp spectrum and ~1095 cm\(^{-1}\) and ~1145 cm\(^{-1}\) for the ppp spectrum appearing. These peaks correspond to the two strongest \(\nu_{\text{AS}}\text{-SO}_4^{2-}\) modes of the bound sulfate anion. The \(\nu_{\text{SS}}\text{-SO}_4^{2-}\) peak is most likely not resolvable for the 0.1 m \(\text{Na}_2\text{SO}_4\) solutions due to a combination of low sulfate concentration and the lower infrared transmission of fluorite at 1000 cm\(^{-1}\) compared to 1150 cm\(^{-1}\). As \(\text{Na}_2\text{SO}_4\) concentration increases above 0.1 m the VSFG response dramatically increases until four peaks are observed in both the ssp and ppp VSFG spectra. The mode centered at 990 cm\(^{-1}\) in both Figures 2.14a and 2.14b is assigned to the \(\nu_{\text{SS}}\text{-SO}_4^{2-}\) mode of adsorbed sulfate surface complexes. The three higher frequency modes present in Figure 2.14 are assigned to the non-degenerate \(\nu_{\text{AS}}\text{-SO}_4^{2-}\) modes of sulfate surface structures.\(^{12}\)

Figure 2.16 gives a schematic of five possible ideal surface structures that sulfate could adopt at the fluorite surface ranging from a non-bonding interaction to bidentate surface complexes where two of the sulfate anion’s oxygens bond directly with a positive calcium center surface site. The symmetry of each representative sulfate surface structure is indicated below the scheme shown in Figure 2.16 and the net effect on the sulfate anion charge is noted. For schemes I and II, corresponding to the non-interactive fully solvated sulfate anion and an outer-sphere hydrogen-bound sulfate anion respectively, no
VSFG activity is expected as in these environments the sulfate anion will retain $T_d$ symmetry. In scheme III, representing monodentate inner-sphere sulfate adsorption, the sulfate anion possesses $C_{3v}$ symmetry which will incompletely lift the degeneracy of the $\nu_{AS-SO_4^{2-}}$ modes resulting in two distinct frequencies for these vibrations. Hence for sulfate surface complexes possessing $C_{3v}$ symmetry three total VSFG peaks would be expected, two $\nu_{AS-SO_4^{2-}}$ peaks and the $\nu_{SS-SO_4^{2-}}$ peak. The final two schemes, IV and V, represent mono-atomic and bridging bidentate inner-sphere sulfate structures, respectively. For both of these structures the sulfate anion symmetry will lower to $C_{2v}$, which completely breaks the $\nu_{AS-SO_4^{2-}}$ degeneracy resulting in three distinct stretching frequencies. Thus, for bidentate inner-sphere sulfate coordination at the fluorite surface, four total VSFG peaks are expected.

As discussed above, four peaks are observed for both ssp and ppp polarization combinations for the three most concentrated Na$_2$SO$_4$ solutions (Figures 2.14a, b) indicating net $C_{2v}$ symmetry for the adsorbed sulfate structures. While the SSP spectra are best fit with four peaks for all but the weakest Na$_2$SO$_4$ concentration solution tested, the peak frequencies are not as distinct as those observed in the ppp spectra (Figure 2.14b). By utilizing different VSFG polarization schemes it is possible to probe different sulfate adsorption structures which may feature varying distributions at the fluorite surface. These sub-distributions of sulfate adsorption structures will preferentially interact with a specific input beam polarization combination due to geometric alignment with the electric-field vectors of the input beams. This alignment will result in the detected sum frequency response for different polarization combinations having greater signal contribution from the preferred sub-distribution of adsorption structures. The presence of
varying sulfate adsorption structures is apparent when comparing the $\nu_{\text{AS-SO}_4^{2-}}$ mode frequencies between the ssp and ppp spectra shown in Figure 2.14, which clearly vary, even though both spectra sets indicate $C_{2v}$ symmetry for the adsorbed sulfate. Sulfate’s $\nu_{\text{AS-SO}_4^{2-}}$ vibrational frequencies are known to vary significantly with molecular environment, even for sulfate anions possessing the same symmetry group, and as such the VSFG spectra in Figure 2.14 reflect the differing distributions of sulfate adsorption structures at the fluorite/solution interface. These distributions, which manifest as frequency differences for the $\nu_{\text{AS-SO}_4^{2-}}$ modes, as well as the difficulties in determining a depolarization ratio for adsorption structures make a detailed analysis of the net sulfate adsorption structure orientation infeasible using the common polarization intensity ratio method. It may be possible to apply the polarization null angle method pioneered by Shultz and coworkers to determine the net sulfate adsorption orientation. However, the application of this technique is experimentally non-trivial and is beyond the scope of the work presented in this dissertation.

The clear presence of four peaks in the ssp and ppp spectra indicates that sulfate adsorbs to the fluorite surface predominantly in a bidentate inner-sphere manner consistent with schemes IV or V shown in Figure 2.16. While it is not possible from the VSFG data to distinguish between mono-atomic versus bridging bidentate coordination, the presence of four peaks clearly indicates that a bidentate adsorption structure is preferred by sulfate at the fluorite surface. In both the ssp and ppp spectra sulfate adsorption is clearly present for the lowest Na$_2$SO$_4$ concentration tested (0.1 mm) indicating that the sulfate anion forms surface adsorption complexes with fluorite even from dilute solutions at 298 K and pH 7.
It is possible to calculate the net free energy of adsorption for the bidentate inner-sphere sulfate complexes by applying a simple Langmuir adsorption model to the ssp and ppp data.\textsuperscript{153,154,159} An important consideration when applying this model to VSFG studies is that the detected VSFG intensity is proportional to the orientation of the adsorbed species as well as the surface number density, Equation 2.1.9. For the purposes of this analysis it is reasonable to assume that the net orientation of the sulfate bidentate inner-sphere complexes remain constant as the concentration of Na\textsubscript{2}SO\textsubscript{4} increases. If the adsorption orientation is constant with an increase in Na\textsubscript{2}SO\textsubscript{4} concentration then the surface number density of adsorption complexes is proportional to the square-root of the VSFG intensity, Equation 2.1.1. Figure 2.17 shows the Langmuir adsorption isotherms generated by plotting the square-root of the detected VSFG intensities for the v\textsubscript{SS-SO\textsubscript{4}^{2-}} peak and the strongest v\textsubscript{AS-SO\textsubscript{4}^{2-}} peak for both the ssp and ppp data sets versus Na\textsubscript{2}SO\textsubscript{4} solution concentration. Then by plotting one over the relative surface coverage (\(\theta\textsubscript{rel}\)) versus one over the solution concentration and fitting the results with a straight line, Figure 2.18, the Gibbs free energy of adsorption can be found using Equation 2.3.1:

\[
\left[ \frac{d\left(\frac{1}{\theta\textsubscript{rel}}\right)}{d\left(\frac{1}{[SO\textsubscript{4}^{2-}]}\right)} \right]^{-1} = \frac{1}{55.5M} \exp\left(\frac{-\Delta G\textsubscript{ads}}{RT}\right) \tag{2.3.1}
\]

where the concentration of water, 55.5 M, is normalized to. Table 2.4 details the results of the Langmuir adsorption analysis, with an average \(\Delta G\textsubscript{ads}^o = -33 \pm 2 \text{ kJ/mole} \) (rounded
to the nearest whole number) determined when fitting all four Na$_2$SO$_4$ concentrations and
$\Delta G^\circ_{ads} = -29 \pm 2$ kJ/mole when fitting just the three most concentrated Na$_2$SO$_4$ solutions
as shown in Figure 2.18. The Langmuir analysis was carried out for just the three most
concentrated Na$_2$SO$_4$ solutions for comparison purposes as the 0.1 mM solution VSFG
peak intensities have the highest uncertainty due to the weakness of the VSFG response
for this Na$_2$SO$_4$ concentration.

While the limited number of Na$_2$SO$_4$ concentrations tested and the assumption of
constant orientation for the adsorbed surface structures make the application of a
Langmuir adsorption analysis here somewhat physically questionable, the agreement
between the calculated adsorption free energies between the ssp and ppp data when both
four and three Na$_2$SO$_4$ concentrations were fit, Table 2.4, indicate that a Langmuir
analysis is not completely unreasonable. That the degree of splitting observed for the
three $\nu_{AS-SO_4^{2-}}$ peaks with ssp and ppp polarization combinations is quite different and
yet the $\Delta G^\circ_{ads}$ values calculated from both data sets are so similar is a surprising result. It
is reasonable to expect that larger splitting for the $\nu_{AS-SO_4^{2-}}$ peaks would be the result of
a stronger interaction between the adsorbed sulfate and the fluorite surface. However, this
is not what is observed for the surface free energies of adsorption calculated with a
Langmuir analysis, highlighting the oversimplification of ion adsorption processes by the
Langmuir model. A first-approximation for the $\Delta G^\circ_{ads}$ for sulfate at the fluorite surface,
and it is stressed that this value should be taken as a first-approximation only, is
determined to be $-31 \pm 3$ kJ/mole by averaging the values listed in Table 2.4. It is also
worth noting that an average value for $\Delta G^\circ_{ads} = -31 \pm 3$ kJ/mole, which is approximately
as strong as several hydrogen bonds, is quite reasonable considering the reversibility of
sulfate adsorption at the fluorite surface and is in good agreement with literature values for reversible simple inorganic ion adsorption at charged mineral surfaces.\textsuperscript{22,153,154}

These findings help explain recent work on resolving water structure near the charged fluorite surface for a variety of simple inorganic salt solutions, including $\text{Na}_2\text{SO}_4$, carried out by Hopkins et al.\textsuperscript{140} In this study the presence of $\text{Na}_2\text{SO}_4$ was observed to retard the ordering effects of the charged fluorite surface on interfacial water to a greater degree than was observed for other inorganic salts (NaCl, NaBr, and NaF) tested beyond what would be predicted by Gouy-Chapman theory.\textsuperscript{140,159} The VSFG results presented in here (Chapter 2, Section 3), indicating that sulfate predominantly forms bidentate inner-sphere adsorption complexes with the fluorite surface, provides insight into the underlying physical forces behind the water disordered effects observed at the fluorite/sulfate solution interface by Hopkins et al. In forming bidentate inner-sphere adsorption complexes at the fluorite surface sulfate not only replaces adsorbed water at the fluorite surface but also effectively removes the net charge of the positive fluorite surface terminations. This reduces the local electric field responsible for water ordering near a charged mineral surface to a greater degree than what could be expected for non-binding ions near the mineral surface. This is a plausible explanation for the observed reduction of interfacial water ordering at the fluorite/solution interface by aqueous sulfate beyond what would be predicted by Gouy-Chapman theory.\textsuperscript{140,159}

\subsection*{2.3.4. Conclusions}

The direct observation of sulfate adsorption to a charged mineral, fluorite ($\text{CaF}_2$), surface at the buried mineral/solution interface is reported in this section using VSFG
spectroscopy. The use of VSFG to study adsorption phenomena at buried interfaces has the advantage over conventional vibrational spectroscopic techniques in that it is inherently interface-specific allowing for the resolution of adsorbed sulfate surface structures from non-bound fully solvated sulfate near the interface. Sulfate is found to predominantly adsorb in a bidentate inner-sphere manner with an average net surface free energy of adsorption for these complexes calculated to be $\Delta G_{ads}^{\circ} = -31 \pm 3 \text{ kJ/mole}$ using a Langmuir adsorption analysis. These findings have significance toward geochemical and atmospheric phenomena such as competition between sulfate and other aqueous anions for mineral adsorption sites as well as the water uptake and reaction of sulfate-coated mineral dust aerosols.\textsuperscript{18,19} The application of the VSFG method toward the study of sulfate adsorption onto other environmentally relevant minerals at the buried mineral/solution interface is the subject of on-going work.
Figure 2.13. Normalized infrared and Raman spectra from (A) 1 m Na₂SO₄ solutions at pH 7 and 298 K and (B) solid, anhydrous Na₂SO₄ at 298 K. Spectral assignments are indicated above the respective peaks. Vertical dashed lines indicate respective peak centers.
Figure 2.14. Normalized VSFG spectra (A - ssp and B - ppp) of the CaF₂/Na₂SO₄ solution interface for a range of Na₂SO₄ concentrations in 1 m NaCl background electrolyte at pH 7 and 298 K. Spectral assignments are indicated above peaks. The markers are data and solid lines are best fits to the data. Spectra offset for clarity. Vertical dashed lines indicate respective peak centers.
Figure 2.15. Representative VSFG spectra, A-ssp and B-ppp (both are the 100 mm Na$_2$SO$_4$ solution set), showing four typical Lorentzian fit components used to fit the data. Data are markers, solid black line is total fit to the data, and red solid lines are individual Lorentzian fit components. Peaks are labeled 1-4 from left to right. Complete fitting results for all VSFG spectra are listed in Table 2.3.
Figure 2.16. Cartoon representation of possible interaction schemes for $\text{SO}_4^{2-}$ at the CaF$_2$/Na$_2$SO$_4$ solution interface with symmetry of the sulfate anion for each scheme indicated next to the Roman numeral. Note that the blue background represents bulk aqueous solution. Scheme I: non-interacting, Scheme II: outer-sphere coordination, Scheme III: monodentate inner-sphere coordination, Scheme IV: mono-atomic bidentate inner-sphere coordination, and Scheme V: bridging bidentate inner-sphere coordination. Scheme IV and V are boxed to indicate preferred sulfate adsorption structure at the fluorite surface. The effective charge of the $\text{SO}_4^{2-}$ anion is noted for each possible surface structure beside the sulfur atom of $\text{SO}_4^{2-}$. Dashed line in Scheme II represents hydrogen-bond, solid lines in Schemes III, IV, and V represent direct bond with fluorite surface site.
Figure 2.17. Langmuir adsorption isotherms generated by plotting the square-root of the VSFG peak intensity versus Na$_2$SO$_4$ solution concentration. Peaks chosen correspond to the 996 cm$^{-1}$ and 1160 cm$^{-1}$ peaks for the ssp data and 1000 cm$^{-1}$ and 1150 cm$^{-1}$ peaks for ppp data. Markers are data, error bars are plus/minus one standard deviation, and solid lines are fits using Langmuir equation.
Figure 2.18. Reciprocal of relative surface coverage ($\theta_{rel}$) versus reciprocal of sulfate solution concentration from Langmuir adsorption analysis for the four isotherms shown in Figure 2.17. Data are markers, solid lines are fits to all four Na$_2$SO$_4$ concentrations, and dashed lines are fits to three highest (100, 10, and 1 mM) Na$_2$SO$_4$ concentrations with $R^2$ values for the fits are indicated in the legend. From the slope of the lines it is possible to calculate the surface free energy of adsorption using Equation 2.3.1.
### Table 2.3

Fitting results for the fluorite/Na$_2$SO$_4$ solution interface VSFG spectra using Equation 2.1.13 with plus/minus one standard deviation noted. A – peak amplitude, $\omega$ – peak frequency in wavenumbers, HWHM – peak half-width at half-max in wavenumbers.

<table>
<thead>
<tr>
<th>Na$_2$SO$_4$ Concentration</th>
<th>Polarization</th>
<th>Real</th>
<th>Imaginary</th>
<th>A (SSP)</th>
<th>$\omega$ (SSP)</th>
<th>HWHM</th>
<th>A (PPP)</th>
<th>$\omega$ (PPP)</th>
<th>HWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 mm</td>
<td>SSP</td>
<td>0.02 ± 0.01</td>
<td>0.10 ± 0.01</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>4.4 ± 1.4</td>
<td>1121.0 ± 2.4</td>
<td>19.3 ± 4.2</td>
</tr>
<tr>
<td></td>
<td>PPP</td>
<td>0.00 ± 0.01</td>
<td>-0.04 ± 0.01</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>1.0 ± 0.3</td>
<td>1144.6 ± 2.3</td>
<td>17.5 ± 4.5</td>
</tr>
<tr>
<td>1 mm</td>
<td>SSP</td>
<td>0.08 ± 0.01</td>
<td>-0.07 ± 0.01</td>
<td>0.30 ± 0.8</td>
<td>1.2 ± 0.3</td>
<td>1070.4 ± 2.7</td>
<td>17.4 ± 2.4</td>
<td>1148.0 ± 2.3</td>
<td>17.5 ± 4.5</td>
</tr>
<tr>
<td></td>
<td>PPP</td>
<td>-0.01 ± 0.01</td>
<td>0.02 ± 0.01</td>
<td>0.03 ± 0.6</td>
<td>2.4 ± 0.8</td>
<td>1095.3 ± 2.1</td>
<td>17.1 ± 3.7</td>
<td>1144.6 ± 2.3</td>
<td>17.5 ± 4.5</td>
</tr>
<tr>
<td>10 mm</td>
<td>SSP</td>
<td>0.10 ± 0.01</td>
<td>-0.08 ± 0.01</td>
<td>0.30 ± 0.8</td>
<td>1.2 ± 0.3</td>
<td>1070.4 ± 2.7</td>
<td>17.4 ± 2.4</td>
<td>1148.0 ± 2.3</td>
<td>17.5 ± 4.5</td>
</tr>
<tr>
<td></td>
<td>PPP</td>
<td>-0.01 ± 0.01</td>
<td>0.03 ± 0.03</td>
<td>0.30 ± 0.6</td>
<td>2.4 ± 0.8</td>
<td>1095.3 ± 2.1</td>
<td>17.1 ± 3.7</td>
<td>1144.6 ± 2.3</td>
<td>17.5 ± 4.5</td>
</tr>
<tr>
<td>100 mm</td>
<td>SSP</td>
<td>0.10 ± 0.01</td>
<td>-0.09 ± 0.01</td>
<td>0.30 ± 0.6</td>
<td>1.2 ± 0.3</td>
<td>1070.4 ± 2.7</td>
<td>17.4 ± 2.4</td>
<td>1148.0 ± 2.3</td>
<td>17.5 ± 4.5</td>
</tr>
<tr>
<td></td>
<td>PPP</td>
<td>-0.01 ± 0.01</td>
<td>0.03 ± 0.03</td>
<td>0.30 ± 0.6</td>
<td>2.4 ± 0.8</td>
<td>1095.3 ± 2.1</td>
<td>17.1 ± 3.7</td>
<td>1144.6 ± 2.3</td>
<td>17.5 ± 4.5</td>
</tr>
</tbody>
</table>
Table 2.4. Langmuir Adsorption Analysis For VSFG of Fluorite/Na$_2$SO$_4$-Solution Interfaces Results.

<table>
<thead>
<tr>
<th>Peak Frequency (cm$^{-1}$)</th>
<th>Polarization</th>
<th>$^{a}$d(1/$\theta$)/d(1/[SO$_4^{2-}$])</th>
<th>$^{b}\Delta G_{\text{ads}}$ (kJ/mole)</th>
<th>$^{a}$d(1/$\theta$)/d(1/[SO$_4^{2-}$])</th>
<th>$^{b}\Delta G_{\text{ads}}$ (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>996</td>
<td>SSP</td>
<td>(1.2 ± 0.2) x 10$^{-4}$</td>
<td>-32.3 ± 0.4</td>
<td>(3.3 ± 2.1) x 10$^{-4}$</td>
<td>-29.8 ± 1.9</td>
</tr>
<tr>
<td>1160</td>
<td>SSP</td>
<td>(1.3 ± 0.1) x 10$^{-4}$</td>
<td>-32.1 ± 0.3</td>
<td>(3.4 ± 0.4) x 10$^{-4}$</td>
<td>-29.7 ± 0.3</td>
</tr>
<tr>
<td>1000</td>
<td>PPP</td>
<td>(7.8 ± 4.5) x 10$^{-5}$</td>
<td>-33.4 ± 1.6</td>
<td>(7.3 ± 2.2) x 10$^{-4}$</td>
<td>-27.9 ± 0.5</td>
</tr>
<tr>
<td>1150</td>
<td>PPP</td>
<td>(7.8 ± 1.8) x 10$^{-5}$</td>
<td>-33.4 ± 0.6</td>
<td>(3.1 ± 1.3) x 10$^{-4}$</td>
<td>-30.0 ± 1.1</td>
</tr>
</tbody>
</table>

$^{a}$ Slope of line-of-best fit for one over relative surface coverage ($\theta$) vs. one over Na$_2$SO$_4$ solution concentration from Figure 2.18 using four or three Na$_2$SO$_4$ concentrations with plus/minus one standard deviation.

$^{b}$ Calculated surface free energy of adsorption using Equation 2.3.2 with plus/minus one standard deviation.
Chapter 3. Vibrational Spectroscopic Characterization of Hematite, Maghemite, and Magnetite Thin Films Produced by Vapor Deposition


3.1. Introduction

Iron oxides constitute an important class of materials that are ubiquitous in nature. There are sixteen various iron oxide-oxyhydroxide polymorphs that display a wide range of properties and behavior in the environment. Due to this assortment of physical properties, iron oxides are of great interest to a variety of scientific disciplines for various applications that range from opto-electronics, medicine, environmental remediation, pigments, corrosion protection, and gas sensing, among others. Three of the most common and important iron oxide polymorphs are hematite (α-Fe₂O₃), maghemite (γ-Fe₂O₃), and magnetite (Fe₃O₄).

Hematite is the most common iron oxide polymorph found in nature due to its high thermodynamic stability. It is isostructural with corundum (α-Al₂O₃) having a hexagonal unit cell based on anion hcp packing. Due to its ubiquity in nature, the adsorptive properties of hematite are of great importance for the study of transport of
contaminants in water and the remediation of waste. Maghemite, similar to hematite, is a fully oxidized iron oxide polymorph where all iron is in the $\text{Fe}^{3+}$ state. The maghemite crystal structure possesses 2 and 1/3 vacant sites within its unit cell. If these vacant sites are randomly distributed within the crystal structure then maghemite possesses an inverse spinel structure, similar to magnetite. The inverse spinel crystal structure is the most general case for maghemite. It is an important intermediate to hematite formation from the oxidation of magnetite or the dehydroxylation of goethite precursors. Magnetite is a ferromagnetic material that is of importance to the electro-optical industry. Found in nature magnetite produces the magnetic behavior of rocks. Magnetite has an inverse spinel crystal structure, as mentioned above, where each unit cell consists of 8 $\text{Fe}^{2+}$, 16 $\text{Fe}^{3+}$, and 32 $\text{O}^{2-}$ atoms. It is an important precursor to hematite via thermal transformation processes.

$$\begin{align*}
\text{Fe}_3\text{O}_4 & \xrightarrow{\geq 200 \text{ C}} \gamma - \text{Fe}_2\text{O}_3 & \xrightarrow{\geq 400 \text{ C}} & \alpha - \text{Fe}_2\text{O}_3
\end{align*}$$ (3.1.1)

Synthetic thin films of the various iron oxide-oxyhydroxide polymorphs have been widely reported in the literature. General preparation approaches range from ultra-high vacuum epitaxial methods first reported in 1988 by Vuren et al. involving the synthesis of single mono-layers of iron oxides upon an oriented single crystal substrate, generally Pt(111), to high vacuum methods such as chemical vapor and physical vapor deposition (PVD) to non-vacuum methods such as forced hydrolysis and sol-gel synthesis. While the use of ultra-high vacuum epitaxial techniques produce very clean, well defined, single crystal films of iron oxide, the low
pressure requirement limits this method. Wet deposition and chemical vapor deposition techniques have also been shown to produce well defined iron oxide films, however, the use of chemical precursors in these methods can leave contaminants (NO$_3^-$, SO$_4^{2-}$, organics) absorbed onto the thin film of interest.

This is a major weakness of these methods if the thin films produced are to be used in adsorption studies, as is desired for the work presented in this dissertation. One of the earliest reported techniques for generating thin films is PVD by conventional electron-beam evaporation of an elemental metal either onto a hot substrate or followed by an annealing step in air.$^{197}$ This technique seems to be less favored than other iron oxide production schemes as it requires both a high vacuum system, is a two-step process, and generally produces polycrystalline films. However, with the use of conventional electron-beam evaporation and a careful choice of annealing temperature, Equation 3.1.1, it is possible to produce magnetite, maghemite, and hematite films without the presence of chemical precursors.

Raman and Fourier transform infrared (FTIR) spectroscopies have been used to characterize iron oxides for several decades.$^{198-211}$ These analytical techniques can provide clear assignment of the oxide phase as well as a measurement of the degree of crystallinity of the materials under study through the observation of the phonon modes. Raman and IR spectroscopies are also ideal to study films too thin (< 100 nm) to be studied easily by more conventional crystal characterization techniques, e.g. x-ray diffraction (XRD). Raman spectroscopy is generally the vibrational spectroscopy of choice when characterizing oxide powders and films as the various iron oxide polymorphs exhibit distinct Raman signatures and it is possible to take advantage of so-
called phonon confinement effects to better quantify the crystallinity of the sample.\textsuperscript{166,200,201,203,205,206,210,212–221} FTIR has been used less frequently to characterize iron oxide thin films, but can provide additional confirmation of the oxide phase present as well as information on the crystallinity of the film.\textsuperscript{172,175,206}

In this chapter the preparation of polycrystalline thin (40 nm - 250 nm) hematite, maghemite, and magnetite films through the use of conventional electron-beam evaporation is presented. These films are primarily characterized with Raman micro spectroscopy with FTIR providing additional information on the phase of the films excluding the thicker magnetite film. This characterization allows for phase identification as well as insight into the degree of film crystallinity and uniformity. The generation and characterization of iron oxide films free of chemical-precursor contaminants is critical to later studies of sulfate adsorption at iron oxide/solution interfaces.

3.2. Experimental Materials and Methods

Iron oxide films were prepared by depositing a set amount of elemental iron onto KBr substrates via a conventional PVD technique, electron-beam evaporation using a thermal evaporator (Denton, model # DV-502A). Here iron films of 20 nm and 100 nm were deposited via electron beam evaporation from elemental iron slugs (Alfa Aesar, ¼ inch diameter by ¼ inch length, 99.95\% pure) onto KBr substrates in a vacuum chamber at $4 \times 10^{-6}$ Torr. The KBr discs measured 25 mm in diameter by 3 mm thick (Pike Technologies Inc.) and were used as received. Iron film thickness was controlled through the use of a quartz micro-balance within the evaporation chamber. To produce iron oxide phases of interest the iron films were annealed in a conventional muffle furnace (Fisher
Scientific, Isotemp model #550-14) for four hours in an air atmosphere. To produce magnetite films the deposited iron films were annealed in air at 175° C, for maghemite the films were annealed at 350°C in air, and for hematite the films were annealed at 575° C in air. The annealing temperatures chosen resulted in films that were homogeneous in the desired iron oxide phase. Post-annealing, the films were characterized with Raman micro-spectroscopy, FTIR, and ellipsometry.

All Raman spectra were collected using a Renshaw inVia Raman microscope with a 50x objective coupled to a 632.8 nm He-Ne laser excitation source (Renshaw RL633). The resolution of this instrument was approximately 3 cm⁻¹ with an 1800 groove/mm grating. Utilizing this setup the laser power at the sample was approximately 6 mWatts with 100% laser power. Several studies have shown that iron oxides are vulnerable to heat-induced phase changes via the excitation source during the course of collecting a Raman spectrum. In order to address this issue, a line focus was utilized that produces a line shape for the excitation source at the sample surface that is approximately 5 x 40 µm in dimension. This effectively reduces the energy flux felt by any local spot on the sample surface preventing any phase changes in the iron oxide films during the course of a spectral acquisition. The Raman spectra presented in this study were collected with a 30 second acquisition time and 6 mW (100%) laser power over a spectral range from 100 – 1000 cm⁻¹, as all diagnostic phonon modes for the iron oxide phases of interest occur below 1000 cm⁻¹. Using these parameters no phase changes were observed in the Raman spectra during the course of the spectral collection.

FTIR spectra were collected in a Perkin Elmer Spectrum 100 FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The resolution used was 4
cm$^{-1}$. All spectra were collected with 400 scans in transmission mode, then referenced against a 3 mm blank KBr transmission spectrum to yield the absorbance spectra presented. No comparison between films of differing iron oxide phases is reported due to differing film thickness between the iron oxide films produced in this study. The FTIR spectrum of the thicker magnetite film is not reported due to excessive reflection losses from the film’s mirror like surface.

Film thickness was calculated (Appendix A) and measured using ellipsometry with values reported in Table 3.1. Ellipsometry measurements were taken with a Gaertner L116s ellipsometer (Nanotech West Facility, Ohio State University) equipped with a 632.8 nm He-Ne laser. The ellipsometry measurements were carried out with an incident/collection angle of 70° using the thin oxide setting in the software program GEMP. In this setting, it is necessary to provide the software an initial estimate of the oxide film’s refractive index and thickness. Here, bulk values of the refractive index for the iron oxides at 633 nm were provided and the thickness estimate was based upon the calculated estimate of the thickness using a unit cell approach. Thickness characterization was carried out post phase characterization in order to prevent laser induced phase changes during ellipsometry measurements. The estimated and measured thickness, Table 3.1, agree within ±15 nm.
3.3. Results and Discussion

3.3.1. Hematite

Hematite’s irreducible vibrational modes at the first Brillouin zone center are represented by Equation 3.3.1:

\[ \Gamma_{\text{vib}} = 2A_{1g} + 2A_{1u} + 3A_{2u} + 5E_g + 4E_u \]  \hspace{1cm} (3.3.1)

The acoustic \( A_{1u} \) and the \( A_{2u} \) modes are optically silent, the symmetrical modes are Raman active, and the anti-symmetrical modes are infra-red active.\(^{199,206}\) As the hexagonal crystal structure of hematite features an inversion center, no modes are both Raman and infrared active.\(^{223}\)

Figure 3.1 shows the Raman spectra of the iron oxide films produced after heating 20 nm and 100 nm Fe films at 575\(^\circ\)C for four hours in an air atmosphere. These spectra exhibit all seven of the spectral signatures deemed diagnostic for hematite, Table 3.2, and do not contain any peaks associated with either maghemite or magnetite.\(^{166,203,204,206,213}\) The peaks seen at 229 cm\(^{-1}\) and 500 cm\(^{-1}\) are assigned to the \( A_{1g} \) modes.\(^{166}\) The remaining five peaks at 249 cm\(^{-1}\), 295 cm\(^{-1}\), 302 cm\(^{-1}\), 414 cm\(^{-1}\), and 615 cm\(^{-1}\) are assigned to the \( E_g \) modes.\(^{166}\) This indicates that heating for four hours at 575\(^\circ\) C is suitable for transforming the initial Fe films completely to hematite. The weak peak seen at approximately 660 cm\(^{-1}\) has been widely observed in Raman spectra of hematite and is generally attributed to the presence of residual magnetite or maghemite contamination.\(^{203,207–209,213}\)
However, the presence of magnetite or maghemite in the hematite films seems counter-intuitive as the films were heated well above the temperature at which magnetite and maghemite are known to undergo complete thermal transformation to hematite in the presence of air.\textsuperscript{161} This issue has been noted by several other authors who have also observed the 660 cm\textsuperscript{-1} peak for hematite samples at elevated temperatures.\textsuperscript{171,206,210,224} Bersani et al.\textsuperscript{171} showed that only by mixing hematite and magnetite powders together in a 1:1 ratio were they able to achieve the relative intensity for the 660 cm\textsuperscript{-1} peak that they had observed in their hematite film sample. This leads to the rejection of a residual magnetite presence as the source of the 660 cm\textsuperscript{-1} peak and the assignment of the 660 cm\textsuperscript{-1} peak to the Raman forbidden, IR active longitudinal optical (LO) $E_u$ mode of hematite that occurs at the same frequency. This mode is thought to be activated by disorder within the hematite crystal lattice.\textsuperscript{171} This assignment was subsequently confirmed by others and is adopted for this study.\textsuperscript{206,210,224}

Beyond phase assignment via observation of characteristic phonon peaks for oxide samples, Raman spectroscopy has been utilized extensively to investigate the crystallinity of micro- and nano-regimes through phonon confinement effects.\textsuperscript{206,212,214–218,220,221} Briefly, phonon confinement effects describe the phenomena that occurs with the lifting of the phonon momentum selection rule, $q \sim 0$, for the Raman scattering process within ordered media. This generally occurs as crystal domains become very small and manifests as both a frequency shift of the phonon modes and an asymmetrical broadening of the phonon peaks.\textsuperscript{214} An examination of the Raman spectra for the hematite films presented in Figure 3.1 shows that the 250 nm thick film exhibits both blue shifted frequencies and broader FWHM for all seven phonon peaks compared to the
50 nm thick film. This was quantified by fitting both spectra with seven Lorentzian peaks and comparing results, Figure 3.2 and Table 3.3. Figure 3.3 presents just the $A_{lg}$ peak, which is centered at 229 cm$^{-1}$, where the peak blue shifting and FWHM broadening is clearly observed. This is consistent with results for titanium dioxide powders and films where a blue shift of the frequency and a broadening of the FWHM for the phonon peaks represents decreasing crystallite size.$^{214-218}$

The intensity of the Raman scattering increases as the hematite film increases from 50 nm to 250 nm in thickness. This is intuitive as Raman scattering intensity is proportional to the number density of the interacting media. However, the increase of the signal intensity shown in Figure 3.1 between the two films is not proportional to the degree of increase in the film thickness. The reasons for this are not clear; however, as discussed below, IR data do scale appropriately for the hematite films.

Assignments of the six IR active modes of hematite with their respective LO and transverse optical (TO) phonon frequencies are supplied in Table 3.4. The FTIR spectra collected in transmission mode for the two hematite films are presented in Figure 3.4, along with the Lorentzian fits used to quantify the low frequency peak. Spectrum A in Figure 3.4 corresponds to the 50 nm hematite film and spectrum B corresponds to the 250 nm hematite film. The relative absorption intensity between the two spectra shown in Figure 3.4 is appropriately ~ 5 times more intense for spectrum B as the film is ~ 5 times thicker. These spectra feature two prominent peaks at 440 cm$^{-1}$ and 526 cm$^{-1}$. These peaks are assigned to the $E_u$ and $A_{2u}+E_u$ phonon modes, respectively.$^{199,200}$ The weak peak present at ~385 cm$^{-1}$ is attributed to the second $A_{2u}$ mode and is not discussed further.$^{199,200}$
While both the $E_u$ and the $A_{2u}+E_u$ peaks have been used to characterize hematite thin films and particles; Chernyshova et al.\textsuperscript{206} have shown the $E_u$ mode at 440 cm$^{-1}$ to be of greater diagnostic value than the combined $A_{2u}+E_u$ mode at 526 cm$^{-1}$, as it arises from only one phonon mode. This interpretation was adopted for this study. When considering IR spectroscopy of iron oxides, which exhibit high oscillator strengths, it is necessary to consider the contribution to the spectra from surface modes.\textsuperscript{206,225} Surface modes in solids arise when the incoming radiation wavelength is longer than the size of the interacting solid, which is the case for all the thin films investigated here. Due to these induced surface modes, the frequency of the phonon modes within the solid can vary between their TO and LO limits. This effect can be observed as a splitting in the phonon mode peak with contributions from both a TO and a LO component. A greater contribution from the LO component in the peak frequency has been attributed to an increase in the crystallinity of the hematite sample.\textsuperscript{206,225,226}

Following this interpretation, the spectra presented in Figure 3.4 show the $E_u$ mode at 440 cm$^{-1}$ fit with two Lorentzian components, one at $\sim$ 437 cm$^{-1}$ and one at $\sim$ 460 cm$^{-1}$. An increase in the high frequency component at 460 cm$^{-1}$, relative to the component at 437 cm$^{-1}$, has been shown to be correlated with an increase in the degree of crystallinity.\textsuperscript{206} The two spectra shown in Figure 3.4 have relative heights of the low frequency component of the $E_u$ mode of 1.60 and 2.13 for A and B, respectively. This indicates that the 50 nm thick hematite film exhibits a higher overall degree of crystallinity than that of the 250 nm thick sample. As the thickness of the hematite film increases from 50 nm to 250 nm the FWHM for the component peaks of the $E_u$ mode also broadens as indicated by the fitting parameters in the Figure 3.4 insets. These two
findings indicate that the 50 nm hematite film possesses a greater degree of overall crystallinity than the 250 nm thick film which was also shown by the Raman spectra of these two films.

It is not immediately clear why the 50 nm thick hematite film would possess larger crystal domains than the 250 nm thick film. Using conventional vibrational spectroscopic techniques such as Raman micro-spectroscopy and FTIR does not allow for an absolute determination of the crystallite size. More traditional methods of size determination such as transmission electron microscopy (TEM) and XRD are also not optimal choices for these samples given that the films are deposited upon a thick, 3 mm, substrate and the films are very thin, respectively. However, by first comparing my results to Chernyshova et al.\textsuperscript{206}, where both vibrational spectroscopy and TEM/XRD was used to analyze hematite powders of different sizes, it is possible to make an approximation of the size of the crystallites within the thin films presented here.

Chernyshova et al.\textsuperscript{206} report a relative height intensity of 2.1 for the two components of the $E_u$ mode centered at $\sim$440 cm$^{-1}$ for 18 nm hematite powder observed in their FTIR spectra. This is very similar to the value of 2.13 for the relative height of the $E_u$ peak components derived for the 250 nm thick hematite film produced in this study. Based upon this a lower bound of approximately 18 nm is proposed for the crystallite domain size within the hematite films produced in this study. The next largest hematite particle size reported by Chernyshova et al.\textsuperscript{206} was 39 nm in diameter and had a relative height of the $E_u$ component peaks in the FTIR spectra of 1.4. The 50 nm hematite film from this study has a relative height of the $E_u$ component peaks of 1.6. This indicates that the crystal domains within the 50 nm film are not 39 nm in diameter, however, as it
is not possible to quantify the exact size of the domains, 39 nm is proposed as an upper bound on the crystal domain size possessed by the hematite films produced in this study.

Phonon confinement has also been used to quantify particle size with frequency shifts and broadening of the phonon peaks within Raman spectra of titanium dioxide powders. At crystallite sizes above ~10 nm the frequency shifts observed become minor, less than 1 cm\(^{-1}\), and phonon confinement becomes a less useful tool for discerning between crystallite size. Here I observe, on average, a frequency shift of approximately 0.5 cm\(^{-1}\) for the hematite phonon modes between the 50 nm and 250 nm thick films, Table 3.3. This is not sufficient to quantify the degree of crystallite size change between the two films, but is still useful as it indicates that the 50 nm film does indeed possess a greater degree of crystallinity.

The homogeneity of the films was assessed by running a spectral mapping experiment, where a Raman spectrum was collected at every 100 µm point across a large section of the film, ~1.5 mm in length, Figures 3.5 and 3.6. There were no significant detectable differences in peak frequency or FWHM for the spectra collected in this way for either film. This indicates that, within the limit of detection, the phase is homogeneous across the film. While there are differences in scattering intensity between different spots for the 250 nm film, Figure 3.6, this is presumed to arise from differing surface roughness of the film in different spots and not from any compositional change in the phase of the oxide.

The Fe films annealed for 4 hours at 575 °C demonstrate Raman and FTIR signatures that are consistent with an assignment of the oxide phase to hematite. The extraneous peak at 660 cm\(^{-1}\) in the Raman spectra is representative of disorder within the
crystal lattice and not residual magnetite contamination. Both Raman microspectroscopy and FTIR were used to address the crystallinity of the hematite films where the 50 nm film exhibits a greater degree of crystallinity than the 250 nm thick film. Using a comparison with Chernyshova et al. results, a range of 18-39 nm is proposed for the size of the crystallites within the hematite films. By lowering the annealing temperature to 350 °C it is possible to produce the iron oxide polymorph maghemite, instead of hematite.

3.3.2. Maghemite

Maghemite films were prepared by heating the Fe films at 350 °C for four hours, which was sufficient to oxidize the initial Fe films fully, but still avoid hematite formation as indicated by the Raman spectra containing peaks associated with those phases. This temperature selection was important, as heating at 325 °C was insufficient to completely oxidize the film to maghemite and an increase to 375 °C resulted in hematite contamination. Hence, deviation from 350 °C annealing temperature resulted in significant magnetite or hematite formation in the films.

If the vacancies in the maghemite structure are randomly distributed then the net structure will exhibit spinel symmetry. The expected vibrational modes of the first Brillouin zone center of a spinel structure are given by Equation 3.3.2:

$$\Gamma_{vib} = A_1g + E_1g + T_1g + 3T_2g + 2A_2u + 4T_1u + 4T_2u$$ (3.3.2)
All modes are observable except the $T_{1g}$, $A_{2u}$, $E_u$, and $T_{2u}$ modes which are optically silent. The remaining symmetrical modes ($A_{1g}$+$E_g$+$3T_{2g}$) are Raman active and the $4T_{1u}$ modes are infra-red active.\textsuperscript{166,205,227}

The Raman spectra of the two maghemite films are presented in Figure 3.7. The frequency of maghemite’s Raman active phonon modes is known to vary with preparation method and the distribution of vacancies within the maghemite crystal unit cell.\textsuperscript{203} However, the spectra presented in Figure 3.7 match Raman spectra for maghemite previously reported in literature.\textsuperscript{203,204,206,210,226} Maghemite has three observed Raman active phonon modes at 365 cm$^{-1}$ ($T_{2g}$), 511 cm$^{-1}$ ($E_g$), and 700 cm$^{-1}$ ($A_{1g}$), Table 3.2, that exhibit a broad scattering response.\textsuperscript{166,203} The weak Raman signal for the maghemite films in Figure 3.7 is due to maghemite’s poor scattering response.\textsuperscript{203}

For the 45 nm film, Figure 3.7, weak phonon modes at 365 cm$^{-1}$ and 511 cm$^{-1}$ give a very slight scattering response. As the thickness of the maghemite film increases from 45 nm to 230 nm, Figure 3.7, the $T_{2g}$ and $E_g$ phonon modes at 365 cm$^{-1}$ and 511 cm$^{-1}$ become much more pronounced. This weak response is likely due to poor scattering properties of maghemite; zooming in on the spectra presented in Figure 3.7 though shows that the relative height ratio between the $A_{1g}$ peak and the $T_{2g}$ peak is roughly the same value, $A_{1g}/T_{2g}$ $\sim$ 2, for both the 230 nm and the 45 nm films. The roughness of the fits for the maghemite films used here should be stressed as the broadness of the maghemite Raman response makes fitting difficult. Attempts to increase signal to noise in the maghemite Raman spectra by increasing the acquisition time resulted in irreversible hematite formation. For the 45 nm thick maghemite film only the $A_{1g}$ peak at 700 cm$^{-1}$ is pronounced. This is sufficient to assign this film to the maghemite phase as this feature
has been shown to only be associated with maghemite formation.\textsuperscript{166,203,210,213} No features associated with laser induced phase changes can be seen for the maghemite films in Figure 3.7. The homogeneity of the films were checked in a similar manner to that of the hematite films and were found to yield spectra indicative of maghemite phase across the films.

Phonon confinement effects can also be observed for the maghemite films. Similarly to hematite the thinner films exhibit both a red shifted peak frequency and a narrower FWHM for the main $A_{1g}$ peak indicating a greater degree of crystallinity. Due to the very broad Raman scattering response for maghemite and the frequency shifts that can occur with different preparation techniques it appears that phonon confinement is a less useful tool for the investigation of maghemite crystallinity than materials with sharp, strong Raman peaks.

Shown in Figure 3.8 are the FTIR spectra for the two maghemite films. If the maghemite samples possess spinel crystal structure then there are four $T_{1u}$ phonon modes expected at 212 cm$^{-1}$, 362 cm$^{-1}$, 440 cm$^{-1}$, and 553 cm$^{-1}$, of which we are able to observe the highest two frequency modes with our existing experimental setup.\textsuperscript{166} The 230 nm thick film exhibits clearly the two $T_{1u}$ modes expected around 440 cm$^{-1}$ and 550 cm$^{-1}$ for maghemite while the thinner, 45 nm, film exhibits a peak at 546 cm$^{-1}$. The lack of the $T_{1u}$ peak at 440 cm$^{-1}$ for the thinner film is attributed to weak absorption due to the very thin nature of the film. The thicker film exhibits roughly 5x the absorbance of the thinner film for the $T_{1u}$ mode at ~550 cm$^{-1}$, as is expected.

The appearance of the peaks attributed to the two $T_{1u}$ modes confirm that the vacancies in the maghemite crystal structure are randomly distributed resulting in a spinel
crystal structure. If this was not the case many more strongly absorbing vibrational phonon modes would be expected.\textsuperscript{164,165} Additionally, the thicker film shows some spectral structure at \( \sim 430 \text{ cm}^{-1} \) and \( \sim 525 \text{ cm}^{-1} \). These features may be indicative of slight hematite contamination; however, there are no hematite features observed in the Raman spectra presented in Figure 3.7 for the maghemite films. These FTIR spectral features may also potentially arise from minor deviation in the ordering of the vacancies which has been shown to produce additional modes.\textsuperscript{164,165} Yet, the assignment of these low intensity peaks remains ambiguous.

The TO/LO phonon splitting has been calculated for the observed phonon modes from the optical constants for maghemite from Glotch et al.\textsuperscript{164}, Table 3.5, and is \( \sim 13 \text{ cm}^{-1} \) for the \( T_{1u} \) mode centered around \( 440 \text{ cm}^{-1} \) and \( \sim 22 \text{ cm}^{-1} \) for the mode centered at \( 550 \text{ cm}^{-1} \). The observed FTIR phonon frequencies for the maghemite films lie slightly below the TO frequency limit, however, frequency of maghemite phonon modes is known to depend heavily upon preparation method and this is attributed as the source of the observed red shift.\textsuperscript{164,165} The low degree of phonon splitting is expected for solids possessing spinel structure and prevents an analysis of the net crystallinity of the films via FTIR as was done for hematite.\textsuperscript{228} However, the broadening and blue shifting of the \( A_{1g} \) mode in Figure 3.7 as the film thickness increases does indicate that the 45 nm thick maghemite film possesses a greater degree of crystallinity than the 230 nm thick film.

Heating the Fe films at 350 °C for 4 hours produced maghemite films which were then characterized by Raman micro-spectroscopy and FTIR. The phase of the oxide films were confirmed by Raman and FTIR spectra which are indicative of maghemite formation. The FTIR spectra contain two main peaks assigned to the \( T_{1u} \) modes of the
spinel structure. This indicates that the vacancies within the crystal structure are randomly distributed. As the films increase in thickness the signature Raman peaks both broaden and blue shift suggesting that the thinner film possesses a greater degree of crystallinity. To produce the least oxidized phase reported here, magnetite, a much lower annealing temperature of 175 °C was chosen.

3.3.3. Magnetite

Magnetite possesses spinel symmetry similar to maghemite. Hence, the normal modes of vibration for the first Brillouin zone center are expected to be given by Equation 3.3.2 as well. The magnetite films are thinner than both the hematite and maghemite films due to magnetite’s inverse spinel crystal structure which possesses a smaller unit cell than hematite and is free of vacancies, unlike maghemite. The Raman spectra of the two magnetite films produced are shown in Figure 3.9. Choice of laser power and acquisition time is vital for collecting magnetite Raman spectra as phase changes are easily induced in the films by the excitation laser via thermal effects. At acquisition times longer than 30 seconds at 6 mW (100%) laser power, hematite features were observed in collected spectra (data not shown).

The spectra in Figure 3.9 agree well with reported spectra in the literature without any features indicating either maghemite or hematite contamination. The pronounced magnetite feature at 670 cm\(^{-1}\), attributed to the \(A_{1g}\) mode, is visible in both spectra of Figure 3.9. The features at 300 cm\(^{-1}\) and 550 cm\(^{-1}\) are weak in both spectra and are assigned to the \(T_{1g}\) vibrational mode. There is no observable peak shifting in the Raman spectra with an increase in the film thickness from 40 nm to 200 nm, however
the $T_{1g}$ mode at 670 cm$^{-1}$ does broaden as the thickness increases. This broadening indicates that the thinner magnetite film possess greater crystallinity than the thicker film, as is also the result for the hematite and maghemite films. A Raman mapping experiment was conducted indicating that the films are homogenous across a large section of the film similar to observations for the hematite and maghemite films.

FTIR spectra were collected for the magnetite films. However, due to the reflective nature of the films, little transmission intensity was recorded, even for the 40 nm film. It is possible to observe a $T_{1u}$ mode at 560 cm$^{-1}$ for the 40 nm film as shown in Figure 3.10, but the absorbance intensity of the mode is not meaningful due to reflection losses from the film. The frequency of this mode agrees well with reported values by literature.$^{166,205,227}$ The other commonly observed $T_{1u}$ magnetite mode at 350 cm$^{-1}$ is cut off due to absorption by the KBr substrate. Magnetite, like maghemite, exhibits a low degree of TO/LO phonon mode splitting. Using the optical constants for magnetite presented by Glotch et al.$^{164}$, the phonon mode splitting for the $T_{1u}$ mode of magnetite at 560 cm$^{-1}$ was calculated in this study to be $\sim$19 cm$^{-1}$, Table 3.6. This is in excellent agreement with the phonon splitting calculated for various other spinel materials.$^{228}$ The low degree of phonon splitting for magnetite as well as the inability to produce a useable spectrum for the 200 nm thick film makes it difficult to use the FTIR spectrum presented in Figure 3.10 to discuss the degree of crystallinity exhibited by the thin magnetite films.

3.4. Conclusions

In this chapter the preparation of thin films (40 nm-250 nm) of three common iron oxide polymorphs: hematite, maghemite, and magnetite, using a conventional electron
beam evaporation technique is presented. The advantage of producing the oxide films using electron beam evaporation is the absence of any unwanted precursor chemicals. These films were then characterized with the vibrational spectroscopic methods of Raman micro-spectroscopy and FTIR, allowing for clear phase assignment of the thin oxide film produced.

As well as phase assignment, crystallinity of the samples was examined using the phonon confinement phenomena from the Raman results and the degree of splitting of the TO/LO components of the phonon modes present in the FTIR spectra. For films of all three iron oxide polymorphs produced, the thinner films exhibit a greater degree of crystallinity than the thicker films. The explanation of this remains ambiguous. However, this chapter presents the advantages of Raman micro-spectroscopy and FTIR used in conjuncture to characterize and investigate the relative degree of crystallinity possessed by synthetic iron oxide thin films.

Developing a chemical-precursor free procedure to synthesize iron oxide films with controllable thickness and phase was a critical step toward studying adsorption behavior near iron oxide minerals at mineral/solution interfaces. This procedure allows for generation of hematite, maghemite, or magnetite thin films with a wide range of thicknesses on the substrate of choice. In this study KBr plates were used due to the excellent optical transmission of KBr which allowed for the FTIR analysis presented in this chapter. In Chapter 4 this approach is utilized to synthesis hematite films on silica hemispheres with great success.
Figure 3.1. Raman spectra of hematite films. The seven peaks characteristic of hematite are present with no magnetite or maghemite contaminant peaks observed. Peak assignments located above peaks. LO $E_u$ peak at 660 cm$^{-1}$ indicated.
Figure 3.2. Fitting comparison between 50 nm and 250 nm thick hematite films. Black and red solid lines correspond to data, green solid lines are Lorentzian fit components for each of the seven diagnostic phonon modes of hematite.
Figure 3.3. Raman spectra of $A_{ig}$ peak at 229 cm$^{-1}$ for both hematite films showing blue shift and broadening of the phonon mode for the 250 nm film relative to the 50 nm film.
Figure 3.4. FTIR spectra of the two hematite samples with the associated fitting of the $E_u$ mode centered at 440 cm$^{-1}$. Black markers are experiment, red lines are the Lorentzian fitted components. A - 50 nm film. B - 250 nm film. Also shown are the results of the Lorentzian fitting procedure. Here $x_c$ is frequency of component peak, $w$ is FWHM of component peak, and $A$ is amplitude of the component peaks.
Figure 3.5. Raman line map for a 50 nm hematite film. Each spot separated by 100 μm. Inset is the $E_g$ peak at $\sim 413 \text{ cm}^{-1}$ showing that frequency, FWHM, and intensity are fairly constant.
Figure 3.6. Raman line map for a 250 nm hematite film. Each spot separated by 100 μm. Inset is the $E_g$ peak at ~413 cm$^{-1}$ showing that frequency and FWHM are fairly constant while intensity varies. Asterisks are signal due to cosmic rays (spectral artifacts that can be ignored).
Figure 3.7. Raman spectra of maghemite films with the phonon peak assignments indicated. No peaks corresponding to hematite contamination are present.
Figure 3.8. FTIR spectra of maghemite films. A - 45 nm film. B - 230 nm film. Prominent $T_{1u}$ mode observable at 550 cm$^{-1}$ for both films.
Figure 3.9. Raman spectra of magnetite films. Only the $A_{1g}$ mode at 670 cm$^{-1}$ is pronounced. Peak assignments indicated above peaks.
Figure 3.10. FTIR spectrum of 40 nm thick magnetite film. Only $T_{lu}$ mode at 560 cm$^{-1}$ is observed. Recorded intensity is not meaningful due to reflection losses from the oxide film.
Table 3.1. Thickness of Iron Oxide Phases Produced

<table>
<thead>
<tr>
<th>Oxide Phase</th>
<th>Fe Deposited (nm)</th>
<th>Estimated Thickness of Oxide (nm)</th>
<th>Ellipsometric Measured Thickness of Oxide (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>20</td>
<td>49</td>
<td>47.2</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>247</td>
<td>240.4</td>
</tr>
<tr>
<td>Maghemite</td>
<td>20</td>
<td>46</td>
<td>48.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>231</td>
<td>228.4</td>
</tr>
<tr>
<td>Magnetite</td>
<td>20</td>
<td>42</td>
<td>41.2</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>209</td>
<td>194.5</td>
</tr>
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</table>
Table 3.2. Observed Raman Active Phonon Modes for Iron Oxide Phases.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Raman Shift (cm\textsuperscript{-1}) and Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>229 ((A_{1g})), 249 ((E_g)), 295 ((E_g)), 302 ((E_g)), 414 ((E_g)), 500 ((A_{1g})), 615 ((E_u)), 660 (LO (E_u))</td>
</tr>
<tr>
<td>Maghemite</td>
<td>365 ((T_{2g})), 511 ((E_g)), 700 ((A_{1g}))</td>
</tr>
<tr>
<td>Magnetite</td>
<td>310 ((T_{2g})), 554 ((T_{2g})), 672 ((A_{1g}))</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Frequency of the Raman shifts are from this study, assignments from literature values.\textsuperscript{166,171,205}
Table 3.3. Lorentzian Fitting Results for Raman Spectra of Hematite Films.

<table>
<thead>
<tr>
<th>Peak</th>
<th>250 nm Film</th>
<th>50 nm Film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>xc</td>
<td>Value ± 1 stdev</td>
</tr>
<tr>
<td>1</td>
<td>229.43</td>
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<td>4.31</td>
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</tr>
<tr>
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<tr>
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<td>0.13</td>
</tr>
<tr>
<td></td>
<td>5.09</td>
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<tr>
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<td>1.46 x 10^4</td>
<td>765</td>
</tr>
<tr>
<td>3</td>
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</tr>
<tr>
<td></td>
<td>6.11</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>11.2 x 10^4</td>
<td>1989</td>
</tr>
<tr>
<td>4</td>
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<td>7.98</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>6.27 x 10^4</td>
<td>2216</td>
</tr>
<tr>
<td>5</td>
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</tr>
<tr>
<td></td>
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<td>9.38 x 10^4</td>
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</tr>
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<td></td>
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</tr>
<tr>
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</tr>
<tr>
<td></td>
<td>15.03</td>
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Table 3.4. Infrared Active TO and LO Phonon Modes for Hematite From Literature and the Observed Frequencies in This Study.

<table>
<thead>
<tr>
<th>Mode Assignment</th>
<th>$\omega_{TO}$ (cm$^{-1}$)</th>
<th>$\omega_{LO}$ (cm$^{-1}$)</th>
<th>This study (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{2u}$</td>
<td>299</td>
<td>414</td>
<td>385</td>
</tr>
<tr>
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<td>526</td>
<td>662</td>
<td>526</td>
</tr>
<tr>
<td>$E_u$</td>
<td>227</td>
<td>230</td>
<td>N/A</td>
</tr>
<tr>
<td>$E_u$</td>
<td>286</td>
<td>368</td>
<td>N/A</td>
</tr>
<tr>
<td>$E_u$</td>
<td>437</td>
<td>494</td>
<td>436-459</td>
</tr>
<tr>
<td>$E_u$</td>
<td>524</td>
<td>662</td>
<td>526</td>
</tr>
</tbody>
</table>
Table 3.5. TO/LO Splitting for Maghemite IR Phonon Modes Calculated from Glotch et al.\textsuperscript{164} Optical Constants and Experimentally Observed Frequencies for These Modes From This Study.

<table>
<thead>
<tr>
<th>Mode Assignment</th>
<th>$\omega_{\text{TO}}$ (cm\textsuperscript{-1})</th>
<th>$\omega_{\text{LO}}$ (cm\textsuperscript{-1})</th>
<th>Observed (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{iu}(1)$</td>
<td>440</td>
<td>453</td>
<td>439 (230 nm film)</td>
</tr>
<tr>
<td>$T_{iu}(2)$</td>
<td>550</td>
<td>572</td>
<td>546 (45 nm film)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>547 (230 nm film)</td>
</tr>
</tbody>
</table>
Table 3.6. Calculated TO/LO Phonon Splitting From Optical Constants From Glotch et al.\(^{164}\) and Experimentally Observed Frequency for the \(T_{1u}\) Mode From This Study.

<table>
<thead>
<tr>
<th>Mode Assignment</th>
<th>(\omega_{(TO)}) (cm(^{-1}))</th>
<th>(\omega_{(LO)}) (cm(^{-1}))</th>
<th>Observed (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_{1u})</td>
<td>558</td>
<td>576</td>
<td>560 (40 nm film)</td>
</tr>
</tbody>
</table>
Chapter 4. Total Internal Reflection Raman Studies of Sulfate Behavior in Mineral/Solution Systems

4.1. Introduction

As discussed previously in Chapter 2 Section 3, ion interactions at buried mineral/solution interfaces are very important to understand in order to predict the mobility and fate of aqueous contaminants within the environment.\textsuperscript{19} Oxide minerals form the major components of Earth’s upper continental crust, with silicon, aluminum, and iron oxides dominating these components.\textsuperscript{18} Due to the high prevalence of oxide minerals, ion interactions with these minerals are the most important to rationalize with perspective toward understanding the spatial and temporal transport of ions through aqueous environmental systems. In this Section, I present work utilizing TIR-Raman spectroscopy to probe sulfate interactions at silica/solution and hematite/solution interfaces. Despite the environmental ubiquity of these materials there are still unanswered questions regarding the structure and energetics for the sulfate anion’s interactions with buried silica and hematite surfaces.

Generally, mineral/solution interfaces feature some surface charge on the mineral, due to the various surface terminations of the mineral at the interface. Mineral surface charge density will grow or decrease with solution pH depending on the point of zero charge (pzc), i.e. the pH at which the surface of the mineral features a net neutral charge.\textsuperscript{22,159} Hence, electrostatic interactions are considered to be one of the major
driving forces behind ion adsorption onto mineral surfaces such that anions will preferentially adsorb onto positively charged mineral surfaces and will generally not adsorb onto negatively charged mineral surfaces.\textsuperscript{134,153,229–232} Taking advantage of the fact that silica surfaces are negatively charged at near neutral pH values, as silica has a pzc of 2-4 (depending on how it is measured),\textsuperscript{147,149} and hematite surfaces are positively charged at near neutral pH values, pzc ~8.5,\textsuperscript{161} it is possible to investigate how sulfate will interact at mineral/solution interfaces as a function of surface charge. The impact that pH, cation identity, and water content have on sulfate interactions at silica and hematite – solution interfaces will be presented and discussed.

The most common \textit{in situ} spectroscopic techniques for probing ion interactions at buried oxide mineral/solution interfaces are ATR-IR and x-ray absorption spectroscopies.\textsuperscript{128,133,134,139,162} These spectroscopic results provide benchmarks for modeling efforts that ultimately lead to the prediction of contaminant transport and so it is vital that the adsorption structures interpreted from spectroscopic results are correct in order to facilitate accurate models.\textsuperscript{232,233} However, as discussed below, in ATR-IR spectroscopic studies of adsorption at mineral/solution interfacial regimes the probe depth is generally on the order of microns. This signifies that the signal in these studies have contributions from adsorbed species, ions residing in the interfacial electric double layer, and bulk solvated ions. Thus, sulfate adsorption structures determined by conventional ATR-IR studies may be misinterpreted due to spectral features associated with sulfate adsorption potentially being obscured by signal arising from bulk solvated sulfate species.
In this chapter the application of TIR-Raman spectroscopy to study sulfate interaction at both silica/solution and hematite/solution interfaces as a function of pH, cation identity, and water content is presented. A TIR-Raman spectroscopic approach for the study of such systems has advantages over other in situ spectroscopic techniques such as ATR-IR and VSFG in several ways. Compared to ATR-IR spectroscopy, TIR-Raman will feature increased interface sensitivity due to its decreased probe depth; TIR-Raman also has the advantage of decreased experimental obstacles over a VSFG approach. There have been limited reports within the literature of studies utilizing TIR-Raman spectroscopy; with few of these reports probing adsorption and none, to the author’s knowledge, investigating simple ion interaction with mineral surfaces.\textsuperscript{124,126,234–244} Beyond probing sulfate interaction at buried mineral/solution interfaces, this chapter serves to demonstrate the suitability of a TIR-Raman approach to study in situ ion interaction at buried mineral/solution interfaces.

For the silica/solution work presented in Section 4.3 little sulfate adsorption characteristics are expected due to the electrostatic repulsion between the negatively charged silica surface and anionic sulfate, however, the possible presence of ternary silica-cation-sulfate complexes is explored. A cartoon representation of a typical ternary complex, in this case the outer-sphere adsorption of a cadmium-sulfate solvent-shared ion pair, at the silica/solution interface is illustrated by Figure 4.1, although there are many more possible adsorption structures for ternary complexes. Here ternary surface complexes are shown to be present at silica/solution interfaces and are observed to drastically change the interfacial refractive index at the silica/solution interface resulting
in much greater probe depths for the TIR-Raman experiment than predicted by theory.\textsuperscript{236,241}

In the hematite/solution work, Section 4.4, the goal is to probe sulfate adsorption at the hematite/solution surface with minimal contributions from bulk solvated sulfate species. Sulfate interaction with buried hematite/solution interfaces is investigated as a function of pH, cation identity, and water content. Results indicate little adsorption characteristics for sulfate at the hematite surface in the presence of the solution; this is attributed to the detection efficiency for the home-built instrumental apparatus and the signal processing necessary to remove the presence of parasitic scattering peaks. However, upon removal of the solution phase clear sulfate bidentate adsorption signatures are detected almost immediately; this is in direct contrast to literature results using an ATR-IR approach which indicate that monodentate inner-sphere adsorption should be the primary inner-sphere adsorption structure for sulfate at hematite surfaces.\textsuperscript{128,129}
Figure 4.1. Cartoon of a representative ternary adsorption complex at a silica/solution interface. This representative complex shows the outer-sphere adsorption of a solvent-shared cadmium-sulfate ion pair to a deprotonated surface silanol group. Many other ternary complex structures are possible. Two other silanol terminations are shown which may exist at silica surfaces to varying degrees with solution pH. Surface silanol effective charges are indicated. Various other surface silica terminations, such as bridging Si-O-Si siloxanes, are not shown. Blue background represents bulk aqueous solution and slab represents silica bulk.
4.2. Total Internal Reflection Raman Theory and Instrumentation

4.2.1. TIR-Raman Theory

TIR-Raman spectroscopy, as the name implies, harnesses phenomena which occur on the total internal reflection of light from an interface between two media with differing refractive indices to selectively probe interfacial regions. The total internal reflection condition refers to the complete reflection of light that occurs when light passing through a medium with a refractive index, $\eta_1$, is incident on the interface between medium one and a second medium which features a lesser refractive index, $\eta_2$, at an angle greater than or equal to the critical angle ($\theta_c$), Equation 4.2.1.\textsuperscript{245} While light meeting the criteria for total internal reflection is completely reflected from the interface, there is some component of the electromagnetic field (E) which penetrates slightly into the second medium. This portion of the incident light is referred to as the evanescent field, due to its quickly fading behavior. The total internal reflection phenomenon and resulting evanescent field is illustrated in Figure 4.2.

$$\theta_c = \arcsin\left(\frac{\eta_2}{\eta_1}\right)$$

(4.2.1)

The depth that the evanescent field penetrates into the second medium in the $z$ direction from the probe spot is defined by Equation 4.2.2 and given by Equation 4.2.3, where $\lambda$ is
the wavelength of the incident beam and $\theta_i$ is the incident angle for the input beam.\textsuperscript{236,238,240}

\[
d_p \equiv E = E_0 e^{-1}
\]  \hspace{1cm} (4.2.2)

\[
d_p = \frac{\lambda}{2\pi} \left( \frac{1}{\sqrt{n_1^2 \sin \theta_i - n_2^2}} \right)
\]  \hspace{1cm} (4.2.3)

TIR-Raman spectroscopy is based on the detection of the Raman scattered light from the input evanescent field, much as conventional ATR-IR spectroscopy is based on detecting absorption losses from this evanescent field. However, due to the much shorter wavelengths of excitation light used in Raman spectroscopy compared to infrared spectroscopy the penetration depth of the evanescent field in a TIR-Raman experiment is much shorter than in an ATR-IR experiment, Equation 4.2.3. This is a large advantage if one would like to study interfacial processes such as ion adsorption, as the greater the penetration depth the greater the contributions from bulk species to the detected signal. In Figure 4.3 a comparison between the penetration depth of the evanescent field in a typical ATR-IR experimental set-up and a TIR-Raman experiment with a fused silica/water system is presented using Equation 4.2.3. From Figure 4.3 it is clear that in a TIR-Raman experiment the evanescent field will generally have a penetration depth approximately an order of magnitude less than in a typical ATR-IR experiment. Adding to the surface
sensitivity of TIR-Raman is the fact that the detected Raman intensity is proportional to the square of the excitation electric field; due to this 98% of the detected TIR-Raman signal originates from a probe depth equal to \( d_p/2 \), from here referred to as the effective penetration depth.\(^{126,236}\)

TIR-Raman also has the added advantage of Fresnel factor enhancements compared to conventional Raman spectroscopy geometries. The magnitude of the electric fields at an interface is directly related to the incident electric field by the Fresnel factors.\(^{245}\) If the Fresnel factors for reflection in the total internal reflection condition are considered for parallel and perpendicular polarized light, Equation 4.2.3 and 4.2.4, respectively, where \( \eta = \eta_2/\eta_1 \), it is possible to calculate the Fresnel enhancement on adoption of the TIR geometry, Figure 4.4.\(^{245}\)

\[ R_{\parallel} = \frac{\eta^2 \cos\theta_i - i\sqrt{\sin^2\theta_i - \eta^2}}{\eta^2 \cos\theta_i + i\sqrt{\sin^2\theta_i - \eta^2}} \]  
\[ (4.2.3) \]

\[ R_{\perp} = \frac{\cos\theta_i - i\sqrt{\sin^2\theta_i - \eta^2}}{\cos\theta_i + i\sqrt{\sin^2\theta_i - \eta^2}} \]  
\[ (4.2.4) \]

When calculating the Fresnel factor enhancements shown in Figure 4.4 it is important to remember that a parallel polarized beam, or p-polarized, will give rise to electric fields in
the $x$ and $z$ directions, Figure 4.5. The electric fields in the $x$-$y$-$z$ directions are geometrically related to the incident electric fields by Equations 4.2.5-4.2.7.26

$$E^I_y = E^I_s$$

(4.2.5)

$$E^I_x = E^I_p \cos \theta_I$$

(4.2.6)

$$E^I_z = E^I_p \sin \theta_I$$

(4.2.7)

4.2.2. TIR-Raman Instrumentation

All TIR-Raman spectra shown in this dissertation were collected with a home built instrument, Figure 4.6. The beam source for the TIR-Raman instrument is a diode-pumped Nd:YVO$_4$ laser (Millennium II, Spectra-Physics) which produces high quality single mode, TEM$_{00}$, 532.1 nm (2$^{nd}$ harmonic) $p$-polarized, with $> 100:1$ polarization ratio, continuous wave light with output energies of 200 mW – 2 W. The beam source is operated at the minimum energy output of 200 mW to reduce heating artifacts, thin film ablation, and to increase laser life. The 532.1 nm excitation beam is first attenuated to 40 mW by a neutral density filter to further reduce thin film ablation by the beam. The beam is directed to the sample flow cell by a series of four mirrors and a focal lens (5 cm focal length). The last mirror and focal lens are mounted on a goniometer arm in order to
achieve control of the input incident beam angle. If desired, a half-wave plate may be installed in the beam path before the sample flow cell to change the beam polarization from p-polarized to s-polarized; all TIR-Raman spectra shown in this dissertation were collected using p-polarized light. The excitation beam is sent through a TIR element to the element/sample-solution interface at or above the TIR critical angle, Equation 4.2.1, where it is completely reflected. A series of irises is installed to block back reflections from returning to the laser cavity. Post-reflection the excitation beam is sent to a beam dump to minimize scatter. The measured input/output energies of the excitation beam immediately before and after the TIR element were 36/32 mW for all experiments. This slight (~10%) energy attenuation is attributed to absorption losses to the silica TIR element lattice and not from refraction losses.

The sample flow cell is custom made from Teflon with aluminum mounts to clamp a hemispherical TIR element onto the sample exposure reservoir. This flow cell was mounted on an x-y-z translational stage where the sample cell exposure reservoir is supplied by a peristaltic pump (MasterFlex L/S, Cole-Parmer) connecting a solution reservoir, the flow exposure cell, and a waste solution reservoir with Tygon tubing. All TIR-Raman experiments were carried out using a fused silica hemisphere (25.4 mm diameter × 12.7 mm height, surface quality 60/40, ISP Optics Inc.) as the TIR element. A 50× objective lens (infinity corrected, super long working distance (13.8 mm), 0.45 numerical aperture, Nikon) mounted normal to the center of the TIR element and centered on the excitation beam spot was used to collect the TIR-Raman scatter. This collection lens is also mounted on an x-y-z translational stage to ease alignment of the objective lens allowing for greater collection efficiency of the generated TIR-Raman
scatter. It is critical that the point of total internal reflection for the excitation beam be in the focal spot of the collection objective lens; deviation from this resulted in negligible signal collection. The collected TIR-Raman scatter is separated from the Rayleigh scatter by the use of a 535 nm long pass filter (Omega Optical, Custom) before being focused (7 cm focal length) into a monochromator (SpectraPro 500i, Princeton Instruments) equipped with a 1200 groove/mm grating and detected on a liquid N\textsubscript{2}-cooled deep-depletion CCD (1340/400-EB, Roper Scientific) calibrated against the 435.833 nm emission line of a fluorescent Hg lamp.

For TIR-Raman experiments investigating ion behavior near silica surfaces, Section 4.3, the fused silica hemispheres were cleaned by first soaking in a mixture of concentrated sulfuric acid (Fisher, Certified ACS Plus) and ammonium peroxydisulfate (Fisher Scientific, crystalline, certified ACS) for at least four hours followed by copious rinsing with nanopure water (18.3 MΩ, NanoPure, Barnstead/Thermolyne). The silica hemispheres were then sonicated in dry methanol (reagent grade, Sigma-Aldrich) for at least one hour followed by further copious rinsing with nanopure water and drying with house N\textsubscript{2}(g). The silica hemisphere was immediately mounted into the Teflon flow cell following cleaning. All silica/solution TIR-Raman spectra were collected with 90 s acquisition times. The TIR-Raman spectrum of silica/water was checked at the beginning and end of each day that experiments were run to ensure system stability and reproducibility. The TIR-Raman spectra in the S-O stretching region have been background-subtracted to remove contributions from parasitic scatter arising from the silica element to the detected spectra. Figure 4.7 shows the parasitic scattering peaks from the silica hemisphere in the S-O region.
For the hematite/solution TIR-Raman experiments, Section 4.4, a silica hemisphere was cleaned in the manner discussed above. A thin film of hematite was then synthesized on the cleaned hemisphere following the procedure described in Chapter 3. Following thin film synthesis the hematite film was characterized with Raman microscopy to ensure film homogeneity. All hematite/solution spectra shown are the average of nine 2 min acquisitions. Longer acquisition times and more spectral averaging are needed in the hematite/solution experiments to achieve reasonable S/N ratios due to lower TIR-Raman signal in this system compared to the silica/solution system. However, during the course of the drying experiments presented in Section 4.4 spectra were collected in consecutive 10 s increments. The TIR-Raman spectra for the hematite/solution spectra shown in Section 4.4 in the S-O stretching region have also been background-subtracted to remove the parasitic scatter from the hematite-coated silica element. Figure 4.8 shows the parasitic scattering peaks from the hematite-coated silica hemisphere in the S-O region. The presence of the hematite overtone peak at ~1320 cm$^{-1}$ in Figure 4.8 confirms the presence of the hematite film at the excitation beam spot.\textsuperscript{206,246} By monitoring this peak intensity during the course of the spectral acquisitions it is possible to ensure that the hematite film is not ablated from the incident beam spot. The TIR-Raman spectrum of hematite/water was checked at the beginning and end of each day that experiments were run to ensure system stability, reproducibility, and reversibility of ion adsorption.
4.2.3. Experimental Materials and Methods

All conventional Raman spectra were collected using 200 mW output from a 785 nm continuous wave diode laser (Process Instruments, ECL-785-300-SH) coupled to a fiber optic probe (InPhotonics, RPS785/12-5) equipped with a 7 mm focal lens. The fiber optic probe was also used to collect the generated Raman Stokes-scatter in the 0° direction before the collected signal was sent to a monochromator (Princeton, Pixis 400) equipped with a thermo-electrically cooled CCD (Princeton, Acton LS785), calibrated versus the output of a Hg lamp and the conventional Raman spectrum of crystalline naphthalene (Sigma Aldrich, > 99% pure), for detection. All conventional Raman spectra are the sum of a 30 s acquisition.

All salt solutions were prepared by mixing the appropriate amount of salt, Na₂SO₄ (99+% pure, Acros Organics, crystalline, anhydrous), MgSO₄ (> 99.5% pure, Fisher, powder, anhydrous), CoCl₂·6H₂O (> 98% pure, ACS reagent grade, MP Biomedicals, crystalline), CdCl₂ (99% pure, Acros Organics, crystalline, anhydrous), NaCl (>99.5% pure, Sigma-Aldrich, crystalline, anhydrous), MgCl₂·6H₂O (99% pure, Fisher, crystalline), CaCl₂·2H₂O (≥ 99% pure, Acros Organics, crystalline), and/or SrCl₂·6H₂O (≥ 99% pure, Acros Organics, crystalline), with nanopure water (18.3 MΩ, NanoPure, Barnstead/Thermolyne) to the desired concentration. For the pH studies sample solutions were prepared and then brought to the appropriate pH using concentrated HCl (37% wt., Fisher, trace metal grade). The pH of solution was monitored with a standard pH meter (Ag/AgCl glass electrode, Accumet AB15, Fisher Scientific) which had been calibrated following the procedure of Wiesner et al. for high ionic strength solutions.³⁹ The presence of Cl⁻ in the solutions is not predicted to substantially affect the results. The sample
solutions were conditioned overnight at 23 °C prior to use. In a typical TIR-Raman experiment the solution was first transferred to a clean solution reservoir where it was then pumped to the exposure cell. After the exposure cell was filled with sample solution the solution was allowed at least 15 min to equilibrate before spectra were acquired.
Figure 4.2. Schematic of the total internal reflection phenomenon and the resulting evanescent field. $d_p$ refers to the penetration depth of the evanescent field.
Figure 4.3. Penetration depth comparison between a typical TIR-Raman (red trace) using a 532.1 nm excitation beam and a typical ATR-IR (black trace) experiment. For the TIR-Raman experiment the critical angle for TIR is indicated with the dashed line.
Figure 4.4. Fresnel factor enhancements along different coordinates with specific input beam polarizations, $K_{p_x}$ (blue trace), $K_{s_y}$ (red trace), and $K_{p_z}$ (black trace), in a typical silica/water TIR-Raman experiment. The critical angle is noted and indicated with a dashed line.
Figure 4.5. Schematic illustrating relationship between input beam polarization (s – top, p – bottom) and the electric field component in the x-y-z coordinate system.
Figure 4.6. Schematic of home-built TIR-Raman spectrometer. Peristaltic pump, solution reservoir, and waste solution reservoir are not shown.
Figure 4.7. Parasitic scatter from silica hemisphere in the S-O stretching region for silica/water TIR-Raman experiments.
Figure 4.8. Parasitic scatter from 100 nm hematite-coated silica hemisphere in the S-O stretching region for hematite/water TIR-Raman experiments. Note the large hematite overtone peak at ~1320 cm$^{-1}$. 

![Raman Spectrum Graph](image_url)
4.3. Sulfate Interaction at Silica/Solution Interfaces

4.3.1. Results and Discussion

Sulfate interaction at silica/solution interfaces is predicted to be non-adsorptive at most environmentally relevant pH values due to silica’s low pzc. However, the adsorption of cations at the silica surface may enable the formation of ternary silica-cation-sulfate complexes; even in the case of negligible surface over-charging from cation adsorption to the interface.\(^{134,153,230,232}\) Shown in Figure 4.9 are TIR-Raman spectra for a range of sodium (left column) and magnesium (right column) sulfate solution concentrations at three distinct pH values in the S-O stretching region with a 1 m NaCl background electrolyte. The single sharp peak in all spectra shown in Figure 4.9 centered at 980 cm\(^{-1}\) corresponds to the symmetric stretching vibration of sulfate with\(^{104}\) \(T_d\) symmetry, \(\nu_{SS} – SO_4^{2-}\). Immediately apparent is that the MgSO\(_4\) results feature greater \(\nu_{SS} – SO_4^{2-}\) intensity than the Na\(_2\)SO\(_4\) spectra. This intensity difference may indicate the presence of ternary complexes, such as illustrated by Figure 4.1, for divalent cation solutions and this hypothesis will be discussed in detail in the following sections. \(\nu_{SS} – SO_4^{2-}\) intensity is also observed to decrease with a drop in pH; this is attributed to the decrease in bulk sulfate concentration due to sulfate protonation to bisulfate in low pH solutions, Equation 2.2.2. Intensities are comparable between spectra sets in Figure 4.9, and in all TIR-Raman spectra shown in this chapter, even though the intensities have arbitrary units due to subtraction of the parasitic scattering peaks.
The intensities for the ν\textsubscript{SS} – SO\textsubscript{4}\textsuperscript{2−} peak from all spectra shown in Figure 4.9 have been plotted in Figure 4.10 versus solution concentration with one standard deviation indicated by error bars. The data in Figure 4.10 have been fit with a standard linear regression with the R\textsuperscript{2} value for the fit indicated in the legend. The solid traces in Figure 4.10 are third-order polynomial fits to the data and are meant as guides for the eye. Interestingly, the R\textsuperscript{2} values for the line of best fits indicated in Figure 4.10 are lower for all MgSO\textsubscript{4} solutions tested compared to the Na\textsubscript{2}SO\textsubscript{4} solutions and decrease with a drop in solution pH. This deviation from linearity is not observed in conventional Raman spectra of bulk MgSO\textsubscript{4} and Na\textsubscript{2}SO\textsubscript{4} solutions at near neutral or acidic pH values, Figure 4.11. If the peak height for the ν\textsubscript{SS} – SO\textsubscript{4}\textsuperscript{2−} mode from Figure 4.11 spectra is plotted versus solution concentration, Figure 4.12, the resulting curves are all very nearly linear. This indicates that the deviation from linearity for the ν\textsubscript{SS} – SO\textsubscript{4}\textsuperscript{2−} peak response with increased solution concentration and decreased pH observed in the Figure 4.9 spectra does not arise from changes to the Raman tensor strength of the ν\textsubscript{SS} – SO\textsubscript{4}\textsuperscript{2−} mode.

An explanation for these observations might include an increase in the bulk solution refractive index with increased solution concentration as this would increase the penetration depth for the evanescent field, Equation 4.2.3. An alternative explanation would be the presence of surface adsorption complexes, which may result in the local interfacial concentration of sulfate being higher than the bulk solution value or the refractive index of the interface being much larger than its bulk value, or both. The remainder of this section will focus on attempting to rationalize each of these possible
sources for the observed enhancement in sulfate signal at silica/solution interfaces observed in Figure 4.9 for MgSO₄ solutions.

The influence of bulk solution refractive index can be shown to be an insufficient source of the signal enhancement observed in Figure 4.9 if the penetration depth differences arising from refractive index differences between Na₂SO₄ and MgSO₄ solutions are considered. The bulk solution refractive index for an ~0.5 m Na₂SO₄ solution at 589 nm is 1.3435 which results in an effective penetration depth, Equation 4.2.3, of 63.6 nm at the silica/solution interface for the experimental geometry used in this study. However, for a ~0.5 m MgSO₄ solution the bulk solution refractive index is only 1.3451, indicating that the effective penetration depth for this solution will not vary significantly from the 0.5 m Na₂SO₄ solution value. In fact the effective penetration depth for a 0.5 m MgSO₄ solution using its bulk refractive index is 64.1 nm in the current experimental set-up used for this study.

This degree of penetration depth change is insignificant to explain the relative intensity enhancement of ~1.40 observed for 0.5 m MgSO₄ solutions compared to 0.5 m Na₂SO₄ in Figure 4.9. In order to explain the relative enhancement observed the refractive index of the bulk MgSO₄ solution would need to be 1.439, which is greater than refractive indices observed for most bulk salt solutions, even for concentrations exceeding ~5 m. Hence, bulk refractive index change is discarded as a plausible explanation for the enhanced \( \nu_{SS} \) – \( \text{SO}_4^{2-} \) mode intensity in MgSO₄ solutions at silica/solution interfaces.

With the influence of bulk solution refractive index discounted as the origin for the sulfate signal enhancement observed in the TIR-Raman spectra of MgSO₄ solutions
versus Na₂SO₄ solutions at silica/solution interfaces the presence of sulfate adsorption structures needs to be considered. It is known that divalent cations such as Mg²⁺ form adsorption complexes with silica surfaces with varying strengths, generally with adsorption free energies on the order of -10 to -30 kJ/mole, whereas the degree of interaction for monovalent cations such as Na⁺ with the charged silica surface is much weaker. Mg²⁺ cations have also been observed to form ion pairs with sulfate anions in bulk solution with a variety of experimental techniques, unlike Na⁺ ions. These factors would indicate that Mg²⁺ would be a more likely candidate for ternary ion complexation with SO₄²⁻ at silica surfaces than Na⁺. However, due to the strong hydration properties of Mg²⁺ the degree of cation adsorption to silica surfaces is predicted to be weak; this would result in little possible ternary ion complexation and indeed the degree of deviation from linearity (R² = 0.906 – 0.935) for MgSO₄ solutions with increased concentration, Figure 4.10, is not very drastic.

If ternary complex formation is responsible for the signal enhancement observed for MgSO₄ solutions in Figure 4.9, manifesting in deviations from linearity for a plot of signal versus solution concentration, then these effects should increase in the presence of strongly interactive cations. Figure 4.13 shows TIR-Raman spectra for three sets of MgSO₄ solutions at pH 8 at the silica/solution interface where 500 mm CdCl₂ and 500 mm CoCl₂ have been added to a solution set, respectively. Cd²⁺ and Co²⁺ are known to interact strongly with silica surfaces due to properties such as valency and overall geometric size which directly influence their respective hydration propensities, and so should promote the formation of ternary ion complexes with sulfate at silica/solution interfaces. Co²⁺ ions interact so strongly with silica and quartz surfaces that
the presence of kerolite surface precipitates have also been detected after sufficient equilibrium times.\textsuperscript{134,231} Cadmium and cobalt are also very relevant to study as they are both very harmful aqueous environmental contaminants to flora and fauna and as such are actively regulated as EPA primary water contaminants amongst others.\textsuperscript{24}

The degree of signal enhancement for the $\nu_{\text{SS} - \text{SO}_4^{2-}}$ peak centered at 980 cm$^{-1}$ shown in Figure 4.13 with additions of 500 mm CdCl$_2$ or CoCl$_2$ is drastically larger than what is observed for MgSO$_4$ solutions alone. If the Figure 4.13 results are plotted with $\nu_{\text{SS} - \text{SO}_4^{2-}}$ peak intensity versus solution concentration, as was done in Figures 4.10 and 4.12, the deviation from linear behavior observed is significant for the solutions containing CdCl$_2$ or CoCl$_2$. These results promote the idea that ternary ion complexation is important for the observed signal enhancement in the TIR-Raman spectra of silica/sulfate-solution systems with the presence of divalent cations. Interestingly, if the data point corresponding to the highest MgSO$_4$ concentration is discarded from the plots shown in Figure 4.14 a return to linearity is observed. This suggests that ternary complex formation is anisotropic with increases to solution concentration and that there is a critical solution concentration where complex formation rapidly occurs. However, this explanation is speculative and as such will not be explored further.

The enhancement for the $\nu_{\text{SS} - \text{SO}_4^{2-}}$ peak with CdCl$_2$ or CoCl$_2$ additions is so great that signal saturation is observed for the 1 mM MgSO$_4$ solutions in the presence of either addition; the spectrum corresponding to 1 mM MgSO$_4$ with a 500 mM CdCl$_2$ addition is shown in Figure 4.15 illustrating this. Even though the saturation observed in Figure 4.15 makes the interpretation of the $\nu_{\text{SS} - \text{SO}_4^{2-}}$ mode at this concentration infeasible, it
offers key insight into the phenomena responsible for the TIR-Raman signal enhancement. The four asterisks shown in Figure 4.15 indicate Raman modes arising from Teflon. The presence of Teflon scattering peaks in Figure 4.15 indicates that the total internal reflection condition is no longer satisfied, and as no aspect of the experiment has changed except the solution concentration this indicates that the refractive index of the solution must have increased dramatically. In order for the total internal reflection condition to be lifted, with an input angle of 70° and with the bulk refractive index of the silica TIR element equal to 1.547, the refractive index of the solution must be greater than 1.454.

This high degree of refractive index change is simply not feasible for the bulk salt solutions; however, at the interface between a charged mineral surface and a bulk salt solution the solution concentration is not homogeneous. This region of the solution immediately adjacent to the mineral surface is commonly referred to the electric double layer and has a thickness corresponding to the length at which the electric field from the mineral surface has decayed exponentially. The electric double layer is commonly modeled with the Gouy-Chapman model which dictates that its thickness will decrease with salt addition as ions attracted to the charged interface will screen the bulk solution from the mineral surface charge. The refractive index of the electric double layer for the silica/solution systems tested will actually determine the penetration depth of the TIR evanescent field and is a complex function of the molecular environment present. Measuring interfacial refractive indices directly is notoriously difficult, indeed this may be one of the strengths of a TIR-Raman approach but will not be addressed here, however it is not unreasonable to assert that the electric double layer could have a refractive index
as high as 1.454 due to the presence of complex adsorption structures. As this is the only reasonable explanation for loss of TIR with an increase in solution concentration for MgSO₄ solutions with additions of CdCl₂ or CoCl₂ where all other experimental variables were kept static this interpretation is adopted.

These results indicate that the enhancement observed for the sulfate solutions with varying divalent cations is a convolved function of increased sulfate residence due to adsorption complexes and the increase in interfacial refractive index as a result of these adsorption structures resulting in a greater probe depth for the TIR-Raman experiment. This interpretation also explains the static line shape that is observed for the ν₃S–SO₄²⁻ mode even in solutions where ternary complexes involving sulfate should perturb the shape of this band. Perturbation of the ν₃S–SO₄²⁻ peak frequency in Raman spectroscopy has long been associated with ion-pair formation in bulk solutions and similar, if not exaggerated, results would be expected for ternary complexes involving sulfate at silica surfaces. However, number density of surface adsorbed species will be much lower compared to that of the bulk solution species probed by TIR-Raman. This signifies that for the systems probed here it would be reasonable to assert that the increased probe depth which accompanies increased surface adsorption complexation results in the ν₃S–SO₄²⁻ mode lineshape being dominated by sulfate molecules residing outside of the electric double layer. An attempt to quantify relative signal enhancement due to sulfate ternary complex formation from increased probe depth was made by investigating the O-H stretching region for various salt solutions with and without sulfate present and is presented in the following discussion.
By probing the water O-H stretching region at silica/solution interfaces for the solutions under study it is possible to distinguish signal enhancement/refractive index changes due to ternary complexes from cation adsorption. First the role that cation plays on TIR-Raman signal at silica/solution interfaces will be investigated. Shown in Figure 4.16 are the TIR-Raman spectra in the water O-H stretching region corresponding to the concentration series for MgCl₂, CaCl₂, and SrCl₂ solutions at a near-neutral pH. The spectra shown in Figure 4.16 resemble conventional Raman spectra on bulk alkaline earth chloride aqueous solutions except for the large shoulder at ~3700 cm⁻¹.²⁴⁸ This shoulder is attributed to the Si-OH parasitic scatter mode from the bulk silica TIR element as it does not decrease significantly in the presence of aqueous solution as is observed for surface Si-OH species, however the presence of this peak does not affect the interpretation of the results.¹⁴⁹,²⁴⁹ The overall spectral intensity and the ratio between the 3200 cm⁻¹ and the 3400 cm⁻¹ components for the collective O-H modes shown in Figure 4.16 are observed to increase with increased cation size and solution concentration.

Interestingly, the CaCl₂ results, Figure 4.16b, feature the most enhanced signal at 3400 cm⁻¹ for the highest solution concentration in the three alkaline earth chloride salts tested. Adsorption of both Ca²⁺ and Sr²⁺ have been investigated at silica surfaces for pH 7 solutions at 298 K and the surface free energy of adsorption for these two cations were found to be very similar, ~ -29 kJ/mole.²²⁹,²³⁰ With this in mind, the peak area of the collective O-H vibrational band between 3000 cm⁻¹ and 3800 cm⁻¹ was plotted versus solution concentration, Figure 4.18, and the degree of enhancement between the CaCl₂ and SrCl₂ solutions are found to agree within their experimental error for all solutions tested. The spectra presented in Figure 4.16 indicate that cation adsorption complexes
lead to increased interfacial refractive index changes resulting in signal enhancement observed for the water O-H vibrational modes. Only cation adsorption complexes are considered for interpreting the results presented in Figure 4.16 as chloride ions are known to be weakly interactive and as such should not form ternary adsorption complexes.

If solutions where ternary complex adsorption at the silica/solution interface is predicted to occur are examined in the O-H vibrational frequency region striking differences are observed compared to the spectra shown in Figure 4.16. Spectra corresponding to MgSO$_4$ solutions with and without additions of CdCl$_2$ or CoCl$_2$ in the O-H vibrational frequency are presented Figure 4.17. For the spectra shown in Figure 4.17a the TIR-Raman response of the MgSO$_4$ solutions without CdCl$_2$ or CoCl$_2$ additions is observed to be very similar to the spectra for MgCl$_2$ solutions, Figure 4.16a. This implies that for Mg$^{2+}$ containing solutions little surface adsorption is present at the silica/solution interface regardless of the valency of the anion. This result is rationalized by again considering the strong hydration properties exhibited by the magnesium cation which effectively inhibits adsorption.$^{83,116}$

With the addition of CdCl$_2$, Figure 4.17b, or CoCl$_2$, Figure 4.17c, however, the O-H stretching intensity is observed to be greatly enhanced. This is clearly apparent from the spectra but also from plots of O-H peak area versus solution concentration which feature large deviations from linearity, Figure 4.18 top panel. As was observed in the S-O stretching region, the TIR-Raman signal intensity for the most concentrated MgSO$_4$ solution in the presence of CdCl$_2$ or CoCl$_2$ saturated the CCD detector. This indicates that the formation of ternary complexes is most likely responsible for the large signal
enhancement observed in both the S-O and O-H stretching regions for MgSO$_4$ solutions with CdCl$_2$ or CoCl$_2$ additions.

While it is not possible to resolve the structure or energetics for these silica-cation-sulfate ternary complexes the results presented in this section clearly demonstrate their existence at buried silica/solution interfaces for a variety of solution conditions. Based on the loss of TIR conditions for the most concentrated MgSO$_4$ solutions tested in the presence of CdCl$_2$ or CoCl$_2$ and the large signal enhancement observed for MgSO$_4$ solutions relative to Na$_2$SO$_4$ solutions, where ternary adsorption complexes are predicted not to form, the local concentration of ternary structures in the electric double layer is postulated to be quite high and structured. This assertion is based on the necessary refractive index changes for the loss of the TIR condition which is much greater than would be observed for bulk solutions. However, in the interfacial electric double layer an ordered network of ternary adsorption structures, analogous to a highly hydrated crystalline salt, could be rationalized to have a refractive index high enough to push the system out of the TIR condition, although this interpretation is speculative.

4.3.2. Conclusions

Sulfate behavior at buried silica/solution interfaces was examined with interface selective TIR-Raman spectroscopy for a range of solution concentrations and pH values and in the presence of various cations (Na$^+$, Mg$^{2+}$, Cd$^{2+}$, Co$^{2+}$). For MgSO$_4$ solutions the observed TIR-Raman response for sulfate’s $\nu_{SS} – SO_4^{2-}$ mode centered at 980 cm$^{-1}$ is greater than that of Na$_2$SO$_4$ solutions at all concentrations and pH values tested. The
MgSO$_4$ TIR-Raman spectra are also observed to deviate from linearity for plots of signal intensity versus solution concentration. These observations are discussed in light of bulk solution refractive index, interfacial refractive index, and adsorption of ions to the silica surface.

It is shown that bulk refractive index is not responsible for the observed differences in the Na$_2$SO$_4$ and MgSO$_4$ solution spectra. The role that adsorption complex formation and interfacial refractive index play for TIR-Raman spectra at silica/solution interfaces is explored. Ternary silica-cation-sulfate adsorption complex formation is shown to be the fundamental reason behind the increased $\nu_{SS} - SO_4^{2-}$ response for MgSO$_4$ solutions relative to Na$_2$SO$_4$ solutions. Cation adsorption alone is insufficient to explain these results, as demonstrated by the O-H stretching response of water for the systems tested. However, the presence of ternary adsorption complexes also drastically increases the interfacial refractive index resulting in a large increase in TIR-Raman probe depth. This results in negligible lineshape changes to the detected $\nu_{SS} - SO_4^{2-}$ mode precluding the assignment of sulfate structure within ternary complexes or a determination of adsorption energetics. These results still have relevance for understanding sulfate behavior at mineral/solution interfaces as they demonstrate that sulfate can interact strongly even with negatively charged minerals such as silica depending on solution conditions. The silica/solution results presented in this section also serve as experimental controls for later studies on sulfate behavior at iron oxide thin films which have been deposited on the planar silica hemisphere TIR element surface.
Figure 4.9. TIR-Raman spectra for Na$_2$SO$_4$ (*left column*) and MgSO$_4$ (*right column*) solutions with a 1 m NaCl background electrolyte at the silica/solution interface. Solution spectra for three pH values are shown, pH 6-8 (*top panel*), pH 3 (*middle panel*), and pH 1 (*bottom panel*). Vertical dashed line represents peak center for ν$_{SS}$ – SO$_4^{2-}$ mode.
Figure 4.10. Peak height versus solution concentration for $v_{SS} - SO_4^{2-}$ mode from TIR-Raman spectra ($Na_2SO_4$ solutions – top panel; $MgSO_4$ solutions – bottom panel) shown in Figure 4.9. Data (markers) and third-order polynomial fit (solid traces) shown as a guide for the eyes. Error bars correspond to one standard deviation. $R^2$ value for linear regression of data noted indicating deviation from linearity for each data set.
Figure 4.11. Conventional Raman spectra of bulk Na$_2$SO$_4$ (left column) and MgSO$_4$ (right column) solutions at near neutral (top panel) and acidic (bottom panel) pH values. Vertical dashed line represents peak center for $\nu_{SS} - SO_4^{2-}$ mode. Note the similar intensities for spectra from solutions with similar pH.
Figure 4.12. $\nu_{SS} - SO_4^{2-}$ peak height versus solution concentration from conventional Raman spectra of Na$_2$SO$_4$ and MgSO$_4$ solutions at two different pH values shown in Figure 4.11. Data (markers) and lines of best fit (solid traces) are shown. $R^2$ values for lines of best fit are also indicated.
Figure 4.13. TIR-Raman spectra at the silica/solution interface for MgSO₄ solutions at pH 8 (solid traces). Solution spectra correspond to MgSO₄ solutions without additions (top panel), 500 mm addition of CdCl₂ (middle panel), 500 mm addition of CoCl₂ (bottom panel). Vertical dashed line represents peak center for νₜₜ - SO₄²⁻ mode as indicated. Highest concentration of MgSO₄ is not shown in panel B or C due to signal saturation at this concentration.
Figure 4.14. $\nu_{SS} - SO_4^{2-}$ peak height versus MgSO$_4$ solution concentration for TIR-Raman spectra of MgSO$_4$ solutions at pH 8 taken from Figure 4.13. Represented are MgSO$_4$ + 500 mm CoCl$_2$ solutions (top panel), MgSO$_4$ + 500 mm CdCl$_2$ solutions (middle panel), and MgSO$_4$ (bottom panel). Data (markers) lines of best fit (solid traces) with all data fit, and lines of best fit (dashed traces) discarding the highest MgSO$_4$ concentration are shown. $R^2$ values for lines of best fit are indicated.
Figure 4.15. TIR-Raman spectrum of 1 m \( \text{MgSO}_4 \) + 500 mm \( \text{CdCl}_2 \) solution at the silica/solution interface. Boxed area shown in inset highlights saturation for \( \nu_{\text{SS}} - \text{SO}_4^{2-} \) peak. Asterisks indicate peaks arising from Teflon scattering.
Figure 4.16. TIR-Raman spectra in the O-H stretching region for A – MgCl$_2$, B – CaCl$_2$, and C – SrCl$_2$ solutions at pH 8 for the silica/solution interface. Data have been fit and background subtracted.
Figure 4.17. TIR-Raman spectra in the O-H stretching region for A – MgSO$_4$, B – MgSO$_4$ + CdCl$_2$, and C – MgSO$_4$ + CoCl$_2$ solutions at pH 8 for the silica/solution interface. Data have been fit and background subtracted. Highest MgSO$_4$ concentration has been excluded for systems featuring CdCl$_2$ or CoCl$_2$ as saturation of the detector resulted for these solutions.
Figure 4.18. O-H total peak area (3000-3800 cm\(^{-1}\)) versus solution concentration from TIR-Raman spectra shown in Figures 4.16 (bottom panel) and 4.17 (top panel). Data (markers) and third-order polynomial fit (solid traces) shown as guides for the eyes. Error bars correspond to one standard deviation. R\(^2\) values for linear regression of data are noted. Note the large deviations for solutions (MgSO\(_4\) + Cd/CoCl\(_2\)) where ternary complexes are predicted to form.
4.4. Sulfate Adsorption Structure at Hematite/Solution Interfaces

4.4.1. Results and Discussion

Sulfate interactions at iron oxide surfaces have been the subject of many prior spectroscopic studies. Currently most spectroscopic experimental studies probing ion, e.g. sulfate etc., behavior at iron oxide surfaces are focused on using ATR-IR and x-ray absorption techniques as these methods can be applied in situ. While x-ray techniques have, and continue to be, used to study anion behavior at mineral/solution interfaces, vibrational techniques such as ATR-IR seem to be generally more suited to study these systems due to the inherent difficulties of x-ray techniques including the necessity of a synchrotron light source and ambiguities in determining signal contributions from various adsorption structures with similar analyte-mineral distances. The ability to probe mineral/solution interfaces in situ with ATR-IR was first demonstrated by Hug in 1997 and was a critical instrumental advancement as sulfate adsorption structure is very sensitive to molecular environment and has been observed to undergo significant changes on drying. However, as discussed throughout this dissertation, the probe depth of a typical ATR-IR experiment is generally several microns from the ATR element resulting in bulk aqueous species being detected alongside the adsorbed species of interest. This may result in the weaker sulfate adsorption structure signatures being obscured by the broad bulk sulfate infrared response and hence an incorrect assignment of sulfate adsorption structure being adopted.

As TIR-Raman probe depths are much shallower than those in a typical ATR-IR experiment this theoretically allows for a lesser degree of bulk solution contributions to
the detected signal. With this in mind results presented in this section hope to either confirm primarily monodentate inner-sphere adsorption structures for sulfate at the hematite/solution interface as proposed by Hug \cite{128} or demonstrate the existence of other adsorption structures such as a bidentate inner-sphere complexes which may have been obscured in the ATR-IR results of Hug and others.\cite{129,137} Shown in Figure 4.19 are the TIR-Raman results for a series of MgSO$_4$ solutions at a variety of pH values at the hematite/solution interface. In these experiments the hematite film is approximately 100 nm thick and has been deposited on a cleaned silica TIR element as detailed in Chapter 3 and Chapter 4 Section 2. The intense peak centered at ~980 cm$^{-1}$ observed in all spectra in Figure 4.19 is attributed to the $\nu_{SS} - SO_4^{2-}$ response of sulfate. Here the TIR-Raman results shown in Figure 4.19 exhibit primarily bulk solvated sulfate character, that is, a single, strong peak centered at 980 cm$^{-1}$, for all pH values (8, 5, and 3) tested and at all solution concentrations.

If only the effective penetration depth, ~64 nm, for experimental configuration adopted in the TIR-Raman experiments, detailed in Chapter 4 Section 2, is considered the spectra presented in Figure 4.19 are slightly confusing. That is, the film thickness is approximately 0.5 × greater than the effective penetration depth which should result in little bulk solvated sulfate molecules being probed. However, these results can be rationalized by considering that the hematite thin films in question are polycrystalline and quite porous allowing the sulfate solution to fill the interstitial spaces such that bulk solution will be in the effective penetration depth of the TIR-Raman experiment. Also, as demonstrated in the TIR-Raman experiments on silica/solution systems, adsorption complexes will effectively change the refractive index of the interface affecting the
penetration depth of the experiment. This latter situation is exaggerated here as well due to the presence of the hematite thin film which has an unknown effect on the interfacial refractive index. It is not possible to resolve the relative contributions to the detected signal arising from these two issues and taken together they form major weakness in adopting a TIR-Raman approach to study \textit{in situ} sulfate adsorption to hematite surfaces.

If the three lowest MgSO$_4$ solution concentrations spectra from Figure 4.19 for the three different pH values are plotted in the same panel, however, there are several slight spectroscopic signatures which may correspond to adsorption structures, Figure 4.20. In Figure 4.20 the dashed vertical lines indicate respective peak centers with the peak at 975 cm$^{-1}$ assigned to the $\nu_{SS} - SO_4^{2-}$ mode of bulk sulfate. Here two potential adsorption peaks are also indicated by $\nu_{SS} - SO_4^{2-}$ and $\nu_{SS} - SO_4^{2-}$ at 993 cm$^{-1}$ and 1005 cm$^{-1}$, respectively, where $\nu_{SS} - SO_4^{2-}$ can been seen in the 50 mm pH 5 spectra, Figure 4.20a, and the $\nu_{SS} - SO_4^{2-}$ peak is observed for all pH 3 spectra shown in Figure 4.20. Great care must be taken in interpreting such weak spectral features in the TIR-Raman spectra shown in Figure 4.20 due to the background subtraction procedure which can introduce artifacts into the spectra. However, the peaks indicated by $\nu_{SS} - SO_4^{2-}$ and $\nu_{SS} - SO_4^{2-}$ correspond to frequencies that would be expected for monodentate inner-sphere and bidentate adsorption complexes, respectively.$^{104, 250}$ Supporting this interpretation is the observed disappearance of the $\nu_{SS} - SO_4^{2-}$ peak and appearance of the $\nu_{SS} - SO_4^{2-}$ mode for pH 3 solutions which may indicate sulfate’s preference for bidentate adsorption at hematite surfaces with a higher mineral surface charge density, and this is quite intuitive. To reiterate, while the $\nu_{SS} - SO_4^{2-}$ and $\nu_{SS} - SO_4^{2-}$ peaks
indicated in Figure 4.20 are suggestive of sulfate adsorption structure peaks, this result should be treated with heavy skepticism based on the possibility of spectral artifact contamination until clearer indications of sulfate adsorption is demonstrated.

To investigate the possible synergistic role that cation identity may play for sulfate adsorption at hematite/solution interfaces MgSO$_4$ solutions were tested in the presence of either CdCl$_2$ or CoCl$_2$ at pH 8. These spectra are presented in Figure 4.21 where, again, the spectra are dominated by the $\nu_{SS} - SO_4^{2-}$ response of bulk sulfate species. Similar to the TIR-Raman results for silica/MgSO$_4$ solutions in the presence of CdCl$_2$ or CoCl$_2$, a large enhancement is observed for the $\nu_{SS} - SO_4^{2-}$ peak intensity for these solutions. Interestingly, unlike the silica/solution results, signal saturation is not observed for the most concentrated MgSO$_4$ solution (1 m) tested. The reasons behind this discrepancy are opaque but attributing them to the complexities of the interfacial refractive index for adsorption structures on the thin film of hematite seems to be a logical, if speculative, explanation.

A careful examination of the spectra presented in Figure 4.21 reveal that there are slight spectral features which differ in the presence of CdCl$_2$ or CoCl$_2$ from the binary MgSO$_4$ solutions. Figure 4.22 presents the spectra corresponding to solutions of 300 mm MgSO$_4$ without (black trace) and with CdCl$_2$ (red trace) or CoCl$_2$ (pink trace) additions at the hematite/solution interface. Here the $\nu_{SS} - SO_4^{2-}$ peak from bulk aqueous sulfate is centered at 975 cm$^{-1}$ and indicated with a vertical dashed line. However, there are two possible peaks in the CdCl$_2$ (red trace) or CoCl$_2$ (pink trace) solution spectra not observed in the MgSO$_4$ solution spectrum, each centered at 942 cm$^{-1}$ and 1010 cm$^{-1}$, respectively. These peaks are also indicated by vertical dashed lines. These peaks are possibly
indicative of some adsorbed or solution phase metal-sulfate ion pair (as noted for Co\(^{2+}\)) for the peak at 942 cm\(^{-1}\) and/or some unknown adsorption phase for the peak at 1010 cm\(^{-1}\). However, as these peaks fall far outside the range of Raman frequencies observed for sulfate salts and sulfate adsorption complexes they are most likely artifacts from the spectral processing of the raw TIR-Raman data.\(^{114,128,250,251}\)

As little adsorption signatures were observed for hematite/solution interfaces probed with TIR-Raman a drying experiment was conducted to investigate if it was possible to resolve any adsorption features for sulfate at hematite surfaces with the TIR-Raman method. In these experiments the solution exposure reservoir was filled with 0.5 m Na\(_2\)SO\(_4\) solution at pH 6 (Na\(_2\)SO\(_4\) was used to eliminate contributions from ternary complex adsorption) and then the solution was removed from the sample cell. With solution removal TIR-Raman spectra were immediately collected in 10 s acquisitions. It is important to state that in this way the sulfate concentration on the hematite film was not concentrated, only sulfate which was in contact with the film will remain after the bulk solution is removed. Figures 4.23 and 4.24 detail the results for the drying experiments where Figure 4.23 shows the \(\nu_{SS} – SO_4^{2-}\) peak region spectra while Figure 4.24 presents spectra in the \(\nu_{AS} – SO_4^{2-}\) region.

From Figure 4.23 almost immediate changes are observed for the \(\nu_{SS} – SO_4^{2-}\) peak with drying. At 10 s after removal of the Na\(_2\)SO\(_4\) solution the spectrum resembles the solution spectra detailed in Figure 4.19a; however, within another 20 s the \(\nu_{SS} – SO_4^{2-}\) peak becomes bimodal with a shoulder at 975 cm\(^{-1}\) and the main peak drastically blue shifted to 995 cm\(^{-1}\), indicated by \(\omega_2\). The main peak at 995 cm\(^{-1}\) observed with 30 s
drying in Figure 4.23 resembles the peak frequency observed in solid sulfate salts where the sulfate anion resides in a $C_{2v}$ symmetry site for the $\nu_{SS} - SO_4^{2-}$ mode. This is indicative of bidentate inner-sphere adsorption structures for sulfate at the hematite surface. With further drying another peak becomes apparent at 991 cm$^{-1}$, $\omega_3$, before $\omega_2$ and $\omega_3$ converge to a single peak centered at 988 cm$^{-1}$, $\omega_4$. This complicated behavior observed for the $\nu_{SS} - SO_4^{2-}$ peak of adsorbed sulfate complexes with drying time illustrates the sensitivity of sulfate’s vibrational modes to local molecular environment. This ensemble of peaks indicates that several molecular environments are experienced by sulfate molecules within the probe spot at the same time; indeed it is not until greater than two minutes have passed that the shoulder at 975 cm$^{-1}$ originating with solvated sulfate disappears. However, the spectra presented in Figure 4.23 do not unambiguously point to a specific adsorption structure symmetry as several peaks are observed in the $\nu_{SS} - SO_4^{2-}$ frequency region, even for long, $\geq 2$ mins, drying times. It is worth noting that no $\nu_{SS} - SO_4^{2-}$ peak frequencies are observed in Figure 4.23 to exceed 995 cm$^{-1}$ indicating that the higher frequency peaks observed in Figures 4.20 and 4.22 are most likely spectral artifacts.

If the drying spectra are examined for the $\nu_{AS} - SO_4^{2-}$ frequency region, Figure 4.24, a much clearer interpretation of sulfate adsorption structure before, during, and after drying is possible. For the first two time points of the drying experiment, 10 s and 20 s, no peaks are observed in the $\nu_{AS} - SO_4^{2-}$ frequency region. The reasons behind this are unclear, but most likely arise due to insufficient detection sensitivity of the current TIR-Raman spectrometer. However, at 30 s drying time clear peaks are observed at 1075 cm$^{-1}$,
1130 cm\(^{-1}\), and 1198 cm\(^{-1}\) indicated in Figure 4.24 by \(\omega_1\), \(\omega_2\), and \(\omega_3\), respectively. The clear presence of three \(\nu_{AS} - SO_4^{2-}\) peaks indicates that the adsorbed sulfate possesses \(C_{2v}\) symmetry and as such is adsorbed in a bidentate inner-sphere complex following the discussion in Chapter 2 Section 3.

As the drying time continues the \(\omega_1\) and \(\omega_3\) peaks converge to 1100 cm\(^{-1}\) and 1150 cm\(^{-1}\), respectively, while the \(\omega_2\) peak frequency remains essentially constant. The final \(\nu_{AS} - SO_4^{2-}\) peak frequencies indicated by \(\omega_1\), \(\omega_2\), and \(\omega_3\) agree very well with the Raman frequencies of solid Na\(_2\)SO\(_4\) crystalline powder, Figure 2.13b, indicating that sulfate has completely dried on the hematite surface. It is important to note that the spectra shown in Figures 4.23 and 4.24 are not entirely reproducible at each time point tested, this is due to the inherent anisotropy of the drying process. That is, on repetition of the drying experiments different time points showed different lineshapes; however, the general trends observed in Figures 4.23 and 4.24 are reproduced in each drying experiment indicating that the discussions on sulfate adsorption behavior in this section are reasonable.

The results shown in Figure 4.24 clearly indicate only bidentate adsorption for sulfate at the hematite surface. While these results do not correspond to \textit{in situ} measurements in the strictest sense it is reasonable to assume that if monodentate inner-sphere adsorption complexes were the predominant adsorption structure for sulfate at hematite surfaces there would be some spectral signatures suggesting this at early drying times. That only bidentate inner-sphere adsorption signatures are observed in these experiments is in direct contrast with the ATR-IR results for sulfate adsorption at hematite/solution interfaces demonstrated by Hug.\(^{128}\) The existence of other inner-sphere
adsorption complexes for sulfate at hematite surfaces is a vital consideration for theoreticians seeking to model adsorption processes as these models rely on reproducing experimental benchmarks.\textsuperscript{233} However, the current lack of \textit{in situ} sensitivity for sulfate adsorption structures at iron oxide/solution interfaces in the TIR-Raman experiments is a large source of uncertainty and makes clear interpretation of sulfate behavior at iron oxide/solution interfaces difficult. Addressing this issue is of prime importance to future studies using TIR-Raman spectroscopy to investigate anion adsorption at iron oxide/solution interfaces and is the focus of ongoing efforts.

\textbf{4.4.2. Conclusions}

The interaction and subsequent adsorption of sulfate at hematite/solution interfaces for a variety of solution conditions (pH, cation identity, and water content) were investigated with TIR-Raman spectroscopy. Little unambiguous adsorption signatures were observed in the TIR-Raman spectra of the hematite/solution interfaces tested. This is attributed to bulk solution dominating the detected signal arising from complex interfacial refractive index effects that are non-trivial to interpret or remove. However, on removal of the solution almost immediately large spectral changes associated with adsorption are observed. These spectral signatures only indicate bidentate inner-sphere adsorption complexation for sulfate at the hematite surface although the presence of several distinct molecular environments are suggested to coexist by the wide range of frequencies observed for both the $\nu_{SS} - SO_4^{2-}$ and $\nu_{AS} - SO_4^{2-}$ peaks. While these results do not correspond exactly to an \textit{in situ} situation they are significant in that they
suggest that bidentate inner-sphere adsorption complexation may actually be the preferred adsorption structure for sulfate at hematite surfaces. This is in direct contrast to the currently accepted interpretation of sulfate behavior at hematite/solution interfaces which indicate a monodentate inner-sphere adsorption structure to be preferred by sulfate. If sulfate does indeed prefer bidentate inner-sphere adsorption at hematite surfaces this would necessitate a rethinking of current models rationalizing sulfate behavior in mineral/solution systems. Improving the current TIR-Raman spectrometer detection efficiency is a prime focus of on-going work in order to adequately investigate true in situ sulfate behavior at iron oxide/solution interface.
Figure 4.19. TIR-Raman spectra for a range of MgSO₄ solution concentrations at different pH values, A – pH 8, B – pH 5, C – pH 3, at the hematite/solution interface. Vertical dashed line represents peak center for the v₃S₅ – SO₄²⁻ mode.
Figure 4.20. TIR-Raman spectra for MgSO$_4$ solution concentrations for the three pH values tested (pH 5 – red trace, pH 3 – green trace, pH 8 – black trace) at the hematite/solution interface. A – 50 mm, B – 100 mm, C – 300 mm. $\nu_{SS-SO_4^{2-}}$ mode centered at ~975 cm$^{-1}$ assigned to “free” $Td$ sulfate, * $\nu_{SS-SO_4^{2-}}$ and **$\nu_{SS-SO_4^{2-}}$ correspond to possible sulfate adsorption complexes. Respective peak centers are indicated by vertical dashed lines.
Figure 4.21. TIR-Raman spectra for a range of MgSO$_4$ solution concentrations with and without 500 mm CdCl$_2$ or CoCl$_2$ additions at pH 8 at the hematite/solution interface. A – MgSO$_4$, B – MgSO$_4$ + CdCl$_2$, C – MgSO$_4$ + CoCl$_2$. $\nu_{SS}$ – SO$_4^{2-}$ mode centered at $\sim$975 cm$^{-1}$ is assigned to “free” $Td$ sulfate with peak center indicated by the vertical dashed line.
Figure 4.22. TIR-Raman spectra for 300 mm MgSO₄ solutions without (black trace) and with either 500 mm CdCl₂ (red trace) or CoCl₂ (pink trace) additions at pH 8 at the hematite/solution interface. νₜₐₜ – SO₄²⁻ mode centered at ~975 cm⁻¹ is assigned to “free” T₄ sulfate, νₜₐₜ – [Co²⁺-OSO₃²⁻] tentatively assigned to either adsorbed or solvated cobalt-sulfate ion pair, and νₜₐₜ – ? indicates a possible sulfate adsorption peak of unknown origin. Respective peak centers are indicated by vertical dashed lines.
Figure 4.23. TIR-Raman drying spectra of adsorbed $\nu_{SS} - SO_4^{2-}$ mode as a function of drying time (noted) at hematite/air interface. $\omega_1$- $\omega_4$ refer to the respective peak centers of the peak components (indicated by vertical dashed lines). Note the $\nu_{SS} - SO_4^{2-}$ peak centers do not appear at frequencies greater than ~995 cm$^{-1}$ indicating that peaks observed at greater frequencies in Figures 4.20 and 4.22 are likely due to subtraction artifacts.
Figure 4.24. TIR-Raman drying spectra of adsorbed sulfate $v_{AS} - SO_4^{2-}$ modes as a function of drying time (noted) at the hematite/air interface. $\omega_1$, $\omega_2$, and $\omega_3$ indicate the respective peak centers of first observed adsorption $v_{AS} - SO_4^{2-}$ modes. $\omega_1'$ and $\omega_3'$ indicate new $v_{AS} - SO_4^{2-}$ peaks observed with drying whereas $\omega_2$ frequency is static. Peak centers are indicated by vertical dashed lines. Note only bidentate adsorption structure signatures are observed (at least three $v_{AS} - SO_4^{2-}$ peaks).
Chapter 5: Summary and Future Outlook

5.1. Summary

Work presented in this dissertation has focused on investigating behavior for the simple inorganic anion sulfate at a variety of environmentally relevant interfaces. Two different vibrational spectroscopic techniques, VSFG and TIR-Raman, were the primary tools used for these investigations due to the interface sensitivity exhibited by both methods; this instrumental criterion was shown to be critical for the unambiguous study of inherently interfacial processes such as dehydration and adsorption. VSFG was first used to study bisulfate dehydration at vapor/solution interfaces as a function of cation identity and then to investigate sulfate adsorption to a model mineral, fluorite, at the buried mineral/solution interface. Following this the ability to generate thin films of various iron oxide polymorphs free of chemical precursors was demonstrated. Finally TIR-Raman was used to study sulfate interaction at the silica/solution and hematite/solution interfaces. TIR-Raman was chosen as the primary method to investigate buried oxide mineral/solution interfaces, in place of VSFG, due to the difficulty in accessing these interfaces with infrared light.

In Chapter 2 Section 2 HSO₄⁻ behavior was observed at vapor/solution interfaces via the νₜₜ-SO₃ response of interfacial HSO₄⁻ molecules. VSFG results for 0.4 x H₂SO₄ solutions agree well with literature results from Morita and co-workers⁶²,⁸⁰,⁸¹ which indicate the νₜₜ-SO₃ peak frequency occurs at 1050 cm⁻¹ which is ~15 cm⁻¹ blue shifted
from the bulk solution frequency. This blue shift is attributed to the perturbation of \( \text{HSO}_4^- \) hydration as a consequence of residing within the interfacial region where water’s hydrogen bond network is asymmetric. With the addition of \( \text{Na}^+ \) or \( \text{Mg}^{2+} \) the \( \nu_{\text{SS}}\text{-SO}_3^- \) peak blue shifts to an even greater degree than observed for \( \text{H}_2\text{SO}_4 \) solutions. This is attributed to increased dehydration of \( \text{HSO}_4^- \) molecules by the cations with \( \text{Mg}^{2+} \) cations being more disruptive than \( \text{Na}^+ \), in accordance with the strong hydration properties of \( \text{Mg}^{2+} \). These results have implications for atmospheric acidic aerosols, which have been shown to play important roles in catalyzing the production of secondary organic aerosols and chloride radicals, etc. \(^{11,14}\) That is, if \( \text{HSO}_4^- \) molecules residing in the surface of an acidic aerosol have their hydration perturbed by nearby cations the acid dissociation of bisulfate (Eq. 2.2.2) may be retarded effectively inhibiting the important chemical reactions which are acid catalyzed at the aerosol surface.

The last section of Chapter 2 is devoted to the study of \( \text{SO}_4^{2-} \) behavior at a model buried mineral/solution interface using VSFG. Fluorite was chosen as the model mineral of choice due to its high industrial relevance as well as its large transmission for both visible and infrared light, a necessary condition for VSFG studies of buried mineral/solution systems. Here sulfate is found to adsorb preferentially with a bidentate inner-sphere structure. The net adsorption strength of these adsorption complexes was determined to be \( \Delta G_{\text{ads}}^\circ = -31 \pm 3 \text{ kJ/mole} \), in good agreement with literature values for reversible adsorption of simple ions at mineral/solution interfaces, from a simple Langmuir analysis. \(^{22,154,229}\) In this study two different polarization combinations, ssp and ppp, was used for the VSFG experiments. Different polarization combinations revealed that there is a distribution of adsorption geometries for sulfate adsorption complexes at
the fluorite surface which all still possess net $C_{2v}$ symmetry. This resulted in frequency discrepancies in the VSFG spectra corresponding to the adsorption structures detected by ssp light versus ppp light. The results on sulfate adsorption to fluorite presented here are significant in that they help elucidate why sulfate is more perturbative to water ordering at mineral/solution interfaces than halide salts. In forming adsorption complexes at the mineral surface sulfate effectively removes the mineral surface charge responsible for water ordering within the interface; this may help explain why sulfate coatings reduce the ice nucleating properties for some mineral dusts as water ordering has been suggested to be a key step in mineral dust ice nucleation.

Chapter 3 demonstrates the ability the produce thin films of three different iron oxide polymorphs, hematite, maghemite, and magnetite, with controllable thickness free of chemical precursors. These films were characterized using the widely available conventional vibrational spectroscopic methods FTIR and Raman microscopy. Results indicated that thinner films generally possessed a higher degree of crystallinity than the thicker films produced. This procedure was necessary to develop in order to study sulfate behavior at iron oxide/solution interfaces as absorption losses to the excitation beams when using both VSFG and TIR-Raman spectroscopies render the use of a bulk iron oxide sample infeasible. By using a thin film of the iron oxide polymorph of choice, however, absorption losses from the excitation beams can be minimized.

The use of TIR-Raman to investigate sulfate behavior at silica/solution and hematite/solution interfaces is presented in Chapter 4. TIR-Raman is used for these studies instead of VSFG due to the added experimental difficulties with accessing buried oxide mineral/solution interfaces with infrared light; a required condition for VSFG
spectroscopy. Results for the silica/solution interfaces studied indicate that sulfate forms ternary adsorption structures as a function of cation identity with ternary ion complexation increasing in the presence of Co$^{2+}$ > Cd$^{2+}$ > Mg$^{2+}$ > Na$^+$. Little adsorption character is observed with TIR-Raman for sulfate within hematite/solution interfaces as a function of both pH and cation identity. This troubling result is attributed to the low detection efficiency of the home-built TIR-Raman spectrometer. However, almost immediately upon removal of the solution, sulfate bidentate inner-sphere adsorption signatures are observed at the hematite surface. This is significant as sulfate is generally accepted to form monodentate inner-sphere complexes with hematite from ATR-IR results;\textsuperscript{128,129} however no evidence supporting this interpretation is found here. If sulfate does indeed prefer bidentate inner-sphere adsorption at hematite surfaces this would necessitate a rethinking of current models rationalizing sulfate behavior in mineral/solution systems.\textsuperscript{233}

To recap the themes explored in this dissertation, behavior exhibited by the simple inorganic anion sulfate at interfacial regimes is actually quite complex. The development and implementation of interface sensitive spectroscopic techniques allows for the investigation of such behavior often revealing non-intuitive results. Interfacial behavior for sulfate is vital to understand in order to rationalize the wide range of environmental phenomena which sulfate takes part in. These phenomena have consequences for local, regional, and global issues such as water and air quality and climate change.
5.2. Future Outlook

All areas of work presented in this dissertation represent first attempts to study sulfate behavior at a wide variety of interfacial systems. As such, each section of this dissertation has a wide variety of future directions that are possible where the scientific outlook is bright. In this section I will briefly detail what I believe the best next steps for each area under study would be and the challenges in adopting these steps. The areas will be listed in order of appearance in the dissertation body, however, no future outlook is given for the work presented in Chapter 3 as this work was conducted as a means to an end and is not the focus of the current area under study.

5.2.1. VSFG of Ion Modes at Vapor/Solution Interfaces

Presented in Chapter 2 Section 2 is work presenting VSFG on bisulfate behavior at vapor solution interfaces revealed by bisulfate ion vibrational modes. The direct interrogation of ion modes by VSFG is under-reported within the literature, most likely due to the experimental difficulties with producing an infrared beam at low enough frequencies to access ion vibrational modes. However, current advancement in VSFG instrumentation has made this limitation a much easier obstacle to overcome and so the wealth of information available from directly probing interfacial ions with VSFG techniques should be readily accessible to future researchers. In general, improvements in VSFG instrumentation have focused on broad band VSFG instruments; these differ primarily from scanning VSFG spectrometers, used for all VSFG work in this dissertation, in that the infrared beam used to elicit a sum frequency response has a broad bandwidth, typically 100-700 cm$^{-1}$ FWHM. This allows for the excitation of all VSFG
active oscillators within this bandwidth using one laser shot enabling much faster spectral acquisition times compared to a scanning VSFG instrument, which must scan over the infrared frequency range of interest.

Broad band VSFG instruments typically utilize a femtosecond infrared pulse and a ~2 ps visible pulse, both with a kHz repetition rate.\textsuperscript{35,72,74,77} The shorter visible pulse length and higher repetition rates compared to those used in a typical scanning VSFG experiment can have consequences for the study of ion modes within vapor/solution interfaces. Shown in Figure 5.1 are the broad band VSFG spectra for solutions of SDS, methanesulfonic acid (MSA), and H\textsubscript{2}SO\textsubscript{4}. In panels A-C of Figure 5.1 the raw collected broad band VSFG spectra and their accompanying background spectra for these solutions are shown while panel D presents the normalized (background subtracted and divided by GaAs profile) spectra. SDS, MSA and H\textsubscript{2}SO\textsubscript{4} are an interesting comparison as they primarily differ in number of attached hydrocarbons with SDS having a CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{11}-chain, MSA having one CH\textsubscript{3}- moiety, and H\textsubscript{2}SO\textsubscript{4} having zero hydrocarbons attached, however, they should all feature a v\textsubscript{SS}-SO\textsubscript{3} VSFG response at ~1050 cm\textsuperscript{-1}. The hydrocarbon component differences of these compounds results in differing surface propensities where SDS is well known to form monolayers at vapor/waters interfaces,\textsuperscript{38} MSA is strongly surface enriched,\textsuperscript{56} and HSO\textsubscript{4}\textsuperscript{-} concentration (the prevalent chemical species in 0.4 x H\textsubscript{2}SO\textsubscript{4} solutions) is weakly enhanced at vapor/solution interfaces.\textsuperscript{81}

Varying surface residence between these compounds manifests in differences for the background spectra collected for each solution, Figure 5.1 black traces. This background signal (collected with temporal mismatch between input visible and infrared beams) has contributions from all non VSFG light making it to the detector. What is
interesting is that for the MSA and \( \text{H}_2\text{SO}_4 \) solutions the background spectra are clearly structured; this structure is attributed to the \( f \) the anti-Stokes Raman scatter generated by the input visible beam. For the \( \text{H}_2\text{SO}_4 \) solution spectra the anti-Stokes signal is strong enough to completely obscure the VSFG signal from this sample resulting in negligible signal observed in the normalized spectrum, Figure 5.1d.

Anti-Stokes scatter is not an issue when using a scanning VSFG spectrometer to investigate ion modes at vapor/solution interfaces, as presented in Figure 5.2 and Chapter 2 Section 2. The ability of scanning VSFG to probe ion modes is most likely due to either a combination of lower peak power and repetition rate for the input visible pulses or the increased collection distance used as anti-Stokes Raman scatter will occur in a diffuse cone from the input visible beam spot. Addressing these issues is a subject of on-going work within our laboratory and is non-trivial. This must be overcome if recent advances in broad band VSFG instrumentation are to be used to investigate ion modes at vapor/solution interfaces. Until these issues have been addressed, only scanning VSFG spectrometers, where producing low frequency infrared light is experimentally challenging, will be able to access ion modes at vapor/solution interfaces.

### 5.2.2. VSFG of Ion Modes at Mineral/Solution Interfaces

Like vapor/solution interfaces, the application of VSFG techniques to directly probe ion vibrational modes at buried mineral/solution interfaces is sorely under-represented in the literature. The reasons for this stem primarily from difficulties in accessing buried interfaces with an infrared beam at the frequencies necessary to probe ion modes, generally below 1500 cm\(^{-1}\). This is especially true for oxide minerals which
are the most important minerals for environmental study due to their ubiquity within the Earth’s crust. However, this limitation can be overcome by careful selection of some optically transparent substrate material, such as fluorite, and the deposition of a thin film of the mineral of interest onto this substrate.

This approach has been reported, to the author’s knowledge, only once within the literature by Waldrup and Williams and so is a ripe area of potential research. While this approach is very promising, it is not without experimental complexities which must be overcome. Early attempts made during the course of my dissertation work to apply this approach will be discussed below illustrating several aspects of these difficulties. Shown in Figure 5.3 is a series of ssp and ppp VSFG spectra of a 100 nm hematite film on a 10 nm silica film on a CaF$_2$ plate substrate in contact with air (Figure 5.3a), water (Figure 5.3b), and 100 mM Na$_2$SO$_4$ solution (Figure 5.3c).

The silica film is necessary to prevent hematite film delamination which occurs rapidly on exposure to water for hematite films deposited on bare CaF$_2$ surfaces. This is most likely due to poor adhesion between surface CaF$_2$ groups and hematite potentially arising from lattice mismatch. The addition of a small silica layer seems to effectively prevent hematite film delamination; however, this silica layer adds complexity to the interface in question complicating data interpretation. For the hematite film studies illustrated by Figure 5.3 the VSFG spectra all appear very similar. This is most likely due to non-resonant and hematite lattice resonant contributions. While there are no allowed phonon modes for hematite in this region, as discussed in Chapter 3, there are slight peaks visible in the hematite Raman spectrum (Figure 3.5) possibly corresponding to forbidden phonon modes arising from hematite lattice disorder. Regardless of the origin
for these peaks, they render the interpretation of the spectra presented in Figure 5.3 very challenging. Addressing these issues forms the next logical step in implementing a VSFG approach to study ion adsorption at buried oxide mineral/solution interface.

5.2.3. TIR-Raman Studies of Ions at Mineral/Solution Interfaces

Since the TIR-Raman effect was first demonstrated in the 1970s there have been relatively few studies utilizing this method, and even less investigating adsorption onto minerals. However, all adsorption studies reported in the literature to date, to the author’s knowledge, have reported on surfactant adsorption with no reports of simple inorganic ion interaction at mineral/solution interface. This is in huge contrast to studies utilizing ATR-IR, the sister technique of TIR-Raman, where dozens of reports on inorganic ion behavior at mineral surfaces are published every year. The primary reasons for this are the lack of awareness for the power of a TIR-Raman approach within the scientific communities interested in such processes and the unavailability of a commercial TIR-Raman instrument.

In the discussions presented in Chapter 4 the power and advantages for adopting a TIR-Raman approach for the study of ion interactions at buried mineral/solution interfaces. This approach has the large advantage over ATR-IR techniques in that the probe depth for a TIR-Raman experiment can be as much as an order of magnitude less than a typical ATR-IR experiment. TIR-Raman is also experimentally easier and less expensive to implement than a VSFG approach. However, there are serious detection efficiency issues which must be addressed before TIR-Raman’s full potential for the in situ study of ion behavior at buried mineral/solution interfaces is realized.

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For the home-built TIR-Raman spectrometer in the Allen laboratory several areas of the instrument are suggested to be modified in order to increase the detection efficiency for the instrument. Changing the TIR element from amorphous silica to a crystalline substrate such as sapphire or cubic zirconia is the first suggested modification for improvement. By changing the TIR element from silica two improvements are gained; first the large parasitic scattering peaks from silica (Figure 4.7) will be removed facilitating better background subtractions and secondly the refractive index of the TIR element will increase, as silica has a lower refractive index for a solid of ~1.5, which will decrease the penetration depth of the TIR evanescent field. The next areas for instrumental improvement all reside within the detection branch of the TIR-Raman spectrometer. In the current set-up the objection lens used for collection is aligned by visually inspecting the TIR reflection spot on a business card projected out of the objective lens. In this way the collection lens may be slightly misaligned resulting in less than ideal collection efficiencies. By the implementation of a optical microscope stage into the detection stage would allow for a more accurate alignment of this collection objective lens. If these relatively straight-forward steps are taken the investigation of in situ ion adsorption at mineral/solution interfaces with the Allen lab TIR-Raman spectrometer will be greatly facilitated.
Figure 5.1. Comparison between broad band VSFG spectra for SDS, MSA, and H$_2$SO$_4$ solutions which differ primarily by hydrocarbon chain length. Shown are raw VSFG spectra (red traces) and background spectra (black traces) for $1.5 \times 10^{-4}$ x SDS (A), 0.1 x MSA (B), and 0.4 x H$_2$SO$_4$ (C) solutions. Note increasing background signal with decreasing surface residence (hydrocarbon chain length). Shown in panel D are the normalized spectra for the three solutions with $1.5 \times 10^{-4}$ x SDS (green trace), 0.1 x MSA (blue trace), and 0.4 x H$_2$SO$_4$ (pink trace) indicated. Wing intensities vary for spectra shown in panel D due to different IR profiles on the different days the spectra were collected. All MSA data are courtesy of Dr. Xiangke Chen.
Figure 5.2. Scanning VSFG spectra of $1.5 \times 10^{-4}$ x SDS (A) and 0.4 x H$_2$SO$_4$ (B) solutions.

Shown are normalized VSFG spectra (red circles) and background spectra (black squares).
Figure 5.3. Scanning VSFG spectra corresponding to a 100 nm hematite film on a 10 nm silica on a CaF$_2$ plate in contact with air (A), neat water (B), and 100 mM Na$_2$SO$_4$ solution at pH 6 (C). PPP (blue markers) and SSP (red markers) are shown. Note that PPP spectra more intense than the SSP data for A and B but less intense for panel C spectra; the reasons for this are unclear.
References


(225) Tolstoy, V. P.; Chernyshova, I. V.; Skryshevshy, V. A. *Handbook of Infrared Spectroscopy of Ultrathin Films*; Wiley-VCH: Hoboken, New Jersey, **2003**.


(245) Born, W.; Wolf, E. *Principles of Optics*; 7th ed.; Cambridge University Press: Cambridge, United Kingdom, **1999**.


Appendix A: VSFG Software Modification for EMCCD Implementation

It was necessary to modify the existing home written Labview software program which controlled the 20 Hz scanning VSFG spectrometer in order to implement an EMCCD into the detection system. This was necessary to generate VSFG spectra with acceptable S/N ratios in a reasonable amount of time due to the VSFG weakness of sulfate ion modes, particularly at vapor/solution interfaces. Specifically the sub-.vi program “SFGfinder.vi” was modified to accommodate the EMCCD. Shown below is the relevant block diagrams of SFGfinder.vi that were modified with the changes and effects noted.
Pre – Modification: EMCCD area inputs were not connected to EMCCD array builder.

Simple constant values input for beta testing purposes.

Post – Modification: Wires connect EMCCD area inputs to array builder.
Post – Modification: Area indicated by red dashed box had wires correctly connected.

Area indicated by blue dashed box had “Call Library Function: Get Acquired Data” added. Area indicated by green dashed box had array generation modified to increase data processing speed.
Appendix B: Iron Oxide Film Thickness Calculation

Iron oxide film thickness in Chapter 3 was estimated by calculating the approximate number of Fe atoms present in the film:

\[
D \left( \frac{g}{cm^3} \right) \times A_{substrate} (cm^2) \times d(cm) \times \frac{1}{amu_{Fe}} \left( \frac{mol}{g} \right) \times 6.02 \times 10^{23} \left( \frac{atoms}{mol} \right) = \# Fe \ atoms. \quad (A.1)
\]

where D is the density of iron, A is the area of the substrate, and d is the thickness of the initial deposited Fe film. This allows the calculation of the number of oxide unit cells present as the number of iron atoms per unit cell is known:

\[
\frac{Total \ #Fe \ atoms}{\# Fe \ atoms \ per \ unit \ cell} = \# oxide \ unit \ cells. \quad (A.2)
\]

By examining the cross-sectional area of a sample unit cell and the total area of the substrate the number of unit cells needed to form one layer on the substrate is calculated:

\[
\frac{A_{substrate}}{A_{unit \ cell}} = \# \ unit \ cells \ to \ form \ one \ layer. \quad (A.3)
\]

With the total number of unit cells present in the film and the number of unit cells needed to form a layer the total oxide film thickness is calculated as:
Here C is the third axis of the unit cell not picked to calculate the cross-sectional area of the unit cell. Results from this estimate agree well with our measured ellipsometry thicknesses.
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