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Vibrational Spectroscopic Investigation of Dehydrogenation on Supported Platinum Nanoparticles, and Photoelectron Spectroscopy to Probe Chemistry at the Aqueous Interface

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Vibrational Spectroscopic Investigation of Dehydrogenation on Supported Platinum Nanoparticles, and Photoelectron Spectroscopy to Probe Chemistry at the Aqueous Interface

Dissertation

submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

Marijke H. C. Van Spyk

Dissertation Committee:
Professor John C. Hemminger, Chair
Professor Wilson Ho
Professor Reginald M. Penner

2014
DEDICATION

To

my husband, parents, siblings, in-laws and friends

for unflinching support,

good examples and advice,

motivation,

encouragement,

and perspective.
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to document the integration of administrative and laboratory safety regulations.
  • Completed chemical inventory audits and supervised hazardous waste storage, labeling, and
disposal.
  • Enforced safety training and compliance with administrative and laboratory safety
regulations.
  • Recommended and executed corrective changes in processes and equipment to improve
safety.

  • Designed and installed a fast entry load lock and removable sample holder with resistive
heating and cryogenic cooling for existing ultrahigh vacuum chamber (UHV).
  • Refurbished a high resolution electron energy loss spectroscopy (HREELS) UHV chamber.
  • Completed vibrational and Auger spectroscopic analysis of several supported nanoparticle
systems and studied heterogeneous hydrocarbon catalysis on oxide-supported nanoparticles
using HREELS.
  • Member of two national chemistry societies, one integrated research unit, one national
honors society for chemists and one national chemistry fraternity.

Visiting Researcher at Advanced Light Source (ALS), Lawrence Berkeley National Laboratory,
Berkeley, California (1/2012 – 12/2013)
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photoelectron spectroscopic studies of interfacial aqueous chemistry with a custom-designed
liquid microjet.
  • Completed LJ-XPS studies on concentration dependence of surface propensity and
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• Laser induced breakdown spectroscopy laboratory
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2014 University of California Regent’s Dissertation Fellowship
2011 honorable mention Ford Foundation Predoctoral Fellowship

PUBLICATIONS


ORAL PRESENTATIONS


ABSTRACT OF THE DISSERTATION

Vibrational Spectroscopic Investigation of Dehydrogenation on Supported Platinum Nanoparticles, and Photoelectron Spectroscopy to Probe Chemistry at the Aqueous Interface

By

Marijke H. C. Van Spyk

Doctor of Philosophy in Chemistry

University of California, Irvine, 2014

Professor John C. Hemminger, Chair

This work focuses on determining the fundamental chemistry of molecules at interfaces important to catalysis and atmospheric chemistry using electron-detection based techniques. Instruments were either retrofitted, or designed and constructed to facilitate the study of interfaces in ultrahigh vacuum (UHV) or in near-ambient pressures. Chapters two and five overview theory and instrumental development for high resolution electron energy loss spectroscopy (HREELS) and liquid-microjet X-ray photoelectron spectroscopy (LJ-PES), respectively.

Chapters three and four cover vibrational spectroscopic studies completed at UC Irvine. The dehydrogenation of cyclohexane over alumina-supported platinum nanoparticles was found to differ from that over platinum surfaces in HREELS studies. HREELS was also used to test cleaning or activation protocols for nanoparticles supported on highly oriented pyrolytic graphite (HOPG). These are the first HREELS studies for cyclohexane dehydrogenation over supported nanoparticles, and results provide fundamental information about reactivity for this system.

Chapters six through eight cover LJ-PES studies on aqueous solutions completed at the ALS synchrotron facility in California, and at the BESSY synchrotron in Berlin, Germany. Here,
the relative concentrations and chemistry of aqueous solutes at the air-water interface and in the bulk of solution were probed using LJ-PES. Chapter six investigates the interfacial deprotonation of aqueous ammonium, which varies with pH so that ammonium is depleted at the interface at low pH. Chapter seven describes the distribution of dications in magnesium chloride or sulfate solutions. It is found that sulfate ions “pull” magnesium cations away from the interface. These results are compared with ionic distributions for sodium chloride solutions that have well understood interfacial chemistry. Chapter eight focuses on interfacial solute distributions in ternary aqueous organic and ionic solutions. The addition of ethanol perturbs the ionic distribution for magnesium or sodium chloride solutions, in contrast to ethylene glycol addition, which does not. Additional studies on the interfacial behavior of acetonitrile and propionitrile (including the effects of potassium chloride on this behavior), and the distribution of lithium halide salts in aqueous solution are briefly mentioned. Results have ramifications for aqueous atmospheric aerosol chemistry, but are also interesting from a fundamental standpoint.
1. Surface Science

Importance of Interfaces

Chemistry happens at surfaces, and interfaces between surfaces are everywhere. Any heterogeneous interface between vacuum, air, water, metal, metal oxide, or insulator surfaces tend to enables unique chemistry compared to that in bulk material. Indeed, even our bodies need interfaces to function such as the air-lung interface. There is a saying that “a chemist never dies, they simply reach equilibrium” to which I would add “across interfaces”. This work reveals chemistry at the air – water interface relevant for atmospheric aerosols, and the vacuum – nanoparticle interface important for industrial catalysis.

Why are interfaces different from bulk material? Surfaces have broken symmetry so that molecules may align in a particular orientation (e.g. acetonitrile orients near the air-water interface with hydrophobic groups directed away from water), rendering them active for one reaction, but not for another. This organization is driven by energetic gains, and is highly dependent on the type of interface and local environment. For example, solutes like large anions may have a higher concentration near the surface of aqueous solution, which is referred to as surface enhancement. Interfaces can also bridge materials with differing electronic properties, creating a unique environment. Metallic interfaces can have different structures that are active for different reactions, and which have different types of defect sites.

Although interfaces are omnipresent, studying them is often challenging because they can be around 0.1 nm thick. This is a million times smaller than the width of a human hair. The field of Surface Science has developed many tools capable of selectively probing interfaces to address this challenge, and several techniques will be discussed in the next section of this chapter.
Surface Analytical Techniques

Specialized surface science instruments are required to detect interfacial structure or reactivity. The type of probe used, and the experimental conditions are important factors. This section will overview some of the technology required for surface studies and will introduce terminology used throughout this work.

Gentle probes including radiation and electrons are used in surface experiments because they are attenuated by bulk material. HREELS is a surface-specific technique that probes interactions occurring at the interface using a monochromatic electron beam (see Chapter two). X-ray photoelectron spectroscopy (XPS or PES) uses monochromatic light to probe the near-surface region, and not just the surface. Here the probe depth corresponds to the energy of ejected photoelectron (see Chapter five). In both cases, the penetration of electrons through material determines the specificity for the interface.

Surface sensitive experiments are often undertaken using specialized equipment to provide a vacuum environment that facilitates sample surface cleanliness and reduction in attenuation of electrons by collision with gaseous molecules. Vacuum further reduces gas phase signal intensity for studies of the gas interfaces, leading to a better sensitivity towards molecules adsorbed at the surface. The distance between molecular collisions, termed the mean free path ($\lambda$), is maximized in vacuum:

$$\lambda = \frac{kT}{\frac{1}{4.14}P\sigma}$$  \hspace{1cm} (1.1)

Where P is pressure in Pascal, k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J/K}$), $\sigma$ is the collision cross section in square meters, and T is the temperature in Kelvin. Although SI units for pressure are used in this equation, experimental pressures will be discussed in the units of torr (1 torr = (1/760) * 1 atm ~ 133.3 Pa). Collisions between molecules are effectively eliminated at pressures
below \(1 \times 10^{-4}\) torr, but vacuum pressures below \(1 \times 10^{-6}\) torr are necessary to operate the channeltron detector for electrons, and further reduction of pressure below \(1 \times 10^{-9}\) torr is required to maintain a clean surface. This is because the coverage (Equation 1.2) of molecules on a surface depends on the molecular flux (Equation 1.3), and sticking probability (Equation 1.4).

\[
\theta = \frac{\text{Actual surface coverage}}{\text{Saturation surface coverage}} \tag{1.2}
\]

\[
F = \frac{p}{\sqrt{2\pi mkT}} \tag{1.3. Hertz-Knudsen formula}
\]

\[
F = \frac{p}{\sqrt{2\pi mkT}} \tag{1.4}
\]

Where all unit are SI. Full monolayer (ML) coverage of surfaces is defined as the maximum surface concentration of an adsorbed species on a surface. This occurs on the order of seconds in high vacuum (HV) between \(1 \times 10^{-6}\) to \(1 \times 10^{-8}\) torr, but may take hours in ultra high vacuum (UHV) below \(1 \times 10^{-9}\) torr because the flux of molecules to the surface is much lower. Thus, experiments that require a particularly clean surface are undertaken in UHV. ML coverages can be complicated to determine, and so the exposure of a surface to a gaseous molecule is a simple and useful value often described in units of Langmuir (1 L = \(1 \times 10^{-6}\) torr⋅s).

Pressure regimes used in this work are summarized in Table 1.1, and full descriptions of the techniques can be found in subsequent chapters. Bench top atomic force microscopy (AFM) is undertaken in the presence of air because the cantilever is relatively robust when compared to electrons and photons which are attenuated by inelastic scattering with air molecules. Ambient pressure PES (AP PES) can be undertaken in rough vacuum around 1 torr, but only when coupled with differential pumping to eliminate gasses from the analyzer. Scanning electron microscopy (SEM) requires HV pressures which are achievable using turbomolecular pumps. High resolution electron energy loss spectroscopy (HREELS) and Auger electron spectroscopy (AES) require UHV for a clean sample, but can be undertaken in HV below \(1 \times 10^{-8}\) torr for surface
characterization. These pressures are reached using an ion pump for continuous capture of gas molecules coupled with a titanium sublimation pump for periodic pumping speed enhancement.

Table 1.1. Pressure regimes for surface techniques

<table>
<thead>
<tr>
<th>Technique</th>
<th>Regime</th>
<th>Pressure (torr)</th>
<th>Probe (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AES</td>
<td>UHV</td>
<td>$3 \times 10^{-10}$</td>
<td>Electrons, 2000</td>
</tr>
<tr>
<td>AFM</td>
<td>AP</td>
<td>760</td>
<td>Cantilever</td>
</tr>
<tr>
<td>AP PES</td>
<td>Near AP*</td>
<td>1</td>
<td>Photons, 100-1500</td>
</tr>
<tr>
<td>HREELS</td>
<td>UHV</td>
<td>$3 \times 10^{-10}$</td>
<td>Electrons, 3.698</td>
</tr>
<tr>
<td>LJ-PES</td>
<td>HV</td>
<td>$1 \times 10^{-8}$</td>
<td>Photons, 100-1500</td>
</tr>
<tr>
<td>SEM</td>
<td>HV</td>
<td>$1 \times 10^{-8}$</td>
<td>Electrons,</td>
</tr>
<tr>
<td>XPS</td>
<td>HV</td>
<td>$1 \times 10^{-8}$</td>
<td>Photons, 100-1500</td>
</tr>
</tbody>
</table>

It must be mentioned that attaining low pressures require that equipment is free of hydrocarbon contamination including fingerprints. Thus, equipment is handled with gloves or wiped down with ethanol or acetone. For UHV studies, water is removed by baking the chamber above 100 °C under vacuum until the desired pressure is reached.
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2. High Resolution Electron Energy Loss Spectroscopy (HREELS)

This chapter will discuss HREELS and AES techniques. It will also describe modifications to the HREELS instrument that were completed to enable the studies in Chapters three and four.

HREELS Technique Overview

High resolution electron energy loss spectroscopy (HREELS) is a surface-sensitive electron scattering based vibrational spectroscopic technique. The fundamental physics were presented by Harald Ibach and Douglas L. Mills in 1982, and have been subsequently reviewed by Wilson Ho, and Larry Kesmodel. The delicate nature of low energy electrons ensures that signal is only generated at the surface because the electrons lack the kinetic energy required to penetrate into the sample. For incident electrons with 10^2 eV KE, the depth from which scattered electrons can escape from the surface (inelastic mean free path (IMFP)) is about 1 nm, or several atomic monolayers. HREEL spectrometers thus must incorporate μ-metal shielding to reduce electromagnetic noise, and operation is restricted to UHV (2 × 10^-10 torr) to minimize electron attenuation by collision with gas molecules. HREELS has several advantages over photon based vibrational spectroscopy techniques resulting from the physical properties and detectability of low energy electrons. Electrons possess both mass and charge and so interact more strongly with adsorbates than photons, and can thus probe phonon excitations which are invisible in IR spectroscopy. Electrons are more efficiently detected by channeltron electron multiplier devices (10^8 gain) than photons are by photon multiplier tubes (10^6 gain), but there is a trade off in the spectral resolution which is limited by the monochromator’s ability to make the electron beam single energied.

For HREELS, an electron beam is generated by thermionic emission from a lanthanum hexaboride (LaB6) filament as electrical current is applied. The electrons are collimated into a
beam using electron optics – several carbon-coated metal electrodes to which an electric potential is applied to direct electrons through a gap between two optics. The energy of the electron beam is then selected using two monochromators containing additional electron optics, before being focused and accelerated to collide with the sample. The scattering geometry is shown in Figure 2.1. The scattered electron beam is then steered into an electron energy analyzer that scans the electron energies present in the beam using electron optics. The electronic signal is collected by a channeltron and filtered using analog signal processing before being presented as spectra on the computer.

![Figure 2.1. Schematic of HREELS experimental technique.](image)

HREELS spectra include energy losses from several electron scattering mechanisms, each with unique selection rules which aid in the interpretation of spectra. Dipole scattering losses result from long range Coulombic interactions of incident electrons with the oscillating dipole moment of adsorbates, and are most intense in the specular direction and at low beam energies. For dipole scattering, vibrational modes parallel the sample surface are not detected due to charge cancelation.
by image charges. The specular direction is defined by setting the angle of the rotatable analyzer equal to the angle of the incident electron beam with respect to the sample surface normal. Impact scattering losses result from electron collisions with the surface and are broadly distributed off specular. HREELS spectra are plotted as the number of electrons collected versus energy lost by the electron relative to initial energy in electron volts, later converted to wavenumbers (1 meV = 8.01 cm\(^{-1}\)). Spectra are normalized to the peak intensity and position of the elastically scattered electrons (no energy change and \(\theta_f = \theta_i\)). Spectral resolution is quantified by measuring the full width at half maximum (FWHM) of the elastically scattered energy loss peak. Although low resolutions have been attained using HREELS (around 5 cm\(^{-1}\)), the resolution for present studies was 70 cm\(^{-1}\) on average. This resolution is limited by the low electron scattering signal provided by samples with nanoscale roughness.

The vibrational frequency of energy losses are specific to the type of vibrational mode excited (Table 2.1). Shifts in the energy loss frequency for a particular molecule can indicate changes in molecular interactions, and are often used to determine the type of bonding between a molecule and atoms in a surface. In this work, carbon monoxide gas (CO) is used as a probe molecule for determining the type of available sites on platinum surfaces because the energy loss peak position is indicative of the CO binding configuration (Figure 2.2). CO is a uniquely valuable probe molecule because the large dipole moment normal to the surface provides high signal in HREEL spectra.
Table 2.1. Energy losses for select vibrational modes.

<table>
<thead>
<tr>
<th>Vibrational Mode</th>
<th>Interaction</th>
<th>Energy Loss (cm⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν_C-O</td>
<td>CO - Pt(111) bridge site</td>
<td>350, 480, 1920-1800</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>CO - Pt(111) top site</td>
<td>390, 480, 2100-1920</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>CO - Pt NP / Al₂O₃ / NiAl(100)</td>
<td>2040</td>
<td>This work</td>
</tr>
<tr>
<td>ν_Pt-C</td>
<td>C₆H₁₂ – Pt(111)</td>
<td>380, 430 symm.</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>560, 700 asymm.</td>
<td></td>
</tr>
<tr>
<td>ν_C-H</td>
<td>C₆H₁₂ – Pt NP / Al₂O₃ / NiAl(100)</td>
<td>2930</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>C₆H₆ – Pt NP / Al₂O₃ / NiAl(100)</td>
<td>3045</td>
<td>This work</td>
</tr>
<tr>
<td>ν_Al₂O₃</td>
<td>Al₂O₃ / NiAl(100)</td>
<td>418, 600, 895</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>410, 620, 850</td>
<td>11</td>
</tr>
<tr>
<td>Pt(111)</td>
<td></td>
<td>250, 470, 680</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>140</td>
<td>9</td>
</tr>
<tr>
<td>TiO₂(110)</td>
<td></td>
<td>339, 436, 637</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>365, 445, 755</td>
<td>14</td>
</tr>
</tbody>
</table>

Figure 2.2. Carbon monoxide stretching modes on Pt(111). ⁸

Identities and quantities of reaction intermediates are determined from HREELS energy loss peak positions, and intensities, respectively. Reaction mechanisms can be understood by completing annealing profiles where reaction intermediates are monitored with increasing
temperature. Here, the sample is cooled to cryogenic temperatures before exposure to probe molecules and subsequent heating to a specified temperature for a set amount of time. The sample must be re-cooled to cryogenic temperature for spectra acquisition to freeze out further reactivity and to isolate the sample from electrical current used during resistive heating. This process is repeated for sequential temperatures as desired to monitor initial reactant adsorption, reaction steps, and decomposition or desorption of products. The saturation exposure of molecules to samples can be determined by completing a coverage profile experiment. Here, a sample is cooled to cryogenic temperatures, and then exposed to a measured amount of gas before spectra acquisition. The process is repeated, and the peak height as a function of exposure is used to determine the gas exposure required to saturate the sample surface.
Auger Electron Spectroscopy

Auger electron spectroscopy (AES) is a complementary surface analysis technique invented by Pierre Auger in the early 1950s that detects secondary electrons to determine elemental composition and relative atomic abundance in a sample. The emission process is described in Figure 2.3. AES is used in this work to determine sample cleanliness, nanoparticle composition, and oxide-layer thickness. The second derivative of the number of detected electrons is plotted as a function of Auger electron KE ($-d^2I(E)/dE^2$), and peak positions are elementally specific.

Figure 2.3. Diagram showing the emission of an Auger electron. A 2 keV electron beam bombards the sample surface (step a), ejecting a core-level electron (step b) from an atom in the sample having an energy of $E_1$. An electron from a higher orbital (with energy $E_2$) relaxes to fill the core hole, providing enough energy to emit a secondary electron from a higher shell with energy $E_3$ (step c). The last step is concerted, meaning that relaxation and emission occur simultaneously. The energy of the emitted secondary electron equals the difference in orbital energies.
Previous HREELS Chamber Design

The HREELS chamber in the Hemminger Laboratory was homebuilt from an existing vacuum system base, a two-level custom bell jar, and custom manipulators, as detailed elsewhere.\textsuperscript{16} The 981-0000 Varian Vacuum System at the base of the chamber contains five ion pumps with 40 liter per second pumping speeds, an all-metal isolation valve for the gas manifold, a poppet valve, an ion gauge, and a Varian titanium sublimation pump. The bell jar’s two-level design places sample processing and characterization tools in the upper level, and an LK Technologies L2000 HREELS spectrometer in the lower level. The bell jar was equipped with a Varian LEED system, a UTI 100C quadrapole MS for trace gas analysis, a Varian Ion bombardment gun for argon bombardment of samples, and a Perkin-Elmer AES system for determination of sample elemental composition. The sample was mounted to a manipulator equipped with resistive heating and conductive cooling from a liquid nitrogen reservoir. In the past, inserting a sample in the HREELS chamber entailed up to a month of venting, baking, and prolonged sample cleaning by sputtering and annealing.

The HREELS electron optics were previously controlled by electronics which required iterative manual optimization of 49 pots, and all electron optic voltages were recorded by hand. This process is time-consuming and detrimental to the cleanliness of the experiment.

Subsequent to the initial construction, the chamber was equipped with heating elements and dedicated variacs for bakeout, and an Oxford Scientific EBE 1 “OS-Vap” electron beam platinum evaporator with an Inficon front load bakeable sensor QCM for monitoring the deposition of platinum. The complete description of the heating element circuitry can be found in the HREELS user operation manual.\textsuperscript{17}
HREELS Refurbishment and Electronics Upgrade

Modifications were made to the LK2000 HREELS spectrometer in 2010 to improve the operation and ease of use of the spectrometer. Specifically, upgraded LK2000-DAC digital electronics enable auto-tuning and digital tuning file storage, and a spectrometer refurbishment restored optimal capabilities. These improvements were made by LK Technologies in Bloomington, Indiana, and then the spectrometer was reassembled on-site at UC Irvine.

The spectrometer was removed from the UHV chamber at UC Irvine, and prepared for shipping according to instructions provided by LK Technologies. The spectrometer was mounted in a homemade coaxial plywood shipping container that was also designed by LK Technologies, and shipped via an air-ride truck to minimize vibrational damage to LK Technologies in Bloomington, Indiana for $1,473.24 roundtrip. Counting electronics were packaged separately in cardboard boxes with bubble-wrap insulation. The LK2000-DAC digital electronics package cost $38,700.00 and included a replacement for the main power supply, a filter box, a Keithley 6485 picoammeter, a Sorensen regulated DC power supply for the LaB6 filament, a lens voltage controller, a new sample grounding cable which allows sample current to be monitored, software, two computer interface cards, and a modified preamp. The $3,500.00 spectrometer refurbishment included re-coating of the electron optics inside the spectrometer, a new LaB6 filament and channeltron, and optimization of the signal using a HOPG sample.

The updated configuration and operation of the HREELS spectrometer will be summarized here. The HREELS set-up is composed of the internal spectrometer, external counting electronics, and external digital controls. The Sorensen regulated DC power supply in the electronics rack provides power to the filament inside the chamber. The LK Technologies main power supply powers the voltage control box which sets the lens voltages on all electron optics in the
spectrometer through the filter box. The voltage control box is controlled by the computer software and is interfaced to the computer through a Keithley KPCI 3140 card. The electron signal is collected by a channeltron in the spectrometer, which is powered by an Ortec 556 high voltage power supply in the electronics rack. Electric signal travels from the channeltron through a preamp which enhances the signal, before entering an Ortec 9302 amplifier discriminator which allows one to amplify the signal, and an Ortec 583 constant fraction differential discriminator where high and low pass filters are applied to remove dark noise. The amplified signal is displayed in the HREELS software via a Keithley KPCI 488A IEEE-488 GPIB card and on an Ortec 449 log/lin rate meter. The raw signal is also displayed on the Keithley 6485 picoammeter, which can also be set to show the beam current to the sample using the HREELS software. It should be noted that a separate HREELS computer is required because the GPIB cards cannot function concurrently with the National Instruments 488.2 GPIB card which is used to interface the pressure and temperature signals with labview software on the existing HREELS computer. Additionally, the video card for the HREELS computer was replaced with one from another Dell Dimension 8300 tower due to incompatibility with the motherboard.

The main advantage of the new HREELS software is the autotuning feature and digital saving of tuning files. Complete instructions are found in the accompanying documentation supplied with the electronics. Initial tuning of the spectrometer may still take a week for location of the beam, and tuning for each experiment may take up to four hours. The autotuning process is essentially similar to that described in the instruction manual, except that several optics can be scanned to optimize signal once the signal has been found. The signal may also be enhanced by spectral averaging, where successive scans are averaged together to increase the signal to noise, or the integration time for each point is increased.
Load Lock and Removable Sample Holder: Design and Installation

The HREELS chamber was modified to include a removable sample holder to expedite analysis of samples generated \textit{ex situ}. In the original design, exchanging samples required that the chamber be vented and baked, limiting samples to those which could be cleaned after bakeout such as single crystals. The removable sample holder additionally facilitates removal of the sample for analysis by SEM or XPS and rapid repair of some sample connectivity problems.

The new removable sample holder and fast-entry load lock were based on a previous design by Dr. Ronald Grimm which was modified to satisfy the geometry of the HREELS chamber. The width of the sample holder was reduced to allow insertion through the 1.25” slit in the double layer $\mu$-metal shield around the HREEL spectrometer which acts to minimize electromagnetic noise within the spectrometer. $\mu$-metal is a nickel-iron alloy with high magnetic permeability which must be annealed in a magnetic field and hydrogen atmosphere in order to shield against radiation, precluding any cold-cutting modifications to widen the opening in the shield. In addition, the connections for conductive cooling on the sample holder were minimized and inverted from the Grimm design to retain the liquid nitrogen reservoir’s previous position outside of the $\mu$-metal shielding. The sample holder is shown in Figure 2.4, and detailed design schematics can be found in Appendix A. Nonmagnetic materials with low degassing rates and were selected for this project to minimize electromagnetic noise near the electron beam. All custom parts were produced by the UC Irvine Physical Sciences Machine Shop with non-magnetic materials including OFHC copper, and 316 and 304 stainless steel. Components which enter the HREELS spectrometer were demagnetized using a degaussing coil prior to installation.
Figure 2.4. Removable sample holder. Part schematics are available in the Appendix (Figure A.1 - Figure A.16).

One very large hurdle to this project was to ensure good connectivity between the sample, and the electrical and conductive connections while insulating the sample from ground. Several design considerations for connectivity will be discussed here, beginning with sample cooling. The sample is isolated from ground using alumina washers (Kimball Physics part # Al₂O₃-SP-C-025),
tubes (Kimball Physics part # Al₂O₃-TU-C-125), and 0-80 hat washers (McAllister part # 10001609) which are inserted between the physical support for the sample holder, and the active components of the sample holder. The active components refers to those involved in heating and cooling. This includes the two copper sides (p) in the removable portion of the sample holder which are mutually electrically isolated by a machinable high density Macor® ceramic block (t), and the sample and two supporting tungsten wires which are the only connection between the two copper blocks. When inserted into the chamber, these copper blocks are pressed by hand-made 316 stainless steel springs to sit tightly on two copper tracks (k), each of which is bolted to one double, coaxial copper braid (e,g,and h). One copper braid is bolted directly to the bottom of the copper liquid nitrogen reservoir using a custom copper screw (f), and the other is secured to the liquid nitrogen reservoir with a ceramically insulated copper screw and a sapphire insulating washer. This configuration ensures that both braids are in thermal contact with the reservoir while one copper braid is electrically connected to the liquid nitrogen reservoir and the other is electrically isolated. The copper braids and tracks were designed to maximize contact area for efficient heat transfer from the sample when the liquid nitrogen reservoir is filled.

In this configuration, sample temperatures as cold as 160 K have been measured by a K-type cromel-alumel thermocouple spot welded into a slit in a NiAl(100) single crystal. Thermocouple connections are made by threading the fiberglass insulated chromel and alumel wires through the sample holder where they are spot-welded to larger wires which are inserted into the bottom of the Macor® block and bent to form L-shapes (o) directed towards the sides of the sample holder. When the sample holder is inserted into the chamber, the bottom of each L slides into a chromel or alumel clip (n) which is attached to an insulated chromel or alumel wire (i) leading to the thermocouple feedthrough. The clips are extracted from a regular female
thermocouple connection plug, and are electrically isolated from the chamber by a custom Macor® platform (m). The temperature signal is directed to a National Instruments SC 2345 box which connects to a computer using a National Instruments 488.2 PCI card, and the temperature is monitored with Labview software.

Resistive sample heating entails passing an electrical current through the sample from outside the chamber. An electrical circuit is created by bolting the electrically isolated copper braid to another braid leading to a copper electrical feed through, and by bolting the liquid nitrogen feedthrough to a copper braid leading to a separate electrical feed through. Thus, the current flows from one copper braid, to a copper track, to a copper block, through a supporting tungsten wire, through the sample, then out the other tungsten wire, out the other copper block, and up the other copper wire. In this configuration, temperatures up to 1150 °C have been obtained using a NiAl(100) single crystal by supplying electrical current with a SCR Power supply.

A second removable sample holder was constructed for large, flat, square samples such as 12 mm HOPG sheets (as shown in Figure 2.4). The operation of this sample holder is similar to that previously described, with the exception of the thermocouple and tungsten wire connections to the sample. Tantalum foil clips with tantalum screws and molybdenum nuts are used to sandwich the thermocouple and tungsten wires between the sample and a sacrificial sheet of HOPG. Sample heating varies with the thickness and connectivity of the sample, and so different currents may be required for thinner or thicker samples to achieve similar temperatures.

Two additional components were installed in the HREELS chamber to facilitate sample transfer: a “pusher” functions to stabilize the internal components of the sample holder, and a custom wobble stick attachment allows the user to manipulate the sample holder in vacuum. Custom parts were made from aluminum for the wobble stick (VG Scienta, ZWS075). The pusher
was made from a custom steel T-shaped rod attached to a Varian rotary feed through mounted on a linear motion drive (VG Scienta, ZLTM50 2-3/4”, $1,122.00).

The load lock is comprised of a MDC MT-12 linear transfer arm with a custom took connection for the sample holder, and is connected to the main chamber by a VAT 01032-UE01-0002 gate valve and held under vacuum by an Oerlikon Turbomac 50 turbo pump. The load lock contains a Varian ion gauge and is supported by custom metal rods leading to the chamber platform. This configuration has the added benefit that the main chamber may be pumped by the load lock turbo for the initial stages of bakeout, eliminating the use of the Agilent HS-2 diffusion pump (Varian) with liquid nitrogen cooled baffles, and stabilizing the ion pump at pressures above $1 \times 10^{-8}$ torr. A custom, two-level pump cabinet was constructed to accommodate the extra mechanical pump, and portions of the gas manifold were re-built using Kwick-Flange fittings (Figure 2.5). The extension cords powering the mechanical pumps were replaced due to thermal damage with blue SJEOOW cords from McMaster Carr Supply Co. that have a higher temperature rating. It should be noted that the diffusion pump was refurbished because the heating element remained on for several years after the mechanical pump was turned off. This resulted in crystallization of the diffusion pump oil which had to be mechanically removed from the pump, and replaced with Santovac 5 diffusion pump liquid, a polyphenyl ether with low vapor pressure. Additionally, a PHD6 CO detector and 50 ppm calibration gas were purchased through EH&S from SKC-West, INC. CO gas (airgas, research grade) was attached to the manifold using a High-Purity single stage regulator with CGA 350 fittings.
Figure 2.5. Schematic of the gas handling configuration for the HREELS chamber. The load lock is evacuated using a turbomolecular pump, backed by a dedicated mechanical rough pump. The gas manifold may be evacuated by mechanical pump, or by a diffusion pump. Several probe molecules and gasses are attached to the gas manifold and may be introduced into the HREELS vacuum chamber via a leak valve or a directional doser.

Sample transfer is accomplished by loading the sample holder in the load lock, pumping the load lock, and transferring the removable sample holder onto the internal portion of the sample holder. The electrical connections on the removable part of the sample holder are checked on the bench top with a multimeter before loading it on the transfer took facing the linear transfer arm. Then the load lock is pumped to rough vacuum (at least $1 \times 10^{-2}$ torr) through the turbo pump by a mechanical oil pump before the turbo pump is started. The load lock is pumped for approximately two hours, or until the pressure reaches $1 \times 10^{-6}$ torr and the internal component of the sample holder is positioned for transfer with the pusher positioned behind it. The transfer took is inserted into
the chamber and the wobble stick is used to slide the sample holder onto the copper tracks. Electrical connectivity and proper thermocouple readings are confirmed, and the heating is tested. Abnormalities these tests may indicate insufficient contact between the sample holder and the copper tracks and the sample should be re-adjusted before attempting an experiment because good contact is required for efficient cooling and heating, and to obtain HREELS spectra.

Several analytical components have been moved and modified to accommodate the load lock, pusher and wobble stick while preserving their optimum operational geometry, and the resulting chamber configuration is diagramed in Figure 2.6. The load lock and wobble stick are positioned where the platinum evaporator and QCM were previously. To reposition these components in the chamber, the LEED electron optics were removed to make way for the evaporator, and the MS was shifted towards the back of the chamber to attach the QCM. The pusher is attached to a port which was not in use.
Some common problems with sample transfer can be easily fixed. First, it should be noted that although sample transfer may be smooth when the chamber is vented, it may become difficult under vacuum. This problem was resolved by providing extra clearance for the track-slits in the removable section of the sample holder, and by making the transfer took and copper tracks narrower. Although these changes were made by the machine shop, small modifications can be
made by hand using a buffing attachment and polish with a Dremel tool. The Dremel tool can also be used to smooth all parts for tight electrical connections and to reduce friction on moving parts. Also, some components on the removable portion of the sample holder can be adjusted with the wobble stick if they shift. For example, by placing the wobble stick below the sample holder, one can gently push up to reposition alumina spacers between the copper blocks and the Macor® block. The wobble stick may also push or pull the closest side, the top, or the bottom of the sample holder in order to realign the removable portion of the sample holder on the copper tracks in the case that sample transfer becomes difficult due to misalignment or if it is impossible to slide the wobble stick entirely onto the sample holder. After the sample is seated on to the transfer-arm, the wobble stick may be used to level the L-shaped portions of the thermocouple connections. These connections tend to drop and may catch on the copper gasket at the entrance to the load lock.
References


3. Catalytic Dehydrogenation of Cyclohexane over Oxide-Supported Platinum Nanoparticles

Introduction to Cyclohexane Dehydrogenation

Platinum (Pt) is a good heterogeneous catalyst for dehydrogenation reactions,\(^1\) which are one of several steps in fuel reforming that increase the energy density of a feed stock by removing hydrogen to create carbon-carbon bonds. To reduce cost and increase productivity, industrial catalysts typically involve small platinum nanoparticles (Pt NPs), a few nanometers in diameter, dispersed on high surface area metal oxide supports such as alumina.\(^2\) This study provides fundamental information on the hydrocarbon dehydrogenation reactivity of Pt NPs / alumina using HREELS. However, because studies on samples containing bulk alumina would be complicated by sample charging during acquisition of HREEL spectra, an ultrathin aluminum oxide film with properties close to bulk metal oxides\(^3\) is used for HREELS experiments.\(^4\) Alumina films on NiAl(100) can be reproducibly grown (between 5-10 nm thick) with long range order to cover the entire NiAl(100) surface.\(^4\) Here, the NiAl buried interface does not influence NP reactivity because the charge transfer between the NiAl and supported NPs is slower than core ionization processes (10\(^{-17}\) s) and the lifetime of the core hole (10\(^{-15}\) s).\(^5\)

Pt nanoparticles deposited on alumina films grown on NiAl(110) have been extensively studied\(^5\)-\(^12\) and serve as a reproducible and well understood substrate for adsorption.\(^10\) Pt NPs supported on metal oxide foils have been studied by HREELS spectroscopy for CO adsorption\(^13\) and ethylene dehydrogenation.\(^14\)-\(^15\) These studies demonstrate the feasibility of vibrational spectroscopy as a tool for the characterization of NP reactivity, and acknowledge the low signal and diffuse scattering challenges which a nanostructured sample poses.\(^15\) Fewer morphology\(^16\)-\(^19\)
and reactivity\textsuperscript{20-21} studies exist for particles grown on NiAl(100)-supported alumina, but both ultrathin alumina films enable electron scattering studies of supported nanoparticles because they are flat and do not exhibit charging like bulk oxides. This study is the first HREELS study for cyclohexane dehydrogenation on Pt NP / Al\textsubscript{2}O\textsubscript{3} / NiAl(100). The peak position of the CH stretching mode, which is indicative of the composition of the adsorbed molecule, was monitored using HREELS as a function of annealing temperature to determine the temperature at which intermediates form.

Cyclohexane dehydrogenation on metallic single crystals is well-understood from surface sensitive experiments under UHV.\textsuperscript{22-25} The lowest energy surface for platinum is Pt(111), a hexagonal surface. Cyclohexane adsorbs to Pt(111) in the chair conformation with the three axial hydrogens pointed at the platinum surface (Figure 3.1).\textsuperscript{26} This is the same configuration adopted by gaseous cyclohexane where the carbon ring bends to allow equatorial hydrogens to exist in the plane of the molecule while three axial hydrogens point out of plane on either side in order to minimize steric hindrance. The interaction of these axial hydrogens with Pt(111) results in CH bond softening with a correspondingly lower energy CH energy loss peak at 2600 cm\textsuperscript{-1} which is often broad.\textsuperscript{27} Reduction of this peak’s intensity at 200 K is indicative of the onset of dehydrogenation and the formation of a C\textsubscript{6}H\textsubscript{9} reaction intermediate.\textsuperscript{28} The last step of cyclohexane dehydrogenation on Pt(111) is the formation of benzene above 300 K.

Figure 3.1. Mechanism for dehydrogenation of cyclohexane upon heating after adsorption to Pt(111) at cryogenic temperatures.\textsuperscript{29-30} Dehydrogenation occurs when one of the axial hydrogens
is transferred to the platinum and as subsequent hydrogens are transferred, the ring undergoes reorientation to form a stable C₆H₉ surface intermediate and then benzene.³¹

Cyclohexane dehydrogenation chemistry varies from that on Pt(111) for Pt{100}(5×20) and Pt{100}(1×1) platinum surfaces, which may be present on nanoparticles and will be covered here. A soft mode at 2550 cm⁻¹ was observed in the HREEL spectra for Pt{100}(5×20) exposed to cyclohexane at 110 K, indicating an activating interaction between axial hydrogens and the Pt surface similar to that observed for Pt(111).³² However, the majority of cyclohexane desorbs molecularly after heating to 220 K instead of undergoing dehydrogenation, corresponding to a weaker Pt – cyclohexane interaction than for Pt(111). In contrast, HREEL spectra for Pt{100}(1×1) exposed to cyclohexane at 110 K did not exhibit a soft mode near 2600 cm⁻¹. This indicates that the unreconstructed Pt{100} surface does not provide the correct symmetry for strong hydrogen–Pt interactions, whereas cyclohexane and both Pt(111) and the reconstructed Pt{100} surface have C₃ᵥ symmetry.³²

In this discussion it is important to consider ensemble requirements which have implications for the activity and specificity of catalysts, as reactions may be favored or hindered based on the type of chemisorption sites available.²⁵, ³³ The ensemble requirement is defined as the size and shape of chemisorption binding sites required for reaction of an adsorbate at a surface.²⁵ Ensemble effects for Pt(111) require 10-12 Pt atoms for cyclohexane to adsorb, undergo dehydrogenation and desorb.³⁴ Blocking these sites at even low coverage (θ_{Bi} < 0.1, where θ_{Bi} is the coverage of bismuth with respect to the number of surface Pt atoms) results in poisoning of Pt(111)’s dehydrogenation activity for cyclohexane, which may have serious implications for Pt NP.²⁴, ³⁵ Indeed, for the comparably spacious Pt(111) surface, increasing the coverage of cyclohexane results in fewer σ-bond interactions between cyclohexane and the surface and
increased activation energy for dehydrogenation (from 9.5 kcal/mol to 13.5 kcal/mol when the coverage is increased from 0.05 monolayer (ML) to 0.30 ML). This study addresses how ensemble effects impact the reactivity of supported NPs whose ensemble size is additionally limited by the three dimensional geometry of the particle.

Further changes in cyclohexane dehydrogenation chemistry over supported nanoparticles are expected because nanoparticles have a high surface-to-volume ratio, defect sites (steps and kinks), and multiple surfaces. For example, nanoparticles can express different percentages of surfaces including terraces or and steps (four nanometer Pt NPs grown in vacuum by vapor deposition on an oxide layer display 68:32 terrace:step CO binding sites. This relation is 50:50 for three nanometer NPs and 0:100 for 2.5 nanometer NPs). Since cyclohexane preferentially reacts at sites of high symmetry such as terrace sites, it is possible that Pt NPs smaller than 3 nm in diameter will have reduced reactivity due to the lack of ensemble sites.

Given the interesting chemistry of cyclohexane dehydrogenation on various single crystals, changes in reactivity can be expected for dehydrogenation on Pt nanoparticles having. In addition, nanoparticle reactivity depends on the material of the particle, particle morphology, oxidation state, density of particles and support interactions. Here, the reactivity of cyclohexane with small, oxide-supported Pt nanoparticles is investigated using HREELS.
Experimental Methods

HREELS experiments were undertaken in a custom built ion–pumped ultra high vacuum (UHV) chamber with a base pressure of $1 \times 10^{-10}$ torr as measured by an ion gauge. The chamber has two levels and is equipped with an LK2000 HREEL spectrometer in the lower level. The upper level houses a Physics Electronics Auger spectrometer (AES), a UTI 100c quadrapole mass spectrometer (QMS), and an EBE-1 Oxford Scientific electron beam evaporator with a Pt rod. The sample holder is removable through a fast-entry load lock and is equipped for resistive heating to 1470 K and conductive cooling from a liquid nitrogen reservoir to 165 K. The temperature is monitored by a K-type thermocouple spot welded to the side of the crystal.

Samples were generated *in situ* before each experiment. An NiAl(100) single crystal is mounted to the sample holder by two tungsten wires which are spot welded to the crystal. Oxygen cleaning followed a previously developed protocol which has been shown to generate complete, ultrathin films of alumina. The NiAl(100) was heated to 1070 K and exposed to 60 L (1 L = $10^{-6}$ torr·s) oxygen (Airgas, research grade) to oxidize carbon compounds. The NiAl(100) was then flashed to 1420 K to desorb contaminants, and then exposed to 60 L oxygen gas at 920 K to grow the ultrathin oxide film. This process was completed two or more times, and cleanliness was confirmed by AES.

The Pt evaporator was degassed prior to use and Pt NP were deposited on the alumina film using an electron beam evaporator (Oxford Scientific EBE-1) operated at 1.4 kV, 4.5 mA, and 10 A. The sample temperature was held below 180 K during deposition to minimize modification of the Al$_2$O$_3$ near the Pt and to limit Pt oxidation. Pt deposition on alumina / NiAl(100) at 90 K results in small disordered Pt clusters and disordering of the oxide as determined in literature by LEED.
The particle size was measured by the intensity of the elastically scattered peak in the HREELS spectra as described elsewhere.\textsuperscript{13} SEM images of a representative sample of Pt NP / Al\textsubscript{2}O\textsubscript{3} / NiAl(100) were collected using an FEM Magellan 400 XHR SEM with a through-lens detector. A beam current of 25 pA was used at 10.0 kV, and the dwell time was set to 30 µs. For these studies, the Pt was deposited \textit{in situ} as previously described, and the sample was then warmed to room temperature overnight, and removed from vacuum via the load lock. Care was taken to ensure the sample was exposed to air for a minimum amount of time, roughly 20 minutes.

Hydrocarbon exposure was completed by backfilling the UHV chamber through sapphire sealed leak valves while the sample was held at cryogenic temperatures in the HREEL spectrometer. HPLC grade cyclohexane (Fisher Scientific, 99.9\% purity) and spectroscopy grade benzene (OmniSolv, 99.7\% purity) were kept in Pyrex bulbs attached to a diffusion pumped gas manifold with a base pressure of $9 \times 10^{-7}$ torr, and were cleaned with three or more freeze pump thaw cycles before use. Hydrocarbon purity was confirmed by QMS.

HREEL spectra are collected immediately after hydrocarbon dosing and are normalized to their respective elastic peak position and signal intensity. The beam energy used for all spectra in this study is 3.689 eV, and scans were collected on specular with 4.5 cm\textsuperscript{-1} step size. These settings resulted in a spectral resolution of 70 cm\textsuperscript{-1}, which is broad compared to scattering studies on single crystals, but is on par with those observed for similar systems with nanoscale roughness.\textsuperscript{13} Region spectra were averaged up to 20 minutes to obtain a signal to noise of 6.7 (peak height / RMS noise). To collect annealing profiles, the sample was heated to the desired temperature for five minutes and then cooled below 170 K to record spectra. Coverage profiles were collected by iteratively exposing particles to molecules, and scanning the appropriate region and elastic peak.
Properties of Al$_2$O$_3$ / NiAl(100)

HREEL spectra were taken of an Al$_2$O$_3$ film grown in-situ on NiAl(100) (Figure 3.2). Al$_2$O$_3$ films offer insulating ordered surfaces which were utilized in previous studies with the original LK 2000 electronics.\textsuperscript{38-41} The HREELS spectra in Figure 3.2 shows three peaks at 418, 600 and 895 cm$^{-1}$ which correspond to Fusch-Kliewer phonons of alumina.\textsuperscript{42} These losses result from electron interactions with the long range electric field from the displacement of infrared-active longitudinal optical surface phonons.\textsuperscript{43} The peaks between 1300 – 1800 cm$^{-1}$ correspond to the ($\nu_3+\nu_1$), ($\nu_3+\nu_2$) and (2$\nu_3$) overtone bands.\textsuperscript{38} The alumina film used in this study is found to be 4 Å thick by comparison of the ratio of the intensity of the Al$_2$O$_3$ peak at 895 cm$^{-1}$ to the elastic peak intensity from experiment to the known film thickness from literature.\textsuperscript{44} Alternatively, comparison with AES spectra of alumina on NiAl(100) (Figure 3.3) with literature yields a film thickness of 8 Å ± 2.5 Å.\textsuperscript{45} The AES spectra for an alumina film on NiAl(100) is characterized by the O peak at 487 eV, the Ni peak at 809 eV, the Al peak at 1330 eV (Figure 3.3).\textsuperscript{46} The O/Ni peak signal intensity ratio is consistent with previous studies on ultrathin alumina films.\textsuperscript{40,45}
Figure 3.2. HREEL spectra of an Al₂O₃ film.⁴⁵

Figure 3.3. AES spectra of an alumina film on NiAl(100).
Cyclic Hydrocarbons Do Not Interact with Al$_2$O$_3$ / NiAl(100)

A background study was undertaken to determine if cyclohexane or benzene adsorbs to or reacts on the Al$_2$O$_3$ substrate used in these studies. Alumina films were exposed to cyclic hydrocarbons at cryogenic temperatures and HREEL spectra were recorded to detect any reactions occurring on the alumina. The annealing profile for the alumina film after exposure to 40 L cyclohexane at 170 K is shown in Figure 3.4. Neither the $\nu_{\text{C-H}}$ energy loss peak near 2930 cm$^{-1}$ nor the $\nu_{\text{C-O}}$ peaks near 2000 cm$^{-1}$ were observed after dosing a fresh Al$_2$O$_3$ film with 40 L cyclohexane at 170 K. This indicates that the alumina is unreactive in regards to cyclohexane. An annealing profile was completed, and no further energy loss peaks developed, indicating that cyclohexane does not adsorb to Al$_2$O$_3$ films at 170 K, and that no reabsorption occurs after warming to 300 K. The absence of CO peaks has an added importance because it indicates that the alumina film is highly uniform with few defects which would have otherwise provided CO adsorption sites.$^{47}$ Lastly, the lack of a $\nu_{\text{O-H}}$ peak indicates that the gas manifold is clean, and that any OH seen in future studies results from the dehydrogenation of cyclohexane. This study was repeated for benzene, and the results were consistent.
Figure 3.4. a. Alumina film on NiAl(100) at 300 K, b. film after cooling to 170 K, c. film after exposure to 40 L cyclohexane at 170 K, and after subsequent annealing to d. 200 K, e. 260 K and f. 300 K.
Characterization of Pt NP / Al₂O₃ / NiAl(100)

Pt NP deposition is quantified by the reduction in HREELS elastic peak signal intensity. Rough particles diffusely scatter electrons, and the elastic signal measured on specular results from the elastic scattering from the exposed alumina.\textsuperscript{13} In a typical experiment, the elastic peak intensity of the clean alumina film is on the order of several hundred thousand counts per second. After Pt deposition, the elastic peak intensity is reduced to tens of thousands of counts per second. This corresponds to an EELS peak amplitude ratio between 0.1 and 0.2, corresponding to a Pt deposition of 11-13 atoms / nm\textsuperscript{2} which forms Pt islands 1 nm to 1.25 nm in diameter.\textsuperscript{13} Pt deposition was also examined by AES after each annealing profile and a representative spectrum is shown in Figure 3.5b and c where small Pt peaks may be observed.

![Figure 3.5. AES spectra for Al₂O₃ / NiAl(100) a. before, and b. after Pt deposition. c. shows a zoomed-in region from b.](image)

Figure 3.5. AES spectra for Al₂O₃ / NiAl(100) a. before, and b. after Pt deposition. c. shows a zoomed-in region from b.
SEM images show the structure of Pt NP / Al₂O₃ / NiAl(100) and are used to determine particle size and coverage (Figure 3.6). Figure 3.6a shows oxide ordering consistent with literature¹⁹, 48-49 and Figure 3.6b and c show the roughly 2 nm Pt nanoparticles that are uniformly dispersed on the oxide film. A line scan of the image pixel intensity confirms a diameter around 2 nm (Figure 3.7).

Figure 3.6. SEM images of Pt NP / Al₂O₃ / NiAl(100) showing alumina structure and ~2 nm nanoparticles.

Figure 3.7. SEM image of Pt NP / Al₂O₃ / NiAl(100) showing alumina structure and ~2 nm nanoparticles. Contrast was enhanced using Image J software. Line scan confirms particle diameter.
CO Coverage Profile

A carbon monoxide coverage profile was undertaken to determine the relative Pt coverage on Pt NP / Al₂O₃ / NiAl(100) versus on a single crystal. After exposure to CO, a single νₕC-O peak was observed at 2040 cm⁻¹ consistent with top bonded carbon monoxide (Figure 3.9).⁵⁰ The lack of bridge-bonded CO molecules is expected based on the small size of terrace sites for Pt NPs.

Figure 3.8 shows the relative intensity of the νₕC-H peak, which differs by only 0.005 CPS between 0.1 L and 5 L exposures of CO. The saturation of Pt nanoparticles with carbon monoxide by 0.1 L of CO exposure indicates that the Pt coverage is less than complete by comparison with a Pt(111) crystal where the saturation exposure is 2 L.⁵¹ The annealing profile for alumina supported Pt nanoparticles after exposure to 5 L of CO (Figure 3.9) reveals that CO remains adsorbed to the Pt nanoparticles below 400 K. This trend is also seen in Figure 3.8. Desorption or decomposition of CO occurs by 500 K, in agreement with an alumina film coated with between 2.34 Å and 7.8 Å Pt.¹⁰

![Figure 3.8](image-url)  
Figure 3.8. Intensity of the νₜC-O peak at 2040 cm⁻¹ normalized to alumina phonon peak intensity at 1770 cm⁻¹ as a function of CO exposure for Pt / Al₂O₃ / NiAl(100).
Figure 3.9. HREELS annealing profile for Pt NP / Al₂O₃ / NiAl(100) after exposure to 5 L carbon monoxide at 166 K, and annealing to b. 200 K, c. 300 K, d. 400 K, and e. 500 K.
Hydrocarbon Adsorption on Pt NP / Al$_2$O$_3$ / NiAl(100)

Adsorption of hydrocarbons on freshly deposited Pt NPs / alumina at 177 K was accomplished by dosing a saturation amount (25 L benzene or 40 L cyclohexane) and is evidenced by the appearance of the ν$_{C-H}$ peak at 2930 cm$^{-1}$ for cyclohexane and at 3025 cm$^{-1}$ with a shoulder near 2870 cm$^{-1}$ for benzene (Figure 3.10A). The C-H peak at 2930 cm$^{-1}$ is consistent with the vibrational frequency of gas phase cyclohexane and is higher than literature values for cyclohexane on Pt(111) and (1×1) Pt{100} at 160 K.$^{28,52}$ The soft CH loss peak was not observed near 2600 cm$^{-1}$, which agrees with cyclohexane on (1×1) Pt{100} at 160 K supporting the idea that the nanoparticles have a majority of coordinately-unsaturated Pt atoms.$^{28,32}$ Figure 3.10B shows the spectra for cyclohexane or benzene on Pt NP / alumina, each annealed to 300 K for five minutes. The CH peak for cyclohexane on Pt NP remained at 2930 cm$^{-1}$ upon annealing to 300 K. This indicates that as in the (1×1) Pt{100} case, a stable C$_6$H$_9$ intermediate may form. Further studies will examine the dehydrogenation of the intermediate to benzene at temperatures over 300 K.

The shape and position of the CH peak is indicative of the type of chemisorption sites present on the sample. The ν(C-H) peak position at 3025 cm$^{-1}$ for benzene on Pt NPs is higher than that for benzene on Pt(111), and is likely from a benzene monolayer as multilayers desorb form Pt(111) below 160 K.$^{32,53-54,55}$ This is also 45 cm$^{-1}$ higher than observed for benzene adsorbed to Pt{100}(1×1),$^{56}$ but given our spectral resolution of 70 cm$^{-1}$, we have assigned the 3045 cm$^{-1}$ peak to benzene on the Pt particles. The shoulder near 2870 cm$^{-1}$ is absent in HREEL spectra of benzene on Pt(111) at 300 K.$^{57}$ The shoulder is visible in spectra for benzene on Pt{100} and on Pt NP / alumina where it is assigned to the minority population of benzene molecules which exhibit σ interactions with the Pt.$^{32,55-56}$ This interaction is in contrast to the more commonly accepted π interactions where electron density from the benzene highest occupied molecular orbital is donated
to the Pt NP’s lowest unoccupied molecular orbital. Benzene also adsorbs at hollow sites and bridge sites on Pt(111), and the difference in vibrational frequency of 25 cm$^{-1}$ between two sites could account for the width of the CH peak.
Figure 3.10. HREEL spectra for Pt NP / Al₂O₃ / NiAl(100) after exposure to a. 25 L benzene or b. 40 L cyclohexane at A. cryogenic temperatures and B. after annealing to 300 K.
Cyclohexane Coverage Profile

The adsorption of cyclohexane to the supported particles at 171 K was investigated by recording spectra after exposure to increasing amounts of cyclohexane. The spectra in Figure 3.12 show the growth of a $\nu_{\text{C-H}}$ peak at 2930 cm$^{-1}$ with increasing cyclohexane exposure. Figure 3.11 shows the increasing trend for clarity.

Figure 3.11. HREELS signal intensity at 2930 cm$^{-1}$ as a function of cyclohexane exposure to Pt NP / Al$_2$O$_3$ / NiAl(100).
Figure 3.12. HREEL spectra for Pt NP / Al₂O₃ / NiAl(100) exposed to a. 0.25 L cyclohexane, b. 0.5 L cyclohexane, c. 0.75 L cyclohexane, d. 1 L cyclohexane, e. 2 L cyclohexane, and f. 5 L cyclohexane.
Benzene Dehydrogenation

The dehydrogenation of benzene was investigated to determine the temperature at which benzene desorbs or decomposes. Figure 3.14 shows the annealing profile for Pt nanoparticles on alumina after exposure to 25 L benzene at 165 K. Decomposition or desorption of benzene is illustrated in Figure 3.13 by the decrease of the peak intensity corresponding to the benzene peak at 3045 cm\(^{-1}\). This information will later be used to distinguish between benzene and cyclohexane energy loss peaks for the supported particles, and will be compared to the observed loss in peak intensity during annealing experiments.

![Graph](image)

**Figure 3.13.** Peak intensity at 3045 cm\(^{-1}\) for annealing profile of benzene on Pt NP / Al\(_2\)O\(_3\) / NiAl(100).
Figure 3.14: Annealing profile for Pt NP / Al₂O₃ / NiAl(100) after a. exposure to 25 L benzene at 165 K, and subsequent annealing to b. 300 K, c. 350 K, d. 400 K, e. 500 K, f. 550 K, g. 600 K, and h. 700 K.
Cyclohexane Dehydrogenation

HREELS signal strength is dependent on the surface area covered by cyclohexane because HREELS is an averaging technique. As such, studies were undertaken for Pt nanoparticles exposed to 40 L cyclohexane to maximize the signal by saturating the Pt with cyclohexane. The intensity of the $\nu_{\text{C-H}}$ peak at 2930 cm$^{-1}$ in Figure 3.16 decreases with annealing temperature to reveal a smaller benzene $\nu_{\text{C-H}}$ peak at 3045 cm$^{-1}$ which becomes the majority component after annealing to 450 K. The benzene peak becomes apparent at 350 K and decreases at higher temperatures due to decomposition or desorption of benzene (Figure 3.15). The peak corresponding to benzene is not observed at 600 K, in agreement with the benzene annealing profile in Figure 3.14.

![Figure 3.15](image.png)

Figure 3.15. Peak intensity at 2930 cm$^{-1}$ and 3045 cm$^{-1}$ for annealing profile of 40 L cyclohexane on Pt NP / Al$_2$O$_3$ / NiAl(100).
Figure 3.16. Annealing profile for Pt NP / Al₂O₃ / NiAl(100) after a. exposure to 40 L cyclohexane at 165 K, and subsequent annealing to b. 300 K, c. 350 K, d. 400 K, e. 450 K, f. 500 K, g. 550 K, h. 600 K.

When considering ensemble effects contributing to cyclohexane chemistry, it is apparent that the energetics of dehydrogenation may be cyclohexane-coverage dependent. To study this, the annealing profile was undertaken for Pt nanoparticles on alumina after exposure to 1 L of cyclohexane at 167 K (Figure 3.18). The spectra in Figure 3.18 show a shift of the νC-H peak to higher frequency after annealing to 300 K, and loss of signal after annealing to 600 K. Figure 3.17
illustrates the 60% increase in the benzene peak intensity at 3045 cm\(^{-1}\) after annealing to 260 K, and the linear decrease in intensity thereafter that results from the desorption or decomposition of benzene. Interestingly, the cyclohexane peak at 2930 cm\(^{-1}\) is seen to exhibit the same changes in intensity.

Figure 3.17. Peak intensity at 3045 cm\(^{-1}\) and 2930 cm\(^{-1}\) for annealing profile of benzene on Pt NP / Al\(_2\)O\(_3\) / NiAl(100).
Figure 3.18. a. HREEL spectra for Pt NP / Al₂O₃ / NiAl(100) after exposure to 1 L of cyclohexane at 167 K and after annealing to b. 220 K, c. 260 K, d. 300 K, e. 400 K, f. 500 K, and g. 600 K.
Conclusions

These studies show that the reaction mechanism for cyclohexane dehydrogenation to benzene on supported Pt nanoparticles is similar to that on Pt\{100\}(1×1) single crystals, resulting from the large percentage of coordinately unsaturated Pt atoms on both surfaces. Here, 0.58 nm diameter cyclohexane has a high probability of interacting with the low coordination Pt atoms on the edges of the 1.25 nm diameter Pt NPs because of the relative sizes, as depicted in Figure 3.19. Our HREELS data confirms that nanoparticle surfaces are more disordered than Pt(111) single crystals, as no activating Pt–H interaction (soft $\nu_{\text{C-H}}$ mode at 2600 cm$^{-1}$) is observed for our Pt nanoparticles at low and high cyclohexane exposures below 170 K.

![Figure 3.19. Schematic showing relative size of cyclohexane (green circles) and Pt NPs (grey circles) on Al$_2$O$_3$.](image)

The dehydrogenation activity for oxide-supported Pt nanoparticles can be determined by the temperatures and C-H vibrational frequencies of reactants, intermediates, and products (Table 3.1). The dehydrogenation of cyclohexane to benzene on Pt nanoparticles confirms that nanoparticles are more reactive towards dehydrogenation than Pt\{100\}(5×20). The benzene formation temperature of 300 K for our sub-saturation studies is consistent with that on Pt(111)
and Pt\{100\}(1\times1), which indicates that our nanoparticles are at least as active for cyclohexane dehydrogenation as these single crystals.

Results show that cyclohexane dehydrogenation occurs at different temperatures for different exposures, in agreement with ensemble site studies. As mentioned previously, cyclohexane undergoes dehydrogenation with low activation energy on ensemble sites containing more Pt atoms than are required for adsorption\(^{34}\). A 40 K difference in the temperature of benzene formation was seen for the two extreme cases – a low exposure and a saturation exposure of cyclohexane. The exposure-dependent change in benzene formation temperature reflects the increased activation energy for dehydrogenation when sufficiently large sites are not available on the platinum. In addition, the benzene peak signal intensity remained lower than the cyclohexane peak signal intensity until 450 K for the saturation exposure study, and 300 K for the sub-saturation exposure study. This results from the ensemble site-blocking effect of the saturation coverage of cyclohexane. To the best of my knowledge, these studies are the first HREELS studies on cyclic hydrocarbon dehydrogenation on supported nanoparticles. This technique presents opportunities for future studies on nanoparticle size effects in dehydrogenation chemistry.
Table 3.1. Compiled HREELS data for cyclohexane dehydrogenation. Each cell represents a spectra recorded after reaching a certain step in the dehydrogenation. The annealing temperature T, and the $\nu_{\text{C-H}}$ vibrational frequencies are noted.

<table>
<thead>
<tr>
<th></th>
<th>Pt(111)</th>
<th>Pt NP / Al$_2$O$_3$ / NiAl(100)</th>
<th>Pt{$100$}{$(1\times1)$}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$H$_6$</td>
<td>$T^{57} = 300$ K 3000 cm$^{-1}$</td>
<td>$T = 300$ K 2870 cm$^{-1}$ 3045 cm$^{-1}$</td>
<td>$T^{32} = 300$ K 2870 cm$^{-1}$ 3000 cm$^{-1}$</td>
</tr>
<tr>
<td>Product formation</td>
<td>$T^{28} = 300$ K $\sim 2900$ cm$^{-1}$ 2980 cm$^{-1}$</td>
<td>$T \geq 300$ K 3045 cm$^{-1}$</td>
<td>$T^{32} &gt; 300$ K $\sim 2970$ cm$^{-1}$ 3000 cm$^{-1}$</td>
</tr>
<tr>
<td>C$_6$H$_9$ formation</td>
<td>$T^{28} = 220$–280 K 2946 cm$^{-1}$</td>
<td>$T = 170$ - 300 K 2930 cm$^{-1}$</td>
<td>$T^{32} = 220$-300 K 2950 cm$^{-1}$</td>
</tr>
<tr>
<td>C$<em>6$H$</em>{12}$ exposure</td>
<td>$T^{28} \leq 160$ K 2600 cm$^{-1}$ $\leq 2915$ cm$^{-1}$</td>
<td>$T = 170$ K 2930 cm$^{-1}$</td>
<td>$T^{32} = 110$ K 2915 cm$^{-1}$</td>
</tr>
</tbody>
</table>
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4. Activation of HOPG Supported Nanoparticles

Introduction to Graphite Supported Nanoparticles

As discussed in Chapter three, surface-sensitive experiments provide fundamental understanding of reactivity on supported nanoparticles that are vital for modern industrial catalysis. This chapter focuses on the development of catalytically active platinum particles with chemically inert HOPG (highly oriented pyrolytic graphite) supports for electron scattering spectroscopic studies. The motivation for these studies will be presented here, followed by the experimental methods elected for this work. Lastly, results will be presented for samples produced in situ and ex situ at UC Irvine, and ex situ at the University of Central Florida.

There is an interest in activating supported nanoparticles that are inherently catalytically inactive due to their physical state directly following production. Inverse micelle encapsulation, for example, can be used to grow size and shape-controlled nanoparticles in solution which remain coated by ligand molecules after deposition onto supports. In this work, we address particles that are inactive for dehydrogenation reactivity due to ligand presence, oxidation, or carbon passivation.

One of the motivations for this work was to activate platinum nanoparticles decorating titanium dioxide (titania, TiO$_2$) nanoparticles (Pt NP / TiO$_2$ NP / HOPG) because the nanoscale interface between the titania and platinum nanoparticles provides interesting electronic support effects. For comparison, the interface between bulk TiO$_2$ and bulk Pt exhibits a Shottkey barrier as shown in Figure 4.1b that prevents the sharing of electrons from TiO$_2$ to Pt.$^2$-$^3$ When both materials are nanoscale as in the Pt NP / TiO$_2$ NP system, this barrier is removed so Pt may accept electrons from TiO$_2$, resulting in a lower activation energy for many reactions and potential for use as a photocatalyst (Figure 4.1c).$^4$ However, the particles for this study must first be activated
by removal of contaminants from ex situ generation without encapsulation of the Pt by TiO$_2$ as often occurs following the strong metal-support interaction effect (SMSI).$^{4-5}$

![Figure 4.1] Electronic diagram of a. Pt – TiO$_2$ interface before contact, b. bulk materials interface after contact, and c. nanoscale materials interface after contact. $E_C$ is the conduction energy level, $E_F$ is the Fermi energy level, $E_V$ is the valence band energy. Figure adapted from references 2 and 3.

In this work, samples were prepared on HOPG by various methods and molecular interactions were monitored using HREELS. Additional techniques and sample systems are summarized in Figure 4.2. Systems of interest included HOPG supported linear arrays of titania nanoparticles with and without photodeposited Pt nanoparticle decoration,$^6$ and inverse micelle encapsulation generated Pt nanoparticles with HOPG support.$^1$ HOPG supported platinum and titania films were also investigated because the high surface coverage of maximizes HREELS and AES signal intensities for ease of observation during activation treatments.

This work focused on developing cleaning methods to remove surface oxides, contaminants, or ligands to provide a clean sample for dehydrogenation studies. Oxygen cleaning,
annealing in vacuum, and argon ion sputtering methods were investigated, and cleanliness was monitored using AES, and HREELS adsorptions studies with CO as a probe molecule for Pt. These studies reveal that in-situ cleaning by these methods cannot be utilized to produce a chemically reactive supported nanoparticle system due to passivation of particles by oxide or carbonaceous films, or by encapsulation following the SMSI effect in the case of the Pt NP / TiO$_2$ NP / HOPG system.

Figure 4.2. Schematic showing the methods used in this study to characterize HOPG supported particles and films.
Preparation of Platinum and Titania Nanoparticles and Films on HOPG

HOPG

HOPG samples were generated from 12 × 12 mm HOPG (Grade ZYB, Momentive Performance) which were manually cleaved using scotch tape. Samples were degassed at 200 °C before spectroscopic investigation or in situ particle deposition.

TiO2 NP / HOPG and TiO2 Film / HOPG

Linear arrays of uniform, ordered, and separate titania nanoparticles were fabricated on HOPG by physical vapor deposition (PVD) of Ti using an Edwards 306 Coating System following protocols described in literature.7 Ti shot was loaded in a tungsten basket which was resistively heated to around 1000 °C by an external power supply. The HOPG was degassed to 200 °C in a home-made sample holder before being held over 300 °C for Ti deposition at pressures of 1 × 10⁻⁶ torr. The deposition is undertaken at HV so that the Ti is oxidized to form TiO2 NPs. Ti deposition thickness was measured with a quartz crystal microbalance (QCM, Edwards FTM5).

HOPG supported titania films were grown by the same method used to prepare HOPG supported titania nanoparticles, except that the HOPG was held at 200 °C during Ti PVD. This lower substrate temperature limits the mobility of Ti adatoms and results in a more uniform film.

Pt NP / TiO2 NP / HOPG

Platinum nanoparticles were photodeposited onto the HOPG supported titania nanoparticles previously described. Photodeposition entailed immersing a TiO2 NP / HOPG sample in a solution of 0.25 mM Potassium tetrachloroplatinate(II) (K2PtCl4) and 0.5 mM trisodium citrate for 30 minutes under 365 nm ultraviolet irradiation.7 Ultraviolet light is used because it has energy larger than the TiO2 band gap (roughly 3.0 and 3.3 eV for rutile and anatase, respectively). Photogenerated electrons and holes at the surface of the titania participate in redox
reactions including the reduction of $\text{K}_2\text{PtCl}_4$ to metallic platinum and oxidation of trisodium citrate. This results in evenly spaced Pt particles a few nanometers in diameter that encapsulate rod like TiO$_2$ NPs. The size of these particles can be modulated by varying the photodeposition time. The small size and distribution of these Pt particles and the relatively small volume of support material make a unique architecture which has not been previously tested for catalytic behavior.

Pt NP / HOPG

Micelle encapsulated platinum nanoparticles were distributed on a HOPG support by students in the laboratory of Dr. Beatriz Roldán Cuenya at the University of Central Florida.\textsuperscript{1} The 10 nm reverse micelle encapsulation generated Pt NPs were plasma treated after deposition on HOPG to remove the surface ligands.

Pt Film / HOPG

Deposition of a Pt film of undetermined thickness on HOPG was accomplished \textit{in situ} using an electron beam evaporator (Oxford Scientific EBE-1) operated at 1.4 kV, 4.5 mA, and 10 A emission current. Deposition was verified by AES.
Experimental Methods for Sample Activation

This section will explain the complementary techniques utilized to understand sample composition and reactivity. Material deposition on HOPG was quantified using room temperature AES (2 kV, and 2 mA). Molecular bonds and phonons were monitored with HREELS (room temperature, beam energy 3.689 eV, 6 meV resolution and analyzer angles from 0° to 16° off specular). Morphology was monitored with SEM (LEXI FESEM).

Three types of activation protocols were tested including annealing, oxygen cleaning, and argon ion bombardment. For annealing studies, samples were heated in UHV to remove ambient contaminants and adsorbates, and to recrystallize particles. Samples were resistively heated to the desired annealing temperature and held there for the annealing period before being allowed to cool to 30 °C. CO was used as a probe molecule to detect the presence of Pt because it has a strong dipole scattering mode detectable in HREELS. CO was dosed onto samples using a directional doser and an exposure of $4 \times 10^{-7}$ torr for four minutes equating to 96 L. After each annealing cycle HREELS and AES spectra were recorded.

Oxygen cleaning of HOPG supported particles was accomplished by resistively annealing the sample and exposing it to oxygen through a directional doser. Then the sample was flashed to 1000 °C to remove residual oxygen. Before dosing, the gas manifold was refilled with 20 psi of O$_2$ and pumped out three times to ensure gas cleanliness.

Argon (Ar) sputtering was accomplished using a Varian ion gun operated at 1 kV and 20 mA emission current for 5-15 minutes. The sample was positioned roughly below the ion gun. The chamber was filled with $1 \times 10^{-5}$ torr of Ar, and the beam position and focusing were adjusted to ensure it was hitting the sample.
HOPG

Studies on HOPG show that in addition to being chemically inert, HOPG substrates have the advantage of providing nearly blank spectral backgrounds. Auger spectra of HOPG do display a prominent carbon peak at 260 eV (Figure 4.3). HREELS spectra of HOPG is blank except for the elastic energy loss peak and the C-H energy loss peaks at 1434 cm\(^{-1}\) and 2860 cm\(^{-1}\) which are easily removed by heating the sample to 900 °C (Figure 4.4). Additionally, no new peaks emerge when the spectra are recorded off specular, despite the expected reduction in signal intensity. The elastic peak does widen off specular by almost 6 cm\(^{-1}\). These blank spectra make HOPG an ideal substrate for spectroscopic studies because phonon or molecular energy losses are not obscured.

Figure 4.3. AES spectra for room temperature HOPG. The sole carbon peak at 260 eV leaves the remainder of the spectrum blank so that any supported material can be detected without spectral overlap.
Figure 4.4. HREELS spectra for HOPG after a flash to 900 °C provides a blank background that slopes down from the elastically scattered peak. The FWHM is denoted to the left or the elastic peak for the specular (0°) and off-specular spectra (4°).
The titania films and nanoparticles used in this study have been characterized by SEM and TEM, and readers are referred to the published work for specific details. The particles are rod-like and roughly spherical rutile particles oriented in straight lines along HOPG step edges with a mean diameter of 18 nm and a standard deviation of 8 nm. Auger Spectra of a 2 nm thick TiO$_2$ film display Ti peaks at 352 and 383 eV and an O peak at 470 eV, indicating the presence of TiO$_2$ (Figure 4.5c). Supported titania nanoparticle samples lacked these strong peaks due to the low coverage of titania (Figure 4.5a), but did show a silicon (Si) contamination by AES at 75 eV in some cases. Complementary techniques including PES and EDS would be more effective for spectroscopic studies on titania.
Figure 4.5. AES spectra for a. titanitia nanoparticles with HOPG support, b. HOPG, c. titania film with HOPG support.

HREELS spectra were recorded for HOPG with and without PVD deposited titania films or nanoparticles (Figure 4.6). The HOPG sample has a FWHM of ~ 60 cm\(^{-1}\), but after particle or film deposition the FWHM increases to ~75 cm\(^{-1}\), reflecting the increased roughness of the surface. HREELS spectra of the TiO\(_2\) film exhibit C-H energy loss peaks, but did not show the dominant rutile TiO\(_2\) peak expected at 752 cm\(^{-1}\). This may be due to the amorphous structure of the film. The this particular sample with titania particles shows strong SiO\(_2\) phonon HREELS loss peaks at 395, 805, and 1065 cm\(^{-1}\).
Figure 4.6. HREELS spectra for a. titania nanoparticles with HOPG support, b. HOPG, c. titania film with HOPG support.
HREELS spectra were collected off-specular to investigate the hysteresis of the signal and contributions from impact scattering. This is of particular interest because HREELS is typically applied to samples with flat surfaces, and it is important to understand how the signal is modified when a sample has nanoscale roughness. An example set of spectra for titania nanoparticles on HOPG is shown in Figure 4.8, and results for the elastically scattered peak’s intensity and FWHM for HOPG, TiO$_2$ NP / HOPG, and TiO$_2$ Films / HOPG are compiled in Figure 4.7. It was found that the counts behaved normally for these rough samples, being highest on specular and diminishing off specular (Figure 4.7A). The elastic peak FWHM (Figure 4.7B) increased linearly with angle for the titania film, but fell off for blank HOPG and particles, corresponding to coverage.

Figure 4.7. Behavior of the HREELS elastic peak as a function of angle for HOPG supported titania films and nanoparticles. a. elastic peak signal intensity, and b. FWHM.
Figure 4.8. HREEL spectra for room temperature titania nanoparticles on HOPG showing change in peak intensities off specular.
The TiO₂ NPs were annealed at 400 °C and oxygen cleaned by exposure to 100 L O₂ at 400 °C to crystalize the NPs and remove Si contamination (Figure 4.9). These spectra were recorded 8° off-specular to enhance the energy loss peaks at 710, 1425, and 2860 cm⁻¹. The removal of Si was not evident in the spectra.

Figure 4.9. HREELS spectra for TiO₂ NP / HOPG recorded 8° off specular a. as-prepared, b. after heating to 400 °C, and c. after oxygen cleaning at 400 °C.
Pt NP / TiO₂ NP / HOPG

After Pt photodeposition on the titania particles, a large Si signal is seen in both the HREELS (Figure 4.10a) and AES spectra. The sample was exposed to 100 L of CO at room temperature to determine if Pt was present in a large enough coverages that C-O energy loss peaks from adsorbed CO are evident in the HREEL spectra (Figure 4.10b). The absence of the CO energy loss peaks near 2000 cm⁻¹ indicates that the Pt coverage is below the limit of detectability, or the Pt is passivated. The sample was sputtered with Ar plasma for five minutes (Figure 4.10c), and then heated to 1000 °C to crystalize the NPs, but again, the C-O energy loss peak was not observed after exposure of the sample to 100 L of CO (Figure 4.10d).

![Figure 4.10. HREELS spectra for a. As-prepared Pt / TiO₂ NP / HOPG, b. after exposure to 100 L CO, c. after 5 min of Ar plasma sputtering, and d. after heating to 1000 °C and exposure to 100 L of CO at room temperature.](image-url)
Pt NP / HOPG

Micelle generated Pt NP / HOPG were investigated for potential methods to activate the Pt for catalytic studies. The particles are estimated to be roughly 10 nm in diameter based on AFM images taken after ligand removal by plasma treatment (Figure 4.11).

Figure 4.11. AFM images provided by Dr. Beatriz Roldán Cuenya at the University of Central Florida. These particles have been pre-treated to remove the ligand.

HREELS spectra were recorded before and after exposure of these particles to 50 L of CO (Figure 4.13a,b), and the absence of the CO energy loss confirmed passivation of the platinum. The sample was annealed in UHV up to 500 °C to reduce Pt and desorb adventitious carbon (Figure 4.12c). However, the Pt remained oxidized after 500 °C, and the removal of carbon cannot be confirmed due to the signal from the graphite support.
Figure 4.12. AES spectra for annealing profile of HOPG-supported micelle generated Pt nanoparticles after exposure to 50 L CO. Annealing temperatures include a. 150 °C, b. 200 °C, c. 300 °C, d. 400 °C, and e. 500 °C.

The sample was cleaned with cycles of oxygen treatment ($1 \times 10^{-6}$ torr) at elevated temperatures (400 °C to 550 °C) and annealed in UHV (500 °C to 600 °C). After three cycles, the
sample was exposed to 50 L of CO and HREEL spectra were recorded, but the CO energy loss peak was not observed, perhaps due to surface contamination (Figure 4.13d). After heating to 500 °C, the elastically scattered peak intensity dropped to several thousand counts per second, opposed to several hundred thousand. This may be due to diffuse scattering of the electron beam from large Pt particles formed during the cleaning process (Figure 4.14c).

Figure 4.13. HREEL spectra for reverse micelle encapsulation generated Pt NP / HOPG a. as-prepared, b. after exposure to 50 L CO, c. after heating to 500 °C, d. after re-heating to 500 °C and subsequent exposure to 50 L CO upon cooling, and e. after three oxygen cleaning cycles and subsequent exposure to CO at room temperature.

Pt4f and O1s XPS spectra and SEM images were collected after the cleaning protocol, showing a clear reduction of surface oxide to metallic platinum and progressive sintering of the nanoparticles (Figure 4.14). It was determined that the sintering of Pt NPs on HOPG by 600 °C
together with the apparent passivation of the particles, precludes HREELS dehydrogenation studies on samples generated by inverse micelle encapsulation on HOPG.

Figure 4.14. SEM of Pt/HOPG heated to (a) 400 °C and (b) 600 °C (during oxygen cleaning).
Pt Film / HOPG

Pt films were formed in situ on HOPG to determine the sensitivity of the HREELS signal to CO on low coverages of Pt / HOPG. HREEL spectra of a Pt film after exposure to 100 L of CO (Figure 4.15a) show diffuse scattering exemplified by the low signal intensities, likely caused by nanoscale roughness of the Pt film deposited by electron beam evaporation as shown by STM.10

The Pt film was annealed and adsorbed molecules and film morphology were monitored as a function of temperature (Figure 4.15). The CH stretch energy losses are removed at 300 °C, the bridge bonded CO peak at 400 °C and the top bonded CO by 600 °C. This study confirms that the C-H contamination may be removed by heating to low temperatures which do not significantly change the binding properties of the Pt. This is particularly important for cyclohexane reactivity because it is desirable that the CH signal reflect only hydrogens from cyclohexane. This study on a Pt film also confirms that detectable CO signals are possible with a high coverage of Pt on HOPG.

The Pt film was then annealed to 800 °C for 10 minutes to flatten the surface to recover the angular dependence of dipole and impact scattering. Annealing flattened the surface as evidenced by a 100 fold increase in HREELS elastic peak signal intensity, but seems to have dirtied the surface because successive spectra lacked loss peaks after CO dosing. Oxygen cleaning and sputtering were not able to restore CO adsorption.

SEM data (Figure 4.16a) reveal Pt platelets, some of which have apparent Pt(111) structure. XPS spectra revealed an oxide-like species in the Pt4f spectra, however no O1s signal was observed. These findings are consistent with the formation of a passivating layer such as a carbide film, but the chemical composition was not revealed by XPS.
Figure 4.15. HREEL spectra for a. Pt Film / HOPG after exposure to 100 L CO, b. Pt Film / HOPG after heating to 300 °C, c. Pt Film / HOPG after annealing for five minutes at 400 °C, and d. Pt Film / HOPG after annealing for five minutes at 600 °C.
Figure 4.16. a. XPS spectra of thick Pt film on HOPG after annealing to 800 °C, oxygen cleaning and sputtering, shows an oxide-like species. b. SEM image shows islands between up to 100 nm in diameter.

Dendritic Pt films were also grown by PVD (Figure 4.17). Initial HREEL spectra showed a small CO adsorption, but CO adsorption was not restored after cleaning steps, in agreement with passivation of the in situ Pt film / HOPG. The sample was heated to 800 °C, oxygen cleaned (120 L O₂ at 700 °C), flashed to 900 °C, and exposed to 100 L CO. This process was repeated without adding additional CO, then the sample was oxygen cleaned (360 L O₂ at 700 °C), annealed for 30 minutes at 530 °C, and exposed to 120 L CO. Then the sample was oxygen cleaned (360 L O₂ at 700 °C), annealed for 30 minutes at 530 °C, and exposed to 120 L CO. The sample was then sputtered for 15 minutes, flashed to 500 °C, and exposed to 120 L CO. Next, the sample was oxygen cleaned (500 L O₂ at 400 °C), annealed for 30 minutes at 550 °C, flashed to 900 °C, and exposed to 120 L CO. Lastly, the sample was sputtered for 20 minutes, oxygen cleaned (1200 L O₂ at 400 °C), annealed 30 minutes at 550 °C, and exposed to 120 L CO. SEM images (Figure 4.17b) show significant disruption of the Pt film resulting from this cleaning protocol.
Figure 4.17. SEM image of PVD Pt film on HOPG a. as-prepared, and b. after heating to 800 °C and Ar plasma treatment.
Conclusions on Reactivity of HOPG Supported Platinum and Titania

These studies focused on activating HOPG supported platinum and titania films and nanoparticles using oxygen cleaning, annealing, or ion sputtering. In some cases these cleaning methods resulted in particle morphology changes. The inertness of these particles to CO adsorption after heating in UHV indicates that a permanent oxide or carbide species is likely present on the Pt surface, making these particles inactive for dehydrogenation chemistry. It was generally found that heating of HOPG supported particles and films removed C-H stretching modes in HREELS spectra, but did not restore reactivity with respect to CO. Further, it was found that cleaning processes could not remove silicon contamination from samples grown by PVD using these methods. Platinum particles were shown to be reactive for CO adsorption if deposited in situ as in the studies described in Chapter three.
References


5. Liquid Microjet Photoelectron Spectroscopy (LJ-PES)

LJ-PES Introduction

Although aqueous solution chemistry is relatively well understood for bulk solution, the behavior of molecules adjacent to the liquid-vapor interface varies significantly from that in bulk solution. The anomalous chemistry of interfacial nitrates and ions contributes to reactivity at the surface of aqueous atmospheric aerosols, and thus impacts environmental reactions and air quality. Interfacial aqueous molecular interactions have been examined using sum frequency generation nonlinear optical spectroscopy (SFG), and molecular dynamics (MD) simulations, respectively. SFG is limited by a static (and sometimes complicated) probe depth, and MD simulations require experimental validation to ensure that force fields correctly reflect known chemistry. LJ-PES studies provide experimental confirmation of the relative density of solutes as a function of depth into solution from the photoelectron spectra peak intensities. Additionally, shifts in the elementally-specific photoelectron binding energy indicate molecular interactions, as will be discussed below.

LJ-PES couples a fast flowing aqueous microjet of sample solution with synchrotron-based X-ray photoelectron spectroscopy (PES) to probe the chemistry of solutes near and below the liquid water–vapor interface. PES was developed in the 1960s by Kai Siegbahn as a chemical analysis tool using monoenergetic X-ray irradiation to eject photoelectrons from surfaces in UHV following from the photoelectric effect. Analysis of photoelectron kinetic energies for core level photoelectrons identifies and quantifies elements or chemical species on surfaces. The technique was originally termed electron spectroscopy for chemical analysis (ESCA), but is commonly referred to as photoelectron spectroscopy (PES) or X-ray photoelectron spectroscopy (XPS) to differentiate the technique from Auger electron spectroscopy (AES). Siegbahn also pioneered the
first PES studies on liquids including low vapor pressure organics like ethylene glycol. For his work on PES, Siegbahn received the Nobel Prize in chemistry in 1981.8

In 1989, Manfred Faubel developed a laminar liquid jet driven by gas pressure in a solution reservoir that has been well suited for LJ-PES studies.9-10 This liquid jet has a laminar flow region of several millimeters that is constantly renewed to circumvent beam damage that has been observed for PES studies on static water droplets.11 The thin jet allows for investigation of liquid samples in vacuum, which is required for PES, by minimizing the region of gas surrounding the jet. In 2004 Richard Saykally adapted LJ for X-ray adsorption spectroscopy studies on beamline 9.3.2. at the ALS to take advantage of the highly-brilliant monochromatic photon source.12 Later, the Hemminger laboratory studied an aqueous KF microjet on beamline 11.0.2. at the ALS, but further experiments were prohibited due to instrumental constraints.13 In 2008, David Starr completed a successful droplet train study on the external ambient pressure endstation at beamline 11.0.2 at the ALS.14 In 2009, Bernd Winter constructed an LJ-PES setup at BESSY II at the Helmholtz center for Materials and Energy.6 Here, the liquid jet technology was updated by Faubel and his company Microliquids GmbH to use a pulse-dampened dual piston HPLC pump to drive the jet solution. Several studies were completed at BESSY in collaboration with Winter’s team including acid2-3,15 and base16 dissociation studies, and carbon dioxide uptake experiments.17 In 2013, the Swiss light source constructed a liquid jet with the ability to operate at pressures up to 15 torr.18

AP-PES was previously adapted to beamline 11.0.2 at the ALS synchrotron facility at LBNL and has characterized the distribution of ions in saturated solutions from deliquesced ionic single crystals.5 Previous ambient pressure PES studies on deliquesced solutions on KI single crystals show an excellent agreement between PES depth profile results and MD simulations.11
This tool bridges the gap between UHV used in traditional surface analytical techniques, and moist conditions. However, this experimental set up has several limitations for the study of aqueous solutions including beam damage on the stagnant solution, restricted concentration ranges, and restricted temperatures.

This work presents the design of an AP LJ-PES instrument for ALS beamline 11.0.2 that circumvents the issues in the deliquesced crystal experiments. Specifically, the liquid microjet has a dynamic surface that circumvents charging and beam damage, and possess a laminar flow region which has been claimed to be in equilibrium with its gas phase.\textsuperscript{19,20} The ALS AP LJ-PES instrument is distinct from the LJ instruments at BESSY,\textsuperscript{21} SLS,\textsuperscript{18} and MAX-Lab\textsuperscript{22} because the chamber is constructed from $\mu$-metal, allowing for studies of photoelectrons with kinetic energies as low as 40 eV with only mild re-optimization of the differentially pumped Phobios 150 electron energy analyzer. The chamber was designed to run experiments in the 1-5 torr pressure range, although high vacuum studies would be possible with a liquid nitrogen-cooled trap to collect the jet solution (as is the case at BESSY). This enables investigation of both gas and liquid phase molecules, and also permits studies of solutions with high vapor pressures. One of the long term goals is to run experiments under full equilibrium conditions so that the solution trap, jet and vapor equilibrate in the absence of pumping. This design may also accommodate gas uptake experiments.

Construction of the AP LJ-PES chamber began in 2011, and the first successful data was gathered in January 2012.\textsuperscript{23} The LJ chamber is mounted on the external AP-PES endstation at beamline 11.0.2 that was developed for the study of humid systems, and in particular has been used for droplet train studies.\textsuperscript{14} Many of the design choices for the ALS AP LJ-PES set up stem from the successes of the droplet train studies. In particular, the designs for the LJ chamber and
the liquid collection configuration are reflective of the droplet train equipment, and will be described in detail in the experimental section.

The ALS AP LJ-PES set up is particularly suited for the investigation of solutes adjacent the liquid-vapor interface as a function of relative depth. In traditional lab-based PES, the probe depth can be altered by varying the sample geometry, but in synchrotron based PES the probe depth is altered by variation of the incident photon energy, as will be described later in this chapter. These LJ-PES studies reveal fundamental information about solubility and solvation, ionic and molecular interactions, protonation, and the relative density of solutes as a function of depth into solution.

Data was gathered at Synchrotron facilities at BESSY in Berlin, Germany, and at the ALS at LLNL in Berkeley, CA. Results from the two facilities have been compared for an aqueous acetonitrile system and have been found to be consistent, and are discussed shortly later in this chapter. Studies were also completed to investigate the salt effects of KI or NaCl on the behavior of interfacial aqueous acetonitrile or propionitrile that show a salting in of acetonitrile by KI, and a salting out of propionitrile by KI and NaCl. LJ-PES studies also found that lithium cations are present at the interface of aqueous solution, contrary to the known behavior of cations like sodium that are repelled from the interface. Several additional studies will be presented in detail later in this thesis to highlight the interfacial chemistry of aqueous organics, bases, and salts.

Chapter six describes studies on aqueous ammonia completed at BESSY. Here, the deprotonation of ammonia at the aqueous interface is found to be different from that in the bulk of solution, and is dependent on solution pH. At low pH ammonium is depleted at the interface relative to bulk solution. The effects of counter ions required for pH selection are also discussed.
Chapter seven discusses the interfacial distribution of ions in aqueous magnesium sulfate or chloride solutions.\textsuperscript{29} Results are comparable to MD simulations showing that magnesium is drawn to the bulk by sulfate,\textsuperscript{30} and the distribution of ions in magnesium chloride in solution is similar to that for sodium chloride.\textsuperscript{31-33} These results indicate that ion pairing has a strong effect on the distribution of magnesium near the interface.

Chapter eight presents studies on ternary solutions of aqueous ethanol or ethylene glycol with NaCl or MgCl\textsubscript{2} (aq) that discern the distribution of ions with and without added organics.\textsuperscript{34} Results are compared with previous deliquescence studies where the presence of an organic (\textit{e.g.} butanol, acetone or isopropanol) suppresses the surface enhancement of an anion (\textit{e.g.} iodide from KI).\textsuperscript{35-36} In ALS AP LJ-PES studies, the addition of ethanol greatly changed the solvation of Mg\textsuperscript{2+} (aq), as exemplified by the 0.2 eV increase in binding energy of the Mg2s peak. This effect was not observed for NaCl (aq) where ion-ion interactions are stronger, and solvation is weaker, relative to MgCl\textsubscript{2} (aq). These studies show that the dication behaves differently in the presence of organics than previously observed for monovalent cations.
LJ-PES Technique Overview

Linearly polarized soft X-rays are generated when a beam of electrons in the synchrotron is accelerated by an electromagnet so that its trajectory is bent. This results in highly brilliant, monochromatic synchrotron radiation that can be focused to provide large photon fluxes. This light illuminates the aqueous jet with energies sufficient to ionize atoms and eject photoelectrons from atomic core orbitals following the equation:

\[ h\nu = BE + KE + \phi \]

- \( h\nu \) = X-ray photon energy (eV)
- \( BE \) = binding energy of the photoelectrons (eV)
- \( KE \) = kinetic energy of the ejected (eV)
- \( \phi \) = spectrometer work function (eV)

The liquid microjet is formed by injecting a sample at a constant pressure using an HPLC pump into vacuum through a temperature-controlled feedthrough with a thin quartz capillary at the end. The microjet sample is 24 microns in diameter with a flow rate of up to 10 mL/min. Rapid renewal of gas in the region surrounding the jet ensures that the solution is in thermodynamic equilibrium with the gas phase, and prevents sample charging. However, gaseous molecules surrounding the jet attenuate X-rays and photoelectrons through adsorption and inelastic scattering, respectively. To minimize attenuation of the photoelectrons ejected from the microjet, a micron-sized aperture at the detection angle separates the experimental chamber from differentially pumped electrostatic re-focusing lenses. This equipment refocuses the electrons, and reduces the pressure by use of differential pumping before focusing the electrons into a hemispherical electron energy analyzer that detects photoelectron current as a function of photoelectron kinetic energy by variation of the potential between two hemispherical metal plates.
Figure 5.1. Schematic of LJ-PES experimental technique. Synchrotron X-rays illuminate the liquid jet to produce core-level photoelectrons which are detected by differentially pumped electron energy analyzer.
Depth Profiling

Photoelectron attenuation by inelastic scattering in solution, together with the variable photon energy of synchrotron radiation, enable measurements that selectively probe the interface of solution or deeper into the bulk of solution. As depicted in Figure 5.2, higher energy photons can excite higher energy photoelectrons which have a larger probability of escaping from deeper into solution without undergoing inelastic scattering. This probability falls off as

\[ I = I_0 e^{-\frac{z}{\lambda \cos \theta}} \]

*I* = Final number of photoelectrons which do not undergo inelastic scattering

*I*₀ = Initial number of photoelectrons generated

*z* = depth into solution

*λ* = material and electron energy dependent term

*θ* = angle to surface normal

Thus, photoelectrons detected with low kinetic energies (about 100 eV) have low electron attenuation lengths and must originate in the near-surface region.³⁸ Photoelectrons generated in the bulk with low kinetic energies are not detected due to inelastic scattering. Photoelectrons detected with high kinetic energies (up to 900 eV) originate both at the near-surface and in the bulk, and the signal results predominantly from electrons from the bulk which is more voluminous than the interfacial region. Thus, photoelectrons with kinetic energy greater than or equal to 600 eV will be referred to as photoelectrons from the bulk of solution and those with kinetic energy less than or equal to 200 eV will be denoted as surface photoelectrons. It is important to note that measurements for 600 eV photoelectrons integrate signal from both the surface and bulk, and it is not trivial to separate the individual contributions to the total signal. Despite this, the validity of LJ-PES bulk measurements are confirmed by good agreement with known bulk chemistry.²
Figure 5.2. Illustration of tunable x-ray energies for depth studies in aqueous solution using LJ-XPS. Photoelectrons which are not attenuated by scattering are detected by the hemispherical electron energy analyzer.

The precise probe depth for any given photoelectron kinetic energy is a topic of current research, and will likely be elucidated through a combination of MD simulation and detection angle dependent liquid jet studies. However, it is likely that no universal curve for the probe depth depending on photoelectron kinetic energy exists for aqueous solutions as solute composition and concentration impact the trajectory of photoelectrons. Two liquid microjet studies have currently examined the relationship between IMFP and photoelectron kinetic energy.
Data Analysis

Photoelectron spectra may be normalized to account for experimental factors including electron ring current, experiment geometry, X-ray attenuation by gasses, atomic ionization cross sections, β-factors, and photon flux. Flux is measured during each beam time using a photodiode (OPTO Diode Corp., REV X2, AXUV100G, $650.00) with ceramic holder (OPTO Diode Corp., REV X2 AXUV100CS, $52.00). The flux calculation method is overviewed in the Appendix, and a representative photon flux curve is shown in Figure A.23. If X-rays are severely attenuated by gaseous molecules, the vapor phase can be suppressed by cooling the liquid jet to reduce the amount of gaseous molecules adjacent the analyzer. The atomic ionization cross sections and β-factors are also estimates, as solution phase interactions and experimental geometry are expected to alter these values. Recent LJ-PES studies highlight slight discrepancies in atomic subshell photoionization cross sections at various detection angles and between atomic anisotropy factors (β) and those determined for aqueous solutions. These small differences are a topic of current research and may be applied to findings retrospectively. However, past experience and current results confirm that the normalization method described here provides results that are in good agreement with literature and MD simulations.

Measurements taken at the magic angle (photoelectron detection at 54.7 degrees from the X-ray polarization), are assumed to be largely independent of the β factor, and thus peak areas can be directly compared. Here, peak area ratios of same-symmetry orbitals quantify relative concentrations. Care is taken when describing a ratio of heterogeneous atomic orbitals which can be understood as relative concentration measurements because of the different orbital symmetries involved. For spectra recorded away from the magic angle, peak area ratios of dissimilar orbitals provide relative concentration measurements which are in agreement with literature.
PE peaks are fit using CASA-XPS software (CASA Software LTD.). Binding energies are normalized to the water oxygen 1s (O1s) photoelectron peak position at 538.1 eV for bulk spectra, and to the water 1b1 valance peak at 11.16 eV for surface spectra. This normalization does not account for binding energy shifts in the oxygen spectra resulting from ionic interactions or photoelectron perturbation by ionic fields in solution.

Photoelectron spectra peaks are fit with Gaussian curves after subtracting Shirley backgrounds. Duplex d or p orbital peaks resulting from spin-orbit coupling are constrained so that the peak area ratios satisfy those expected by quantum mechanics, and the FWHMs are set to be equal because the analyzer resolution is constant for peaks close in energy. Gas phase FWHMs for liquid spectra are constrained within 0.1 eV of the measured values for the gaseous molecule, and the splitting between two gas phase peaks are also constrained (e.g. O1s (g) splitting between water and ethanol is 1.16 eV). The gaseous molecular spectra is recorded by translating the jet away from the analyzer aperture until only the gas phase signal is observed. Solution phase peak areas are constrained stoichiometrically for each molecule when occurring in the same spectra (e.g. C1s peaks for methyl and cyano carbons in acetonitrile are 1:1). When liquid phase spectral peaks overlap, binding energy and FWHM constraints are drawn from spectra of standard solutions containing only one component.

Integrated peak areas quantify the relative concentration of species at the surface or in the bulk of solution, and relative photoelectron binding energies (peak positions) can differentiate between chemical species. This method has consistently produced bulk measurements in agreement with literature, and can also reveal interfacial information.
Experimental Set-up at BESSY

The LJ-PES experiment at BESSY in Berlin, Germany was designed by Dr. Bernd Winter using liquid microjet technology developed by Manfred Faubel. This experimental set-up has been described, and will be overviewed here. Light from the U41 PGM undulator beamline passes through a differentially pumped region before entering the experimental chamber which is held around $3 \times 10^{-5}$ torr by two liquid nitrogen traps and a large turbopump. The light is focused to $23 \times 12$ µm$^2$ to illuminate the liquid microjet which is held at 5 °C. Photoelectrons generated within the jet travel through a 0.1 mm copper aperture into a differentially pumped hemispherical electron energy analyzer which is positioned at 54.7° with respect to the polarization of the photons. A Helmholtz coil encircles the entire experimental endstation to counter stray electromagnetic fields that would otherwise perturb low energy electrons, and alter the experimental results.
Design and Construction of ALS LJ-PES Chamber

The ALS LJ-PES chamber (Figure 5.3) is attached to the 11.0.2 external ambient pressure photoemission spectroscopy (APPES) endstation which includes a Phobios 150 electron energy analyzer from Specs with custom three-stage differential pumping and electron refocusing lenses.\textsuperscript{14} This configuration allows an approximately eight order of magnitude pressure differential between the LJ chamber and the analyzer. Subsequent to the development of the endstation, this analyzer has become commercially available.

Photons at beamline 11.0.2 are generated by an elliptically polarizing undulator between 75 to 2150 eV (when the ALS energy is 1.9 GeV).\textsuperscript{37} These experiments utilize the first and third harmonics of the undulator. The optics along the beamline are covered elsewhere, and only those vital to this experiment will be mentioned. The grating in the monochrometer can be alternated between 150 and 1200 lines per millimeter for increased photon flux below 400 eV, or for stable flux at higher energies, respectively. The resulting calculated value for the photon energy resolution is 150-540 meV between photon energies of 253-1135 eV. Kirkpatrick-Baez (KB) mirrors form the exit slits and the vertical and horizontal settings focused the beam to $60 \times 50 \, \mu m^2$ to selectively illuminate the jet, and not the surrounding gas. Light enters the endstation through a 100 nm thick silicon nitride window that preserves vacuum in the beamline. Spectra are recorded at 20 eV pass energy with 0.1 ms dwell time and 0.05 eV per point.

Synchrotron X-rays from beam line 11.0.2 illuminate the 6 °C liquid jet with the light polarization at 20 degrees with respect to the angle of detection. The chamber pressure is maintained around 1 torr using a dry pump and a temperature-controlled cold trap. The design of the chamber and experimental components will be described below.
LJ-PES experiments require the detection of low energy electrons which are susceptible to stray electromagnetic fields. To minimize these effects, a custom μ-metal chamber was manufactured by VG Scienta (6301001-4) for $5,283.90 based on schematics for the droplet train chamber provided by Dr. Hendrik Bluhm. VG Scienta was selected as the vendor for this chamber because of their long history with manufacture of quality μ-metal components. Several modifications were made to the design from Dr. Bluhm including lengthening the chamber to optimize the electromagnetic shielding provided by the μ-metal, and lengthening some ports to attach rotatable flanges. The chamber design parameters will be discussed here and the final design schematics may be found in the Appendix (Figure A.17 - Figure A.22). The length of the chamber was determined by setting the distance from the 6” viewport door to the liquid jet to be at least as far as the diameter of the opening of the 6” viewport door (the penetration depth of magnetic fields through a hole in μ-metal equals the diameter of the opening). The nonmagnetic 304 stainless steel flanges were welded to the chamber after treating the μ-metal with high temperature
annealing to strengthen its magnetic permeability, and the chamber was UHV cleaned and helium leak checked to $7.5 \times 10^{-11}$ torr.

A stationary 8” flange is used to attach the chamber to the end station using either a copper or Viton gasket with bolts or threaded rods with nuts. More bolts are recommended for use with the copper gasket, but it is not possible to use all bolt holes due to steric hindrance from the ports on the chamber. The chamber fits with the 8” flange centered on the 0.1-0.3 mm foil aperture (Beam Dynamics, type 11.0 copper skimmer with gold coating, $1170.00) that separates the chamber from the 1st stage of the analyzer. The port used to introduce X-rays into the chamber is angled down 3 degrees with respect to horizontal and forms a 70 degree angle with the axis of the analyzer. This configuration allows the X-ray port to be attached using M6 threaded rods and 11mm nuts to the X-ray source which is a thin tube with a silicon nitride window at the end that separates the beam line UHV from the atmosphere inside the LJ chamber. The remaining 2-3/4” flanges from the top and going clockwise are used to attach the manipulator for the jet, two viewports, the pumping lines, and the trap with chopper, respectively. Two 1-1/3” CF flanges provide room for a viewport used for photodiode alignment, and the thermocouple pressure reader which is oriented horizontally. The front of the chamber is a 6” M8 tapped flange to which a MDC QD-600-VP-CH viewport door is attached. The knob on this door has jammed on occasion due to corrosion from salt and moisture exposure, and the threaded rod used to attach the knob may need to be re-threaded at some point.

After considering a home-made option, it was decided to order a pre-manufactured liquid jet assembly to ensure a functioning and stable liquid microjet. A liquid microjet assembly was purchased from Microliquids GmbH for 32500 Euros (about $46,367.75), including the jet, XYZ manipulator, Rheodyne sample injection valve (9725-999), Peek Watrex P102 HPLC pump, and
some associated fittings and tubing. A second Peek Watrex P102 HPLC pump was later purchased from Microliquids for $4,147.35 to ensure one working pump during beam time in the case of mechanical failure. The XYZ manipulator was re-designed to fit the height of the chamber and to reorient one of the linear motion drives to provide clearance for an additional port on the LJ µ-metal chamber. The length of the jet was set so that the tip of the quartz capillary reaches 114.8 mm from the knife edge of the 2-3/4” CF flange on the top of the LJ chamber to the center of the chamber when the manipulator is positioned in the middle of its linear motion range. This was done so that the end of the capillary is at the same level as the analyzer aperture when the manipulator bellows are halfway compressed. The jet and manipulator were mounted to the top flange on the LJ chamber, and an Accel 500LT cooling/heating recirculating chiller ($3,900.00 from Thermo Electron Corporation) filled with 50:50 ethylene glycol:water was attached to the temperature control coaxial feedthrough on the jet. This ethylene glycol-based chiller was selected because the temperature is variable from -25°C to 80°C. In an equilibrium experiment where the sample is also used in the cold trap, this chiller could maintain both the jet and the temperature controlled cold trap (discussed later) at the same temperature.

The LJ-PES chamber is evacuated using an Alcatel Adixen ACP 15G dry pump with a base pressure of $2.2 \times 10^{-2}$ torr. This pump was chosen because dry pumps are required on ALS equipment to prevent hydrocarbon contamination from oil-based mechanical pumps. In addition, the ACP 15G can be used to pump water vapor using a purge valve to introduce a flow of air or nitrogen to help prevent water condensation inside the pump. The purge option limits the base pressure to $7.5 \times 10^{-2}$ torr. Experiments are run with continuous pumping, resulting in approximately 1 torr of water vapor in the LJ chamber from the temperature controlled catch basin and microjet. Pressure is measured using a thermocouple gauge attached to the LJ chamber, and
one attached to the pump. A combined thermocouple and ion gauge (Brooks Automation, Granville-Phillips 329 Micro-ion plus gauge with 1-1/3” CF, $1,394.00) was also purchased, but was not used due to problems with pressure calibration. A Baratron pressure gauge may give an accurate pressure reading for future studies.

The pressure in the experimental chamber is regulated by a variable temperature cold trap at the base of the chamber which also functions to contain the output solution from the jet. This custom copper trap was manufactured by the Machine shop at UCI by silver soldering a copper tube around a closed stainless steel cylinder with a KF 40 or KF 25 flange on the top and bottom, respectively. A full copper version and a glass version were also produced, but have not been utilized. For experiments, the trap is filled with 40 wt % NaCl solution to prevent freezing of the microjet upon impact of the jet on the cooled solution, and it is cooled to 10 °C using an ethanol chiller provided by beamline 11.0.2. It is useful to boil the 40 wt % NaCl solution before use to ensure saturation. A valve and a home-made “chopper” are added between the chamber and the temperature controlled trap to isolate dangerous samples during chamber venting and clean up, and to break ice-crystals which sometimes grow up from the trap, respectively. The “chopper” consists of a 1-1/3” CF rotation feedthrough with a sickle-shaped metal rod attached inside the chamber which sweeps out a path to knock over ice crystals. A gate valve (VAT, 01032-UE01-0002) has been used as the isolation valve, but due to a leak and immobility from corrosion, it was replaced with a stainless steel ball valve (Kurt J. Lesker, BV-150QF40-S, $616.50). The ball valve affords corrosion resistance and is simple to disassemble for cleaning after each beam time.

The jet is visualized using a CMOS color USB camera (Edmond Optics, EO-5012C ½” NT59-668, $945.00) with a zoom video lens (Edmond Optics, VZM 450i NT54-671, $895.50) and a laptop computer. The camera and lens are secured to a chamber viewport using a custom
aluminum mounting rod. These tools are useful for telling if the jet is running straight down into the trap. If the jet runs at an angle, the quartz capillary can be sonicated in water to remove any blockages.

All components were assembled at UC Irvine for testing before transportation via U-Haul truck to the staging area in building 7 at LBNL which is adjacent to the ALS in building 6. The liquid jet chamber must be assembled on the external ambient pressure end station at beamline 11.0.2 for each beamtime (Figure 5.4), and disassembled and washed afterwards. The outside of flanges for the pumping lines are marked with permanent marker before dismantlement for ease of alignment during re-assembly. The pumping lines have been assembled so that the chamber and the first stage of the analyzer can be pumped independently or simultaneously. This is important for venting and pumping from atmosphere because pumping is not efficient through the micron-sized aperture connecting these two regions. All chamber components are rinsed into the appropriate waste, then washed with tap water, Milli-Q water (18.2 MΩ), then dried with ethanol and covered with aluminum foil. It is advisable to pump the mechanically-formed bellow pumping lines for several hours before storage as they retain water, increasing pump-down time at a subsequent beam time.
Figure 5.4. Photographs of liquid jet chamber.
Experimental Methods

Solutions are prepared using standard pyrex glassware that is washed with soap and triple rinsed with MilliQ water (18.2 MΩ), and materials are massed using an analytical scale. MilliQ water is used because it contains few contaminant ions. Solutions are filtered using 60 mL Luer-Loc syringes and 0.45 μm polyethersulfone membrane sterile syringe filters (part numbers BD309653 and 28145-505 from VWR), and are degassed by sonication before loading in the sample injection loop to prevent bubbles. Small bubbles are compressed when flowing through the jet, but larger bubbles can momentarily cause the jet to stop flowing into the chamber and usually leads to freezing of the jet. The jet may be restarted by increasing the jet temperature to melt the ice, or by tapping to dislodge the ice, but can also require immediate venting of the chamber.

Samples can be pushed or pulled into the clear PFA sample injection loop through the injection valve using a syringe (Figure 5.5). During sample loading, the valve connects the flow of the mobile phase from the HPLC pump directly to the inlet for the microjet feedthrough. The sample reservoir or syringe is used to fill the loop until excess overflows out the waste port. Once the valve is switched to inject the solution, the mobile phase is directed into one end of the sample loop to push the sample solution out to the microjet feedthrough. Depending on the length of tubing between the valve and the chamber, it can take up for two minutes for the sample solution to enter the chamber.
The chemical properties of desired samples are considered before running through the jet in the chamber. Viscous samples like ethylene glycol may require a larger in-line filter, or larger diameter quartz microjet capillary (~ 28 µm). It is always best to flow new samples through the jet in the hood to ensure the pump pressure is stable. Samples with higher vapor pressures (e.g. acetonitrile) may be run to higher concentration at the ALS because the differential pumping before the analyzer is more efficient than at BESSY.
Chemicals used in LJ-PES experiments include:

- acetonitrile (Sigma, ≥ 99.9% purity)
- ammonium chloride crystals (Sigma Aldrich, 99.5 % purity)
- ammonium hydroxide solution (Sigma Aldrich, 28 % in water)
- ammonium iodide (Sigma Aldrich, 99 % purity)
- ethanol (Sigma, > 99.5% purity)
- ethylene glycol (Sigma, > 99.5% purity)
- hydrochloric acid (Sigma, 24.5 – 26.0% purity) and (Sigma Aldrich, 37 % in water)
- lithium bromide (Sigma)
- lithium chloride (Sigma)
- lithium iodide (Sigma, ≥ 99% purity)
- magnesium chloride (Sigma, ≥ 99% purity)
- magnesium sulfate (Sigma, ≥ 99.5% purity)
- potassium bromide (Sigma, ≥ 99.0% purity)
- potassium chloride (Sigma)
- potassium iodide (Sigma, ≥ 99% purity)
- propionitrile (Sigma, ≥ 99.0% purity)
- sodium hydroxide (Sigma Aldrich, 10 M)
Comparison of Results from BESSY and ALS

The operational pressure of the liquid jet chamber, and the experimental geometry differ significantly between the LJ-PES assemblies at BESSY and the ALS. Data interpretation must account for these differences which impact the photoelectron peak areas for different orbitals and physical states. Specifically, at the ALS the gas phase signal intensity is higher and angular anisotropy is particularly important because experiments are not undertaken at the magic angle. For these reasons, the peak area ratios for dissimilar orbitals provide relative trends and not absolute molecular ratios in ALS studies.

Acetonitrile solutions were probed at BESSY and the ALS, allowing for a direct comparison of the experimental findings. The differentially pumped analyzer at the ALS enables investigation of pure acetonitrile microjets which cannot be studied at BESSY where the high vapor pressure of acetonitrile increases the analyzer pressure to such an extent that the photoelectron signal is lost.

Aqueous acetonitrile solutions were prepared at various concentrations in order to observe the heterogeneous phenomena in solution. Data from BESSY and the ALS show the formation of a saturated surface layer of acetonitrile at 0.3 mf bulk concentration. Figure 5.6a shows Langmuir fits to the nitrogen 1s and carbon 1s data, representing the signals from acetonitrile in water. For both studies, acetonitrile signal saturates at 0.3 mf.

Figure 5.6b shows the binding energy splitting between gaseous and aqueous N1s peaks for acetonitrile as a function of bulk acetonitrile concentration mole. This change in binding energy splitting indicates that the electronic dipole of acetonitrile at the surface changes direction upon saturation of the interface with acetonitrile. The agreement of the BE shift below 0.4 mole fraction of acetonitrile for ALS and BESSY experiments suggests that the equilibrium for
acetonitrile and water mixtures is reached at pressures of $1 \times 10^{-4}$ torr or 1 torr, in agreement with independent ambient pressure studies.45

The insert in Figure 5.6b shows the N1s PE spectra from BESSY and the ALS. The gas phase signal is much higher at the ALS, but the signal is still less than what one would expect given the chamber pressure. Suppression of the vapor phase signal may result from narrow focusing of the beam onto the jet, or from low pressure near the aperture caused by differential pumping through the aperture. Regardless of the gas phase signal intensity, the observed acetonitrile chemistry remains the same at 6 °C for BESSY and ALS studies.

![Figure 5.6](image)

Figure 5.6. a. Langmuir fits for LJ-PES N1s (red) and C1s (blue) PE peak areas for acetonitrile solutions studied at BESSY (filled markers) and ALS (open markers). b. The difference between the N1s binding energy in the gas and solution phase peaks for aqueous acetonitrile from BESSY (blue markers) and ALS (red markers) indicates that a dipole shift is observed when the surface of solution is saturated with acetonitrile. Inset N1s acetonitrile spectra from ALS and BESSY are shown to emphasize the different relative intensities of the gas and liquid phase peaks. Figures are adapted from references 23 and 24.
Challenges

The ALS AP LJ-PES technique would benefit from in-depth studies of the dynamics of PES in liquids, and with a gaseous environment. First, absolute binding energy calibration would be useful for determination of changes in binding energies for aqueous solutes. These binding energy changes can be indicative of chemical interactions which alter the electronic structure of molecules in solution. Currently, binding energy calibration to water O1s and 1b1 valence binding energies is sufficient for solutions with ample water. However, this calibration is less applicable when water is the minority species, or when the O1s BE appears shifted due to electric field effects from aqueous molecules. Binding energies are summarized in the Appendix.

ALS AP LJ-PES studies provide measures of relative concentration as a function of relative depth into solution. It is possible to compute the solution-specific absolute probe depth by comparison of MD simulation calculations to LJ-PES studies using a ruler calibration approach. Here, the experimental peak area ratios are initially plotted as a function of photoelectron kinetic energy. This photoelectron kinetic energy can be converted to depth into solution by comparison with IMFP vs. PE KE calculations.

Lastly, these studies utilize two commonly accepted approximations in the normalization factor for PE peak areas. The calculated atomic orbital anisotropy β factor values are used because the solution-dependent molecular values have not been tabulated.41 The β factor may actually vary both with experimental geometry and with solution composition. Recent photoelectron angular distribution studies have used angle-dependent LJ-PES studies to determine the PE KE dependent β factor for neat water.39 It was found that β is fairly uniform for O1s photoelectrons with 100 eV kinetic energy or greater, but the magnitude was found to be ¼ lower for H2O O1s (aq) than that for H2O O1s (g). This method has promise for the determination of β factors for other solutions.
Calculated atomic ionization crossections are used as an approximation in the normalization factors.\textsuperscript{41} Solution phase ionization crossections may differ for molecules, and in particular for solvated molecules. As mentioned in the experimental section, the experimental geometry, or the angle between photoelectron detection and the X-ray polarization vector, can be varied by changing the polarization of the photons. In order to gauge the impact of these anisotropies on these results, spectra for LiI and NaI (aq) were recorded at both 20 and 54.7 degrees. Results show little change in the anion to cation ratio for LiI and NaI for the two detection angles, indicating that orbital anisotropy contributes minimally to the recorded spectra and may effectively be ignored. Although these results were observed for ionic species in solution, the orbital anisotropy cannot be ignored for organic solutes that may have multiple species present. The lack of angular anisotropy was not experienced for studies under vacuum, and may result from gaseous effects on X-rays or photoelectrons.
Summary and Potential Applications

The ALS AP LJ-PES technique builds on liquid photoelectron spectroscopic studies dating back to the 1970s, but allows for the investigation of solution in the presence of vapor. Using LJ-PES, the interfacial structure of aqueous organic, ionic, and mixed organic and ionic solutions are probed to better understand chemistry for environmentally important systems. LJ-PES studies provide complimentary information to SFG and MD studies to further understand chemistry adjacent to the liquid-vapor interface. Specifically, photoelectron peak area ratios and binding energy trends are used to learn about surface saturation, depth-dependent concentration, and molecular interactions. In particular, these studies have shown interesting new chemistry for lithium ions near the aqueous interface.

The ALS AP LJ-PES instrument is well suited for future gas uptake experiments or In situ organic chemistry or photochemistry. Here, reactant mixing can be achieved by colliding two jet streams, or combining two solvent sources using the HPLC pump. Additionally, investigations of colloidal particles can expand the understanding of the liquid-vapor interface and fundamental reactivity of aqueous nanoparticles that abound in tropospheric waters. Several colloidal nanoparticle studies have recently been published using the LJ-PES technique.46-47

Several challenges are presented that would benefit from further studies from a physics standpoint. As mentioned earlier, the binding energy calibration to water oxygen may be refined by incorporating any concentration or solute effects which impact the actual water binding energy. LJ-PES studies provide information as a function of relative depth into solution, and further work is required to determine the exact probe depth into solution. Additionally, the impact of experimental geometry may be fully explored.
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6. pH Dependent Deprotonation of Interfacial Ammonium

The LJ-PES technique has previously been used to study differences in the protonation for nitric acid at the aqueous interface,\textsuperscript{1-2} and has studied the bulk protonation for sulfuric acid.\textsuperscript{3} This work is interesting from a fundamental perspective, and is also important for understanding chemistry at atmospheric aqueous surfaces. This chapter presents new work on the deprotonation of interfacial ammonium.

Introduction to Aqueous Ammonia

Ammonia is an abundant strong base in the atmosphere which is responsible for neutralizing reactions such as that with sulfuric acid as shown below in Equation 6.3.\textsuperscript{4} Although ammonia is emitted to the troposphere naturally, human production of ammonia for fertilizer has increased emissions since the discovery of the Haber-Bosch process for ammonia production in 1920.\textsuperscript{5-6} Increases in ammonia levels have led to various environmental problems which differ for aqueous and gaseous ammonia.\textsuperscript{5} Reactive ammonia can be found in both dry and aqueous atmospheric aerosols, in the gaseous form, and it has been found to exchange from the atmosphere to the ocean where it is toxic to aquatic life.\textsuperscript{7-10} Given the omnipresent role of water in atmospheric chemistry, and the high solubility of ammonia in water (Henry’s Law constant = 127.66 kg atm mol\textsuperscript{-1} at 10 °C), there is an interest in understanding the liquid-vapor interfacial behavior of aqueous ammonia in aerosols (Equation 6.1).\textsuperscript{11-12}

\[
\begin{align*}
\text{NH}_3 (g) + \text{Aqueous aerosol} & \rightleftharpoons \text{NH}_3 (aq) & (6.1) \\
\text{NH}_3 (aq) + \text{H}_2\text{O (aq)} & \rightleftharpoons \text{NH}_4^+ (aq) + \text{OH}^- (aq) & (6.2) \\
2 \text{NH}_4\text{OH (aq)} + \text{H}_2\text{SO}_4 (aq) & \rightleftharpoons (\text{NH}_4)_2\text{SO}_4 (aq) + 2 \text{H}_2\text{O} & (6.3)
\end{align*}
\]
Enhancement or depletion of NH$_4^+$ (aq) at the surface of aqueous atmospheric aerosols may have a large impact on the rates and energetics of reactions with other solutes, or with gaseous molecules impacting at the interface. For example, this is the case for bromide ions on the surface of sea-spray aerosols where surface enhancement of bromide was correlated with a higher than expected activity for the destruction of ozone. In another instance, a difference in dissociation behavior was demonstrated for nitric acid and sulfuric acid near the aqueous interface compared to the bulk solution, as a function of concentration.

For bulk solution, the equilibrium between ammonia and the ammonium ion (see Equation 6.2) is quantitatively well understood (Figure 6.1). As the pH of ammonium based solutions is increased, ammonium dissociates to ammonia which partially degasses from solution because it is less soluble. It has been shown that pH, ammonia concentration, and temperature impact the equilibrium between NH$_4^+$ (aq) and NH$_3$ (aq) in bulk solution. To illustrate the role of temperature, the pKa of ammonia has been experimentally determined to decrease from 9.90 to 9.24 when the temperature is increased from 5.0 °C to 25.0 °C. In bulk aqueous solution, the concentration of ammonium and ammonia are equal when the pH is to equal the pKa, and ammonium is the dominant bulk species below pH 9.2. In this work, the pH of dilute aqueous ammonium hydroxide and ammonium chloride solutions was varied at 5.0 °C to elucidate how the ammonia–ammonium equilibrium is altered at the liquid–vapor interface, compared to the bulk. In the case of ammonium hydroxide, the absolute number of nitrogen species remains constant at all pHs, and the ion effects from added HCl are discussed. For ammonium chloride solutions, the concentration of nitrogen species decreases as the pH is increased by the addition of NaOH due to the degassing of ammonia, and the effects of both chloride and sodium are considered. Although the absolute
concentrations of ammonia and ammonium vary, the relative concentrations are directly compared for the surface versus the bulk.

Figure 6.1. Relative concentration of ammonium and ammonia in bulk aqueous solution as a function of pH at 5 °C. Figure adapted from reference 15.

It is expected that the \( \text{NH}_4^+ \) (aq) / \( \text{NH}_3 \) (aq) ratio at the surface is unique for ammonia solutions because the structure of interfacial aqueous ammonia is distinct from that in bulk solution. \textit{Ab initio} studies show that the hydrogen-bond strength between ammonia and water near the aqueous surface is greater than in bulk solution, resulting in surface ordering of ammonia with water.\textsuperscript{17-18} SFG studies confirm this strong interfacial hydrogen bonding, and further determine that the lone pair of ammonia forms a hydrogen bond with water, which is directed towards the interface, away from the solution.\textsuperscript{19-20} Specific ordering of ammonia at the interface is quantified by a O-H\( \cdots \)N bond axis tilt angle between 25° and 38° relative to the surface normal. How these properties affect the ammonia–ammonium equilibrium at the solution surface is unknown, and will be explored here.
In this study, the relative concentrations of ammonium and ammonia at the surface and in the bulk of aqueous solution were determined as a function of pH using X-ray photoelectron (PE) spectroscopy of a liquid microjet. The inelastic mean free path (IMFP) for electrons strongly depends on photoelectron kinetic energy which can be selected to be 140 eV for surface sensitive measurements, and 600 eV for measurements that probe sufficiently deep into solution to investigate bulk solution behavior.\textsuperscript{1-2, 14, 21} Furthermore, PE spectroscopy distinguishes between aqueous ammonium and ammonia based on their unique N1s electron binding energies which differ by approximately 1.3 eV, and the PE signal intensities are compared to infer the relative amount of ammonium versus ammonia both at the surface and in the bulk of solution.

The effects of ions in the as-prepared solutions, and ions formed during the neutralization reactions of NH\textsubscript{4}OH with HCl or NH\textsubscript{4}Cl with NaOH are discussed. OH\textsuperscript{-}, Na\textsuperscript{+} and Cl\textsuperscript{-} ions are inevitably introduced into ammonia or ammonium solutions when adjusting the pH by adding NaOH or HCl. Na\textsuperscript{+} and Cl\textsuperscript{-} ions are known to form an electrical double layer at the neat water surface,\textsuperscript{22} which may influence the interfacial chemistry in ammonia – ammonium solutions. Chloride may also interact favorably with NH\textsubscript{4}\textsuperscript{+} (aq) in bulk solution, and the resulting stabilization can modify the equilibrium between NH\textsubscript{4}\textsuperscript{+} (aq) and NH\textsubscript{3} (aq), at the solution surface.\textsuperscript{23} In addition, there might be a competition between NH\textsubscript{4}\textsuperscript{+} (aq) and the smaller Na\textsuperscript{+} (aq) ions for propensity near the interface.\textsuperscript{24} Finally, NH\textsubscript{3} has been observed to be “salted out” from aqueous solution by the addition of NaCl, which would suggest a lower relative concentration of ammonium at the surface at high pH.\textsuperscript{25}
Experimental Methods

Experiments were completed at the U41 PGM undulator beamline at BESSY as previously discussed in Chapter five. N1s PE spectra were recorded at 545 eV and 1005 eV for surface and bulk spectra, respectively probing about 10 Å or 50 Å into solution. A Shirley background was subtracted from the spectra which were fit with Gaussian peaks. Cl2p spectra were also collected for 600 eV photoelectrons (corresponding to bulk solution). Cl2p peaks were fit using two Gaussian peaks with areas constrained in a 1:2 ratio. O1s peaks were fit using two unconstrained Gaussian peaks. Binding energies were calibrated to the oxygen 1s PE peak of water at 538.1 eV for spectra recorded at high photoelectron kinetic energies, or to the valence H2O (aq) peak at 11.16 eV for spectra recorded at low photoelectron kinetic energies.
Results

In order to prepare ammonia-based solutions over a range of bulk pHs, studies began with an acidic 4 M NH$_4$Cl solution which was gradually titrated by adding 10 M NaOH, and a 6 M NH$_4$OH solution which was titrated using 12 M HCl. The N1s spectra for NH$_4$Cl are shown in Figure 6.3 and representative PE spectra for NH$_4$OH solutions are shown in Figure 6.4. Bulk spectra are shown in the Appendix (Figure A.24 and Figure A.25). These studies were undertaken to gain information about the pH and counter-ion effects on the distribution of ammonia species at the interface, as will be discussed later.

The N1s PE spectra were deconvoluted into three peaks representing aqueous ammonium (NH$_4^+$ (aq)), aqueous ammonia (NH$_3$ (aq)), and ammonia gas (NH$_3$ (g)). From previous studies, it was determined that the high-binding energy species is the protonated species,$^{30}$ and the low binding energies species is NH$_3$ (aq).$^{31}$ The N1s line shape and binding energy for NH$_4^+$ (aq) was determined from unconstrained fits of reference N1s spectra for NH$_4$I and several other reference solutions (Figure 6.2). These solutions provide the N1s line shape for NH$_4^+$ (aq) because they can be assumed to contain only NH$_4^+$ (aq). For ammonium studies, the FWHM and the NH$_4^+$ (aq) N1s binding energy were constrained within 0.05 eV of the corresponding NH$_4$I reference values. The resulting NH$_4^+$ (aq) binding energy is 406.94 ± 0.1 eV, and the FWHM is 1.73 ± 0.1 eV. The exact values used in fitting are shown in Table 6.1.

The line shape for NH$_3$ (g) N1s PE spectra was measured by moving the jet out of the x-ray beam so that only the gas phase peak is observed. NH$_4$OH was chosen for this measurement because higher concentration (6 M) is attainable which contains mostly ammonia due to its high pH, leading to a large gas-phase NH$_3$ signal. The resulting NH$_3$ (aq) binding energy is 404.88 ±
0.1 eV, and the FWHM is $1.64 \pm 0.1$ eV. No noticeable change in the FWHM or BE was observed for the different photoelectron kinetic energies, or with changes in pH.

Table 6.1. Fitting parameters for N1s line shapes.

<table>
<thead>
<tr>
<th></th>
<th>NH$_4^+$ (aq) (eV)</th>
<th>NH$_3$ (g) (eV)</th>
<th>NH$_3$ (aq) (eV)</th>
<th>NH$_3$ (aq) - NH$_4^+$ (aq) Splitting (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FWHM Surface</strong></td>
<td>1.65 ± 0.05</td>
<td>0.62 ± 0.05</td>
<td>1.55 ± 0.05</td>
<td>2</td>
</tr>
<tr>
<td><strong>FWHM Bulk</strong></td>
<td>1.8 ± 0.05</td>
<td>1.15 ± 0.05</td>
<td>1.7 ± 0.05</td>
<td>2.2</td>
</tr>
<tr>
<td><strong>BE</strong></td>
<td>406.99 ± 0.1</td>
<td>405 ± 1.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 6.2. Reference spectra used to determine the N1s lineshape for NH$_4^+$ (aq): a. 2.8 M NH$_4$I (aq) surface PE spectrum, b. 2.8 M NH$_4$I (aq) bulk PE spectrum, c. 4 M (NH$_4$)$_2$SO$_4$ (aq) surface PE spectrum, d. 4 M (NH$_4$)$_2$SO$_4$ (aq) bulk PE spectrum, e. 4 M NH$_4$NO$_3$ (aq) surface PE spectrum, f. 4 M NH$_4$NO$_3$ (aq) bulk PE spectrum. Spectra were recorded at 545 eV and 1005 eV photon energies for surface and bulk, respectively.
Figure 6.3. Surface (545 eV photon energy) N1s PE Spectra for NH₄Cl (aq) solutions titrated using NaOH to pH a. 4.56, b. 8.25, c. 8.98, d. 9.20, e. 9.46, f. 9.54, g. 9.74, and h. 10.0.
Figure 6.4. Surface (545 eV photon energy) N1s PE Spectra for NH₄OH (aq) solutions titrated using HCl to pH a. 8.06, b. 8.87, c. 9.08, d. 9.24, e. 9.45, f. 9.62, g. 9.83, h. 10.5, and i. 12.2.
From the N1s photoelectron signal intensities in Figure 6.3 and 6.4, NH$_4^+$ (aq) is seen to be the major component at low pH as expected, and NH$_3$ (aq) prevails as pH is increased. More NH$_3$ (g) is generated as the pH increases which enhances the gas-phase signal. However, variations in the gas-phase signal intensity do not precisely correlate with the large degasing of NH$_3$, because they also reflect the slight changes in the position of the liquid jet with respect to the X-ray beam. This has no effect on the solution ratios considered in this study though, as will be discussed below.

The experimental NH$_4^+$ (aq) / NH$_3$ (aq) ratios were quantified by taking the ratio of the NH$_4^+$ (aq) N1s and the NH$_3$ (aq) N1s PE peak areas. These values are displayed in Table 6.2 and Figure 6.5, and error values (precisions) were determined from multiple measurements under nominally identical experimental conditions. The NH$_4^+$ (aq) / NH$_3$ (aq) ratio decreases with increasing pH for both solutions. The decrease for the bulk measurements (Figure 6.5a, blue and red dots) agrees quantitatively with the NH$_4^+$ (aq) / NH$_3$ (aq) experimental ratio previously reported (Figure 6.5a, black line). The curve from literature is the empirically found function reported for the temperature dependent pK$_a$ for the equilibrium of aqueous ammonium and ammonia for a solution temperature of 5 °C and pK$_a$ = 0.09018 + 2729.92/T.\textsuperscript{16} From this relation, it is determined that:

\[ \text{pK}_b(5^\circ\text{C}) = e^{-\left(14 - (0.09018 + \frac{2729.92}{T})\right)} \]  \hspace{1cm} (6.4)

For the aqueous equilibrium of ammonia (Equation 6.2), the dissociation constant, K$_b$

\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \]  \hspace{1cm} (6.5)

is then rearranged to provide a ratio of components:

\[ \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = \frac{K_b(5^\circ\text{C})}{10^{-(14-pH)}} \]  \hspace{1cm} (6.6)
where the substitution $[\text{OH}^{-}] = 10^{-pH}$ has been made. There is some discrepancy at pH = 8.9 where this study finds a larger $\text{NH}_4^+ / \text{NH}_3$ ratio, but this is probably due to the error in fitting the very small ammonia peak at this pH. The otherwise good agreement of this data for bulk solution with literature indicates that this method for using the PE peak areas (in the magic-angle geometry) to determine the $\text{NH}_4^+ / \text{NH}_3$ ratio provides a method for the accurate detection of these ratios. This agreement indicates that the method can also be used for a reliable quantification of the $\text{NH}_4^+ / \text{NH}_3$ ratio for the surface.

Figure 6.5. Ammonium to ammonia ratios as a function of pH. a. Bulk $\text{NH}_4^+ / \text{NH}_3$ ratios are shown for 4M NH$_4$Cl titrated with 10 M NaOH (red dots) and 6 M NH$_4$OH (aq) titrated with 12 M HCl (blue dots). Experimental bulk data from literature (black dots and dotted line) are shown to confirm agreement of these studies with literature.\textsuperscript{16} b. $\text{NH}_4^+ / \text{NH}_3$ surface (orange dots) and bulk (green dots) ratios for 4M NH$_4$Cl titrated with 10 M NaOH. c. $\text{NH}_4^+ / \text{NH}_3$ surface (orange dots) and bulk (green dots) ratios for 6 M NH$_4$OH (aq) titrated with 12 M HCl. Green data points are replicated from a.
Table 6.2. Ammonium/Ammonia ratio for Aqueous NH₄OH and NH₄Cl Solutions

<table>
<thead>
<tr>
<th>Solution</th>
<th>pH</th>
<th>140 eV KE NH₄⁺ (aq) / NH₃ (aq)</th>
<th>600 eV KE NH₄⁺ (aq) / NH₃ (aq)</th>
<th>NH₄⁺ (aq) / NH₃ (aq) (Emerson et al.)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄OH &amp; HCl</td>
<td>8.06</td>
<td>7.66</td>
<td>70.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.87</td>
<td>7.68</td>
<td>10.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.08</td>
<td>2.72 ± 0.5</td>
<td>4.14 ± 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.13</td>
<td>4.61</td>
<td>5.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.24</td>
<td>2.80 ± 0.1</td>
<td>4.40 ± 0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.28</td>
<td>3.05</td>
<td>5.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.45</td>
<td>2.11 ± 0.1</td>
<td>3.10 ± 0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.62</td>
<td>1.76</td>
<td>2.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.80</td>
<td>1.03 ± 0.2</td>
<td>1.79 ± 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.6</td>
<td>0.29</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.1</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>NH₄Cl &amp; NaOH</td>
<td>8.25</td>
<td>-</td>
<td>45.72</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.98</td>
<td>5.52 ± 1.7</td>
<td>15.09 ± 2.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.20</td>
<td>2.62 ± 0.4</td>
<td>7.39 ± 3.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.46</td>
<td>2.22</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.54</td>
<td>1.32 ± 0.1</td>
<td>2.34 ± 0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.74</td>
<td>0.98 ± 0.2</td>
<td>1.32 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.02</td>
<td>0.64 ± 0.1</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.38</td>
<td>0.20</td>
<td>0.32</td>
<td></td>
</tr>
</tbody>
</table>

*Values from Emerson et al.¹⁶ have been taken from a power fit of the original data points.

Differences in the ammonia – ammonium equilibrium at the surface versus the equilibrium in the bulk can now be quantified by numerical values for the NH₄⁺ (aq) / NH₃ (aq) PE signal ratio from measurements recorded at the surface and in the bulk of solution. The NH₄⁺ (aq) / NH₃ (aq) ratio for the surface (orange dots) and the bulk (green dots corresponding to red dots in Figure 6.5a) for NH₄Cl aqueous solution are shown in Figure 6.5b, and analogous data for NH₄OH are shown in Figure 6.5c. The surface NH₄⁺ (aq) / NH₃ (aq) ratio for NH₄Cl solutions (Figure 6.5, orange dots) is observed to be noticeably smaller than the bulk ratio, and this effect is enhanced at low pH. This indicates that the equilibrium between NH₄⁺ (aq) and NH₃ (aq) for bulk solution will not be suited to describe the interfacial chemistry. The observed NH₄⁺ (aq) / NH₃ (aq) ratio is
argued to mainly arrive from ammonium depletion. Signal changes of NH$_3$ (aq) associated with ammonia evaporation are not taken into account here.

Reduced amounts of NH$_4^+$ (aq) at the surface versus the bulk is in agreement with MD simulations from literature which find that ammonium and chloride are not enhanced at the aqueous surface.\textsuperscript{32} This result is confirmed for ammonium hydroxide solutions by the qualitatively lower ammonium signal relative to water O1s signal, especially at low pH (Figure 6.6). The closer agreement of surface and bulk data at high pH indicate that the surface depletion of ammonium is proportional to the amount of ammonium relative to aqueous ammonia. This effect cannot be decoupled from the salting out of NH$_3$ by Na$^+$ (aq) and Cl$^-$ (aq) ions, which exacerbates degassing of ammonia from solution as pH is increased.

![Figure 6.6](image)

Figure 6.6. NH$_4^+$ (aq) / O1s (aq) peak area ratios for 6 M NH$_4$OH titrated with 12 M HCl. Surface ratios (orange dots) are three times lower than those for the bulk (green dots) at pH = 9, and this difference decreases towards higher pH in agreement with Figure 6.5.
In order to present the enhancement of the surface depletion of NH$_4^+$ (aq) more clearly, the absolute difference between the surface NH$_4^+$ (aq) / NH$_3$ (aq) ratio and the respective bulk ratio at each pH is plotted in Figure 6.7. The trends in these differences, \( \left( \frac{\text{NH}_4^+}{\text{NH}_3} \right)_{\text{bulk}} - \left( \frac{\text{NH}_4^+}{\text{NH}_3} \right)_{\text{surface}} \), can be attributed to the respective Cl$^-$, Na$^+$, and OH$^-$ relative concentrations in the various solutions as depicted in Figure 6.7a-d. Ion effects will be discussed in the context of the titration of NH$_4$Cl with NaOH (Figure 6.7a → Figure 6.7b), and the titration of NH$_4$OH with HCl (Figure 6.7d → Figure 6.7c).

Figure 6.7. Absolute surface NH$_4^+$ (aq) depletion as a function of pH and schematic for relative concentrations, molecular distributions and interactions (Ion pairing is shown as a dotted line) contributing to the surface ammonium depletion in NH$_4$OH and NH$_4$Cl aqueous solutions. Surface ammonium depletion is calculated by taking the absolute difference of the bulk and surface NH$_4^+$ (aq) / NH$_3$ (aq) ratio at each pH. a. Chloride-ammonium interactions stabilize ammonium in low pH NH$_4$Cl bulk solution. b. Ion pairing of sodium and chloride reduce bulk stabilization of ammonium (as seen in a) for high pH NH$_4$Cl solution. c. Low pH NH$_4$OH solutions have similar
chloride-ammonium interactions occur as in a., but relative chloride concentration is less and thus the surface ammonium depletion is less. d. High pH NH₄OH solutions have few ion interactions.

When the as-prepared NH₄Cl solution, with pH = 4.5 to 5.5, is titrated to higher pH by the addition of NaOH (Figure 6.7a → Figure 6.7b), it contains more chloride than ammonia and ammonium together, due to outgassing of ammonia. Even for NH₄Cl solutions at pH = 8 - 9.5 (little NaOH added), there will always be more chloride than ammonium. The very high concentration of chloride at low pH appears to correlate with the larger surface ammonium depletion for acidic NH₄Cl solutions (Figure 6.7a), in agreement with Figure 6.5. At high pH, however, the relative concentration of Na⁺ (aq) approaches that for Cl⁻ (aq) (up to 3 M), and formation of Na⁺ (aq) – Cl⁻ (aq) ion pairs would decrease the effective Cl⁻ concentration (Figure 6.7b), explaining the small surface depletion of ammonium (Figure 6.7). Competition between NH₄⁺ (aq) and Na⁺ (aq) for existing at the surface seems to be of minor importance as inferred from the very low surface ammonium depletion at high pH, where the solution is rich in sodium. Also OH⁻ (aq) appears to have little or no effect on the ammonium depletion, consistent with the findings for NH₄OH solutions considered next.

NH₄OH solutions with pH = 11.7 are titrated with HCl to produce solutions with even higher pH than those previously discussed. In this case, the chloride concentration is always less than the sum of the ammonia and ammonium concentrations, and it decreases towards higher pH (Figure 6.8). Basic NH₄OH solutions contain little or no Cl⁻ (aq) and very little OH⁻ (aq), and as HCl is added (Figure 6.7d → Figure 6.7c), water is formed, and the dilute chloride interacts with ammonium as described above. The lower relative concentration of chloride in acidified NH₄OH solutions, would correlate with the smaller surface ammonium depletion compared to NH₄Cl (aq) at low pH.
Counter-ion studies indicate a strong effect of Cl$^-$ which can be associated with a lower energy for the formation of $[\text{NH}_4^+]\cdot[(\text{Cl}^-)_m\text{H}_2\text{O})_n]$ in the bulk solution as compared to the total energy of solvation of the individual species at the solution surface. This observation is consistent with MD simulations of aqueous ammonium chloride which predict slight bulk propensity for both ions, in contrast to simulations for aqueous sodium chloride which predict an enhancement of chloride at the water interface.$^{22-23}$
Conclusions

LJ-PES studies demonstrate a method for quantifying the relative concentrations of ammonia and ammonium both at the surface and in the bulk of aqueous ammonium solutions over a pH range of 9.2 – 11.9. The NH$_4^+$ (aq) / NH$_3$ (aq) ratio at the surface is considerably smaller than that in the bulk, which will have crucial consequences for environmental chemistry. Experiments indicate that the surface equilibrium depends sensitively on co-dissolved ions, but the exact interactions are yet to be explored. Specifically, comparison of the absolute ammonium depletion and relative concentrations of ions indicates that Cl$^-$ (aq) may interact favorably with ammonium in the bulk of solution, and Na$^+$ (aq) may interact strongly with chloride in solution and thus reducing the effective chloride concentration. Further computational studies would be very useful to better understand ionic interactions in ammonia and ammonium mixed solutions with chloride and sodium counter-ions.

It is interesting to connect these results to ongoing discussions about the acidity or basicity of aqueous solution interfaces.$^{33}$ One view of this issue – exemplified here by NH$_4^+$ (aq) / NH$_3$ (aq) – is that the change in the ammonium–ammonia ratio at the surface is a change in equilibrium, but should not be mistaken for a change in pH. pH is constant, because the chemical potential of a solution is constant across the solution interface at equilibrium by definition. The varying ratio corresponds to a change in the activity coefficient. Note that even though there are different relative amounts of species at the surface than in the bulk, this will not lead to an increase or decrease in the overall chemical reactivity. For instance, if there are more molecules, they will be less reactive according to their activity coefficient. However, surface species will not be exactly the same as in bulk solution due to differences in hydration structure. This may account for changes in the reactivity which affect the overall reaction kinetics.
References


6. Haber, F. The Synthesis of Ammonia from its Elements.  
   (accessed July 18).


7. Aqueous Chemistry of Salts Revealed by LJ-PES

Interfacial Distributions of Aqueous Ions

Although the chemistry of ions in aqueous solution is generally well-understood, the distribution of ions at and near the air-water interface has recently been discovered to vary depending on the ions present. A complicated scenario was presented in Chapter six involving mixtures of multiple ions and volatile bases. There, the discussion of the surface propensity was limited by the complexity of solution. This chapter will examine the issue of interfacial ionic distributions more closely by probing aqueous solutions of individual salts.

Several works review interfacial ionic behavior\(^1\)\(^-\)\(^3\) that has significant atmospheric importance. In one particular case it was found that the increased activity of atmospheric aerosols for ozone destruction upon arctic sun rise was caused by an enhancement of the bromide ion concentration on the surfaces of aerosols relative to the bulk.\(^4\) Interfacial ionic distribution studies predominantly focus on the enhancement of the concentration of anions at the aqueous interface for single-component ionic solutions.\(^1\)\(^-\)\(^2\),\(^5\)\(^-\)\(^7\) This enhancement of negative ions necessitates a layer of cations below the anions to provide electroneutrality to solution.

Ionic distributions near the air-water interface are described based on the strength of ion-ion interactions, water-ion interactions and ionic polarizability. Ions that are strongly solvated by water (kosmotropes) must pay a higher energetic cost to be dehydrated at the surface, and thus are more likely to be depleted at the interface.\(^8\) Largely polarizable ions (chaeotropes) are more easily dehydrated, and are thus concentrated near the interface (this behavior is also called surface enhancement).\(^9\) These trends agree well with the Hofmeister series, which is an ordering of ions ranked by their ability to denature proteins (abbreviated series are shown in Equations 7.1,2).\(^10\)

\[
F^- \approx SO_4^{2-} > Cl^- > NO_3^- > Br^- > I^- > SCN^- 
\]  

(7.1)
\[
\text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}
\] (7.2)

This work aims to understand exceptions occurring when strong ion-ion interactions exist in solution (Figure 7.1). One example is contact ion pairing where two ions exist together in solution with the water solvent shell encircling the two together. Other ion-ion interactions play less of a role, but should be mentioned here. This includes solvent-shared ion pairing, where two ions have independent first solvent shells of water and share second or third solvent shells, and solvent separated ion-pairs. The Hofmeister series can also qualitatively describe a pair of ion’s likelihood to form solvent-separated, solvent-shared or contact ion pairs. Anions which are high in the series are more likely to form contact ion-pairs, like \(\text{Mg}^{2+} \cdot \text{SO}_4^{2-}\). This interaction can significantly vary the distribution of solutes with respect to the interface, contrary to what one would expect from the general polarizability and solvation strength trends.

Contact ion-pair  
Solvent shared ion-pair  
Solvent separated ion-pair

Figure 7.1. Illustration of ion pairing interactions including contact, solvent-shared, and solvent separated ion pairs. The blue regions surrounding the anion (green) and cation (orange) represents several solvent shells, in this case the solvent being water. For solvent shared ion pairs, the first solvation shell for each ion may be complete with the water molecules in the middle existing in the first solvation shell of both ions.

The impact of specific ion effects (including anion or cation effects) on ionic distributions are another focus of this work.\textsuperscript{5, 7-8} Here, the presence of different cations may alter the distribution of an anion, or vice versa, due to the strength of ionic interactions in solution. Additionally, ionic concentrations can change the interfacial distribution of ions.\textsuperscript{11} The distribution of cations in
solution has been explored using AP-PES and MD simulations for RbCl, RbBr, and NaCl. Here, the size of the cation impacts bonding with water, with larger cations having a lesser effect on water molecules than small ones. The anion to cation ratio was insensitive to cation size, but the ion to oxygen ratios show that the smaller cation provides a larger chloride surface enhancement. Following from this, we would expect that chloride would have a higher enhancement at the surface of MgCl₂ (aq) solutions than in NaCl (aq) solutions, but the matter is complicated by the additional charge of Mg²⁺ compared to Na⁺.

Salts were selected for these studies for their environmental importance or unique spectral properties. Specifically, iodide salts were utilized for low photoelectron kinetic energy studies because of the high atomic iodine 4d photoionization cross section. Cation-specific ion effects were examined in the context of lithium and potassium aqueous solutions to corroborate MD simulations showing an unprecedented enhancement of lithium near the aqueous interface. This chapter, however, will focus mainly on the interfacial distribution of aqueous magnesium ions, as will be described below.

Magnesium salts were investigated because magnesium is a small, highly charged kosmotrope, making it an interesting component in sea-salt aerosols. The Mg²⁺ cation has unusually strong solvation by six water molecules in the first solvation shell, and weak interactions with anions including chlorine. This strong solvation is exemplified by the magnesium ion’s large Gibbs free energy of solvation (-1830 KJmol⁻¹), and the increased time for electron transfer events between water molecules in the presence of Mg²⁺, as well as its position at the right of the Hofmeister series for cations. These interactions impact the interfacial distribution of magnesium, as will be described here.
Molecular dynamics simulations revealed the density profiles of several magnesium-containing solutions, including MgCl$_2$, which is the second most abundant oceanic salt after NaCl (Figure 7.2). In MgCl$_2$, multiple layers of opposite-charged ions were observed at the interface, which cannot be experimentally confirmed by surface potentiometry (PS) or SFG. Here, Mg$^{2+}$ was predicted to have a twofold surface enhancement versus the bulk. Additionally, the surface enhancement of Cl$^-$ (aq) in MgCl$_2$ (aq) is similar to that in NaCl (aq) solutions, despite ion pairing in the latter.$^{14-15}$

![Figure 7.2. Qualitative sketches of simulated ion density profiles: a. 2 M Mg(NO$_3$)$_2$ (aq), b. 1.9 M MgCl$_2$ (aq), c. 2 M Mg(OAc)$_2$ (aq). The density profile data was adapted from references 14 and 19.](image)

The interfacial solute density of several other aqueous magnesium solutions with ion-pairing anions have been simulated (Figure 7.2a and c). It was found that Mg$^{2+}$ in aqueous 2 M magnesium acetate solutions exhibits enhancement of Mg$^{2+}$ just below the surface because it strongly ion pairs to acetate, which is driven to the air-water interface by hydrophobic
interactions. In contrast, surface depletion of Mg$^{2+}$ was observed for a 2 M Mg(NO$_3$)$_2$ (aq) solution which exhibited minimal contact ion pairing. Although MD simulations can be used to predict the behavior of Mg$^{2+}$ in solution, these simulations require experimental validation because of the long half-life of water-ion and ion-ion interactions that can render opposing results depending on the force-fields in use. Additionally, the method for accounting for surface capillary waves at the interface strongly impacts MD results.
Experimental Methods

Experiments utilized the external ambient pressure end station on beamline 11.0.2 at the ALS at LBNL that is described in Chapter five. To summarize, a custom-built \( \mu \)-metal chamber was designed to house a liquid microjet system from Microliquids GmbH. The chamber was held at approximately 1 torr of water vapor pressure during experiments by a temperature controlled cold trap containing 500 mL of 40 wt % NaCl solution (\( \geq 99 \% \), Sigma Aldrich) at -10 °C. The electron energy analyzer used to record spectra (Phobios 150, Specs) was maintained in high vacuum by differential pumping. A 0.1 – 0.3 mm foil aperture separates the experimental chamber from the first differentially pumped stage which contains the pre-lens for the electron energy analyzer.

Solutions were prepared from MilliQ water (18.2 M\( \Omega \)), and the appropriate salt. Solutions were filtered with a 0.45 \( \mu \)m Millipore syringe filter to remove particulates, and then sonicated to sparge gas bubbles before introduction into the chamber through a 28 \( \mu \)m quartz capillary mounted on a temperature controlled liquid feedthrough maintained at 21 °C by an ethylene glycol chiller. A constant 0.5 mL/min flow of solution was achieved using a P 102 Watrex HPLC pump. A switching valve and external sample loop allowed injection of concentrated solutions while ensuring a constant liquid flow into the chamber and preventing exposure of the HPLC pump to sample solution.

The liquid microjet was positioned within 0.5 mm of the foil aperture and illuminated with X-rays from beam line 11.0.2, which provides monochromatic light between 75 eV and 2150 eV. The light entered the chamber through a silicon nitride window (100 nm thick) and was focused to 50 \( \times \) 60 \( \mu \)m\(^2\), and the I\( \text{4d} \) photoelectron intensity from a 4 M KI solution was optimized by tuning the analyzer electron optics. A concentrated salt was used for optimization because iodide
has a large photoionization crosssection that produces high photoelectron signal, and no presence in the vapor phase. This protocol ensures that the photon beam is focused on the jet to provide high signal from the liquid phase. Ejected photoelectrons were detected at 70° with respect to the incident photons (20° with respect to the light polarization), and the electron energy analyzer was optimized for signal at a pass energy of 20 eV.

The distribution of ions in solution was measured using LJ-PES as a function of relative depth into solution by variation of incident X-ray photon energies. In this study, photon energies were selected to produce photoelectrons with 200 eV, 300 eV, 400 eV, 600 eV, and 700 eV kinetic energies to probe the solution at various relative depths. These measurements provide integrated photoelectron signal from the solution surface, down to the maximum escape depth for the photoelectron kinetic energy being sampled.

Spectral intensities were normalized to the photon flux, orbital specific photoionization cross sections and beta parameters,\textsuperscript{13} and X-ray transmission through 1 torr of water.\textsuperscript{22-23} Although experiments were not performed at the magic angle, the ratios of integrated peak areas for 2p, 4d, 2s and 1s core photoelectrons are compared without correction for the angular dependence of the beta parameter. In this work, peak area ratios for dissimilar orbital symmetries reflect relative changes of solute propensity in solution. Error bars result from several data points gathered under nominally identical conditions.

Binding energies were calibrated to the O1s (aq) core level photoelectron peak at 538.1 eV,\textsuperscript{24} or the H$_2$O (aq) highest occupied molecular orbital (HOMO) valence peak (1b$_{1}$) at 11.16 eV.\textsuperscript{25} Photoelectron peaks were fit using Gaussian curves and a Shirley background was subtracted in CasaXPS software. 2p peaks were fit with two Gaussians, and the peak area ratios were constrained in a 1:2 ratio with FWHMs set to be equal. 2s photoelectron peaks were fit with one
unconstrained Gaussian curve. I4d spectra were fit with two Gaussian curves, and the area was constrained in a 2:3 ratio. O1s photoelectron spectra for 2 M MgSO₄ (Figure 7.7) showed three peaks which were separated by about 1 eV, and were assigned to sulfate oxygen, liquid water, and gaseous water. The liquid phase water peak FWHM for 2 M MgSO₄ solutions was constrained within 0.05 eV of the FWHM for water O1s photoelectron peak.
Enhancement of Lithium Concentration near the Air-Water Interface

LJ-XPS experiments have shown the surface enhancement of lithium cations relative to potassium cations in 2 M aqueous solutions (Figure 7.3). Results were confirmed with MD simulations, and are consistent with previous studies. Importantly, these MD simulations account for the instantaneous interface of solution so that the depth into solution is calculated from the surface of capillary waves, not an average surface.

Figure 7.3. Anion to cation ratios for lithium salts show an interfacial lithium enhancement. Figure is adapted from reference 26.
Low Photoelectron Kinetic Energy Studies

The absolute probe depth of LJ-PES experiments has been approximated for NaI solutions, but is largely unknown.\textsuperscript{28} LJ-PES studies were undertaken for potassium iodide and sodium iodide solutions for photoelectron kinetic energies between 40 and 800 eV (Figure 7.4). However, interpretation of data in terms of absolute depth by comparison with MD simulation is complicated by experimental geometry and orbital anisotropy in aqueous solutions.\textsuperscript{29}

Figure 7.4. PE peak area ratios for aqueous 2 M NaI. Or 2 M KI relative to water O1s.
Aqueous Distribution of Magnesium and Sodium Ions

Figure 7.5 shows S2p, Mg2s, and Cl2p photoelectron spectra collected for 2 M MgSO4 and 2 M MgCl2 at 600 eV photoelectron kinetic energy (835 eV, 696 eV, and 803 eV photon energies, respectively). Integrated photoelectron spectral peak areas were measured and ratios were taken to determine the relative concentration of each species as a function of photoelectron kinetic energy, or relative depth into solution.

Figure 7.5. PE spectra showing Mg2s, S2p, and Cl2p peaks for photoelectrons with 600 eV kinetic energy for aqueous 2 M MgCl2 and 2 M MgSO4.

The increased Mg2s / O1s (aq) ratio for surface measurements (200 eV photoelectrons) shown in Figure 7.6a indicates a twofold surface enhancement of Mg2+ for MgCl2 solutions, but not for MgSO4 solutions. Studies are currently being completed to confirm this enhancement, as it is unexpected based on the strong repulsion of a doubly-charged ion from its image charge. These results suggest that Mg2+ has a larger surface propensity in the absence of ion-pairing
interactions, consistent with MD predictions for 2 M MgNO₃⁻ (aq) that suggest ion-pairing with nitrate “pulls” magnesium to the bulk.

Figure 7.6. Photoelectron peak area ratios for 2 M MgSO₄ (blue dots) and 2 M MgCl₂ (red dots).

a. Cation to O1s (aq) ratio. b. Anion to O1s (aq) ratio.

The anion to O1s (aq) peak area ratios are shown in Figure 7.6b. The relative Cl⁻ signal was observed to be higher at the surface, whereas SO₄²⁻ signal is slightly lower at the surface. These findings are consistent with Hofmeister series surface propensity trend where sulfate has bulk propensity, and chloride has surface propensity. The relative distribution of sulfate as a function of depth into solution can also be estimated from the ratio of the sulfate O1s peak to that from liquid water (Figure 7.7). These findings for the bulk ratio of sulfate to water agree with what we would expect when calculating the molar ratio for a 2 M MgSO₄ solution, and the amount of sulfate oxygen decreases near the interface. This approach reveals an approximately 50% surface depletion in SO₄²⁻ (aq).
Figure 7.7. a. PE spectra showing O1s peaks for photoelectrons with 600 eV kinetic energy and b. sulfate O1s to water O1s (aq) ratio for aqueous 2 M MgSO₄. The blue Gaussian is the H₂O (g) peak, the red Gaussian is the H₂O (aq) peak.

Figure 7.8 shows the anion to cation ratio for aqueous 2 M MgSO₄ and 2 M MgCl₂. In the bulk (700 eV photoelectron kinetic energy), the anion to cation peak area ratios approach the stoichiometric values for bulk solution: Cl⁻ / Mg²⁺ approaches two and SO₄²⁻ / Mg²⁺ approaches one. The surface Cl⁻/Mg²⁺ peak area ratio is slightly lower near the surface (200 eV photoelectron kinetic energy), which reflects the tentative surface enhancement of magnesium. The SO₄²⁻ / Mg²⁺ ratio remains fairly constant over all photoelectron kinetic energies sampled, which may indicate that the ions exist in a 1:1 pair in the bulk and at the surface, as would be expected for ion-pairs.
Figure 7.8. Anion to cation photoelectron peak area ratios for 2 M MgSO\(_4\) (blue dots) and 2 M MgCl\(_2\) (red dots).
Specific Ion Effects: Cation Effects

Studies were undertaken to determine the difference between ionic distributions in MgCl₂, and NaCl, and several relevant photoelectron spectra peak area ratios are plotted in Figure 7.9. The Na₂s (aq) / O₁s (aq) peak area ratio is slightly lower near the surface, indicating that Na⁺ (aq) is depleted at the surface as we would expect from the formation of an electrical double layer with chloride, which is typically enhanced at the air-water interface. The anion to cation PE peak area ratios show similar relative concentrations for NaCl and MgCl₂ solutions at the surface (200 eV photoelectron kinetic energy), and the ratio approaches the expected bulk stoichiometric values for spectra recorded with 600 and 700 eV PE KEs. These results suggest that sodium and magnesium have similar density profiles when in the presence of chloride despite their very different solubility and ion-interaction energetics.

Figure 7.9. Photoelectron peak area ratios contrasting 2 M MgCl₂ (aq) (red dots) and 2 M NaCl (aq) (blue dots) as a function of photoelectron kinetic energy. a. Cation to O₁s (aq) ratio. b. Anion to O₁s (aq) ratio. c. Anion to cation ratio.
Binding Energy Trends

Binding energies were plotted versus photoelectron kinetic energies for 2 M MgSO₄ (aq), 2 M MgCl₂ (aq), and 2 M NaCl (aq) (Figure 7.10). Slight deviations were observed. Deviations in the binding energies are seen at 400 eV because the reference spectra are recorded at low flux, and thus have greater noise.

Figure 7.10. Photoelectron binding energies for Cl₂p, S₂p, and Na₂s photoelectrons from 2 M MgCl₂ (aq) (red dots), 2 M NaCl (aq) (light blue dots), and 2 M MgSO₄ (aq) (blue dots) as a function of photoelectron kinetic energy.
Conclusions

This chapter explored the interfacial ionic distributions of aqueous ionic solutions using LJ-PES. Surface enhancement of lithium cations was observed, showing that these fundamental studies are required to discover exceptions to the general Hofmeister trends. Low PE KE studies investigated the probe depth in solution, but results are complicated by fundamental photoionization crossection issues that are beyond the scope of this work.

The magnesium dication was found to be slightly more concentrated near the interface of aqueous solution compared to the bulk, except when a bulk-segregated anion like sulfate offered ion-pairing opportunities as depicted in Figure 7.11. These studies show that sulfate has an almost 50% lower concentration within the first few angstroms of solution compared to bulk solution up to ~ 50 angstroms deep. The observed depletion of sulfate and magnesium near the interface may indicate that the energy stabilization conferred by ion-pairing is greater than the energy to fully solvate magnesium in water. However, this is tentatively stated as more studies are underway to confirm these results.

Figure 7.11. Schematic depiction of solute distributions in 2 M MgCl₂ and 2 M MgSO₄ showing the effect of ion pairing.
This work also experimentally confirmed that the interfacial behavior of magnesium or sodium chlorides are very similar, as predicted by MD simulations.\textsuperscript{14-15, 30} It should be mentioned that this work is in good agreement with the alternating magnesium and chloride layers predicted at the interface of MgCl\textsubscript{2} solutions despite the lack of a second magnesium enhancement below the first. Signal from this second magnesium enhancement is suppressed because this experimental technique also integrates photoelectrons generated at the surface when probing higher kinetic energy photoelectrons from the bulk.

This work provides a complimentary investigation to prior SFG studies, MD simulations, and PS experiments on magnesium solutions, with the capability to determine the density profile of aqueous solutes. Direct comparison of these results with previous findings may lead to an understanding of the surface potential. Further correlation with MD simulations to determine the thickness of the ionic layers at the interface requires analysis of the probe depth of the LJ-PES technique.
References


Introduction to Ternary Solutions

The interaction of aqueous ions and organics is particularly interesting in the context of atmospheric aerosols such as oceanic spray. These small droplets contain organics from biogenic and natural sources, and have been shown to have significantly different surface chemistry compared to pure ionic solutions. Studies have been completed to investigate the chemistry of salts or organic molecules at the surface of aqueous solutions, but relatively few probe the surface chemistry of mixtures containing both ions and organics.

One study that is particularly relevant to the topic of ternary organic-salt-water solution chemistry elucidated the surface-specific behavior of aqueous potassium iodide with the addition of 1-butanol using AP PES at beam line 11.0.2 at the ALS. Here, a potassium iodide (KI) single crystal was cooled in the presence of water vapor (-10 °C, 78% relative humidity) until a droplet formed from deliquescence, that was then exposed to butanol vapor. Iodine (I4d) to potassium (K2p) PES peak area ratios were determined as a function of photoelectron kinetic energy (eV), a measure of relative depth into solution. The I4d to K2p ratio for aqueous KI decreased by factor of two to three when exposed to butanol, depending on the degree of butanol exposure. Results were compared to MD simulations and surface tension measurements for aqueous NaI with butanol. It was found that butanol resides at the surface of solution with the alkyl chain directed away from solution. In this orientation, the oxygen from butanol interacts with cations in solution, and the hydroxyl hydrogen interacts with anions in solution, increasing the concentration of ions near the interface in a stoichiometric relationship.
The work presented here will expand on the topic of salts and organics near the aqueous interface through discussion of several aqueous systems: acetonitrile and potassium iodide, propionitrile and potassium iodide, ethanol and sodium chloride, ethanol and magnesium chloride, and ethylene glycol with sodium chloride. The first two systems will be mentioned briefly here as they have been covered elsewhere, and the last three systems will be emphasized.

It is useful to have a perspective on the known chemistry of single-component solutions before discussing the mixtures investigated here. SFG studies found that acetonitrile or propionitrile undergo concentration-dependent reorientation at the aqueous interface. Acetonitrile orients with the methyl group directed away from solution at a 40° angle with respect to surface normal below 0.07 mf. At higher concentration, this angle tilts to 70° with a corresponding loss of hydrogen bonding with water. A reorientation from 40° to 50° is seen for propionitrile solutions above 0.011 mf. However, MD simulations predict that the orientation of acetonitrile depends strongly on the curvature of the liquid interface. These reorientations are indicative of structural changes at the interface, including changes in hydrogen bond strengths.

The addition of chloride salts to nitrile solutions results in bulk phase separation, or salting out, of acetonitrile from bulk aqueous solution. As such, KI was chosen for these studies because it is ineffective for salting out of acetonitrile. Indeed, KI was found to salt-in acetonitrile.

Ethylene glycol and ethanol solutions were examined as models for automotive pollution in oceanic aerosols where salt concentrations approach 2 M after evaporation. The interfacial behavior of aqueous 2 M sodium and 1 M magnesium chloride solutions upon addition of ethylene glycol or ethanol were examined as a function of depth into solution by LJ-PES. Studies were also completed for ethanol or ethylene glycol solutions with very little salt (0.01 M) to rule out
ion-dependent changes in the interfacial behavior of ethanol and ethylene glycol over the concentration range of interest (0 – 0.2 mf).

Interfacial aqueous ethanol has been modeled using MD simulations, and SFG experimental studies reveal the nature of the alcohol-water interaction. It is accepted that ethanol is concentrated at the surface of solution where it hydrogen bonds to fewer water molecules compared to the bulk and orients so that the alkyl group is directed away from solution. This ordering results in a depletion layer directly under the first (similar “hydrophobic packing” is seen for aqueous methanol). Ethylene glycol solutions have been studied by SFG and DFT computations, and it is found that ethylene glycol also accepts hydrogen bonds from water near the aqueous interface, resulting in highly viscous solutions.

Mixtures of salts with aqueous ethanol or ethylene glycol have previously been investigated for bulk behavior. Salts have been long used in phase separation of organics and water because ions often outcompete organics for interaction with water, driving the organic to form homogeneous clusters away from water. The competition results from the higher solubility of the salt in water (Table 8.1). For instance, sodium chloride is less soluble in ethanol–water mixtures and ethylene glycol-water mixtures than in neat water. Additionally, aqueous ethanol is salted out of solution by NaCl.
Table 8.1. Solubilities for select organics and ions.

<table>
<thead>
<tr>
<th>Solubility in water (g/100 g at 25 °C)</th>
<th>Solubility of NaCl in solvent (g / 100 mL at 25 °C)</th>
<th>Solubility of MgCl₂ in solvent (g / 100 mL at 25 °C)</th>
<th>Solubility of KI in solvent (g / 100 mL at 20 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Miscible</td>
<td>36.09 (ref 22)</td>
<td>144.0 (153.2 ) (ref 22) (59.67) wt % (ref 24)</td>
</tr>
<tr>
<td>MeCN</td>
<td>Miscible</td>
<td>0.0003 (ref 25)</td>
<td>- (1.9) wt % (ref 24)</td>
</tr>
<tr>
<td>PropCN</td>
<td>5-10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Miscible</td>
<td>0.065 (ref 25)</td>
<td>4.5 (ref 24)</td>
</tr>
<tr>
<td>Butanol</td>
<td>8.15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>Miscible</td>
<td>7.09 (ref 22)</td>
<td>50.0 (ref 24)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.0 (ref 24)</td>
<td>50.58 (ref 22)</td>
</tr>
</tbody>
</table>
Experimental Methods

Solution surfaces were probed using LJ-PES with and without the addition of salt to aqueous solutions of acetonitrile, propionitrile, ethanol, or ethylene glycol. Experiments were undertaken on the ALS LJ-PES setup, with the exception of acetonitrile solutions without salts that were studied at BESSY, as described in Chapter five. PE spectra were recorded at photoelectron kinetic energies of 200 and 600 eV at the ALS. Spectra were fit with Gaussian peaks and a Shirley background was subtracted. The peak areas for chlorine (Cl2p) peaks were constrained in a 1:2 ratio. Sodium (Na1s), carbon (C1s) peaks for ethylene glycol, and magnesium (Mg2s) peaks were fit with unconstrained Gaussian peaks. Oxygen (O1s) peaks were fit with two unconstrained Gaussian peaks for the gas and solution phase, except for ethanol solutions where a third oxygen species was observed. Here, the O1s gas phase peak splitting was set to 1.16 eV. Two ethanol (g) C1s peaks were constrained within 0.05 eV of the gas phase peak width, with splitting between the peaks set to equal the gas phase splitting of 1.5 eV. The peak areas for the ethanol (aq) C1s peaks were set to be equal.

Data is presented in terms of relative concentrations represented by the ratio of peak areas at a particular photon energy, or in Langmuir plots. Care must be taken when interpreting PE peak area ratios for dissimilar orbitals because these experiments were not undertaken at the magic angle and so the geometrical dependence of the angular anisotropy has not been taken into account, nor has the solution or gas phase effects on the beta factor. Langmuir plots were constructed by taking the ratio of peak areas relative to the total signal for species in solution. To calculate the Langmuir point for ethanol with magnesium chloride, the average was taken for the ethanol C1s PE peak area divided by the sum of the water O1s (aq), ethanol C1s (aq) and Mg2s or Cl2p peak area ratios. The average is taken to account for differences between the Mg2s or Cl2p peak areas.

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Aqueous Acetonitrile or Propionitrile

Interfacial acetonitrile behavior has been described elsewhere. Briefly, aqueous solutions containing either acetonitrile or propionitrile were investigated by LJ-PES with and without 2 M KI to probe interfacial and bulk chemistry. Figure 8.1 shows C1s PE spectra for acetonitrile solutions recorded at the surface (200 eV photoelectrons) and bulk (600 eV photoelectrons). The higher binding energy species is dominant for measurements probing the surface, and is identified as gaseous acetonitrile. Saturation of the C1s (aq) / O1s (aq) for acetonitrile occurred by 0.2 mf, corresponding to the formation of a surface monolayer. The Helmholtz equation was used to calculate a surface angle for acetonitrile between 72° and 53° with respect to surface normal, in agreement with SFG findings.

Figure 8.1. C1s PE spectra for 0.6 mf (a. and c.) and 0.07 mf (b. and d.) aqueous acetonitrile probing the surface (a. and b.) and bulk of solution (c. and d.). C1s spectra are fit with two peaks corresponding to aqueous (blue) and gaseous (red) acetonitrile species that have sufficiently different binding energies to be resolved.
Interactions of Aqueous Acetonitrile and Propionitrile with KI

The effect of KI on aqueous acetonitrile or propionitrile has been examined using LJ-PES, and the results are explored elsewhere.\textsuperscript{29} Aqueous nitrile solutions were investigated using depth-dependent LJ-PES with either a small amount of salt (0.01 M KI) to correct for solution charging during irradiation, or large amounts of salt (2 M KI) to elicit a salt-effect. Briefly, it was found that acetonitrile is salted in from the surface to the bulk by KI, whereas propionitrile is salted out by KI (Figure 8.2), as one would expect.

![Figure 8.2. Illustration of salting in or out of acetonitrile or propionitrile by KI, respectively.](image)

This section will focus on the impact of salt concentration on acetonitrile behavior near the liquid-vapor interface. PE spectra were collected for a 0.1 mf aqueous acetonitrile solution as a function of added KI concentration, and PE peak area ratios provide measures of the relative concentration of solutes at the surface or in the bulk for photoelectrons with 200 eV and 600 eV KE, respectively. Results show a saturation of the salting in effect of KI on 0.1 mf acetonitrile by 1 M KI.
The relative acetonitrile concentration with respect to water for a 0.1 mf acetonitrile solution with varying amounts of KI was monitored at the surface and in bulk solution by establishing the C1s or N1s ratios versus O1s (aq) from water (Figure 8.3). N1s to O1s ratios are lower than C1s to O1s ratios, as expected from the stoichiometry of the molecule (C₂H₃N). The relative acetonitrile concentration probed near the surface (blue) is seen to be approximately double that in the bulk (red), regardless of KI concentration and in agreement with studies on pure aqueous acetonitrile. The relative surface depletion of acetonitrile at high KI concentrations supports the salting in of acetonitrile by KI, and this effect is seen to saturate by 1 M of KI. This result is also observed in the C1s Langmuir plot (not shown).²⁹

Figure 8.3. C1s and N1s PE Peak area ratios relative to O1s (aq) for a 0.1 mf aqueous acetonitrile solution as a function of KI concentration. Surface data (200 eV KE photoelectrons) are shown as blue triangles, and bulk data (600 eV KE photoelectrons) are shown in red.
The relative ion to water (aq) O1s oxygen PE peak area ratios are plotted in Figure 8.4 for a 0.1 mf acetonitrile solution with added KI. Relative to the water O1s signal, the K2p signal increases linearly with added salt at the surface and in the bulk of solution, indicating a uniform potassium concentration. However, the I4d / O1s ratio is four times as high at the surface than in the bulk. This surface enhancement of I (aq) increases with KI concentration, and the relative iodide concentration at the surface is nearly five times greater than that in the bulk of solution for solutions with more than 3 M KI.

Figure 8.4. Ionic PE Peak area ratios for a 0.1 mf aqueous acetonitrile solution as a function of KI concentration. Surface data (200 eV KE photoelectrons) are shown as blue triangles, and bulk data (600 eV KE photoelectrons) are shown in red.
The anion to cation PE peak area ratio is plotted for a 0.1 mfe aqueous acetonitrile solution as a function of KI concentration (Figure 8.5). The bulk ratio (red) is in good agreement with the stoichiometric ratio for all KI concentrations, but the surface ratio (blue) decreases for higher KI concentrations. By comparing these results to those in Figure 8.4, it is clear that the decrease in the relative I / K ratio at the interface for 5 M KI in 0.1 mfe acetonitrile is caused by saturation of I' (aq) at the surface.

![Figure 8.5](image)

Figure 8.5. Anion / cation PE Peak area ratios for a 0.1 mfe aqueous acetonitrile solution as a function of KI concentration. Surface data (200 eV KE photoelectrons) are shown as blue triangles, and bulk data (600 eV KE photoelectrons) are shown in red.
Interaction of Aqueous Ethanol or Ethylene Glycol with Ions

Ethanol and ethylene glycol were selected for this study because they are structurally similar, soluble automotive pollutants that can potentially impact the distribution of ions in solution. Aqueous ethanol solutions have lower densities, viscosities, and surface tensions than ethylene glycol solutions. The concentration of ethanol is enhanced at the surface of aqueous ethanol solutions, and will be shown to have a strong impact on ions at the interface. Ethanol does not restructure at the interface at any concentration, indicating that the strength of ethanol-water hydrogen bonds are constant. Ethylene glycol solutions, however, have interfacial properties that depend on concentration. Ethylene glycol forms complexes with water near the aqueous interface, with an interfacial phase rearrangement occurring for solutions above 0.5 molar ethylene glycol bulk concentration. The surface tension of aqueous ethylene glycol solutions decreases with concentration up to 0.1 molar ethylene glycol, corresponding to breaking of water-water hydrogen bonds.

PE spectra were recorded for photoelectrons with 200 eV KE and 600 eV KE for aqueous solutions of ethanol or ethylene glycol with a small amount of salt (0.01 M NaCl or MgCl$_2$), or a large amount of salt (2 M NaCl or 1 M MgCl$_2$). C1s PE spectra for ethanol solutions show a gas phase species, but those for ethylene glycol solutions do not because it has a low vapor pressure (Figure 8.6). In addition, two carbon species were observed for ethanol (methyl and hydroxyl carbons), whereas ethylene glycol spectra show only one carbon species. The addition of salts including 1 M MgCl$_2$ do not qualitatively alter ethanol C1s PE spectra for photoelectrons generated near the surface (Figure 8.7), or in the bulk (Figure 8.8).
Figure 8.6. C1s photoelectron spectra for 0.01 M NaCl with 0.09 mf ethanol or 0.07 mf ethylene glycol.

Figure 8.7. (on following page) C1s PE spectra recorded for photoelectrons with 200 eV KE for aqueous ethanol solutions with or without salt.  a. 0.05 mf ethanol with 0.01 M MgCl₂, b. 0.05 mf ethanol with 1 M MgCl₂, c. 0.09 mf ethanol with 0.01 M MgCl₂, d. 0.09 mf ethanol with 1 M MgCl₂, e. 0.14 mf ethanol with 0.01 M MgCl₂, f. 0.14 mf ethanol with 1 M MgCl₂, g. 0.2 mf ethanol with 0.01 M MgCl₂, h. 0.2 mf ethanol with 1 M MgCl₂. Spectra are fit with four peaks corresponding to the aqueous ethanol hydroxyl (red) and methyl (black) carbons, and gaseous ethanol hydroxyl (blue) and methyl (green) carbons.
a. 0.05 mf ethanol

b. 0.05 mf ethanol + 1 M MgCl₂

c. 0.09 mf ethanol

d. 0.09 mf ethanol + 1 M MgCl₂

e. 0.14 mf ethanol

f. 0.14 mf ethanol + 1 M MgCl₂

g. 0.2 mf ethanol

h. 0.2 mf ethanol + 1 M MgCl₂
Figure 8.8. C1s PE spectra recorded for photoelectrons with 600 eV KE for aqueous ethanol solutions with or without salt. a. 0.05 mf ethanol with 0.01 M MgCl₂, b. 0.05 mf ethanol with 1 M MgCl₂, c. 0.09 mf ethanol with 1 M MgCl₂, d. 0.14 mf ethanol with 0.01 M MgCl₂, e. 0.14 mf ethanol with 1 M MgCl₂. Spectra are fit with four peaks corresponding to the aqueous ethanol hydroxyl (red) and methyl (black) carbons, and gaseous ethanol hydroxyl (blue) and methyl (green) carbons.
O1s PE Spectra for ethanol show a distinct vapor phase peak for ethanol and water, but only one peak corresponding to water is resolvable for the liquid phase (Figure 8.9).

Figure 8.9. O1s PE spectra for 0.01 M MgCl₂ with 0.2 mf ethanol recorded for 600 eV KE photoelectrons (1135 eV photon energy). The spectra is fit with three peaks corresponding to liquid water (red), gaseous ethanol (green), and water vapor (blue).

C1s to O1s peak area ratios were determined for ethanol and ethylene glycol solutions with added NaCl or MgCl₂ (Figure 8.10). For these ratios, only one carbon species was included so the ratios can be understood as a stoichiometric comparison of the hydrocarbon to water relative concentration. The relative concentration of ethanol at the surface (blue) is nearly double that in the bulk (red), as expected. However, the ratios with and without salt are not significantly different. A similar trend is seen for ethylene glycol, but the surface enhancement is more subtle.
Figure 8.10. C1s to O1s (aq) PES peak area ratios for a. ethylene glycol solutions with and without 2 M NaCl, and ethanol solutions with and without b. NaCl, and c. 1 M MgCl$_2$. Empty circles represent data for solution with 0.01 M salt, crosses represent data after the addition of 1 M salt, and triangles represent data after the addition of 2 M NaCl or 1 M MgCl$_2$. Surface data is shown in blue (200 eV photoelectrons), and bulk data is shown in red (600 eV photoelectrons). Error bars result from multiple experiments under nominally similar conditions.
Surface data show an enhancement of gas phase ethanol upon addition of salt, suggesting an increased vapor pressure (Figure 8.11). This increase is consistent with salting out of ethanol by ions. A comparison to ethylene glycol is not possible because there is no gas phase C1s peak for ethylene glycol.

![Figure 8.11. PES peak area ratios for gas phase C1s relative to aqueous O1s signal for a. aqueous ethanol with 2 M MgCl$_2$, and b. aqueous ethanol with 2 M NaCl. Open circles represent data for solution with 0.01 M salt, and triangles represent data after the addition of salt. Surface data is shown in blue (200 eV photoelectrons), and bulk data is shown in red (600 eV photoelectrons).](image-url)
Langmuir plots for Ethanol with 0.01 M NaCl or MgCl₂ show a surface saturation of ethanol around 0.1 mf (Figure 8.12a, blue open circles), but not for ethylene glycol (Figure 8.13, blue open circles). This could be because the concentrations of ethylene glycol in solution were lower in this study. When 1 M NaCl (Figure 8.12a, yellow triangles), 2 M NaCl (Figure 8.12a, black triangles), or 2 M MgCl₂ (Figure 8.12a, green triangles) are added to ethanol solutions, the relative amount of ethanol at the surface upon saturation decreases, indicating that ions are displacing some of the organic at the interface. This change is not seen for ethylene glycol with the addition of 2 M NaCl (Figure 8.13, purple triangles), where the distribution of ethylene glycol is independent from ionic concentration. Gas phase Langmuir plots show no gas phase ethanol saturation with or without ions at the concentrations investigated (Figure 8.12b).

Figure 8.12. The addition of salt decreases the saturation of ethanol at the solution surface. The C1s (aq) signal is shown relative to the total solution signal for 1 M NaCl (yellow open triangles), 2 M NaCl (black open triangles), 1 M MgCl₂ (green open triangles), and water (blue open circles). Gas phase Langmuir plot shows no saturation at the concentrations in this study. All data is for 200 eV PE photoelectrons.
Figure 8.13. Ethylene glycol does not saturate the surface in the concentration range examined in this study, and is not affected by the presence of ions. The noise at low [EG] is real, and cannot be excluded using the Q-test. This does not affect the conclusion that a saturation layer is not formed at the surface. The Langmuir plot shows data for the ethylene glycol concentration (½ * C1s PE area) relative to total signal for solutions with 0.01 M NaCl (blue), or 2 M NaCl (purple triangles).

Now that the behavior of organics is well-understood, we can move on to investigate the behavior of ions in these solutions. Langmuir plots have been developed for chloride, magnesium, and sodium at the surface in these solutions (Figure 8.14). First, we note that the behavior is very different for ethylene glycol solutions (purple), than for ethanol solutions (green, black, yellow). The relative concentration of sodium or chloride ions at the interface is nearly independent of the amount of ethylene glycol in solution, but decreases as ethanol is added to solution. The change in the sodium Langmuir plot is more extreme than that for magnesium, indicating that sodium is pushed away from the interface with greater force than magnesium, perhaps because magnesium is much smaller. This is in agreement with the formation of a surface layer of ethanol (Figure
8.12a) that pushes ions away from the interface, and also leads to changes in magnesium solvation (Figure 8.16a).

![Graphs showing PE peak area ratios for Cl2p and Na2s](image)

Figure 8.14. The Na2s signal decreases relative to the total solution signal as the ethanol concentration increases, indicating displacement of sodium by ethanol at the surface. Langmuir plots for Na2s and Cl2p are shown for 1 M NaCl (yellow triangles) and 2 M NaCl (black triangles). Langmuir plots are also shown for ethylene glycol with 2 M NaCl (purple triangles).

PE peak area ratios for Cl2p versus O1s from liquid water provide a relative measure of the chloride concentration in solution compared to water (Figure 8.15). The upward trend in the Cl2p to O1s ratio for ethanol solutions is expected for all solutions because the concentration of water decreases as the ethanol or ethylene glycol concentration increases. Solutions with ethylene glycol (Figure 8.15a) have similar distributions of chloride at the surface, and in the bulk of solution because it acts as a surfactant to eliminate surface enhancement of chlorine as seen in neat solutions. For the study with NaCl (Figure 8.15c), both Na⁺ (aq) and Cl⁻ (aq) are stabilized by alcohol at the aqueous interface. The 1 M MgCl2 (aq) and ethanol solution (Figure 8.15b) has
more surface enhancement of chloride compared to the studies with NaCl, contrary to studies on 2 M MgCl₂ without ethanol that suggest the surface enhancement should be similar.³²-³³

Figure 8.15: PES Peak area ratios for Cl₂p to O₁s for aqueous solutions with either a. ethylene glycol with 2 M NaCl, b. ethanol with 1 M MgCl₂ or c. ethanol with 2 M NaCl. Surface data (200 eV KE photoelectrons) are shown as blue triangles, and bulk data (600 eV KE photoelectrons) are shown in red.

The solvation of magnesium is investigated by looking at the binding energy of ejected photoelectrons from the 2s core level. Mg 2s PE binding energy increases by 0.2 eV as ethanol is added to solution (Figure 8.16), corresponding to decreased electron density donation from water as the water concentration decreases. Additionally, the binding energy is greater for the surface data, indicating an even greater dehydration compared to magnesium in the bulk. The increase in binding energy upon dehydration is expected because magnesium is strongly solvated by six water molecules. Binding energies were constant for all other species investigated, indicating that Cl⁻ (aq), Na⁺ (aq), ethanol (aq), and ethylene glycol (aq) interactions with water are weaker, as one would expect.
Figure 8.16: Mg 2s PE binding energy as a function of ethanol concentration. Surface data (200 eV KE photoelectrons) are shown as blue triangles, and bulk data (600 eV KE photoelectrons) are shown in red.

The anion to cation PE peak area ratio is slightly larger at the surface for all solutions (Figure 8.17), as expected. Bulk anion to cation ratios (red triangles) approach the expected stoichiometric ratio for each of the salt solutions. The surface ratios (blue triangles) are slightly higher because chloride is enhanced at the interface, and this difference is largest for MgCl₂ (aq) solutions at high ethanol concentrations. The surface enhancement of chloride relative to magnesium can be explained by surface depletion of magnesium from favorable solvation by water in the bulk. In contrast to past studies, the addition of an alcohol did not significantly reduce the anion to cation ratio at the interface.¹
Figure 8.17: PES Peak area ratios for Cl2p to cation for aqueous solutions a. ethylene glycol with 2 M NaCl, b. ethanol with 1 M MgCl₂ or c. ethanol with 2 M NaCl. Surface data (200 eV KE photoelectrons) are shown as blue triangles, and bulk data (600 eV KE photoelectrons) are shown in red.
Conclusions

This work studied the surface chemistry of ternary solutions of water with acetonitrile, propionitrile, ethanol, or ethylene glycol and sodium chloride, magnesium chloride, or potassium iodide using LJ-PES. The ALS AP LJ-PES technique has also been applied to ternary nitrile and salt aqueous solutions, where a strong surface competition is examined. It was found that acetonitrile was salted in to bulk aqueous solution from the interface by KI, and the converse occurred for aqueous propionitrile. The salting-in effect of KI on aqueous acetonitrile was seen to saturate by 1 M KI.

The presence of ethanol in aqueous solutions was shown to have a large impact on the chemistry of the magnesium ion due to displacement of solvating water molecules. Ethanol influences the chemistry of sodium chloride solutions, by forcing the ions deeper into solution. Additionally, ethanol and ethylene glycol reduced the surface enhancement of chloride compared to that in water. Results are consistent with previous studies on butanol ternary solutions, and are distinct from aqueous MgCl₂, NaCl, ethanol or ethylene glycol solutions. This work expands the understanding of interfacial molecular behavior in ternary aqueous ionic and organic solutions.
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A. Appendix

Abbreviations

AES Auger electron spectroscopy, Auger electron spectrometer.
ALS advanced light source
AP ambient pressure
BE binding energy (eV)
BESSY synchrotron facility, Helmholtz Center for Materials and Energy in Berlin, Germany
CO carbon monoxide (gas)
HOPG highly oriented pyrolitic graphite
HPLC high pressure liquid chromatography
HREELS high resolution electron energy loss spectroscopy
KE kinetic energy (eV)
LaB6 lanthanum hexaboride filament
LBNL Lawrence Berkeley National Laboratory in Berkeley, California
LEED low energy electron diffraction
LJ-PES liquid jet photoelectron spectroscopy
MD molecular dynamics
MS mass spectrometer, mass spectroscopy
OFHC oxygen free high conductivity (Copper)
PE photoelectron
PEEK polyether ether ketone
PES photoelectron spectrometer, photoelectron spectroscopy

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PFA perfluoroether

PMT photomultiplier tubes

PS surface potentiometry

Pt NP(s) platinum nanoparticle(s)

QCM quartz crystal microbalance

SEM scanning electron microscopy

SFG sum frequency generation (spectroscopy)

UCI University of California, Irvine

UHV ultra high vacuum

XPS X-ray photoelectron spectroscopy
HREELS

Schematics for HREELS Components

The following pages contain schematics for the removable sample holder based on those made by Dr. Ronald Grimm for the TPD chamber in the Hemminger Laboratory.

Figure A.1. Coupler (a): used to attach the manipulator rod to coupler (b). Type 304 stainless steel.
Figure A.2. Coupler (b): used to attach coupler (a) to coupler (c). Type 304 stainless steel.
Figure A.3. Coupler (c): used to attach coupler (b) to SS Legs (d). Type 304 stainless steel.
Figure A.4. SS Legs (d) used to attach coupler (c) to SS tracks (i), thermocouple sled (m), and support (l).
Macor® thermocouple sled (m) is oriented so that thermocouple clips line up with holes in Macor® block (t).

Figure A.5. Macor® thermocouple sled (m) and two illustrative photographs. Groves are centered side to side, and the overall length and depth are not vital. The groves go 0.02” into the Macor® piece with holes made with a 1/16” endmill that travels 0.1000” for an overall length of 0.163” and a width of 0.063”.
Figure A.6. Detail of holes in SS legs (d).
Figure A.7. Type 304 SS tracks (j) are used to attach Cu tracks (k) to SS legs (d), and a photograph showing the placement of the tracks relative to other sample holder components.

Bottom-up view of sample holder during construction.
Figure A.8. Summary of copper connections for resistive heating and conductive cooling. All components are OFHC copper, except for the braids (e) extracted from electrical wires and silver soldered to (g) and (h). Braids are insulated with fiberglass.
Figure A.9. Cu track (k)

- Top view
- Front view
- Outside view

0-80 tapped to connect to Cu reservoir connectors (h)

Thru holes
#30 (0.128” dia.) for 1/8” dia. ceramic tubes that insulate the 0-80’s for mounting onto SS track support
Figure A.10. Diagram of alumina spacers used to attach the copper tracks (k) to the stainless steel tracks (j).
Figure A.11. (f) copper screws and aluminum spacers, (h) copper reservoir connectors, and (g) copper track connectors.
Figure A.12. Representative photographs and a schematic of the removable sample holder. The sides are type 101 copper, and the middle block is Macor® with 0.032” holes to hold alumel or chromel wires for the thermocouple (o). 0-80 bolts attach the three components, and 0.025” alumina spacers are in-between the blocks to provide room to thread thermocouple wires. 0-08 screws on the top and bottom provide a grip for the wobble stick to push against to move the sample holder during transfer. Nuts are included on the left side to ensure a close fit with the wobble stick. The copper washers (s) at the front hold the 0.004” tungsten wire legs (f) that are attached to the sample for resistive heating.
Figure A.13. OFHC copper blocks (p).
Figure A.14. Macor® block (t).
(q) SS springs

0-80 thru holes (#53 drill, 0.059” dia)

Bend them to look like this:

- Made out of about 0.005” thick SS Shim

(s) Cu washers

0-80 thru holes (#53 drill, 0.059” dia)

for mounting front of cu block

Figure A.15. Stainless steel springs (q) and copper washers (s).
Figure A.16. Components for the transfer took on the linear motion arm.
HREELS experiment time line

Day 1:

1. Sample cleanliness is checked using AES.
2. One full oxygen cleaning cycle.
3. Sample cleanliness is confirmed with AES.
4. Run the sub pump, and wait two hours for the pressure to recover.
5. Degas Pt Evap for up to five hours or until pressure levels off.
6. Run the sub pump again to ensure pressure drops overnight.

Day 2:

1. Run the sub pump
2. Degas the Pt evaporator for up to five hours or until the pressure levels off.
3. Sample cleanliness is checked using AES.
4. One full oxygen cleaning cycle.
5. Sample cleanliness is confirmed with AES.
6. Run the sub pump, and wait two hours for the pressure to recover.

Day 3:

1. Sample cleanliness is confirmed with AES.
2. Al₂O₃ phonons are checked with HREELS.
3. Degas Pt evaporator.
4. Flash sample to 900 °C
5. Cool sample to room temperature, Re-tune HREELS (the flash lowers counts) and record back ground spectra.
6. Cool the sample to cryogenic temperatures using liquid nitrogen.
7. Retune the spectrometer and scan the sample before Pt deposition.

8. Introduce probe molecules to the chamber and retune.

9. Record annealing profile.

10. Thaw chamber.

Day 4:

1. Turn off the diffusion pump.

2. Record AES to document Pt deposition.

3. Work up data.
Improvements to the HREELS experiment

Auger degasing time and position

It is recommended to turn on the Auger spectrometer while the sample is in scanning position, and to eliminate the “degassing” waiting period of ten minutes. The Auger electron beam will not damage the surface of a Al₂O₃ film, and this protocol reduces the time the pressure in the chamber is elevated by the Auger filament – which will reduce exposure of the sample to background molecules.

Installation of a ventilated hazardous gas cabinet near the HREELS chamber

Given the newly implemented Toxic Gas Program at UCI, a ventilated gas cabinet and two points of chemical detection will be required for all toxic gasses used for HREELS experiments. These precautions will decrease the risk of exposure to gasses for experimenters, and reduce the lab’s liability.

Installation of load lock ion-gauge reading reporting electronics

The load lock ion gauge pressure is currently read by a local, analog control box. The ion gauge can be wired into a multiguage controller, and the pressure can be sent to the computer for reporting to the internet using labview software. It should be simple to replicate the set-up used for the main chamber ion gauge.

Computer upgrade

The HREELS computers are very slow, the software tends to crash, and now Windows XP will not be supported as of April 2014. New computers must be specially ordered to contain
multiple internal PCI slots to accommodate the HREELS and NI technology. This will require two computers due to card incompatibility.

Elimination of the all-metal valve

Currently, there is an all-metal valve connecting the gas-manifold to the HREELS chamber which can be opened to pump the chamber with a mechanical or diffusion pump. This valve leaks so that any changes in the pressure of the manifold result in pressure spikes in the main chamber. The valve could be re-built and replaced. However, the addition of the fast entry load lock with mechanical and turbo pumping capabilities eliminates the need for the valve between the chamber and the manifold. It is suggested that the valve be removed and the chamber and manifold be blanked off.

External control of thermoswitch on the ion pump for bakeout

Two thermoswitches on the HREELS chamber regulate several heating elements based on the temperature at the switch during bakeout – the process of heating the chamber to desorb water. The thermoswitch located on the ion pump is hazardous to operate during bakeout because fiberglass must be manually removed, presenting and inhalation and contact hazards. Here, the experimenter must insert an arm to the shoulder through the fiberglass to access the thermoswitch multiple times per day during bakeout. The thermoswitch should be mechanically coupled to an external rotational control to minimize exposure to the fiberglass insulation.

Replace copper connections for resistive heating
It is recommended to replace the copper part of the heating lead connections for the HREELS chamber with new connections including a safety coating to reduce the risk of electrical shock, and an insulated Allen wrench should be used to tighten the set screws.

Power supply with battery backup for mechanical pumps

The mechanical pumps should be placed on a power supply with a backup battery so that the pumps remain on long enough to be shut down and vented manually in the case of a power outage. This will prevent damage to the mechanical pumps, to the load lock turbo pump, and it will prevent the backflow of oil into the load lock and gas manifold.
### Figure A.17. Design parameters for the ALS LJ-PES chamber © 2011 VG Scienta Ltd.

<table>
<thead>
<tr>
<th>PORT</th>
<th>FLANGE TYPE</th>
<th>TUBE</th>
<th>PORT LENGTH</th>
<th>SKIRT LENGTH</th>
<th>PORT LENGTH TOL ±</th>
<th>FOCAL POINT</th>
<th>FOCAL POINT TOL Ø</th>
<th>ANGLE DETA</th>
<th>ANGLE GAMMA</th>
<th>FLANGE ORIENTATION</th>
<th>PORT USE</th>
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<tr>
<td>1</td>
<td>ZTCL45</td>
<td>Ø 44.45 x 1.50</td>
<td>114.000</td>
<td>11.00</td>
<td>0.00 ± 0.50</td>
<td>2.00 ± 0.50</td>
<td>90.00 ± 0.50</td>
<td>0.00 ± 0.50</td>
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<td>STRADDLED</td>
<td>JET ENTRY (TOP)</td>
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<td>PUMP</td>
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<td>ZCL19NS</td>
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<td>105.916</td>
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<td>1.00 ± 0.50</td>
<td>2.00 ± 0.50</td>
<td>90.00 ± 0.50</td>
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<td>320.00 ± 0.50</td>
<td>STRADDLED</td>
<td>LASER</td>
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<td>2.00 ± 0.50</td>
<td>90.00 ± 0.50</td>
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<td>3-RAY WINDOW</td>
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<td>Ø 152.40 x 3.00</td>
<td>181.400</td>
<td>18.00</td>
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<td>2.00 ± 0.50</td>
<td>90.00 ± 0.50</td>
<td>0.00 ± 0.50</td>
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<td>18.00</td>
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<td>2.00 ± 0.50</td>
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<td>0.00 ± 0.50</td>
<td>360.00 ± 0.50</td>
<td>STRADDLED</td>
<td>CONNECTION TO ANALYSER (BACK)</td>
</tr>
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**Diagram:** Chamber Assembly (not shown in text)
NOTES
1) WELD NOTE.
UNLESS OTHERWISE STATED ALL WELDS TO BE VG STYLE 'B' WITH NO
BURN THROUGH. ARGON GAS BACKING SHOULD BE USED TO
ACHIEVE THIS. ALL PORTS TO BE INSPECTED ON ASSEMBLY TO
DETERMINE IF EXTERNAL TACK WELDS ARE REQUIRED EITHER
FOR SUPPORT OR TO AID ASSEMBLY.

2) LEAK RATE.
THE CHAMBER MUST BE LEAK CHECKED TO BETTER THAN 1x10^-10 mbar Ls
USING A HELIUM MASS SPECTROMETER.

3) FINISH NOTE.
INTERNAL SURFACES TO BE UHV CLEAN. BEAD BLAST EXTERIOR, MASKING
ALL SEALING FACES.

4) SUPPORT NOTE.
IT IS THE RESPONSIBILITY OF THE CUSTOMER TO SUPPORT ANY EQUIPMENT
MOUNTED TO THE CHAMBER.

5) THREADS
ALL THREADS ARE METRIC.

6) PORT 10 A8010 FLANGE TO BE TAPPED M8.

7) PORT 8 ZFCL41R FLANGE TO BE TAPPED M6.

Figure A.18. Port specifications for ALS LJ-PES chamber. © 2011 VG Scienta Ltd.

The following schematics are shown at half-size.
Figure A.19. Front View of ALS LJ-PES chamber. © 2011 VG Scienta Ltd.
Figure A.20. Bottom-up view of ALS LJ-PES chamber. © 2011 VG Scienta Ltd.
Figure A.21. Side view of ALS LJ-PES chamber. © 2011 VG Scienta Ltd.

Figure A.22. (On following page) Manipulator for ALS LJ-PES chamber. © 2011 Microliquids GmbH
Binding Energies

Binding energies from our studies are summarized in Table A.1. Our studies have benefitted from published data for aqueous BEs so it seems only fitting that I present the experimental BEs for posterity. These binding energies are referenced to oxygen, and do not account for binding energy shifts in oxygen due to concentration or electric effects from ions in solution.

Table A.1. Binding energies from ALS AP LJ-PES studies and from LJ-PES studies from literature (*).

<table>
<thead>
<tr>
<th>Species</th>
<th>Binding Energy (eV)</th>
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<tr>
<td>Br2p</td>
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<tr>
<td>KBr (aq)</td>
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<td>3</td>
</tr>
<tr>
<td>LiBr (aq)</td>
<td></td>
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<tr>
<td>C1s</td>
<td></td>
<td></td>
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<tr>
<td>CH₃CN (g)</td>
<td>292.9 ± 0.1</td>
<td>4</td>
</tr>
<tr>
<td>CH₃CN (aq)</td>
<td>291.9 ± 0.2</td>
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<tr>
<td>CH₃CH₂CN (g)</td>
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<tr>
<td>CH₃CH₂CN (aq)</td>
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<tr>
<td>C₂H₆O (g)</td>
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<tr>
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<tr>
<td>LiCl (aq)</td>
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<td></td>
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<td>KI (aq)</td>
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<td>1*</td>
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<td></td>
</tr>
<tr>
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<td>3</td>
</tr>
<tr>
<td>KCl (aq)</td>
<td></td>
<td>3</td>
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<tr>
<td>KI (aq)</td>
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<td>LiI (aq)</td>
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<td>Li⁺ (aq)</td>
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<td>Mg2s</td>
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<tr>
<td></td>
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<tr>
<td></td>
<td>CH₂CH₂CN (aq)</td>
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<td></td>
<td>NaCl (aq)</td>
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<td></td>
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<td>H₂O (aq)</td>
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<td></td>
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<td>S2s</td>
<td>MgSO₄ (aq)</td>
<td>237.4 ± 0.1</td>
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References


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Dynamics in Charge-Transfer-to-Solvent States of Aqueous Chloride Revealed by Cl- 2p

9. Ottosson, N.; Faubel, M.; Bradforth, S. E.; Jungwirth, P.; Winter, B., Photoelectron
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LJ-PES Experimental Time Line

Before Beamtime

There are several things which should be completed before beamtime to ensure optimum use of light. First experiments should be planned and the type of solutions and scans requires are determined. Calculations should be done to evaluate the amount of reagents required to produce the solutions, and supplies should be purchased and shipped to the synchrotron facility. It is important to touch base with the beamline scientist and safety administrator to ensure the experiments are approved. Also, an e-mails should be sent to facilities to check if an equipment inspection or additional training are needed. For ALS work, the AP endstation is rotated into position infront of the X-ray window by using high pressure air to float the platform into place. This can be accomplished by one trained person in under 15 minutes. Experimenters then arrive at the synchrotron facility a day in advance to assemble the LJ-PES chamber on the AP endstation at beamline 11.0.2., and to make solutions in the chemlab (2233 ALS).

During Beamtime

At the beginning of each beam time, the beam must be focused on a sample, and the electron signal detected by the hemispherical energy analyzer must be optimized. Mirrors in the beamline at the ALS are tuned by a beamline scientist, and the light is detected in the chamber using a photodiode. Next, the beamline scientist optimizes the electron signal to the hemispherical energy analyzer. It is advisable to slightly re-optimize the mirrors and electronic optics while monitoring the I4d signal intensity using the SpecsLab software for a 4 M potassium iodide solution. This extra step ensures that the beam is focused on the liquid jet because the iodide ion does not enter the gas phase. Experimenters may fine tune the beam using the KB mirror vertical
and horizontal options in the MotorDisplay.vi labview program, but this will alter the beam and require a new flux measurement if one was already recorded.

Flux measurements (Figure A.23) are taken for normalization of ALS experiments using the photodiode, and it is advisable to record them first thing on the second day of beam time to minimize time spent venting and pumping the LJ chamber. Once the photodiode is in the chamber, one BNC connection is grounded and the other is attached to the signal in on a picoammeter. The signal is also transferred from the picoammeter to the “Aux” reading in the Single Motor Scan software. All viewports must be covered in foil or black cloth to prevent noise from ambient light. The Aux signal is scanned over all photon energies required for the experiment, at all appropriate polarizations and line gratings. The sensitivity of the picoammeter may be adjusted to ensure the signal does not saturate. The measured Aux values are used along with the picoammeter sensitivity, photon energy, and synchrotron ring current to calculate the X-ray Flux:

\[
\text{Flux} = \frac{(\text{Aux}) \times S}{(h \nu / 3.7) / (1.6 \times 10^{-19}) / C / 6}
\]

- Aux = Auxiliary signal measured by the photodiode (A)
- S = Sensitivity programmed in picoammeter 1E-6 (A/V)
- C = Synchrotron ring current (mA)
- \(h\nu\) = X-ray energy (eV)
- \(1.6 \times 10^{-19}\) eV = charge of an electron (eV)
Figure A.23. Flux on beamline 11.0.2 measured on 10-14-13.
At the ALS, the first stage of the analyzer and the liquid jet chamber must be vented or pumped down simultaneously to minimize the pressure differential across the aperture, and changes in pressure are done slowly (5 torr/second) because of the fragility of the silicon nitride x-ray window. The general instructions follow:

1. With the jet turned off in the chamber, fill the trap with 40 wt% NaCl solution and cool it below 0 °C (set chiller for -10 °C).
2. Using valves, connect the jet chamber to the first stage of the analyzer and slowly open these chambers to the ACP 15G mechanical pump. Pressure will drop very quickly at first, but try to keep it at 5 torr/second. Watch the pressure in the beamline (215A on the screen with green pressures) and the analyzer (top on liq jet pressure reader).
3. Once the chambers reach 20 torr, shut the valve to the pump. Isolate the first stage of the analyzer, and slowly pump it out. While this is pumping, start the jet 0.5 mL/min 0.05 M NaCl or MilliQ water.
4. Once the first stage of the analyzer reaches the $9 \times 10^{-2}$ torr, shut the valve to the ACP 15G dry pump, and open the gate valve to the large turbo by inserting the bent wire into the button hole and latching around the back of the button box. This is a dead-man’s switch – if the latch falls off, the valve will close.
5. You can now use the ACP 15G to pump the liquid jet chamber if needed.
6. Once the pressure in the first stage of the analyzer reaches $9 \times 10^{-4}$ torr, open the gate valve between the 1st stage and the 2nd stage.
The chamber at the ALS has to be vented carefully to protect the pressure in the analyzer and the beamline – The delicate x-ray window can break if the pressure increases suddenly. The first stage of the analyzer and the liquid jet chamber must be vented or pumped sown simultaneously to prevent a pressure differential across the aperture.

1. Stop scans in the `speckslab` software. Disconnect the analyzer in the software. Use `BL1102 BR.vi` to shut the valves to the FLEX APPES. It is OK to leave the valves to microscopy open.

2. Shut the manual gate valve to the analyzer.

3. Shut the turbo pump valve on the first stage of the Analyzer by removing the bent wire from the dead-man’s switch.

4. Slowly open the valve to connect the first stage of the analyzer to the jet chamber

5. Connect the gas nitrogen line to the green valve near the X-ray window. Shut the gatevalve on the cold trap. Slowly (10 torr/sec) vent the chamber with nitrogen while watching the pressure in the 1st stage of the analyzer, and the pressures in the beamline. Loosen the front door when the pressure nears atmospheric to prevent over pressurization of the chamber.

To collect spectra at the ALS, first turn on the analyzer by pressing the power buttons on both grey specs boxes and the one on the blue surface concept box located below the beamline to the left of the grey specs boxes. Electron signal will be optimized by sample positioning. In the `Specslab` software you should begin a scan using the photon energy corresponding to the dominant chemical species in your sample, plotting the intensity of electrons with a specific KE (say 200eV) as a function of time (735 light energy and 200eV kinetic energy). Make sure you have a good
view with the video camera or viewports, and check position through the viewport when you’re getting very close.

End of Day Cleanup

At the end of each experimental shift, the chamber is vented so that the jet can be stored externally overnight and the temperature controlled trap can be cleaned. Any chamber component with visible residue should be rinsed with MilliQ water. It is a good general practice to remove and rinse the aperture with MilliQ water to remove particulates which may block signal.

After Beamtime

One day after beamtime should be spent cleaning the LJ-PES chamber as described previously. The BESSY chamber requires a simple wiping-out using water and paper towels. The ALS chamber must be dismantled and all components must be rinsed into the waste with tap water and then MilliQ water before drying with ethanol and re-assembly. All safety paperwork should be completed including waste logs.
Suggestions for Future LJ-PES Experiments

Carts or Pallets for Equipment Transfer

   The liquid jet experiments require transfer of multiple heavy components and equipment from the storage facility in building 7 to the beam line in building 6. This currently entails multiple trips back and forth, and significant heavy lifting as each object needs to be lifted onto a cart, and then set down at the beamline. This process is time consuming and will result in irreparable injury to experimenters. Permanent installation of equipment on carts would reduce the amount of heavy lifting, but would still require multiple trips and would not reduce strain on experimenters from pushing heavy carts over uneven surfaces and door jams. It may be a better idea to produce a fixed shelf structure on a pallet which could be transferred in one step via forklift. This would protect the equipment, expedite set-up, and reduce the instance of injury.

Enlargement of the Cold Trap Flange

   On a future liquid jet chamber, the flange connecting the cold trap should be made larger to improve pumping efficiency of the cold trap, and to reduce the probability of the jet colliding with metal and subsequently freezing.

Splash Protection Cone

   A glass cone can be made to fit in the opening of the connection to the cold trap. This will minimize splattering while permitting visibility.

Aperture Removal Tool
Daily removal of the aperture for cleaning is accomplished by manually removing the aperture from the chamber. This step can be made more efficient by use of a rod with a clipping tool at the end to hold and remove the aperture as the screws are loosened.
Bulk Ammonia PES spectra

Figure A.24. Bulk (1005 eV photon energy) N1s PE Spectra for NH₄Cl (aq) solutions titrated using NaOH to pH a. 4.56, b. 8.25, c. 8.98, d. 9.20, e. 9.54, f. 9.74, g. 10.0, and h. 11.38.

Figure A.25. (On following page) Bulk (1005 eV photon energy) N1s PE Spectra for NH₄OH (aq) solutions titrated using HCl to pH a. 8.06, b. 8.87, c. 9.08, d. 9.24, e. 9.45, f. 9.62, g. 9.83, h. 10.5, and i. 12.2.