EXPERIMENTAL INVESTIGATIONS OF PHYSICAL AND CHEMICAL

PROCESSES AT AIR-ICE INTERFACES

by

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A thesis submitted in conformity with the requirements

for the degree of Doctor of Philosophy

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ABSTRACT

Studies were performed to characterize the physical nature of the air-ice interface, and to clarify its role in processes that occur there. A glancing-angle Raman probe was developed to monitor hydrogen bonding at atmospheric interfaces; we saw enhanced hydrogen-bonding on ice compared to on water. Using glancing-angle laser-induced fluorescence (LIF), we determined that small acids and bases dissociated to similar extents at air-water and air-ice interfaces, but aromatic compounds were less well solvated at air-ice interfaces, resulting in self-association even at low surface coverages.

We measured uptake kinetics of organic compounds using LIF and Raman spectroscopy. The uptake kinetics can be adequately fit by a single-exponential growth equation, but in order to properly describe the self-association of aromatics observed at the air-ice interface, equations accounting for self-association should be incorporated into the uptake model. A simple model was developed for naphthalene which included terms for self-association; good fits to the observed growth of intensity from monomeric and self-associated naphthalene were obtained.

Direct photolysis of aromatics was faster at air-ice interfaces than in bulk ice or aqueous solution. While red shifts in the absorption spectra of benzene and naphthalene
at air-ice interfaces could explain their enhanced reactivity there, the enhanced anthracene photolysis kinetics on ice are likely due to enhanced absorption cross sections or photolysis quantum yields, or to a different photolysis mechanism there.

Oxidation rates of aromatics by photo-formed hydroxyl radicals are suppressed at air-ice interfaces, but not in bulk ice. Similarly, gas-phase OH reacts rapidly with aromatics at air-water interfaces, but no reaction is observed at air-ice interfaces. Conversely, the reactivity of ozone toward phenanthrene is enhanced there. This is not due to temperature effects or to enhanced partitioning of ozone to ice. Ozonation of bromide is also more rapid at air-ice interfaces than at air-water interfaces at environmentally relevant bromide concentrations. This enhancement could be due to exclusion of bromide to the air-ice interface during freezing. The rapid reactions of ozone with bromide and phenanthrene at air-ice interfaces suggest that both reactions could be atmospherically important.
Acknowledgments

There are many people and institutions who deserve my thanks. First and foremost, of course, is my advisor, Jamie Donaldson. I could write paragraphs oozing praise and gratitude, but for now I will simply say: I feel extremely lucky to have worked with you and to have had you as my mentor. Thank you.

The few lines I have space for can not adequately convey the gratitude I feel for my parents. So I will just say thank you both for everything; you have helped me in so many ways throughout this journey.

On a less personal note, I would like to thank the institutions which provided me with funding throughout my PhD: NSERC for postgraduate scholarships; and IGAC, CGCS, and the University of Toronto Department of Chemistry for various travel grants.

I would also like to thank the members of the Donaldson group, from Dr. Thorsten Bartels-Rausch, who was there to keep me company and help me out when I first started, to our current crop of lovely graduate students, and to all those in between.

I had the opportunity to collaborate with a number of people throughout my PhD, and I would like to extend my thanks to them. First, to Dr. Jonathan Reid for sharing his enthusiasm and knowledge while visiting our lab, and for later hosting me at the University of Bristol. I would also like to thank Dr. Jack Dibb for providing me with the opportunity to participate in the GSHOx campaign at Summit, Greenland. My first collaboration during my PhD was with Nana Kwamena; I would like to thank her for this rewarding and enjoyable experience. I had the opportunity to mentor two undergraduate summer students, Klaudia Jumaa and Ran Zhao; working with them was a true pleasure. Finally, I wish to thank Dr. Diego Ardura for his support and assistance during his tenure at the University of Toronto. Most obviously, I must thank him for teaching me how to perform DFT calculations, and for working closely with me on two theoretical chemistry manuscripts; these experiences helped me to grow as a scientist. I also wish to thank him for sharing his passion for teaching with me, and for being a wonderfully supportive friend.
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Preface

The chapters of this thesis are based in part upon a series of manuscripts that have been published, are being considered for publication, or are being prepared for submission. All manuscripts included in this thesis were written by Tara Fayga Kahan, with critical comments provided by D. James Donaldson. The contributions of other authors are described below.

CHAPTER ONE:
Introduction

Contributions:
Written by Tara F. Kahan with critical comments from D. James Donaldson

CHAPTER TWO: PART ONE:
Spectroscopic Probes for the Quasi-Liquid Layer

Published in part as:

Contributions:
The glancing-angle laser-induced fluorescence technique was developed by Baagi Mmereki and optimized for use at the air-ice interface by Thorsten Bartels-Rausch and Tara F. Kahan. The glancing-angle Raman probe was developed by Tara F. Kahan and Jonathan P. Reid. All experiments described in this chapter were carried out by Tara F. Kahan. The manuscript was prepared by Tara F. Kahan with critical comments from D. James Donaldson and Jonathan P. Reid. The portions of this section that do not exist in published form were written by Tara F. Kahan with critical comments from D. James Donaldson.

CHAPTER TWO: PART TWO:
Solvation of Aromatic Species at the Air-Ice Interface
Published in part as:


**Contributions:**

Tara F. Kahan performed all of the experiments described in this chapter. The manuscripts were prepared by Tara F. Kahan with critical comments from D. James Donaldson. The portions of this section that do not exist in published form were written by Tara F. Kahan with critical comments from D. James Donaldson.

**CHAPTER TWO: PART THREE:**

Uptake of Organic Compounds to the Air-Ice Interface

This portion of the manuscript contains no previously published work.

**Contributions:**

The experimental approaches were developed by Baagi Mmereki and Tara F. Kahan. All experiments were performed by Tara F. Kahan. This section of the thesis was prepared by Tara F. Kahan with critical comments from D. James Donaldson.

**CHAPTER THREE: PART ONE**

Photolysis Kinetics of Aromatic Species in Aqueous Solution, in Ice, and at the Air-Ice Interface

Published in part as:


Kahan, T. F.; Donaldson, D. J. (in preparation) Benzene photolysis in ice: Implications for the fate of organic contaminants in the winter.

**Contributions:**

The HPLC methodology was developed by Tara F. Kahan and Derek A. Jackson. All other experimental approaches were developed by Tara F. Kahan. Kinetic measurements acquired offline using a commercial fluorimeter were performed by Ran Zhao and Klaudia B. Jumaa under the guidance of Tara F. Kahan. All other experiments were performed by Tara F. Kahan. Analysis of offline results was performed by Ran Zhao, Klaudia B. Jumaa, and Tara F. Kahan. All other analysis was performed by Tara F. Kahan. Manuscripts were prepared by Tara F. Kahan with critical comments from D. James Donaldson. The portions of this section that do not exist in published form were written by Tara F. Kahan with critical comments from D. James Donaldson.

**CHAPTER THREE: PART TWO**

Investigating the Cause of Enhanced Photolysis Rates at the Air-Ice Interface

Published in part as:


**Contributions:**

The experimental approaches were developed by Tara F. Kahan. Measurements of the photon flux dependence of nitrite in aqueous solution were performed by Ran Zhao under the guidance of Tara F. Kahan. Measurements of the photon flux dependence of anthracene in aqueous solution were performed by Ran Zhao and Klaudia B. Jumaa under the guidance of Tara F. Kahan. All other experiments were performed by Tara F. Kahan. Manuscripts were prepared by Tara F. Kahan with critical comments from D. James Donaldson. The portions of this section that do not exist in published form were written by Tara F. Kahan with critical comments from D. James Donaldson.

**CHAPTER FOUR: PART ONE**

Heterogeneous ozonation of bromide at the air-ice interface

This portion of the manuscript contains no previously published work.

**Contributions:**

The experimental approach was developed by Tara F. Kahan and Klaudia B. Jumaa based on a method developed by Daniel Clifford. Experiments were performed by Klaudia B. Jumaa under the guidance of Tara F. Kahan. Data analysis was performed by Klaudia B. Jumaa and Tara F. Kahan. This section of the thesis was written by Tara F. Kahan with critical comments by D. James Donaldson.

**CHAPTER FOUR: PART TWO**

Heterogeneous ozonation of phenanthrene at the air-ice interface
Published in part as:


**Contributions:**

The experimental approach was developed by Tara F. Kahan. All experiments were performed by Tara F. Kahan. The manuscript was written by Tara F. Kahan with critical comments from D. James Donaldson. The portions of this section that do not exist in published form were written by Tara F. Kahan with critical comments from D. James Donaldson.

**CHAPTER FOUR: PART THREE**

Indirect Photolysis of Aromatics at the Air-Ice Interface

Published in part as:


**Contributions:**

The experimental approach was developed by Tara F. Kahan. All experiments were performed by Tara F. Kahan, except for the offline measurements of benzene indirect photolysis, which were performed by Ran Zhao under the guidance of Tara F. Kahan. Data analysis was performed by Tara F. Kahan, with contributions from Ran Zhao. The manuscripts were written by Tara F. Kahan with critical comments from D. James Donaldson. The portions of this section that do not exist in published form were written by Tara F. Kahan with critical comments from D. James Donaldson.
CHAPTER FOUR: PART FOUR

Heterogeneous Oxidation of Aromatics at the Air-Ice Interface by Hydroxyl Radicals

Published in part as:


Contributions:

The experimental approach was developed by Tara F. Kahan. All experiments described in this section were performed by Tara F. Kahan. The manuscript was written by Tara F. Kahan with critical comments from D. James Donaldson. The portions of this section that do not exist in published form were written by Tara F. Kahan with critical comments from D. James Donaldson.
Chapter One:

INTRODUCTION:

Ice as a Reaction Medium
1.1 Overall Summary

Many atmospherically relevant reactions occur in snow and ice. In polar regions, photochemical reactions in snow and ice can alter the composition of the overlying atmosphere to the extent that traditional gas-phase models cannot correctly predict atmospheric composition. This discovery has led to numerous field campaigns in polar regions, laboratory-based investigations into photochemical reactions in ice, and to the development of new models that incorporate snowpack chemistry.

Despite the importance of ice as a reaction medium, our understanding of its role in atmospherically relevant reactions remains poor. Many questions remain unanswered, with perhaps the most pressing being: Can we accurately predict the fate of species in ice? Measuring kinetics of every relevant environmental process, while robust, is not practical. More straightforward would be to use existing rate constants from aqueous media, accounting for differences due to temperature and reagent concentrations. This approach is regularly used in chemical fate models and atmospheric composition models which include reactions in ice. However, experimental results do not necessarily support the validity of this approximation. While some studies suggest that reactivity is very similar or even identical in aqueous solution and in ice, other results suggest that reactivity in the two media is quite different.

The goal of my PhD research was to investigate ice as a reaction medium. The approach taken in this work was to measure reaction kinetics at air-ice interfaces and to compare the results with kinetics measured in bulk ice, in aqueous solution, and at air-water interfaces. The ultimate goal of this research was to describe the observed kinetics based on the different physical properties of the reaction media. This thesis presents published and unpublished results from my PhD studies which examine ice as a reaction medium. The Introduction summarizes the literature regarding field, laboratory, and theoretical studies of chemistry in ice at Earth’s surface. It also discusses the physical characteristics of snow and ice as they pertain to atmospheric chemistry. The subsequent three chapters present results from the studies that were performed as part of this thesis. They include studies of the physical nature of the air-ice interface, as well as
measurements of reaction kinetics in aqueous solution and in ice, and at air-ice and air-water interfaces. The final chapter summarizes the findings of the previous chapters, and discusses the atmospheric significance of the findings.

1.2 Observations of Chemistry in Snow and Ice

Snow and ice can cover up to 40% of the Earth’s surface.\textsuperscript{1} Until relatively recently, snow and ice were considered solely as physical sinks for trace atmospheric species. In the 1980s, however, significant boundary layer ozone depletion was observed\textsuperscript{2-4} which could not be explained by known gas-phase chemistry. Subsequent studies confirmed that reactive halogens, reactive nitrogen oxides, and volatile organic compounds were being formed within the snow and released to the overlying gas phase.\textsuperscript{1,5-7} Since this discovery, significant progress has been made in understanding snow and ice as reaction media.\textsuperscript{1,8} The following is a brief summary of observations of chemistry occurring in snow and ice in the field and in the laboratory, and of the methods that are being used to model these processes.

1.2.1 Field Observations of Reactions in Snow and Ice

The importance of ice as a medium for tropospheric reactions was first established in the 1980s, when it was discovered that models were not accurately describing the composition of the polar boundary layer.\textsuperscript{5} Subsequent field measurements determined that photochemical reactions within polar snowpacks were releasing products to the overlying gas phase and affecting its composition. These findings prompted a slew of field campaigns and laboratory studies aimed at understanding the physical and chemical processes occurring in environmental snowpacks.

The majority of polar field studies have focussed on the photochemistry of compounds within snow and ice which affect the oxidizing capacity of the atmosphere.\textsuperscript{5,9-11} The concentrations of species such as nitrogen oxides, hydrogen peroxide, and halogens within and above polar snowpacks have been monitored.\textsuperscript{1,6,8} Evidence for photochemical transformation of each of the above-mentioned class of species has been observed in coastal and interior polar regions.\textsuperscript{1} The production of small organics within
polar snowpacks has also received some attention, as compounds such as formaldehyde are important sources of free radicals in the Arctic troposphere, and can be important sinks for bromine atoms, which contribute to Arctic boundary layer ozone depletion.

Other field studies have investigated species such as mercury and organic pollutants which can pose significant health risks. The fate of mercury has received a good deal of attention, because evidence of biomagnification has been seen in many species of Arctic wildlife. While organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) have been detected in the snows of polar regions, few field studies have focussed on their chemical fates. It is likely that reactions involving these species will be much more important in urban snows, where they are abundant, and where their transformations could have significant impacts on human health.

1.2.2 Laboratory Investigations of Reactions in Snow and Ice

A number of laboratory studies have been performed over the past decade to investigate chemistry within snow and ice. As with field studies, these have primarily focused on the photolysis of inorganic species which are expected to affect boundary layer compositions. The photolysis of nitrate has received considerable attention, with various laboratory studies measuring photochemical formation rates of NO$_2^-$, NO$_2$, and OH due to NO$_3^-$ photolysis in snows and ices imported from field sites or prepared in the laboratory. Photochemical production and reactivity of other species in ice such as NO$_2^-$, HONO, and H$_2$O$_2$ have also been studied in laboratory settings. A number of studies have also examined reactions involving halides on ice, as autocatalytic bromine production in the Arctic is responsible for periods of significant ozone depletion. A more in-depth discussion of halogen chemistry is presented in Chapter Four. A few studies have investigated the photochemistry and bimolecular reactions of aromatic species in ice. A more thorough discussion of these studies is presented in Chapters Three and Four.
1.3 The Physical Properties of Snow and Ice

The role of snow and ice as reaction substrates depends largely on the physical characteristics of these frozen media. At the macro scale, structural properties such as porosity and surface area affect the uptake and release of reagents and products to the snow, while grain size and morphology are important in determining the optical depth of the snow or ice. On a molecular level, arrangement of water molecules within bulk ice and at the air-ice interface can significantly affect the manner in which trace atmospheric species interact with the ice and with other compounds, both physically and chemically.

1.3.1 Macromorphology of Snow and Ice in the Environment

Frozen water exists in a wide range of morphologies at the Earth’s surface. It can be divided into the two broad categories of snow and ice. Snow refers to individual crystals which have been deposited on the ground (it can also refer to crystals falling through the atmosphere, but that will not be discussed here). It is a porous mixture of ice crystals and air, with densities ranging from below 0.01 g cm\(^{-3}\) to 0.61 g cm\(^{-3}\). Ice is a largely non-porous medium, with a density of 0.917 g cm\(^{-3}\) at 0 °C. Unlike snow, which contains open networks of pore space, the gas in ice is restricted to unconnected air bubbles. Ice is formed on glaciers and ice sheets through the compression of snow. It can also be formed by the condensation of water vapour onto existing snow, or by the freezing of water or riming. These last two processes are important for oceans and lakes, but also for inland regions (and perhaps especially urban areas) where snow can undergo many freeze-thaw cycles before the spring melt.

An important property of snow and ice with respect to atmospheric reactions is surface area. Since many reagents are introduced through adsorption from the gas phase, higher surface areas will result in higher reagent concentrations. Specific surface area (SSA) is a measure of the ratio of surface area to volume or mass for a given substrate. Fresh snow can have SSAs of up to 1500 cm\(^{2}\), but snow crystals tend to grow as they age, resulting in reduced SSAs. The SSA of ice is very similar to that of liquid water.
The density (or the inversely related variable, porosity) of snow is also important to atmospheric chemistry, because it determines the mobility of gas-phase species within the interstitial air. A high density implies low diffusion rates through the snow, while a low density implies quick diffusion rates and good air-snow exchange. These factors will affect reagent concentrations on snow crystals, as well as the diffusion of gas-phase reagents through the snow, and the release of gaseous products into the overlying atmosphere.

The shape and size of ice granules can affect snowpack photochemistry by scattering incoming solar radiation. This can have two major consequences: The first is that scattering will reduce the depth to which light penetrates the snowpack. The region of the snowpack that receives shortwave radiation is referred to as the photic zone. This is often determined by the $e$-folding depth, the depth at which $e^{-1}$ of radiation has been scattered or absorbed. This depth ranges from ~10 to 20 cm in most snowpacks. Light scattering can also affect the photon flux within an individual ice crystal. In aqueous droplets, scattering has been found to enhance photon fluxes by over 100%. Photon fluxes in snowpacks are also predicted to be enhanced due to scattering. This could greatly affect rates of photochemical reactions within snowpacks.

### 1.3.2 Ice at the Molecular Level

The structure of ice at the molecular level may significantly influence the fate of atmospheric species present there. Ice found at Earth’s surface is $I_h$, one of the solid phases of ice. It consists of hexagonal bilayers of strongly hydrogen-bonded water molecules. In the environment, ice rarely grows in perfect single crystals; therefore, there will exist some heterogeneity in the crystal structure, such as veins or liquid pockets within the ice matrix. Likewise, near the air-ice interface, the disordered region known as the quasi-liquid layer (QLL) replaces the ordered structure of bulk ice, as illustrated in Figure 1.1.
Reactions in ice are thought to occur primarily in the liquid regions within bulk ice and in the QLL. Therefore, it is the physical characteristics of these regions which are of interest for this work. Veins and pockets within bulk ice are liquid water. They often have high reagent concentrations, due to exclusion of solutes from the ice matrix during freezing. The physical properties of the QLL are less clear. Laboratory studies suggest that it presents a distinct environment from both bulk ice and liquid water, but the extent of these differences and their effect on the reactivity of solutes there remains unknown.

Many laboratory experiments have investigated the physical properties of the QLL. Properties such as depth, density, polarity, and orientation of water molecules in the QLL have been probed by a variety of techniques including proton channelling, LEED, atomic force microscopy, infrared spectroscopy, and sum frequency generation. Theoretical techniques have also been employed in recent years to investigate the properties of the QLL. A more thorough discussion of these investigations is given in Chapter Two.

The physical properties of the QLL have also been studied indirectly, by observing the adsorption behaviour of trace atmospheric species to ice. Numerous studies have investigated the ionization and hydrolysis of small inorganic species on ice, while

Figure 1.1. Cross-section of ice I$_h$ near the air-ice interface
others have studied the uptake of organic compounds such as formaldehyde and acetone. The uptake of inorganic and organic species is discussed more fully in Chapter Two.

It should be noted that there are several common usages of the term “quasi-liquid layer”. Many substances other than water, including metals and rare gases, exhibit surface disorder at temperatures near their melting point. This is thought to be due to the weak binding of atoms near a free surface resulting in increased thermal disorder. Also referred to as the premelting layer, this strictly thermodynamic definition of the QLL predicts a thin disordered region at the surface of single crystal ice in the absence of solutes or gas-phase contaminants.

In the environment, ice does not exist in a pristine, single-crystalline form. Therefore, the disordered region at the air-ice interface will likely contain impurities, which can affect properties such as thickness and hydrogen bonding. Some compounds, most notably halide salts, are known to be excluded from ice during freezing, resulting in the formation of highly concentrated brines in liquid impurities within bulk ice and at air-ice interfaces. In this case, it is likely that the disordered region at the air-ice interface is in fact a true liquid solution containing high solute concentrations. To distinguish this from the premelting layer that exists at the surface of pristine ice, this surface region is sometimes referred to as a quasi-brine layer (QBL).

Some researchers define the QLL as any liquid-like region of ice, including liquid veins and pockets within bulk ice. The term liquid-like layer (LLL) is sometimes used in this case, although QLL is the more common term. This definition is used to help explain reaction kinetics in ice: The fraction of ice which exists as a liquid (including the disordered surface region and liquid impurities in the bulk) is referred to as the liquid volume fraction (LVF). All impurities are assumed to be located in the LVF, and therefore all reactions are assumed to occur there. Using this approach, reactions are generally assumed to follow aqueous-phase kinetics. This assumes that the reaction environment at the air-ice interface is identical to that in liquid impurities within bulk ice, and that reactions in both regions of ice occur similarly as in aqueous solution. As we
discuss in Chapters 2 and 3, this assumption is not necessarily valid, and we believe that the disordered region at the air-ice interface should be treated separately from liquid impurities in bulk ice.

We are left then with the premelting layer that exists at the surface of pristine ice, and with QBLs formed from the exclusion of solutes during freezing. To date, there has been no real discussion of how to describe the disordered surface region of ice that exists in the environment in the presence of low concentrations of solutes or adsorbates. Its properties will certainly be distinct from that of a QLL at the surface of a single-crystal ice sample in vacuum. However, calling this region a “brine” suggests that it is a true liquid, which may also not be appropriate.

In this work, we use the QLL to mean the disordered region at the air-ice interface, either in pristine conditions or in the presence of low solute concentrations. If we know that extensive solute exclusion has occurred, such as during the freezing of halide salts, we will use the term QBL rather than QLL. In all other cases, we use the term QLL. While we acknowledge that the surfaces of our ice samples, especially those that contain solutes or adsorbates, do not meet the strict definitions of the premelting layer, we are unaware of a more suitable term for the surface region under the conditions in our experiments or in the environment. Therefore, we use the QLL to mean the disordered region at the surface of ice that is distinct from liquid water. This usage is justified by the results discussed in Chapters Two, Three, and Four of this thesis.

1.4 Predictive Models for Processes in Snow and Ice

Chemical fate models and atmospheric chemistry models serve two main functions in atmospheric chemistry: They are important predictive tools, and they serve as a test of the atmospheric community’s understanding of atmospheric processes. For example, it was discrepancies between modelled predictions and measured values of the tropospheric concentrations of species such as hydroxyl radicals in the Arctic which prompted scientists to explore snowpacks as reaction media, rather than continue to view them solely as physical sinks.
A truly complete model would incorporate all of the factors discussed in the previous sections: Reagent partitioning; reaction kinetics; snowpack morphology; and influences of the QLL on surface processes. Such a model does not currently exist, as these factors remain poorly understood. Several types of models do exist which treat various aspects of chemical fate in snow and ice.

Linear Free Energy Relationships (LFERs) are often used to describe partitioning between phases. A poly-parameter LFER, which combines parameters that reflect the van der Waals and hydrogen bonding between sorbent and sorbate, has been used in recent years to predict the partitioning behaviour of organic species to snow and ice.

Other models focus on chemical, rather than physical, interactions that occur in snow and ice. One method that has been employed is to include only gas-phase processes in the model, and to infer reaction rates within the snow based on the discrepancies between predicted and measured concentrations to snowpack chemistry. Box models combine estimates or known values for parameters such as reagent concentrations, reaction rate constants, and QLL volume to predict reaction rates and product fluxes from ice. A 3-D model incorporating transport and multiphase chemistry, including heterogeneous reactions on snow and ice, was recently developed.

1.5 Overview of Thesis Work

We do not currently understand the role of ice as a reaction medium well enough to predict the fate of atmospheric species present there. For some reactions, kinetics in ice appear to be adequately described by those in liquid water. If this is true for all reactions, then modelling the fate of species in snow and ice becomes very straightforward. The aim of my PhD research was to test the hypothesis that ice and liquid water provide similar reaction environments. I did so by comparing the physical properties of ice and water surfaces, and by comparing kinetics for a range of physical and chemical processes at air-ice and air-water interfaces. These studies are described in the following sections.
1.5.1 Chapter Two: Probing the Physical Nature of the Air-Ice Interface

This chapter describes experiments which investigate the physical properties of the air-ice interface, and how this medium affects solutes present there compared to air-water interfaces. In the first set of experiments, a novel glancing-angle Raman spectroscopic technique was developed to probe the hydrogen-bonding nature at air-ice and air-water interfaces, and the effect of the presence of atmospheric impurities on the physical characteristics of both interfaces was observed. A glancing-angle laser-induced fluorescence (LIF) probe was developed to monitor pH changes in situ at the air-ice interface. We used these probes to observe changes in pH due to the dissociation of small ionizable species on ice, as well as the effects of this dissociation on the hydrogen-bonding nature of the QLL. Studies were also performed to explore the extent of exclusion of acids into the QLL during freezing.

A second set of experiments focussed on exploring the solvating environment presented by the QLL to organic species. Uptake kinetics of organic compounds to ice surfaces were measured, and excitation and emission spectra of aromatic species were compared at air-ice and air-water interfaces. The spectral features allowed us to comment on the extent of self-association of the species at the two interfaces.

1.5.2 Chapter Three: Photolysis of Aromatics at the Air-Ice Interface

To determine the role of the QLL in the photolysis kinetics of aromatic compounds, we measured photolysis rates directly at the air-ice interface for several aromatic species using glancing-angle LIF. In one set of experiments we contrasted photolysis rates of anthracene, naphthalene, and benzene at air-ice interfaces and in aqueous solution or at air-water interfaces. For each compound, photolysis occurred much more quickly at the air-ice interface than in aqueous solution.

In a second set of experiments, we measured anthracene kinetics in ice samples with varying surface areas, by melting samples prior to analysis. This method allowed us to distinguish between reactions occurring in bulk ice and in the QLL. We found that photolysis kinetics were similar in bulk ice and in aqueous solution, but that increasing
the surface area, and therefore the amount of anthracene in the QLL, resulted in enhanced photolysis rates which matched those measured at air-ice interfaces.

In a final set of experiments, we investigated the possible reasons for the enhanced photolysis kinetics measured at air-ice interfaces compared to in bulk ice or aqueous solution. We measured photon flux dependences for PAH photolysis kinetics in aqueous solution and at air-ice interfaces to determine whether increased light scattering by ice was responsible for the increased rates measured at its surface. We also looked for temperature and wavelength dependences for anthracene photolysis on ice, and we compared photolysis rates on various solid and liquid substrates. Our results suggest that none of these factors are responsible for the enhanced anthracene photolysis rates measured on ice. We conclude that while at least some of the enhanced reactivity of naphthalene and benzene on ice is due to increased absorption in the actinic region, anthracene’s enhanced reactivity is likely best explained by changes in its absorption cross section or photolysis quantum yield at air-ice interfaces, or by reaction via a different mechanism.

1.5.3 Chapter Four: Monitoring Bimolecular Reactions at the Air-Ice Interface

In this chapter, we examined bimolecular reactions at the air-ice interface. The first set of experiments explored the heterogeneous ozonation of bromide and phenanthrene at air-ice and air-water interfaces. In both cases, kinetics were much faster at the ice surfaces. The enhancement in bromide’s reactivity can be explained by exclusion of bromide from the ice matrix during freezing, but this is not true for phenanthrene. As with photochemistry, differences in the physical environment presented by the QLL must be responsible for the heightened reactivity there.

We also investigated reactions of aromatic species with photoformed hydroxyl radicals at air-ice interfaces. In a first set of experiments, we used benzene as an OH-trap and measured phenol formation rates in aqueous solution and in ice due to the photolysis of the OH-precursor H₂O₂. We observed similar phenol formation rates in aqueous
solution and in bulk ice samples, but when the surface area of the ice samples was increased, no phenol formation was observed.

To follow up on this result, we developed an in situ probe to monitor phenol formation in real time at the air-ice interface. While we measured expected photolysis rates of NO$_3^-$, NO$_2^-$, and H$_2$O$_2$ in aqueous solution using this technique, we did not observe any reaction at the air-ice interface, regardless of initial reagent concentrations or preparation methods.

In a final set of experiments designed to monitor the reactivity of hydroxyl radicals at the air-ice interface, we monitored heterogeneous reactions between gas-phase OH and aromatics present at air-ice and air-water interfaces. We saw rapid phenol formation at air-water interfaces when OH(g) was introduced to aqueous benzene samples. The same set of conditions at air-ice interfaces yielded no phenol. Likewise, fluorescence intensity from anthracene present at air-water interfaces decreased in the presence of gas-phase OH, but no change was observed at air-ice interfaces under the same conditions.
1.6 References


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Chapter Two:

Probing the Physical Nature of the Air-Ice Interface

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2.1 Introduction

Ice is a complex, poorly understood reaction medium. One of the most atmospherically relevant regions of ice, the QLL that exists at the air-ice interface, remains poorly characterized, and its role as a physical and chemical sink for trace atmospheric species is unclear. We have studied the physical properties of the QLL in several manners. In Part One of this chapter we discuss two spectroscopic probes which we developed to investigate the hydrogen-bonding nature of the QLL, as well as changes in pH at the air-ice interface. In Part Two, we discuss studies of the uptake of aromatic hydrocarbons, and their spectral features at air-ice interfaces. These studies give us insight into the solvating nature of the QLL. In Part Three, we describe our use of glancing-angle Raman spectroscopy to monitor the uptake of organic species to ice, and measure uptake kinetics of aromatic and non-aromatic species to ice at various temperatures. These studies provide a comparison between the physical environment presented to atmospheric species present at air-ice and air-water interfaces.

Chapter Two: Part One
Spectroscopic Probes for the Quasi-Liquid Layer

2.2 Introduction

Understanding the physical properties of the air-ice interface is key to understanding its role as a reaction substrate. As discussed in Chapter One, many studies have probed various physical characteristics of the QLL. Reviews of these studies are provided in Refs. 1-4. The most commonly studied parameter is the depth of the QLL as a function of temperature. Approximately 1 °C below the melting point, measured depths range from 4 Å to up to 500 Å.5,6 Depths above 90 Å have been measured or predicted by ellipsometry,7 proton channeling,8 interfacial force microscopy,9 and glancing angle X-ray spectroscopy6 at this temperature. Conversely, atomic force microscopy10 and infrared spectroscopy5,11 measured depths of less than 35 Å. Molecular dynamics
simulations\textsuperscript{12-14} predict depths on the order of 5 to 10 Å at temperatures within a few degrees of the melting point.

Widely varying measured onset temperatures of the QLL have also been reported. Interestingly, techniques that measured the greatest QLL depths at high temperatures did not necessarily measure the lowest onset temperatures. The onset temperature based on X-ray spectroscopy measurements was 259.5 K,\textsuperscript{6} while atomic force microscopy measurements suggested an onset temperature of 239 K.\textsuperscript{10} On the other hand, photoemission spectroscopy,\textsuperscript{15} elastic helium scattering,\textsuperscript{16} and sum frequency generation\textsuperscript{17-19} measurements predict onset temperatures ranging from 113 K to 200 K. Molecular dynamics simulations\textsuperscript{13,14,20,21} predict an onset temperature of between 173 and 250 K, while thermodynamic treatments\textsuperscript{22,23} predict onset temperatures ranging from 230 K to 262 K.

There are several possible explanations for the large discrepancies in measured and predicted values for QLL depth and onset temperature. The first is that the ice samples used in different experiments could have different properties. Some of the experiments mentioned above were performed on single-crystalline ice, while others were performed on thin ice films or polycrystalline ice. The atmospheres above the ice samples were also quite different: Some experiments were performed in vacuum, while others were performed in atmospheres of air. It has been noted that “impurities” such as air can greatly increase the depth of the QLL. The second possible reason for the wide range of results is that different techniques are sensitive to different physical properties. For example, ellipsometry measures changes in refractive index, while SFG measures changes in the orientational distribution of dangling OH bonds at the ice surface. Different theoretical studies also use different potentials and apply different criteria to their definitions of what constitutes a QLL. A third possible explanation for these discrepancies is that the QLL is not a homogeneous region with clearly defined boundaries. More likely, there is a gradual disordering of water bilayers as the air-ice interface is approached. Thus, there may be no unique value that can be assigned to the QLL’s onset temperature, or to its depth at any given temperature.
Although quantitative measurements of physical properties of the QLL may not be meaningful, or even possible, qualitative measurements can still be made. For example, the extent of solvation of trace species can be compared at air-water and air-ice interfaces. In this section, we developed two spectroscopic probes to qualitatively investigate physical characteristics at the air-ice interface. The first technique, glancing-angle Raman spectroscopy, was used to examine the extent of hydrogen bonding at air-ice interfaces compared to that in bulk water and at air-water interfaces. Glancing-angle LIF of a pH-sensitive fluorescent probe was used to monitor changes in pH at air-ice interfaces.

2.3 Experimental

2.3.1 Apparatus and Data Acquisition

The reaction chamber used for this study is displayed in Figure 2.1. It consists of a ~500 mL Teflon box with side ports through which gases can be introduced and vented. A copper plate on the chamber floor is soldered to copper tubing, through which cooling fluid is circulated. The temperature of the plate is monitored using a thermistor attached to its surface; good thermal contact is assured by using thermal grease. Experiments were carried out at temperatures ranging from $-16^\circ C$ to $24^\circ C$.

Raman scattering was induced by the unfocussed 355 nm output of a frequency-tripled Nd:YAG laser (pulse energy ~ 0.5 mJ). Acridine fluorescence was excited by the 337 nm output of a nitrogen laser (pulse energy ~ 0.25 mJ). Both lasers operated at a repetition rate of 10 Hz. The laser beam entered and exited the Teflon chamber through quartz windows and impinged on the surface of the sample at a glancing angle (> 85° from the surface normal for Raman experiments and > 80° from the surface normal for LIF experiments). The polarization of the input radiation was perpendicular to the surface normal for all LIF experiments. For the Raman experiments the input polarization was varied using a polarization rotator. At an incident angle of 87° from the surface normal, 67% of p-polarized (polarized in the plane of incidence) and 80% of s-polarized (polarized perpendicular to the plane of incidence) input radiation will be reflected at the
air—ice interface, as calculated using the Fresnel equations.$^{24}$ This reflected light samples the surface region; transmitted (refracted) light excites species below the surface. As discussed below, the effective depth of penetration of the probe is greater than $1 – 2$ monolayers, but probably less than a few hundred monolayers.

**Figure 2.1.** Schematic of the reaction chamber used for in situ spectroscopic studies.

Raman scattering and fluorescence were collected perpendicular to the surface using a 7 mm diameter liquid light guide suspended 1 cm above the sample. After passing through a long-pass optical filter with a 370 nm cutoff, the Raman scattered radiation was imaged into a monochromator, and the transmitted intensity was detected by a photomultiplier tube and sent to a digital oscilloscope and computer for analysis. No optical filters were used in the LIF experiments. The digital oscilloscope averaged the intensity vs. time signal over 64 laser shots and then the data were sampled and stored by the computer. Spectra were obtained by manually scanning the monochromator in steps to give approximately $30 \text{ cm}^{-1}$ separation between collected data points over the spectral range of interest.

At the liquid water surface, spectra were measured in the same reaction chamber, but with the water sample contained in a Petrie dish. Raman scattered light was collected from above, as in the ice experiments. Bulk water Raman spectra were measured with the sample in a 1 cm x 1 cm quartz cuvette. The laser beam entered through the side of the
cuvette, and the detected light was collected at 90° to the laser input in the horizontal plane. These experiments were all performed at room temperature.

2.3.2 Sample Preparation

Ice samples, with the exception of the acid-exclusion experiments, were prepared by freezing ~0.5 mL water or aqueous solution on a copper plate placed on the chamber floor. After freezing, the copper plate was briefly removed from the chamber and the ice samples were inverted by hand to present a flat surface to the laser. The surface area of the ice exposed to the air was ~3 cm² and the ice thickness ~1.5 mm. We assume that the thermistor provides an accurate indication of the sample temperature.

For the acid exclusion experiments, aqueous solutions of a known pH containing either HNO₃ or HCl were frozen in a Petri dish suspended in a chilled bath with a temperature between –1 °C and –11 °C. The sample was allowed to freeze slowly, over periods extending to over one hour. After freezing, the sample was transferred to the chilled reaction chamber, and a fluorescence spectrum was acquired immediately.

In some experiments we prepared D₂O ice; here the following steps were taken to reduce contamination by ambient H₂O: The copper plate used as a substrate was soaked in D₂O for several minutes before being placed in the chamber, and the chamber was purged with dry N₂ prior to depositing the liquid D₂O.

Deposition of gas-phase H₂O onto D₂O ice surfaces was accomplished by flowing N₂ at a rate of 1 SLM through a flask containing liquid H₂O heated to ~75 °C before introducing it to the chamber through the side port via ~0.5 m of PTFE tubing at room temperature. Gas phase HCl, HNO₃, and NH₃ were deposited on the ice surface by withdrawing ~2 mL of the vapour present in the headspace of a bottle containing a concentrated aqueous solution of the desired compound into a Pasteur pipette, and then expelling the collected gas onto the ice surface.

Dodecane samples were prepared by spreading a small amount (~0.1 mL) of dodecane on a glass microscope slide and placing it in the reaction chamber. The
chamber was purged for 10 minutes with dry nitrogen prior to inserting the dodecane sample in the chamber, as well as during data acquisition.

Water surfaces were coated with octanol monolayers by pipetting 12 µL octanol into 30 mL water in a Petri dish. The solution was stirred and then left for at least 15 minutes to allow the monolayer to develop.

2.3.3 Chemicals

Acridine (Fluka, ≥ 97.0 %), Dodecane (Sigma Aldrich, ≥ 99 %), octanol (Sigma Aldrich, 99%), concentrated nitric acid (Caledon, ≥ 99.9 %), reagent grade concentrated hydrochloric acid (Baker), ammonium hydroxide (Fisher), and nitrogen gas (BOC, > 99.99 %) were used as purchased. Ice was prepared from 18 MΩ deionized water for all experiments, except those involving acridine, where distilled water was used.

2.4 Results and Discussion

2.4.1 General Features of Raman Spectra at Water and Ice Surfaces

The Raman spectrum of the OH-stretch region of water has been well studied (e.g. Ref. 26 and references therein). Figure 2.2a shows intensity-normalized spectra of bulk water measured using vertically (solid trace) and horizontally (dashed trace) polarized input radiation. In our experimental geometry, the scattered light in the former case contains components with polarization both parallel and perpendicular to that of the input light; the latter contains only the perpendicular polarization component in the scattered signal arising from depolarization. Hence the spectrum shown by the solid trace contains contributions that transform as both symmetric and antisymmetric stretching vibrations in liquid water. The dashed trace arises only from the depolarized scattering from vibrations which transform as antisymmetric stretches. Although we do not separate the parallel and perpendicular components of the scattered light, the solid trace shown in Figure 2.2a is essentially identical to the unpolarized spectrum reported by others, in which the parallel component of the scattered light contributes the greatest part to the observed signal. We shall therefore hereafter refer to this component as the “unpolarized spectrum”.
Whereas in the isolated water molecule the symmetric stretch vibration lies at a lower energy than the antisymmetric stretch, in the liquid state both of these vibrations are red shifted with respect to the antisymmetric stretch of the isolated molecule, due to the extensive hydrogen-bonded nature of the liquid. The large shoulder on the low wavenumber side (≈3200 cm\(^{-1}\)) of the solid trace in Figure 2.2a is assigned\(^{27}\) to vibrations involving more highly hydrogen bonded (“4-coordinate”) molecules, by analogy with the spectrum of bulk ice, in which this feature dominates.\(^{27}\) The higher frequency band has been assigned (for spectra corresponding to that shown in the solid trace) to motions of less strongly hydrogen bonded molecules.\(^{27}\) Because this high frequency component transforms as an asymmetric vibration, it appears in the dashed-line spectrum. A recent reinterpretation of vibrational water spectra by Petersen and Saykally\(^{28}\) posits that there exists a continuum of hydrogen bonding states in the bulk liquid and that the appearance of two bands in the parallel spectrum should not be associated with two distinct hydrogen bonding environments. Consequently, in the following we shall discuss the results as indicating “more” or “less” hydrogen bonded environments, with no further quantification.

Figures 2.2b and 2.2c show intensity-normalized spectra of the OH-stretching band of water taken with the laser impinging respectively on a water surface and on an ice surface, at an incident angle >87° from the surface normal. Here the detection is above the plane of the interface; therefore p-polarized input radiation (vertical polarization) allows detection of the perpendicularly polarized (depolarized) spectrum and s-polarized input light (horizontal polarization) allows detection of both the parallel and perpendicularly polarized scattered light. The solid and dashed lines in these figures represent the spectra measured using s- and p-polarized input radiation, respectively, and can thus be compared directly to the corresponding solid and dashed line traces shown in Figure 2.2a. The spectra illustrated by the solid lines are clearly much narrower for surface scattering than for bulk scattering, primarily due to a significant loss of intensity from the low energy side of the band. The depolarized scattering spectra, shown by the dashed lines, are quite similar in overall shape to the spectra observed using s-polarized radiation for both the liquid and solid water surfaces. It is interesting to note that the
strong polarization dependence observed for bulk water is observed only very faintly for the air-water interface, and is not seen at all at the air-ice interface.

![Raman spectra](image)

**Figure 2.2.** Raman spectra of the OH-stretching region of (a) room temperature bulk water; (b) the air-water interface; and (c) the air-ice interface at $-15$ °C. Solid traces correspond to vertical polarization in the bulk and s-polarized radiation at the surface, and dashed traces correspond to horizontally polarized light in the bulk and p-polarized light at the surface. The insets illustrate the experimental geometry used in each case. Here the solid line shows the input laser and the dotted line shows the scattered light.

In Figure 2.3 the “unpolarized” spectra observed from the water bulk, water surface, ice surface, and solid ice bulk are plotted together for comparison. In the near-surface region, the local environment is expected to contain fewer highly-coordinated water molecules; consequently, if there is a significant contribution to the Raman
spectrum from this region, a less intense red shoulder to the band is expected, and indeed
the s-polarized water spectrum in Figure 2.3 shows significantly less intensity at low
energies than does the unpolarized bulk water spectrum. As well, the ice surface
spectrum is significantly blue shifted compared to the bulk ice spectrum; both ice and
supercooled water are dominated by a feature near 3200 cm⁻¹, with a shoulder at higher
energy which corresponds to the dominant feature in the room temperature liquid. These
spectra suggest that the liquid water surface is the least ordered environment, followed by
the ice surface, then by bulk water and finally bulk ice. Figure 2.4a displays spectra of the
ice surface measured using s-polarized light at temperatures near 0 °C and –15 °C. A
clear increase in the relative intensity of the red shoulder is observed as the temperature is
lowered, consistent with this interpretation.

![Normalized Intensity vs Raman Shift](image)

**Figure 2.3.** Intensity-normalized unpolarized Raman spectra of the OH-stretching region
of room-temperature bulk water (solid blue trace); the air-water interface (dashed blue
trace); bulk ice at –20 °C (dotted red trace); and the air-ice interface at –15 °C (dash-
dotted red trace). The bulk ice spectrum has been redrawn on the basis of Figure 4 of Ref.
30.

To test this further, we measured the Raman spectrum from the water surface at a
laser incidence angle of 40° from the surface normal. At this angle 0.6% of p- and 4.3 %
of s-polarized light is reflected, as compared to 65.5% and 78.8% respectively at 87°
from the surface normal, based on the Fresnel equations. The result, shown in Figure
2.4b, clearly shows a broadening to the red side of the spectrum at the less glancing angle, consistent with a greater contribution from the bulk in this case.

**Figure 2.4.** Intensity-normalized Raman spectra: (a) the OH-stretching region of the air-ice interface at –0.5 °C (solid trace) and –13.5 °C (dashed trace); (b) the OH-stretching region of room-temperature bulk water (blue solid trace) and the air-water interface with an incident laser angle 87.2° from the surface normal (green dashed trace) and 40° from the surface normal (green dotted trace). Experimental geometries are as illustrated in the insets.

Sum frequency generation (SFG) measurements of the ice surface have observed a similar effect of changing the temperature: The orientation of hydroxyl groups in the surface layer of the QLL becomes more disordered as temperatures increase from 200 K to the melting point. Clear differences in the amount of disorder of the surficial water
molecules are observed at the surfaces of ice and of supercooled water at identical
temperatures,\textsuperscript{17} suggesting that the surface region of the air-ice interface is structurally
different than water surfaces, supercooled or otherwise.

The differences observed in the OH-stretch region between bulk and surface
water and between bulk and surface ice suggest that we are seeing different environments
at the surface and in the bulk. This interpretation assumes that there is sufficient intensity
associated with the scattering generated in the surface region to be distinguished from the
bulk contribution. In the following section we will discuss the results of several
experiments that were designed to explore our sensitivity to the ice and water surfaces.

\section*{2.4.2 Observing Water on Dodecane Surfaces}

In one experiment, we measured the water OH-stretch spectrum at the surface of
liquid dodecane. Water is not miscible with dodecane, but will adsorb (or condense) onto
its surface in amounts which depend on the ambient relative humidity. The uptake of
water by this compound has been determined as a function of relative humidity in this
labratory.\textsuperscript{31} Even at a room temperature relative humidity approaching 100%, a
maximum of ~50 monolayers of water are present at the dodecane surface. Figure 2.5
shows two s-polarized Raman spectra measured at a dodecane surface under low relative
humidity conditions, with incidence angles for the excitation laser beam of 80° from the
surface normal (dashed trace) and 87° from the normal (solid trace). The intensity at 2900
\text{cm}^{-1} arises from the dodecane CH-stretch, but the water OH-stretch, appearing at ~3450
\text{cm}^{-1}, is clearly observed in both spectra. This result clearly shows that this technique is
sensitive to a surfacial water layer of ~50 monolayers, or a probe depth of ~15 nm. It
should be noted that this is a conservative estimate, as the cited 50 monolayers of water is
only present under extremely high relative humidity, which was not the case in our
measurements. Further, we have also measured water OH-stretch bands on glass surfaces
at ambient relative humidity, which likely corresponds to fewer than five molecular
layers of water.\textsuperscript{32}

The angle dependence of the dodecane surface spectra shown in Figure 2.5 is also
consistent with the notion that we are sensitive to the dodecane surface region: The
relative intensity of the water OH-stretch increases as the laser angle becomes more glancing. This effect, also illustrated in Figure 2.4b, is consistent with the expectation that at a more glancing incidence angle, more light is reflected from the sample surface, resulting in the observed spectrum containing a smaller contribution from the underlying bulk sample (dodecane in this instance).

**Figure 2.5.** Raman spectra of a room temperature dodecane surface under a flow of dry nitrogen with incident laser angles 87.2° from the surface normal (solid trace) and 80° from the surface normal (dashed trace). The spectra are normalized to the CH-stretch fraction at ~2900 cm$^{-1}$. Experimental geometries are as illustrated in the inset.

### 2.4.3 Monitoring Octanol Monolayers on WaterSurfaces

We acquired Raman spectra of water surfaces coated with a monolayer of 1-octanol. Figure 2.6a shows intensity-normalized Raman spectra of a pure water surface, and of the same sample after the addition of octanol to form a monolayer at the surface ($2.5 \times 10^{-3}$ mol L$^{-1}$). Surprisingly, we see no growth in intensity at 2900 cm$^{-1}$, where the CH-stretch from octanol should appear. Raman spectra of pure octanol, ethanol, and isopropanol all exhibit reduced CH-stretch intensity and enhanced OH-stretch intensity at
the air-organic interface compared to in the bulk, as illustrated in Figure 2.7. We do not currently have an explanation for these observations.

![Figure 2.6](image)

**Figure 2.6.** Raman spectra of a room temperature water surface (solid blue trace); and of the same sample after the addition of $2.5 \times 10^{-3}$ mol L$^{-1}$ octanol (dashed red trace). Panel (a) shows intensity-normalized spectra, and panel (b) shows non-normalized spectra. Experimental geometries are as illustrated in the inset.

![Figure 2.7](image)

**Figure 2.7.** Intensity-normalized Raman spectra in the bulk (solid traces), and at air-liquid interfaces (dashed traces) of (a) anhydrous ethanol; and (b) octanol. Experimental geometries are as illustrated in the inset. The different offsets in the two panels are a consequence of the use of different monochromators and filters.

Although we do not see direct evidence of octanol at the water surface in the form of a CH-stretch, the intensity of the OH-stretch of water is significantly reduced in the presence of octanol. Figure 2.6b shows non-normalized spectra of a pure water surface and the same solution coated with an octanol monolayer; the intensity reduction of the
OH-stretch is evident here. This observation is discussed in more detail with respect to ice in Section 2.12.

2.4.4 Deposition of H$_2$O onto D$_2$O ice

We measured the ice surface spectrum while flowing H$_2$O vapour over D$_2$O ice. Since the Raman OD-stretch appears at lower energies than the OH-stretch (on ice, we observe peak intensities at 2395 cm$^{-1}$ and 3450 cm$^{-1}$ respectively), we can readily monitor the ratio of the intensities of these two peaks as a function of time. A decrease in the OD/OH intensity ratio is expected, due to the condensation of H$_2$O on the D$_2$O ice surface.

Figure 2.8 shows the time dependence of the intensity ratio of these two peaks as H$_2$O vapour flows over a D$_2$O ice sample. In our experimental setup, it was not possible to eliminate a contribution from the OH-stretch to the D$_2$O ice spectra due to condensation of ambient water vapour onto the ice. (Measurements of the bulk liquid spectrum of D$_2$O contained a negligible contribution from OH, however.) Nevertheless, in Figure 2.8 one sees that the OD/OH ratio remains fairly constant over a large time period while dry nitrogen flows across the D$_2$O ice sample, but when H$_2$O vapour is introduced to the nitrogen stream, an immediate and rapid decrease in the OD/OH ratio is observed. The intensity ratio levels off within a few minutes and remains constant thereafter. A reduction in the OD/OH intensity ratio is also seen when ~1 cm$^3$ of air containing ~$6 \times 10^{17}$ molecules of H$_2$O(g) is introduced via a Pasteur pipette. In this instance the decrease is ~15 – 20 % of that observed in Figure 2.8. Assuming the gas introduced to the ice surface is saturated with H$_2$O vapour, and that every water molecule present in the pipette collides with an uptake coefficient between 0.1 and 1 with the ice surface, we estimate deposition of between 20 and 200 molecular layers.

Isotopic switching at the D$_2$O ice surface is expected to rapidly convert both the original D$_2$O and the adsorbing H$_2$O to HOD. Subsequent diffusion of HOD through ice films is believed to be negligible.$^{33}$ Therefore, we interpret the observed decrease in the OD/OH signal as being due to condensation and isotopic scrambling of H$_2$O at the ice surface. This observation, and those discussed in the previous sections, give us
confidence that the glancing-angle Raman probe is sensitive to changes in the surface region of ice over a (conservative) range of tens to hundreds of monolayers.

![Graph showing the ratio of intensity at 2395 cm⁻¹ to that at 3450 cm⁻¹ on D₂O ice at –15 °C under a flow of dry nitrogen (blue squares) and under a flow of water vapour in nitrogen (red triangles).](image)

**Figure 2.8.** Ratio of the intensity at 2395 cm⁻¹ to that at 3450 cm⁻¹ on D₂O ice at –15 °C under a flow of dry nitrogen (blue squares) and under a flow of water vapour in nitrogen (red triangles).

### 2.4.5 Effects of Contaminants on the Spectra

Previously we argued that the glancing-angle Raman technique may be used to infer aspects of the water ice surface environment. In the following, we show how Raman spectra measured at the ice surface are sensitive to changes in the local environment which may be induced by different solutes.

Atmospheric and terrestrial ice is rarely pristine. Gaseous acids, such as HCl and HNO₃, adsorb readily to ice, both on the Earth and in high altitude cirrus clouds (e.g. References 34,35). Sea salt is ubiquitous on sea ice,³⁶,³⁷ and halogen chemistry initiated by oxidation of ice-bound halides is extremely important to ozone loss in the polar boundary layer (see for example Reference 38 and references therein). In addition to being involved directly in ozone destruction, sea salt on ice could affect the structure of the QLL and thus its physical and chemical interactions with pollutants. In urban centres
a wide variety of contaminants, potentially including road salt, could be present in high concentrations.

Figure 2.9. Intensity-normalized Raman spectra of the OH-stretching region of (a) room-temperature bulk water (solid trace), a 1 mol L\(^{-1}\) NaCl solution (dashed trace), and a 4 mol L\(^{-1}\) NaCl solution (dotted trace); and (b) the surfaces of pure ice at –15 °C (solid trace) and a frozen 0.01 mol L\(^{-1}\) NaCl solution at the same temperature (dashed trace). Experimental geometries are as illustrated in the insets.

Figure 2.9a shows the effect of dissolved NaCl on the OH-stretch region of the bulk water Raman spectrum. The low wavenumber region in pure water (solid trace) is diminished in intensity in a 1 mol L\(^{-1}\) solution of NaCl, as displayed by the dashed trace. Increasing the NaCl concentration to 4 mol L\(^{-1}\) (dotted trace) diminishes the intensity in this region even further. Sodium halide salts disrupt the hydrogen-bond network of bulk water, which leads to the observed reduction in Raman intensity at low energies of the OH-stretch region.\(^{27}\) At the air-water interface, a shift in the spectrum toward higher energies has been observed by SFG studies in the presence of NaBr and NaI, although NaCl does not change the spectrum.\(^{39}\) We do not see any effect on the s-polarized
spectrum at the water surface in the presence of up to 4 mol L$^{-1}$ NaCl, but on ice we see a reduction in intensity in the red portion of the spectrum when dilute NaCl solutions are frozen at −15 °C. Figure 2.9b illustrates this for solutions with initial NaCl concentrations of 0.01 mol L$^{-1}$. The decrease in the area under the intensity-normalized curves relative to the pure ice spectrum is ~14%, with the loss occurring almost entirely from the red end of the spectrum. The effect of NaCl on the ice surface spectrum is much greater than that observed for bulk water, where a decrease in the area under the curve of similar magnitude is not observed for NaCl concentrations below 1 mol L$^{-1}$.

Exclusion of NaCl during freezing is a well-known phenomenon, and at the temperatures used in this experiment (ca. −15 °C) this process is expected to result in a combination of pure ice and concentrated NaCl solution (~10 mol L$^{-1}$) at the ice surface or in the QLL. These results could be interpreted as indicating a 1000-fold enhancement of Cl$^-$ at the surface. The decrease in relative intensity at 3200 cm$^{-1}$ could be due to increased surface dis ordering by the Cl$^-$, or it could be due to the formation of liquid water. The effect on the Raman spectrum would be similar in either case, and we are therefore unable to distinguish between the two phenomena using this technique.

The effect of the presence of 1 mol L$^{-1}$ HCl on the Raman OH-stretch band of bulk water, shown in Figure 2.10a, indicates that HCl disrupts hydrogen bonding in the bulk to the same extent as NaCl. Surface Raman spectra of concentrated HCl solutions at room temperature are indistinguishable from those of pure water. However, by contrast, Figure 2.10b shows that depositing gas phase HCl onto an ice surface results in increased intensity at low energies. This small increase (of ~3%) is also observed upon exposure of the ice to HNO$_3$(g), while NH$_3$(g) deposited on the ice surface decreases the intensity at low energies by a similar magnitude.

The dissociation of HCl and HNO$_3$ in the QLL will lead to the formation of hydronium ions, which may be strongly hydrogen bonded to at least three other water molecules, and which are believed to show some propensity for the surface of aqueous solutions. This is a likely explanation for the enhancements in Raman intensity observed at low energies in the presence of HCl and HNO$_3$. Likewise, decreased Raman intensity at low energies in the presence of NH$_3$ can be explained by this molecule’s
propensity to scavenge protons. The resulting \( \text{NH}_4^+ \) is evidently similar to \( \text{Na}^+ \) in its effects on the hydrogen bonding structure at the ice surface.

**Figure 2.10.** Intensity-normalized Raman spectra of the OH-stretching region (a) of room-temperature bulk water (solid trace) and of a 1 mol L\(^{-1}\) HCl solution (dashed trace) and (b) of a pure ice surface at \(-15 \, ^\circ\text{C}\) (solid trace) and of the same ice surface after the deposition of gaseous HCl (dashed trace). Experimental geometries are as illustrated in the insets.

To determine whether these species are in fact dissociating at the air-ice interface, we turn to another surface-sensitive spectroscopic probe. Acridine is a surface-active heteroatom-containing PAH with a pKa of \(~5.5\). Its wavelength-resolved fluorescence spectrum is a convolution of emission from its neutral and protonated forms, which have peak fluorescence intensities at ca. 430 nm and 480 nm respectively. The ratio of the fluorescence intensities at these wavelengths can be used to determine the pH of a solution; this technique has been used to probe the pH of aqueous droplets,\(^{40}\) and has been used in this laboratory to probe pH changes at the air-aqueous interface.\(^{41}\)
Here, we adapt this method to probe the ice surface. The experimental setup is identical to that used for our Raman studies, except that the Nd:YAG laser was exchanged for a nitrogen laser emitting at 337 nm, and ice samples were prepared from distilled water rather than deionized water in order to have a higher initial pH.

While acridine can be used to obtain quantitative pH measurements in aqueous solution, this is not currently possible at air-ice interfaces. The wavelength profile of acridine’s fluorescence spectrum can not be quantitatively related to pH at the air-ice interface, as it is not currently possible to determine its pKa there. Therefore, we use acridine to obtain qualitative information about changes in pH at air-ice interfaces: Although we can not quantify pH, we can monitor changes in acridine fluorescence that indicate increases or decreases in local pH.

![Acridine fluorescence spectra at a pure ice surface at –15 °C (solid blue trace), after deposition of gaseous HNO₃ (dashed red trace), and at the surface of the melted acidic sample (dotted green trace).](image)

**Figure 2.11.** Acridine fluorescence spectra at a pure ice surface at –15 °C (solid blue trace), after deposition of gaseous HNO₃ (dashed red trace), and at the surface of the melted acidic sample (dotted green trace).

Figure 2.11 shows acridine fluorescence spectra acquired at an air-ice interface before and after introducing a maximum of $8 \times 10^{16}$ molecules gas-phase HNO₃ to the surface of a frozen acridine solution. In the present experimental arrangement, we can not quantify the number of gas phase acid molecules which adsorb to the ice surface, as an unknown fraction of the input vapour will be taken up by all the other surfaces present. Upon addition of the acid, the fluorescence spectrum of acridine, shown as the solid blue trace, undergoes a significant red shift, as illustrated by the dashed red trace, indicating a
significant drop in the pH at the ice surface. When the sample is melted, the acridine spectrum shifts back to that of the neutral species, displayed as the dotted green trace in the figure, as the nitric acid dissolves into the bulk sample. Acridine fluorescence also shows a similar decrease in the local pH when either HCl or acetic acid are used as trace probe gases. This spectral shift can be reversed by puffing ammonia onto the acid-doped ice surface. These results, in conjunction with the results discussed in section 2.4.5, suggest that the presence of protons at air-ice interfaces results in a local enhancement of hydrogen bonding.

It is unlikely that surface melting of the ice due to the high partial pressures of acids used in our experiments is occurring. The reduced intensity at 3200 cm$^{-1}$ in frozen NaCl solutions could be due to the formation of a surfacial brine, as discussed above. By contrast, the observed increase in relative intensity at 3200 cm$^{-1}$, shown in Figure 2.10b when HCl(g) and HNO$_3$(g) are introduced to the ice surface, is inconsistent with the idea that surface melting gives rise to a decrease in hydrogen bonding under these conditions. Our Raman spectra at air-water and air-aqueous HCl solution interfaces show significantly lower intensity at 3200 cm$^{-1}$ than do our spectra at air-ice interfaces. Therefore, if surface melting were occurring, and the ice surface was becoming more liquid-like, we would expect the Raman spectra to show decreased intensity at 3200 cm$^{-1}$ in the presence of acids, rather than the increase in intensity which is observed.

In order for changes in pH to occur, the acid must dissociate. The result displayed in Figure 2.11 is important, as it indicates that over the course of an experiment, the adsorbed acids do dissociate to ions, and remain in the surface region. Flowtube studies performed with atmospherically relevant partial pressures of nitric acid and HCl indicate that the majority of the acid is irreversibly adsorbed to ice surfaces, presumably due to ionization of the acid on the surface.$^{42}$ Coupled uptake-ellipsometry experiments indicate that HCl uptake can induce structural disorder at the ice surface, interpreted as being due to formation of a QLL.$^{43}$ Transmission FTIR spectroscopy indicates that nitric acid dissociates on ice surfaces at temperatures below 150 K,$^{44}$ and our results show that dissociation / ionization of these acids takes place at ice surfaces at temperatures warmer than 257 K.
2.4.6 Exclusion of Acids to the Quasi-Liquid Layer

We also used glancing-angle LIF measurements of acridine to determine the extent of exclusion of acids from the ice matrix into the QLL during freezing. Species such as halide salts are known to be excluded into veins and pockets within the ice, as well as to the ice surface, forming concentrated brines. It is often assumed that ionic species such as nitric acid will also be excluded to the QLL, resulting in much higher proton concentrations there than in the original aqueous solution. NMR studies suggest that acids are excluded to grain boundaries during freezing; however, this does not necessarily indicate that they will be excluded to the QLL in significant quantities. To our knowledge, the exclusion of acids and bases to air-ice interfaces during freezing has not been experimentally investigated.

Heightened acidity in the QLL would facilitate important acid-catalyzed reactions, such as the catalytic photo-oxidation of Br\textsuperscript{−} to form BrO, which is thought to be one of the primary protagonists in polar ozone depletion events. To our knowledge, however, exclusion of species such as NO\textsubscript{3}\textsuperscript{−} has not been observed experimentally. Figure 2.12 shows a spectrum of acridine acquired at the surface of a pH 6 aqueous nitric acid solution. The spectrum indicates neutral pH. The second spectrum is that of acridine at the air-ice interface of the same sample after freezing. This spectrum also indicates neutral pH. Based on the expected surface area and volume of the ice sample, and the number of protons present in the aqueous sample, we determined that acridine’s spectrum should indicate an acidic environment at the air-ice interface if 1% of the protons in the aqueous sample was excluded to the QLL. If freezing occurred quickly, the acid might not get excluded, but our method of freezing the samples slowly, as described in Section 2.3.2, suggests that this was not the case in our experiments. It should be noted that the introduction of acid from the gas phase does result in an observed reduction of the surface pH. The lack of change in observed pH suggests that much less than 1% of the initial protons in solution were excluded to the QLL in these experiments. We conclude that it may not be accurate to assume that environmental ice surfaces are acidic based on exclusion.
Figure 2.12. Acridine fluorescence spectra at the surface of a pH 6 aqueous HNO$_3$ solution (solid blue trace), and at the air-ice interface of the same sample after slow freezing at $-7\,^\circ$C (dashed red trace). A spectrum acquired at the surface of a pH 4.9 aqueous HNO$_3$ solution is shown (dotted green trace) for comparison.

2.5 Conclusions

We have developed a novel tool for monitoring the structure of the QLL under different physical conditions. This glancing-angle Raman probe is sensitive to changes taking place within the upper ~50 monolayers of water, and is thus capable of detecting changes occurring at the air-ice interface. A complementary technique using glancing-angle LIF of acridine enables us to see changes in pH at the ice surface. Using these two techniques, we have inferred the ionization of gaseous acids and bases deposited onto ice surfaces, and have related this to structural changes observed in the QLL. The presence of acids appears to enhance hydrogen bonding in the QLL, likely due to the formation of H$_3$O$^+$. These observed structural changes are inconsistent with surface melting leading to greater contribution to the signal from bulk water. Our observations are largely consistent with SFG measurements at the surfaces of ice$^{17}$ and aqueous salt and acid solutions.$^{27,46,47}$ Our results further suggest that acids such as HNO$_3$ and HCl are not excluded to the QLL during freezing in significant amounts.
Chapter Two: Part Two
Solvation of Aromatic Species at the Air-Ice Interface

2.6 Introduction

The results of Section 2.2 show us that the hydrogen bonding environment at air-ice interfaces is distinct from that of liquid water, either in bulk solution or at air-water interfaces. Despite these differences, the dissociation of small acids and bases occurs in a qualitatively similar fashion on ice and water surfaces. It is possible, however, that hydrophobic species such as aromatic compounds will be solvated differently at air-ice and air-water interfaces. In this section, we use PAHs as probes to investigate the solvating ability of the QLL. Self-associated PAHs exhibit different absorption and emission spectra than do the monomers; evidence of self-association has been observed at well below monolayer surface coverages on solids such as silica and alumina, while on liquid water surfaces monomeric emission has been observed at surface loadings of up to at least a monolayer.

2.7 Experimental

2.7.1 Apparatus and Data Acquisition

The reaction chamber for the experiments on ice is the same as that described in Section 2.3.1. Excitation and emission spectra in bulk solution were acquired in 10 mm pathlength quartz cuvettes either by LIF or using a commercial fluorimeter. All surface spectra were acquired by LIF, using the method described in Section 2.3.1. For spectra at air-water interfaces, solutions were contained in Petri dishes either in the open air or in the reaction chamber. Ice samples were contained in the reaction chamber. Table 2.1 lists the lasers used for the LIF experiments, as well as the excitation and emission wavelengths for each compound.
Table 2.1. Excitation and emission wavelengths for spectra of aromatic species in solution and on various substrates

<table>
<thead>
<tr>
<th>Compound</th>
<th>Type of Spectrum</th>
<th>Medium</th>
<th>Wavelength(s) (nm)</th>
<th>Excitation</th>
<th>Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Emission</td>
<td>All</td>
<td>266</td>
<td>300 – 500</td>
<td></td>
</tr>
<tr>
<td>Phenanthrene&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Emission</td>
<td>All</td>
<td>266</td>
<td>335 – 425</td>
<td></td>
</tr>
<tr>
<td>Anthracene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Emission</td>
<td>All</td>
<td>355</td>
<td>360 – 500</td>
<td></td>
</tr>
<tr>
<td>Benzene&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Excitation</td>
<td>Water (bulk)</td>
<td>245 – 273</td>
<td>318</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ice (surface)</td>
<td>245 – 315</td>
<td>318</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Emission</td>
<td>Water (bulk)</td>
<td>261</td>
<td>270 – 450</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ice (surface)</td>
<td>261</td>
<td>280 – 470</td>
<td></td>
</tr>
<tr>
<td>Phenol&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Excitation</td>
<td>Water (bulk)</td>
<td>245 – 289</td>
<td>318</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ice (surface)</td>
<td>245 – 315</td>
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<tr>
<td></td>
<td>Emission</td>
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<td>271</td>
<td>275 – 435</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Ice (surface)</td>
<td>261</td>
<td>280 – 470</td>
<td></td>
</tr>
<tr>
<td>Acridine&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Emission</td>
<td>All</td>
<td>337</td>
<td>390 – 550</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Excitation source was a Nd:YAG laser  
<sup>b</sup> Excitation source was a Nd:YAG-pumped OPO  
<sup>c</sup> Excitation source was a N₂ laser

2.7.2 Sample Preparation

Two methods were used to prepare PAH samples for study. In the first, a few grams of the solid PAH were placed in a round-bottom flask which was immersed in a constant temperature bath. The bath was maintained at room temperature for naphthalene deposition, ~40 °C for phenanthrene deposition, and ~75 °C for anthracene deposition. Prepurified dry N₂ flowed through the round-bottom flask at a rate of (1.2 ± 0.3) L min⁻¹, as determined by a mass flow meter. The resulting mixture of PAH and N₂ flowed through ~50 cm of room temperature ¼” PTFE tubing before entering the sample chamber through a port in the wall. In the second method, samples of known concentration were prepared by diluting a saturated aqueous solution of the aromatic compound to concentrations on the order of 10⁻⁸ – 10⁻⁷ mol L⁻¹. Samples containing acridine, benzene, and phenol were prepared by the second method. Acridine concentrations were on the order of 10⁻⁶ mol L⁻¹, and benzene and phenol concentrations were varied between 10⁻⁶ and 10⁻³ mol L⁻¹.

For experiments on ice, this solution was either frozen, or a few drops (~25 µL total) were deposited from a Pasteur pipette onto the surface of an existing ice sample.
Anthracene was also deposited on ground glass microscope slides by pipetting 15 – 110 µL of an anthracene-in-methanol solution of known concentration on the slide and allowing the methanol to evaporate.

### 2.7.3 Chemicals

Anthracene (Sigma-Aldrich, 99%), naphthalene (Caledon, 98%), acridine (Fluka, ≥97.0%), benzene (ACP, ≥99%), and phenol (ACP, ≥99%) were used as purchased without further modification. Nitrogen was from BOC and had a stated purity of >99.99%. Ice was prepared from 18 MΩ deionized water.

### 2.8 Results and Discussion

#### 2.8.1 Spectra of Polycyclic Aromatic Hydrocarbons

Figure 2.13 shows the chemical structures of each of the aromatic species investigated in this section. Each contains one or more benzene ring, and some include other moieties, such as hydroxyl groups and heteroatoms. Figure 2.14 shows emission spectra of naphthalene in aqueous solution and at an air-ice interface. In water, naphthalene fluoresces between ~310 nm and 380 nm, with maximum intensity at ~340 nm. This emission is also observed on the ice surface, but the major feature there is a new fluorescence band appearing to the red of 370 nm, which shows peaks at 387 nm, 410 nm, and 433 nm. This spectrum resembles the emission from excimeric naphthalene observed at 77 K, and indicates that naphthalene self-associates readily on ice.

Figure 2.15 shows emission spectra of phenanthrene excited at 266 nm on water and ice surfaces. Although peaks occur at the same wavelengths for both substrates, clear differences in the relative intensities of the peaks are observed. Specifically, phenanthrene’s most intense fluorescence is observed at 348 nm and 368 nm on water, but on ice these peaks have only a quarter of the intensity of the peaks at 384 nm and 406 nm. As in the case of naphthalene, the observed shift of fluorescence intensity to higher wavelength peaks is a hallmark of phenanthrene excimer formation.
Figure 2.13. Chemical structures of the aromatic probe molecules.

Figure 2.14. Intensity-normalized emission spectra of naphthalene in aqueous solution (solid blue trace), and at an air-ice interface (dashed red trace).
Figure 2.15. Intensity-normalized emission spectra of phenanthrene at an air-water interface (solid blue trace), and an air-ice interface (dashed red trace).

Figure 2.16 shows anthracene absorption and fluorescence spectra in dilute methanol solution. Its fluorescence spectrum in water is the same and remains unchanged as the solution concentration is increased up to $1.7 \times 10^{-7}$ mol L$^{-1}$ (saturated solution in water) both within solution and at the water surface. In methanol, when the anthracene concentration exceeds $\sim 7 \times 10^{-6}$ mol L$^{-1}$, the fluorescence peak at $\sim 380$ nm begins to decrease in intensity; this feature disappears almost completely once concentrations approach $10^{-3}$ mol L$^{-1}$. Figure 2.17 shows anthracene fluorescence spectra at the surface of various substrates. When anthracene is deposited onto a water surface from the gas phase, the spectrum initially resembles that in water solution, but after 115 min of deposition the $\sim 380$ nm peak is no longer observed. This peak is not seen at all on ice, independent of the manner in which anthracene is introduced to the surface (i.e. deposited from the gas phase or frozen from solution), and also independent of the gas phase deposition time or the solution concentration of anthracene prior to freezing. This spectrum is similar to that seen for anthracene on a glass surface, as shown in Figure 2.17b. Conversely, at low deposition times ($\leq 7$ min) on frozen decanol the 380 nm fluorescence peak has the same relative intensity as that observed at a liquid decanol surface, which in turn resembles that observed in and at the surface of dilute aqueous solutions. At high anthracene concentrations in solution and on all surfaces, a broad peak centered around 480 nm begins to appear.
Fluorescence of monomeric anthracene at low temperatures (< 77 K) displays two major peaks at 381 nm and 403 nm, where the 381 nm peak corresponds to the 0–0 emission band. We observe a similar spectrum in dilute solutions, with broader peaks and with additional peaks appearing at 420 nm and 450 nm. The same spectrum is seen at the air-water interface at low deposition times (< ~30 min) in previous work, and in this work as well, as shown in Figure 2.17a.

In more concentrated solutions, as well as on the water surface after long deposition times, the absolute intensity of the 380 nm peak begins to decrease, while the intensities of the other peaks continue to increase. This spectral shift can likely be attributed to self-association of anthracene: Crystalline anthracene does not fluoresce at 380 nm, and the greatest intensity shifts to the band at 420 nm, as we see at high surface coverages on glass surfaces, and as others have observed on alumina and silica gel surfaces. On ice, the fluorescence spectrum that we see even at the shortest deposition times resembles that of crystalline anthracene.

Anthracene is ~50% more polarizable than naphthalene, and so is more likely to undergo self-association. This is supported by our observation of exclusively monomeric naphthalene emission in aqueous solution at concentrations where anthracene emission shows significant self-absorption of the 380 nm peak. Since naphthalene clearly

Figure 2.16. Absorbance (a) and emission (b) spectra of anthracene in methanol: (a) 3.4 × 10⁻⁴ and (b) 3.4 × 10⁻⁶ mol L⁻¹ concentration.
undergoes self-association at ice surfaces, anthracene’s fluorescence spectrum at ice surfaces most likely arises from the self-associated species as well.

Figure 2.17. Anthracene fluorescence measured (a) at a liquid water surface, after 30 min deposition (solid trace) and 115 min deposition (dashed trace) from the gas phase, (b) on a ground glass surface following evaporation of methanol solvent, (c) on ice, after 10 min deposition (solid trace) and 45 min deposition (dashed trace) from the gas phase, and (d) at the surface of liquid decanol at 24 °C (solid trace) and on solid decanol at –8 °C (dashed trace).

A hallmark of anthracene self-association is a broadening and red shift of the absorption spectrum, as well as the appearance of a new absorption band at 390 nm. Various features of anthracene’s emission spectra on solid surfaces, including the appearance of bands at 420 nm and 450 nm, have also been ascribed to its self-association. However, we observe these bands in dilute aqueous and organic solutions at concentrations that do not give rise to the changes in anthracene’s absorption spectrum assigned to self-association. Further, the fluorescence intensities of these bands in solution show the same linear dependence on anthracene concentration as that displayed by the 403 nm band, which is a feature of monomer fluorescence.
A reduction in fluorescence intensity of the ~380 nm band relative to longer wavelength bands\textsuperscript{48,49} does appear to be due to self-association of anthracene. We observe a relative and an absolute reduction of the intensity of this band in concentrated solutions in methanol and octanol,\textsuperscript{66} as well as after long loading times on water surfaces, consistent with this phenomenon being due to reabsorption of light by self-associated anthracene, due to the red shift of its absorption spectrum.\textsuperscript{48,49}

Emission at 380 nm has been observed on silica and alumina surfaces at surface coverages of up to 1\%, while at higher coverages it is not observed.\textsuperscript{48} We have estimated a maximum surface coverage of ~3\% of a monolayer on ice at low deposition times. This concentration is evidently sufficient to suppress monomer emission. On glass, anthracene surface coverage exceeds that of a monolayer in our experiments, so we would not expect to see emission at 380 nm. The fact that emission from self-associated anthracene is observed at well below monolayer coverages on silica and alumina,\textsuperscript{48,49} as well as after short periods of deposition from the gas phase on ice, could indicate that at sub-monolayer concentrations, anthracene is not distributed evenly across the substrate surface, but rather is present in “islands”.

Anthracene’s propensity to self-associate depends at least to some extent on the nature of the substrate. Although anthracene is quite insoluble in liquid water, it does not appear to self-associate appreciably on the water surface except at high concentrations. On ice and glass, anthracene seems to self-associate very readily, but on frozen decanol the fluorescence spectrum does not indicate more self-association than on liquid decanol. The observed self-association is clearly not strictly a temperature effect either, since the spectra on solid decanol were obtained at the same temperatures as several of those on ice.

2.8.2 Spectra of Benzene and Phenol

Figure 2.18 shows excitation and emission spectra of benzene and phenol in aqueous solution and at air-ice interfaces, as well as an excitation spectrum of neat benzene. As with the PAHs, red shifts in the emission spectra are observed on ice. The benzene emission spectrum matches that of benzene phosphorescence observed in low-
temperature gas matrices, and our excitation spectra of benzene at air-ice interfaces are similar to excitation spectra of neat benzene acquired in this laboratory.

These observations prompted us to suggest that the enhanced self-association observed on ice compared to on liquid water could be due to a reduced number of “free” OH-groups at air-ice interfaces resulting in fewer hydrogen-bonding interactions between the aromatic species and the ice surface. This hypothesis is supported by our glancing-angle Raman measurements, discussed in Section 2.4.1, which show enhanced water-water hydrogen-bonding, and therefore fewer available free OH-groups, at ice surfaces compared to at liquid water surfaces.

Figure 2.18. Intensity-normalized excitation spectra of benzene (solid blue traces) and phenol (dashed red traces) (a) in aqueous solution, (b) at air-ice interfaces, and (c) neat benzene; and intensity-normalized emission spectra of benzene (solid blue traces) and phenol (dashed red traces) (d) in aqueous solution, and (e) at air-ice interfaces.
2.8.3 Molecular Dynamics Simulations

Recently, molecular dynamics simulations were performed in this group\textsuperscript{68} to investigate this hypothesis. The adsorption of a naphthalene molecule to a water or ice surface was investigated; naphthalene’s average binding energy to the water surface was $-10.8(0.2)$ kcal/mol, and that to the ice surface was $-9.7(0.2)$ kcal/mol. The numbers within the parentheses are the standard errors, given by [standard deviation / (number of data points)$^{1/2}$]. Naphthalene also spent a larger proportion of the simulation interacting with water hydrogens at air-water interfaces compared to at air-ice interfaces. Further, the average distances between one water hydrogen on the surface and the center of one of the naphthalene rings were $2.8(0.2)$ Å and $4.8(0.3)$ Å on water and on ice respectively. These results support our hypothesis that fewer dangling OH-groups on ice could lead to less favourable adsorption of aromatics.

In a second set of simulations,\textsuperscript{68} the interactions between two naphthalene molecules were monitored at air-ice and air-water interfaces. The average distance between the two naphthalene molecules was $9.3(0.2)$ Å on the water surface and $7.5(0.1)$ Å on the ice surface. The average binding energies between the naphthalene molecules were $0.48(0.05)$ kcal/mol on water and $1.36(0.08)$ kcal/mol on ice. These results are in agreement with our experimental conclusions that aromatic species self-associate more readily on ice than on water.

2.8.4 Spectra of Acridine

While PAHs, benzene, and phenol exhibit spectral properties at the air-ice interface that can be attributed to self-association, the same is not true for acridine. Figure 2.19 shows acridine emission spectra at air-water and air-ice interfaces at neutral pH and in acidified samples, as well as an emission spectrum of aqueous acridine at high concentrations. At acridine concentrations greater than $\sim 2 \times 10^{-6}$ mol L$^{-1}$, the spectrum is broad and featureless, and not pH dependent. Above this concentration, acridine fluorescence intensity at air-water interfaces is independent of concentration in solution. These observations could be due to self-association. At air-ice interfaces, the acridine emission spectrum resembles that of acridine in aqueous solutions at low concentrations.
Acridine contains a nitrogen heteroatom which is easily protonated. It is possible that this ability to interact with the ice substrate prevents acridine from self-associating at low surface coverages, unlike the other aromatic species we examined.

![Intensit-normalized emission spectra](image)

**Figure 2.19.** Intensity-normalized emission spectra of $10^{-6}$ mol L$^{-1}$ acridine solutions: At neutral pH at air-water (solid blue trace) and air-ice (short-dashed blue trace) interfaces; and at low pH at air-water (long-dashed red trace) and air-ice (dotted red trace) interfaces. The dash-dotted green trace is of a $10^{-4}$ mol L$^{-1}$ acridine solution at the air-water interface of a neutral pH solution.

### 2.9 Conclusions

The results presented in this section show that aromatic hydrocarbons are less well-solvated at air-ice interfaces than at air-water interfaces, leading to enhanced self-association on ice. We suggest that aromatics undergo self-association on ice due to a lack of dangling OH groups which can act as binding sites. The heteroatom-containing compound acridine does not appear to self-associate on ice. It is possible that its acid-base properties allow it to interact favourably with water molecules at ice surfaces. It is clear that species with different physical characteristics are solvated to varying degrees at air-ice interfaces, and that the extent of solvation at air-water interfaces is not always a good indicator of how well a compound will be solvated on ice. Our results suggest that hydrophobic compounds (including, but not limited to, PAHs) may tend to self-associate
on ice surfaces in clumps or islands. This should be considered when interpreting the uptake of organics to ice surfaces.

Chapter Two: Part Three

Uptake of Organics to the Air-Ice Interface

2.10 Introduction

The results discussed in Section 2.8 show that the spectral properties of aromatic species are quite different on ice and on liquid water, likely due to differences in the solvating nature of the substrates. Here we investigate how the differing extents of solvation at liquid water and ice surfaces influences the uptake kinetics of organics from the gas phase. In addition to using fluorescing PAH probes, as described previously, to monitor their surface concentrations, we exploit the way in which adsorbed species perturb the OH stretching spectra of water molecules.

In Section 2.4.5 we saw that the shape and magnitude of the Raman OH-stretch of water and ice could be altered by the presence of impurities which were frozen from solution or deposited from the gas phase. In this section, we develop a method to monitor the uptake of organic species to air-ice interfaces using glancing-angle Raman spectroscopy. In addition to providing uptake kinetics, these experiments enabled us to monitor the effects of trace organics on the structure of water molecules at air-ice interfaces. This work remains in its early stages, but the results discussed below illustrate the potential of glancing-angle Raman spectroscopy to provide important information about the nature of the QLL and the interaction between surfacial water molecules and adsorbates.

2.11 Experimental

The reaction chamber and detection geometry for the uptake experiments to ice were the same as those described above. Uptake experiments to water surfaces were performed in a three-necked round bottom flask, with the liquid light guide suspended
above the sample through the central neck. The laser beam entered the flask through quartz windows in the front and rear. The excitation and emission wavelengths used for the LIF measurements, as well as the laser used for each study are described in Table 2.2.

### Table 2.2. Excitation and emission wavelengths for monitoring the uptake of aromatic species to water and ice surfaces

<table>
<thead>
<tr>
<th>Compound</th>
<th>Excitation Wavelength (nm)</th>
<th>Wavelength(s) Monitored (nm)</th>
<th>Excitation Laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenanthrene</td>
<td>266</td>
<td>348</td>
<td>OPO</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>266</td>
<td>340, 410</td>
<td>OPO</td>
</tr>
<tr>
<td>Acetone</td>
<td>266</td>
<td>289.5</td>
<td>Nd:YAG</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>266</td>
<td>292</td>
<td>Nd:YAG</td>
</tr>
</tbody>
</table>

Raman scattering was induced by the frequency-quadrupled output of a Nd:YAG laser at 266 nm. Phenanthrene and Naphthalene were introduced to the chamber or round-bottom flask in the manner described in Section 2.7.2. Acetone and hexane were introduced to the chamber by flowing dry nitrogen through a bubbler containing the pure compound. The vapour pressure of acetone was controlled by submerging the bubbler in either an ice bath or a dry ice-methanol slurry; n-hexane was delivered at room temperature. The chamber temperature was varied between –5 °C and –33 °C for naphthalene uptake, and was maintained at –20 °C during phenanthrene uptake and –11 °C during acetone and hexane uptake.

The Raman OH-stretch of water was monitored during gas-phase deposition of naphthalene, acetone, and n-hexane. The scattered light intensities at 3200 cm\(^{-1}\) and 3450 cm\(^{-1}\) (289.5 nm and 292 nm respectively) were collected during deposition. For naphthalene uptake, the fluorescence intensities at 340 nm and 412 nm were collected during the same experiment. For some experiments, Raman spectra of the surface were acquired before and after deposition.

The amount of naphthalene deposited to the ice surface was determined in some cases by melting the sample after a known deposition time into a 10 mm pathlength quartz cuvette and measuring naphthalene fluorescence intensity in solution. The fluorescence intensity was related to concentration with a calibration curve of intensity vs. concentration, shown in Figure 2.20.
**Figure 2.20.** Naphthalene emission intensity at 340 nm in aqueous solution as a function of concentration. The solid trace is a linear fit to the data.

All chemicals were used as purchased without further modification. Phenanthrene was purchased from Aldrich and had a stated purity of 98%. Naphthalene was purchased from Caledon and had a stated purity of 98%. Acetone was purchased from ACP and had a stated purity of ≥99.5%. n-Hexane was purchased from Sigma Aldrich and had a stated purity of ≥98.5%. Ice samples were prepared from 18 MΩ deionized water.

### 2.12 Results and Discussion

#### 2.12.1 Uptake Kinetics of Phenanthrene

Figure 2.21 shows phenanthrene fluorescence intensity during gas-phase deposition to water and ice surfaces. An equation for single-exponential growth (Eq. 2.1) described the data well.

\[ I = a(1 - e^{-bt}) + c \]

where \( I \) is the observed fluorescence intensity, \( a \) is a constant that relates fluorescence intensity to concentration, \( b \) represents the first order rate constant for adsorption, and \( c \) reflects an offset in the origin. The observed rate constants for uptake, based on the fits, are shown in Table 2.3. Phenanthrene uptake is approximately twice as fast on water as
on ice. The slower rate on ice could be due in part to self-association, which shifts emission to higher wavelengths and could result in a decrease in the observed uptake rate at 348 nm. It should be noted that the uptake rates measured for all the organic compounds in this section are sufficiently slow that gas-phase diffusion is not considered to be rate-limiting.

**Figure 2.21.** Fluorescence intensity of phenanthrene monitored at 348 nm at an air-water interface (blue circles) and an air-ice interface (red triangles) during gas-phase deposition at –20 °C. The solid traces are fits to Eq. 2.1.

To ensure that submonolayer amounts of phenanthrene were deposited, we estimated the phenanthrene concentration on the ice surfaces. We assumed that phenanthrene’s concentration in nitrogen is given by its room temperature equilibrium value ($4 \times 10^{14}$ molec cm$^{-3}$ based on the room temperature vapour pressure)$^{32}$ when it enters the reaction chamber, and that a steady-state concentration of gas phase phenanthrene is maintained in the reaction chamber during deposition. If this is in equilibrium with the surfaces in the chamber, using an estimated snow-air partitioning coefficient $K_{SA}$ for phenanthrene of $10^{1.03}$ m, $^{69}$ based on a linear free energy relationship, $^{70}$ we then may estimate a phenanthrene concentration on our ice surface of $6 \times 10^{12}$ molec cm$^{-2}$. This value is well below the saturated surface coverage for a film of phenanthrene of $\sim 3 \times 10^{14}$ molec cm$^{-2}$, calculated from the density of solid phenanthrene. Of course, given the evidence for PAH self-association presented above, this sub-
monolayer amount is not distributed uniformly over the surface, but must be present in “clumps” or islands.

Table 2.3. Uptake kinetics of phenanthrene and naphthalene to water and ice surfaces. The uptake rate constants are obtained from fits of Eqs. 2.1 or 2.2 to the data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Water, 295 K</th>
<th>( k_{ob} ) (10^{-3} s^{-1})</th>
<th>Ice, T &lt; 250 K</th>
<th>Ice, T &gt; 250 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenanthrene</td>
<td>0.36 ± 0.09</td>
<td>n/a</td>
<td>0.17 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>Naphthalene (monomer)</td>
<td>n/a</td>
<td>2.5 ± 0.9</td>
<td></td>
<td>2.0 ± 0.9</td>
</tr>
<tr>
<td>Naphthalene (self-associated)</td>
<td>n/a</td>
<td>1.6 ± 0.8</td>
<td>0.6 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>Naphthalene (Raman 3200 cm^{-1})</td>
<td>n/a</td>
<td>3 ± 2</td>
<td>2 ± 2</td>
<td></td>
</tr>
<tr>
<td>Naphthalene (Raman 3450 cm^{-1})</td>
<td>n/a</td>
<td>2 ± 1</td>
<td>2 ± 1</td>
<td></td>
</tr>
</tbody>
</table>

2.12.2 Uptake Kinetics of Naphthalene

Figure 2.22 shows naphthalene fluorescence intensity during deposition to an ice surface. This was determined at two wavelengths, corresponding to the monomeric and self-associated features shown in Figure 2.15. The emission intensity at 340 nm, from monomeric naphthalene, grows in a single-exponential fashion. The intensity at 410 nm, from self-associated naphthalene, displays sigmoidal growth. Both sets of data were fit to Eq. 2.1 to determine formation kinetics; data at low deposition times prior to the appearance of emission at 410 nm were not included in the fits to excimer growth.

Figure 2.22. Fluorescence intensity of naphthalene monitored at 340 nm (blue circles) and at 410 nm (red triangles) at an air-ice interface during gas-phase deposition.
It should be noted that the lowest detected naphthalene surface coverage was above monolayer levels for most of these experiments, based on analysis of melted samples after deposition. In some experiments, the partial pressure of naphthalene was reduced by diluting the saturated stream with dry nitrogen before introducing it to the reaction chamber. The dilution factor was consistent between experiments, but was not quantified; we do not know if surface coverages exceeded a monolayer in these experiments. Diluting the naphthalene flow resulted in a reduction in the observed rate constant of monomeric naphthalene growth of a factor of two, but no reduction in the rate of excimer formation was observed.

Figure 2.23 shows the Raman OH-stretch of water at an ice surface before and after naphthalene deposition. A reduction in intensity is apparent after 10 minutes deposition. The intensity-normalized spectrum shows that the shape of the spectrum also changes after this period of deposition; the low-energy shoulder has reduced intensity relative to the higher-frequency component. This is suggestive of disrupted hydrogen-bonding between water molecules in the surface region. We interpret this observation to mean that surfacial water molecules are interacting with naphthalene rather than with other water molecules.

Figure 2.23. Raman spectra of the OH-stretch region of an air-ice interface before (solid blue trace) and after (dashed red trace) 10 minutes deposition of gas-phase naphthalene. Panel (a) shows the non-normalized spectra, and (b) shows the intensity-normalized spectra.
Figure 2.24 shows the intensity of the shoulder and peak of the Raman OH-stretch during gas-phase deposition of naphthalene. The Raman signal begins to decrease immediately after the introduction of naphthalene. This decrease was well-fit by a single-exponential decay:

\[ I = I_0 e^{-k_{obs}t} + c \]  

where \( c \) accounts for variations in the background signal level and \( k_{obs} \) yields the decay rate due to adsorption.

![Raman intensity at 3450 cm\(^{-1}\) (open blue circles) and 3200 cm\(^{-1}\) (closed red circles) at an air-ice interface during deposition of gas-phase naphthalene. The traces are fits to Eq. 2.2.](image)

Figure 2.24. Raman intensity at 3450 cm\(^{-1}\) (open blue circles) and 3200 cm\(^{-1}\) (closed red circles) at an air-ice interface during deposition of gas-phase naphthalene. The traces are fits to Eq. 2.2.

Figure 2.25 shows the temperature dependence for the observed rate constants measured at 3450 cm\(^{-1}\) (rates at 3200 cm\(^{-1}\) were often slightly faster, but were the same within error), as well as the observed rate constants for monomeric and excimeric naphthalene growth as determined by fits to the emission data, as a function of temperature. The observed uptake rate constants are displayed in Table 2.3. The observed formation rate of monomeric naphthalene was independent of temperature between –3 °C and –33 °C. The excimer growth rate was constant above –20 °C, but below –25 °C, it increased by over a factor of two. The kinetics of the Raman signal decrease did not show a temperature dependence, and appeared to more closely mirror the monomer kinetics than the excimer.
Figure 2.25. Observed naphthalene uptake rate constants at air-ice interfaces measured by naphthalene emission at 340 nm (closed blue circles), 410 nm (closed red triangles), and by Raman intensity at 3450 cm$^{-1}$ (open green squares) as a function of temperature.

We propose two possible reasons for the observed decrease in Raman intensity during naphthalene deposition. It could be due to naphthalene molecules shielding underlying water molecules. It is also possible that the loss of Raman intensity is not due to a simple blanketing effect of the naphthalene, but to interactions between naphthalene and surfacial water molecules. As mentioned above, the relatively greater loss in intensity at the low-energy shoulder of the OH-stretch of water compared to the peak suggests that hydrogen bonding is being disrupted, likely due to interactions between the water molecules and naphthalene. Molecular dynamics simulations performed in our group measured interaction energies between surfacial water molecules of ice and monomeric and self-associated naphthalene. The total interaction energy for two isolated naphthalene molecules with ice was calculated to be 19.4 kcal/mol, compared to 25.7 kcal/mol for two complexed naphthalene molecules. Thus, it appears that self-associated naphthalene interacts more strongly with ice than does monomeric naphthalene. These observations are not sufficient to determine whether the loss of Raman intensity is due to simple physical coverage or to interactions between surfacial water molecules and naphthalene. We will discuss this further in the following section.
2.12.3 A Model to Describe Naphthalene Uptake Kinetics

To better understand the measured naphthalene uptake kinetics, we developed a model to explain the behaviour of both monomeric and self-associated naphthalene, considering the following processes:

\[ A(g) \rightleftharpoons k_1 A(surf) \]  \hspace{1cm} (R2.1)
\[ 2A(surf) \rightleftharpoons k_2 AA(surf) \]  \hspace{1cm} (R2.2)

Where \( A \) is the monomeric aromatic species and \( AA \) is the self-associated species. Reactions 2.1 and 2.2 describe equilibrium processes in which \( A \) undergoes adsorption and desorption from the ice surface, as well as reversible self-association on the ice surface. The following rate expressions describe these processes:

\[
\frac{d[A(g)]}{dt} = k_{-1}[A(surf)] - k_1[A(g)] \quad (2.3)
\]

\[
\frac{d[A(surf)]}{dt} = k_1[A(g)] + k_{-2}[AA(surf)] - k_{-1}[A(surf)] - k_2[A(surf)]^2 \quad (2.4)
\]

\[
\frac{d[AA(surf)]}{dt} = k_2[A(surf)]^2 - k_{-2}[AA(surf)] \quad (2.5)
\]

At low deposition times, \([AA(surf)]\) is zero. Therefore we can rewrite Eq. 2.4:

\[
\frac{d[A(surf)]}{dt} = k_1[A(g)] - k_{-1}[A(surf)] - k_2[A(surf)]^2 \quad (2.6)
\]

We integrated Eq. 2.6 using standard methods to get Eq. 2.7, which was used to fit the data for monomeric naphthalene uptake.

\[
[A(surf)] = a(1 - e^{-bt})^2 + c \quad (2.7)
\]

where \( a \) is a constant relating emission intensity to concentration, \( b \) represents \( k_1 \), and \( c \) is a constant that accounts for an offset in the origin. Since \([A(g)]\) was kept constant during these experiments, it is also reflected in \( a \).

Equation 2.5 can be rewritten in the following manner:
\[ [AA(\text{surf})]_i = (d[A(\text{surf})]^2 - f[AA(\text{surf})]_{i-1})dt + [AA(\text{surf})]_{i-1} \] (2.8)

where \([AA(\text{surf})]_{i-1}\) refers to the concentration of \(AA\) at the previous time step. The constants \(d\) and \(f\) represent \(k_2\) and \(k_{.2}\) respectively. It should be noted that the values used in the equation can not be directly related to the actual rate constants and concentrations, since we did not measure concentration, but rather measured fluorescence intensity at the air-ice interface. The ratio of the two values can give a rough equilibrium constant for self-association, however.

Substituting Eq. 2.7 into Eq. 2.8 yields Eq. 2.9, which was used to fit the data measured at 410 nm.

\[ [AA(\text{surf})]_i = (d[a(1-e^{-br})^4 + c] - f[AA(\text{surf})]_{i-1})dt + [AA(\text{surf})]_{i-1} \] (2.9)

The values for the constants \(a\), \(b\), \(d\), and \(f\) are given in Table 2.4. The constant \(c\) was varied for each experiment based on the observed offset in the baseline. The best fit to the data was obtained with a value of \(b\) of \(4 \times 10^{-3}\) s\(^{-1}\); this is a factor of two greater than \(k_i\) determined from fits of Eq. 2.1 to the fluorescence growth at 340 nm. The best fit to the data acquired at 410 nm was obtained with values of \(d\) and \(f\) of \(5 \times 10^{-4}\) s\(^{-1}\) and \(1 \times 10^{-5}\) s\(^{-1}\) respectively. These values correspond to \(k_2\) and \(k_{.2}\) respectively. The value of \(d\) used in this model is quite close to the excimer formation rate constant determined from Eq. 2.1 \((6 \times 10^{-4}\) s\(^{-1}\)).

| Table 2.4. Values used to fit naphthalene uptake data using Eqs. 2.7 and 2.9 for temperatures greater than 250 K. |
|---|---|---|---|
| **Constant** | **Value** | **a** (arbitrary units) | **b** (s\(^{-1}\)) | **d** (s\(^{-1}\)) | **f** (s\(^{-1}\)) |
| **Value** | 2.5 \(\times\) 10\(^{-2}\) | 4.0 \(\times\) 10\(^{-3}\) | 5.0 \(\times\) 10\(^{-4}\) | 1.0 \(\times\) 10\(^{-5}\) |

A free energy of formation of -2.00 kcal/mol was predicted\(^{68}\) for naphthalene dimer formation from monomers on ice based on molecular dynamics simulations. Using this value as \(\Delta G^o\), we calculated an equilibrium constant for naphthalene self-association at 260 K:
The value of $K_2$ calculated from Eq. 2.10 is 48. This is (likely coincidentally) extremely close to the ratio of the constants $d$ and $f$ from Eq. 2.9 of 50.

Figure 2.26 shows the fits to our data based on Eqs. 2.7 and 2.9 for monomeric and self-associated naphthalene growth on ice. Despite the simplicity of the model, the fits to the data are very good. Equation 2.9, which is based on the rate expression developed in 2.7, and not on measured monomer fluorescence intensity, accurately captures the initial lag in the growth of self-associated naphthalene. The good fits to the data suggest that we are properly accounting for the processes involved in naphthalene uptake to ice.

These results strongly suggest that naphthalene adsorbs to the ice surface in monomeric form, but that once it is on the surface, it can undergo self-association. As a further test of this, we monitored fluorescence intensity after stopping the flow of naphthalene into the chamber, as shown in Figure 2.27. The intensity at 340 nm quickly reached a plateau, but the intensity at 410 nm continued growing linearly. This strongly
suggests that self-association occurs after deposition, in agreement with the molecular dynamics simulations\textsuperscript{68} discussed in Section 2.8.3.

**Figure 2.27.** Fluorescence intensity of naphthalene monitored at 340 nm (blue circles) and at 410 nm (red triangles) at an air-ice interface during gas-phase deposition. The arrow indicates the point at which the naphthalene flow was turned off. The solid lines are included to guide the eye.

Although phenanthrene also self-associates after deposition to ice surfaces, Eq. 2.1, which was used to describe phenanthrene uptake kinetics, does not include a term for self-association. We could not fit the phenanthrene data to Eq. 2.7, which includes a term for self-association, because emission from monomeric and self-associated phenanthrene overlap, as shown in Figure 2.15, and so self-association will not affect emission intensity at 348 nm in a straightforward fashion. However, as stated above, Eq. 2.1 provides good fits to phenanthrene uptake to water and ice.

**2.12.4 Uptake of Acetone and n-Hexane**

Figure 2.28 shows Raman intensity at 3450 cm\textsuperscript{-1} during acetone and n-hexane deposition to ice, as well as Raman intensity when dry N\textsubscript{2} is flowed across an ice surface. The loss rate during N\textsubscript{2} flow was \(\sim 4 \times 10^{-5} \text{ s}^{-1}\), as was the loss rate during hexane deposition. The loss rate during acetone deposition was \((7 \pm 4) \times 10^{-4} \text{ s}^{-1}\), an order of magnitude higher. The loss rate at 3200 cm\textsuperscript{-1} was consistently faster, although the
average rate, \((1.2 \pm 0.9) \times 10^{-3} \text{ s}^{-1}\), was statistically indistinguishable from that at 3450 cm\(^{-1}\). We did not acquire Raman spectra before and after acetone deposition, but the faster rate of decrease of the shoulder suggests that, as with naphthalene, deposition disrupts the hydrogen-bonding network of the surfacial water molecules.

![Figure 2.28](image.png)

**Figure 2.28.** Logarithmic decay profiles of Raman intensity at 3450 cm\(^{-1}\) at air-ice interfaces during exposure to pure N\(_2\) (open blue circles), to n-hexane (closed red triangles), and to acetone (closed green diamonds). The traces are linear fits to the data.

The decrease in Raman intensity is almost certainly due to the adsorption of acetone to ice, as in the cases of naphthalene and phenanthrene. As discussed in the previous section, the decrease in intensity could be due to a shielding effect of the organics, or it could be due to interactions between the adsorbate and the substrate. If the first explanation is correct, then the lack of decrease in Raman intensity during the deposition of n-hexane would suggest that hexane was not partitioning efficiently to the air-ice interface. A decrease in the free-OD IR stretch of D\(_2\)O ice has been reported to occur in the presence of strongly-interacting species such as acetone, but not in the presence of weakly-interacting species such as 1-hexene.\(^7\)

If the second explanation is correct, that suggests that the PAHs and acetone interact with the ice surface, but that n-hexane does not. This is quite plausible, since the PAHs could interact with the water molecules through the pi electron cloud, and the carbonyl group of acetone can participate in hydrogen bonding. Based on the structure of
n-hexane, one would not expect it to interact strongly with water molecules. Interestingly, n-hexane has been shown to adsorb strongly to ice, and a contact angle study suggested that it significantly alters the structure of the underlying water molecules in order to maximize the adsorption energy. Based on our experimental data and theoretical calculations, as well as on the results of IR adsorption studies, however, we suggest that n-hexane does not strongly interact with the ice surface. Since n-hexane adsorption to ice has been experimentally observed, we conclude that the decrease in Raman intensity at the air-ice interface in the presence of PAHs and acetone is due to interactions between these species and the ice substrate, rather than to a simple shielding effect.

### 2.13 Conclusions

We have measured uptake kinetics of phenanthrene and naphthalene to ice using glancing-angle LIF. The uptake kinetics of naphthalene are well-described by a simple model that accounts for adsorption and desorption of the monomeric species, as well as self-association at the air-ice interface. No temperature dependence to the uptake kinetics is observed above –30 °C, but below that the observed rate of self-association increases. The uptake rate of the monomer is independent of temperature in the range studied here.

Uptake kinetics of strongly-interacting organic species can be measured by monitoring the intensity of the OH-stretch of water at the ice surface using glancing-angle Raman spectroscopy. The uptake rate of naphthalene measured using this technique is identical to that measured using glancing-angle LIF. We have also measured acetone uptake using this technique, but no change in the intensity or shape of the OH-Raman stretch was observed during the deposition of n-hexane. We conclude that the decrease in Raman intensity is due to interactions between the adsorbed compound and the ice.

The self-association of hydrophobic compounds at air-ice interfaces at sub-monolayer coverages could have significant environmental implications. Common descriptions of uptake kinetics and surface coverages may not be applicable, and the reactivity of the self-associated species could be different from that of the monomers. It should be noted that gas-phase organic compounds partitioning to ice are likely to
encounter a mixture of organics at the surface, rather than one sole species, as was the case in our experiments. Although we are unaware of any studies of the uptake or self-association of mixtures of organic compounds on ice, based on our results, we believe that it is likely that hydrophobic compounds will associate with one another on ice in a similar fashion to the aromatic compounds we studied. Hydrophobic compounds, whether of a single species or a mixture, will likely exist on ice surfaces in islands, even at submonolayer coverages; predictions of pollutant fate may need to account for this behaviour.
2.14 References

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Chapter Three

The Role of the Quasi-Liquid Layer in the Photolysis Kinetics of Aromatic Species

Portions of this chapter are reproduced in part from the following publications, with permission from the respective journals:


Kahan, T. F.; Donaldson, D. J. (in preparation) Benzene photolysis in ice: Implications for the fate of organic contaminants in the winter.


3.1 Introduction

In Chapter Two, we investigated physical properties of air-ice interfaces, and used inorganic and organic probe molecules to investigate the solvating nature of the QLL. We found that the uptake and solvation of aromatic compounds occurs very differently on ice surfaces compared to on water surfaces. In this chapter, we investigate chemical transformations of aromatic compounds on ice.

Polycyclic aromatic hydrocarbons are formed primarily as products of incomplete combustion. These organic pollutants, which consist of two or more fused benzene rings, often have allergenic, mutagenic, and carcinogenic effects. Some PAHs, such as the two-member ring naphthalene, are found almost exclusively in the gas phase, while the larger five- and six-member ring PAHs such as benzo[a]pyrene (BaP) are associated with condensed phases, primarily particulate matter. The three- and four-member ring compounds such as anthracene and pyrene are semivolatile, and therefore partition between the gas and particle phases. Organic pollutants such as PAHs are found in snows of both urban and remote regions.

PAHs in the gas phase react predominantly with hydroxyl radicals with rate coefficients on the order of $10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$. Other reactions have much smaller rate coefficients and are therefore generally considered to be atmospherically unimportant. Because the larger, more toxic PAHs are found primarily on surfaces, heterogeneous reactions of these compounds such as photo-oxidation, ozonation, and nitration are expected to be much more important than gas-phase reactions with OH.

In natural waters, direct photolysis can be a major removal pathway for organic species which absorb in the actinic region. While the photoionization of PAHs in ice has been studied in the context of astrochemistry, interest in photochemical transformations of pollutants in or on frozen media under atmospherically relevant conditions is much more recent. Several recent studies show that direct photolysis could be an important transformation process for organic species in snow and ice.
Nonsoluble reagents such as organic pollutants are expected to be excluded from the ice matrix during freezing, resulting in enhanced concentrations in liquid pockets within the ice, as well as in the QLL. Therefore, reactions involving such species are expected to take place primarily in these two regions of ice. Although the physical properties of the QLL are distinct from those of liquid water (see for example Refs. 31,32), reaction kinetics are often assumed to be identical in the two media. Some studies\textsuperscript{30} support this assumption, while other studies show different reaction rates in ice and at ice surfaces compared with rates in or on liquid water, both for direct photolysis\textsuperscript{25,26,33} and bimolecular reactions\textsuperscript{26,34-36} Our results from Chapter Two indicate that the physical environment of the QLL is quite different from that of a liquid water surface, and that aromatic species are solvated less efficiently there.

In this section, we explore the role of the QLL on the photolysis kinetics of three aromatic species. We measured kinetics both by melting the samples and performing offline analysis following irradiation, and by using glancing-angle LIF to measure kinetics in situ, in real time, at air-ice and air-water interfaces. The following sections contain descriptions of these experiments.

**Chapter Three: Part One**

**Photolysis Kinetics of Aromatic Species in Aqueous Solution, in Ice, and at the Air-Ice Interface**

**3.2 Introduction**

As discussed in Section 3.1, some studies report photolysis rates of aromatic species in ice which are identical to those in aqueous solution, while others report enhanced kinetics in ice. As discussed in Chapter One, reactions in ice are thought to occur primarily in liquid pockets and veins within bulk ice, and in the QLL at the air-ice interface. Since our results from Chapter Two indicate that the QLL presents a very different environment to aromatic species than does liquid water, we hypothesized that
photolysis could occur quite differently in the QLL than within liquid pockets and veins within bulk ice. To test this hypothesis, we measured anthracene photolysis rates in aqueous solution and in ice samples with different surface areas.

**Experimental**

**3.3.1 Effect of Specific Surface Area**

Figure 3.1 shows the experimental geometries used for this set of experiments. Samples were irradiated with the output of a 75 W xenon arc lamp which passed through a 295 nm long-pass cutoff filter. Aqueous solutions were irradiated in 10 mm pathlength quartz cuvettes at room temperature, with the lamp output striking the cuvette horizontally such that the sample was illuminated uniformly. Ice samples were irradiated in an aluminum reaction chamber with copper tubes attached to circulating chillers running beneath the copper floors of the chamber. The lamp’s output was directed by a first-surface mirror with maximum reflectance at 355 nm through an opening in the chamber roof. The distance between the lamp and the sample was ~50 cm. Temperatures within the chamber were maintained at approximately –15 °C.

![Figure 3.1. Schematics of the experimental setups used for photolysis of samples to be analyzed offline: (a) in aqueous solution; and (b) ice samples.](image-url)
For these experiments, kinetic measurements were performed ex situ by melting the ice samples after known time periods of irradiation and collecting anthracene fluorescence spectra with a commercial fluorimeter. Samples were excited at 355 nm and emission was monitored between 370 and 470 nm; photolysis kinetics for aqueous samples and melted ice samples were determined by monitoring the fluorescence intensity of the 380 nm emission peak of anthracene as a function of irradiation time.

Aqueous anthracene solutions were prepared by diluting saturated anthracene solutions (Sigma-Aldrich, 99% purity) in 18 MΩ deionized water. Anthracene concentrations were on the order of $10^{-8}$ to $10^{-7}$ mol L$^{-1}$. Ice cubes were prepared by freezing ~5 mL aliquots of aqueous anthracene solution in an ice cube tray or Petri dish and then transferring them to the reaction chamber to undergo photolysis. The ice cubes were semi-spheres with radii of ~1.5 cm. High surface area samples were prepared by crushing the ice cubes with a pestle on the chilled chamber floor prior to photolysis; the ice granules that were formed had radii of approximately 2 mm.

### 3.3.2 In Situ Measurements of Photolysis in Solution and at the Air-Ice Interface

The experimental geometries for these experiments are displayed in Figure 3.2. Photolysis of aqueous samples was performed in 10 mm pathlength quartz cuvettes. Ice samples were photolyzed in the reaction chamber described in Section 2.3.1. Samples were irradiated with the output of a 75 W or 100 W xenon arc lamp. The lamp’s output was directed onto the sample by a first-surface mirror with maximum reflectance at 355 nm. For ice samples, the lamp’s output entered the chamber through a quartz window in the roof. The distance between the lamp and the sample was ~90 cm for both aqueous and ice samples. With the exception of experiments designed to measure the wavelength dependence of the kinetics, this light passed through a 295 nm long-pass optical filter prior to entering the chamber. With this filter in place, the total radiant power entering the chamber in the UV-VIS region of the spectrum was ~0.2 W, as measured by a power meter using an energy-absorbing head optimized between 250 and 400 nm. Unless otherwise stated, the temperature within the reaction chamber was maintained at approximately $–15$ °C during photolysis.
Figure 3.2. Schematics of the experimental setups used for in situ photolysis measurements of samples (a) in aqueous solution; and (b) at substrate surfaces.

Fluorescence intensity was detected using LIF and glancing-angle LIF. The excitation and emission wavelengths used to monitor fluorescence, as well as the laser used, are detailed in Table 3.1. Anthracene, naphthalene, and benzene photolysis was monitored by following the loss of emission intensity as a function of irradiation time. Phenol growth rates were monitored by following phenol emission intensity as a function of irradiation time.

Table 3.1. Excitation and emission wavelengths used to monitor the photolysis kinetics of aromatic compounds in aqueous solutions and at air-ice interfaces

<table>
<thead>
<tr>
<th>Compound</th>
<th>Excitation Wavelength (nm)</th>
<th>Wavelength(s) Monitored (nm)</th>
<th>Laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>355</td>
<td>379, 403, 420</td>
<td>Nd:YAG</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>266</td>
<td>333</td>
<td>Nd:YAG</td>
</tr>
<tr>
<td>Benzene</td>
<td>261</td>
<td>340</td>
<td>OPO</td>
</tr>
<tr>
<td>Phenol</td>
<td>271 (aq), 261 (ice)</td>
<td>318</td>
<td>OPO</td>
</tr>
</tbody>
</table>

Aqueous samples were prepared as described in Section 2.7.2. Ice samples were generally prepared by freezing the reagent from solution, although anthracene was delivered from the gas phase for some experiments, by the method described in Section 2.7.2. For some experiments involving phenol growth, gas-phase benzene was deposited
onto a pure ice surface by sampling the headspace above liquid benzene with a Pasteur pipette, and then “puffing” the gas onto the ice surface.

### 3.3.3 HPLC Measurements

Melted samples from the experiments described in Section 3.3.1 were analyzed for the presence of phenol using a Waters HPLC-UV with a diode array detector. The column was a C18 (Jones Chromatography, 25 cm x 4.6 mm x 4 µm). A 90:10 acetonitrile-water mixture was run isocratically at a flow rate of 1 mL min$^{-1}$. Absorption was monitored at 210 nm. Phenol eluted at 3.6 min, and benzene eluted at 5 min.

### 3.3.4 Chemicals

All chemicals were used as delivered. Anthracene was purchased from Sigma-Aldrich and had a stated purity of 99%. Naphthalene was purchased from Caledon and had a stated purity of 98%. Benzene was purchased from ACP and had a stated purity of ≥99.0%. Phenol was purchased from ACP and had a stated purity of ≥99%. Ice samples were prepared from 18MΩ deionized water. Nitrogen gas was purchased from BOC and had stated a purity of >99.99%.

### 3.3 Results and Discussion

#### 3.4.1 Anthracene Photolysis in Aqueous Solution, in Ice, and at the Air-Ice Interface

Figure 3.3 shows representative decay profiles of anthracene as a function of irradiation time in aqueous solution, in ice cubes, and in ice granules. To determine reaction kinetics, fluorescence intensity vs. time data were fit to Eq. 2.2. When plotted logarithmically, this expression predicts that a linear dependence with time should be observed, if the reaction is first-order with respect to reagent concentration. First order kinetic expressions fit the data very well, but for saturated anthracene solutions, second order kinetics provided equally good or better fits. Therefore, the reported rate constants were all obtained using dilute anthracene solutions for which first order expressions provided the best fits.
The measured rate constants are summarized in Table 3.2. Anthracene decayed most slowly in aqueous solution, with a rate constant of $2.4 \times 10^{-4}$ s$^{-1}$. In the ice cubes, the rate was slightly faster ($4 \times 10^{-4}$ s$^{-1}$). When the ice sample was crushed into granules prior to photolysis, the rate increased to $1 \times 10^{-3}$ s$^{-1}$. Anthracene loss in the dark amounted to less than 10% over four hours for all samples. Thus, its contributions to the kinetics were deemed to be negligible and were not considered.

Table 3.2. Photolysis rates of aromatic compounds in aqueous solution, in ice, and at air-ice interfaces

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>$k_{obs}$ (10$^{-3}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>Aqueous solution$^{a}$</td>
<td>0.25 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>Air-water interface$^{b}$</td>
<td>0.17 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>Ice cubes$^{a}$</td>
<td>0.4 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Ice granules$^{a}$</td>
<td>1.0 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>Air-ice interface$^{b}$</td>
<td>1.04 ± 0.08</td>
</tr>
<tr>
<td>Benzene</td>
<td>Aqueous solution$^{a,b}$</td>
<td>0$^c$</td>
</tr>
<tr>
<td></td>
<td>Air-ice interface$^{b}$</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>Aqueous solution$^{b}$</td>
<td>0.024 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>Air-ice interface$^{b}$</td>
<td>0.22 ± 0.05</td>
</tr>
</tbody>
</table>

a) kinetics were measured offline by fluorimetry
b) kinetics were measured in situ by LIF or glancing-angle LIF
c) only one measurement was performed
Figure 3.4 shows representative decay profiles of anthracene fluorescence during photolysis at air-water and air-ice interfaces. First order photolysis rate constants obtained for anthracene measured at the air-ice and air-water interfaces using glancing-angle LIF are documented in Table 3.2. When anthracene was introduced to the liquid or solid aqueous surface from the gas phase, exponential decays were observed at both 403 nm and 420 nm, and the data were well fit using Equation 2.2. When experiments were carried out using anthracene prepared in solution, either on water or on ice, first order kinetic expressions fit the data very well, but in some cases second order kinetic expressions also provided reasonable fits to the data. The fact that we measure the same kinetics when anthracene is frozen from solution as when it is deposited from the gas phase is important, as it indicates that we are measuring reactions at the surface, and that contributions from reactions in bulk ice are negligible.

The anthracene photolysis rate constant at the air-ice interface is $1.04 \times 10^{-3}$ s$^{-1}$, the same as that measured in ice granules for similar illumination conditions. This supports our hypothesis that PAH photolysis occurs more rapidly at the air-ice interface than in liquid regions within bulk ice. To further test this hypothesis, we calculated the relative rates expected in ice cubes and ice granules, assuming that the observed kinetics
contain contributions from photolysis at the air-ice interface and from liquid inclusions within the ice. The surface area of the ice granules samples was approximately 4.4 times greater than that of the ice cubes. Given that the rate constant we measure at the air-ice interface using glancing-angle LIF is a factor of 4 greater than that measured in aqueous solution, we calculated the relative rates of photolysis in the ice granules and ice cubes. We calculated this ratio for different anthracene distributions between the bulk and surface, ranging from anthracene being completely present in the bulk to it being excluded entirely to the surface. These calculations predict a maximum rate enhancement in the ice granules of ~2.3, which is obtained if approximately 25% of the anthracene is at the air-ice interface. This is in very good agreement with our measured rate enhancement of 2.5 in the ice granules.

Based on these results, it appears that anthracene in liquid regions within bulk ice undergoes photolysis at rates similar to those in aqueous solution, but that photolysis in the QLL is much faster. We note that anthracene photolysis kinetics are the same at air-water interfaces as in bulk aqueous solution, which indicates that the enhanced reactivity in the QLL is not strictly a surface effect. Other possible factors that could account for the increased rates are explored in Part Two of this chapter.

### 3.4.2 Benzene Photolysis at the Air-Ice Interface

Table 3.2 shows the observed photolysis rate constant for benzene measured at the air-ice interface. Benzene does not undergo photolysis in aqueous solution at the Earth’s surface, because it does not absorb wavelengths above 295 nm, as shown by Figure 2.18. The fact that it undergoes photolysis at the air-ice interface can be explained by a red-shift in its absorption there, as shown in Figure 2.18.

In the presence of high energy photons, gas-phase benzene has been observed to ionize and react with molecular oxygen to form phenol. Recently, the same mechanism was invoked to explain phenol formation from pure benzene placed under direct sunlight. To determine whether this mechanism was responsible for our observations on ice, we irradiated aqueous and ice samples containing benzene at wavelengths below 295 nm either by removing the long-pass filter in front of the xenon lamp or by irradiating the samples with the 261 nm output of the OPO. Figure 3.5 shows emission spectra at an ice
surface for frozen samples containing benzene before and after irradiation with the 261 nm output of the laser, as well as with the 295 nm-filtered output of the xenon arc lamp. When benzene is irradiated at wavelengths above 295 nm, there is a clear decrease in benzene emission intensity after photolysis, while the spectrum acquired after irradiation with wavelengths below 295 nm, either from the laser or the xenon arc lamp, shows an increase in emission intensity in the wavelength region around 310 nm, where phenol emits on ice (see Figure 2.18). Figure 3.5 also shows excitation spectra of an aqueous benzene solution prior to and after irradiation with the full output of the xenon lamp; phenol formation is evident.

Figure 3.5. (a) Glancing-angle LIF emission spectra of a frozen solution containing $1 \times 10^{-5}$ mol L$^{-1}$ benzene (solid blue trace), and of the same sample after irradiation by the 261 nm output of a laser (dotted green trace); (b) glancing-angle LIF emission spectra of a frozen solution containing $1 \times 10^{-5}$ mol L$^{-1}$ benzene (solid blue trace), and of the same sample after irradiation by the 295 nm-filtered output of a 100 W Xe arc lamp (dotted green trace); and (c) excitation spectra of a $2.1 \times 10^{-3}$ mol L$^{-1}$ aqueous benzene solution (solid blue trace), of the same solution after irradiation by the full output of a 100 W Xe arc lamp (dotted green trace), and an excitation spectrum of aqueous phenol (dashed red trace). The sharp peaks at ~285 nm in (a) and (b) are due to Raman scattering from the ice.
We confirmed the presence of phenol in the samples irradiated at low wavelengths by acquiring excitation spectra of the melted samples, as shown in Figure 3.6, and by HPLC analysis. The involvement of $O_2(g)$ in phenol formation was tested by flushing the solutions with $N_2$ prior to freezing, as well as the reaction chamber during freezing and irradiation. No phenol growth was observed in these conditions, confirming the role of molecular oxygen in the mechanism.

**Figure 3.6.** Excitation spectrum of a melted ice sample that had benzene introduced to its surface from the gas phase after 30 minutes irradiation by the full output of a 100 W Xe arc lamp (dotted green trace). Excitation spectra of aqueous benzene (solid blue trace) and phenol (dashed red trace) are shown for comparison.

**Figure 3.7.** Growth of phenol fluorescence intensity during irradiation of $10^{-3}$ mol L$^{-1}$ benzene in aqueous solution and a frozen $10^{-5}$ mol L$^{-1}$ benzene solution at the air-ice interface by the full output of a 100 W Xe arc lamp. The solid traces are fits of Eq. 2.1 to the data.
Figure 3.7 shows phenol emission intensity in aqueous solution and at an air-ice interface during irradiation by the full output of a 100 W xenon arc lamp. The kinetics are identical in the two media. Although this reaction does not occur at wavelengths relevant to the Earth’s surface, it is interesting to note that this is the only reaction that we have observed to date which displays similar kinetics at air-ice interfaces and in aqueous solution.

3.4.3 Naphthalene Photolysis at the Air-Ice Interface

The observed naphthalene photolysis rate constants in aqueous solution and at air-ice interfaces are displayed in Table 3.2. As with anthracene and benzene, the rate is significantly higher on ice than in water. Like benzene, naphthalene exhibits significant self-association on ice. Crystalline naphthalene’s absorbance spectrum is red-shifted with respect to the monomer. Monomeric naphthalene absorbs only very weakly above 295 nm, but crystalline naphthalene absorbs much more strongly up to ~303 nm. This shift in absorbance is likely to enhance the naphthalene photolysis rate we observe, because in our system light at wavelengths below 295 nm is cut off by an optical filter. Therefore, the increase in naphthalene photolysis rate on ice compared to in water could be at least partially explained by a possible red shift in its absorbance spectrum on ice, where it is present primarily in a self-associated form.

Crystalline anthracene also shows a red-shift in its absorption spectrum compared to the monomeric form, but since anthracene already absorbs well above 295 nm, this red shift will likely have much less of an impact on anthracene’s photolysis kinetics than the effects observed for naphthalene and benzene. In section 3.8.4 we explore the wavelength dependence for anthracene photolysis on ice, and conclude that the red-shift in anthracene’s absorption spectrum is not responsible for its enhanced kinetics at the air-ice interface.

3.4 Conclusions

The photolysis rate constant of anthracene measured at air-ice interfaces is the same as that measured in ice granules, but faster than that measured in ice cubes and in,
or at the surface of, aqueous solution. Benzene and naphthalene also exhibit greatly enhanced photolysis rates at the air-ice interface compared to in aqueous solution. In fact, benzene does not undergo photolysis at wavelengths relevant to the lower atmosphere in aqueous solution; its photolysis on ice presents a previously unreported transformation mechanism in the environment. While a red-shift in the absorption spectra of benzene and naphthalene due to self-association at air-ice interfaces could explain their enhanced photolysis rates there, it is not clear that the same is true for anthracene. The remaining sections in this chapter discuss experiments designed to determine the reason for the rate enhancements observed at the air-ice interface.

Chapter Three: Part Two

Investigating the Cause of Enhanced Photolysis Rates at the Air-Ice Interface

3.6 Introduction

Our results from Part One of this chapter indicate that photolysis rates of some aromatic species are enhanced at the air-ice interface compared to in bulk ice or in aqueous solution. In this section, we explore several possible reasons for this enhancement. We first investigate the effect of enhanced photon fluxes due to scattering and reflection by the ice. For this study, we developed an in situ chemical actinometry technique to determine the photon fluxes from the lamps used for photolysis, and measured anthracene and benzene photolysis rates in aqueous solution and at air-ice interfaces as a function of lamp power. These results were compared to measurements of nitrite photolysis kinetics as a function of lamp power.

It is also possible that the photolysis of aromatic species could occur more quickly on solid surfaces than on liquids, or that self-associated species might be more reactive than monomers. We measured anthracene photolysis kinetics on a range of solid and liquid substrates to determine whether this was the case.
In Part One of this chapter we noted that although red-shifts in the absorption spectra of naphthalene and benzene on ice due to self-association could explain their enhanced photolysis kinetics there, enhanced anthracene photolysis rates could not definitively be related to a red-shift in its absorption on ice. Here we investigated the wavelength dependence of anthracene photolysis kinetics at air-ice interfaces to determine whether a change in its absorption spectrum could explain the enhanced rates.

We also investigated other factors that could affect anthracene photolysis rates including temperature, polarity of the substrate, and pH. Finally, we investigated the role of oxygen in the photolysis kinetics of anthracene at air-water and air-ice interfaces.

3.7 Experimental

3.7.1 Development of an In Situ Chemical Actinometer

We used chemical actinometry to determine the photon flux of the lamps used for photolysis in the wavelength regions of interest. Several groups have performed chemical actinometry by measuring the photolysis kinetics of species such as nitrate or nitrite with an OH-trap (e.g. Refs. 44-48). We used nitrite as a chemical actinometer and monitored the growth of phenol formed from reactions between OH and benzene.

Aqueous solutions containing $4 \times 10^{-4}$ to $8 \times 10^{-3}$ mol L$^{-1}$ benzene and $10^{-5}$ to $10^{-3}$ mol L$^{-1}$ NaNO$_2$ were prepared daily. Aqueous samples were contained in a 10 mm pathlength quartz cuvette, and irradiated with the output of the 100 W xenon arc lamp which passed through a 295 nm long-pass cutoff filter. The experimental geometry was the same as that described in Section 3.3.2 and illustrated in Figure 3.2.

Phenol was detected using LIF. The sample was excited by the 271 nm output of the OPO, and emission was detected at 318 nm. 271 nm was chosen as the excitation wavelength to minimize interferences from benzene emission, which overlaps completely with that of phenol (see Figure 2.18). Phenol concentrations were determined from calibration curves, shown in Figure 3.8. The detection geometry and acquisition methods
were identical to those described in Section 3.3.2 and illustrated in Figure 3.2. Laser-induced fluorescence intensity was collected automatically every 20 s.

![Figure 3.8](image.png)

**Figure 3.8.** Calibration curve for phenol concentration in aqueous solution for offline fluorimeter measurements (open triangles), and *in situ* LIF measurements (closed circles). The traces are linear fits to the data. Error bars represent one standard deviation about the mean of at least three trials.

### 3.7.2 Photon Flux Dependence

Aqueous nitrite solutions were prepared by combining $1.2 \times 10^{-3}$ mol L$^{-1}$ benzene and $3.5 \times 10^{-5}$ mol L$^{-1}$ NaNO$_2$ in 18 MΩ deionized water. Aqueous anthracene solutions were prepared as described in section 3.3.1. Ice samples were prepared by freezing benzene or anthracene solutions in the reaction chamber described in Section 2.3.1.

The experimental geometries for photolysis in aqueous solution and at interfaces were the same as those described in Section 3.3.2. Photolysis was effected by the output of a 75 W or 100 W Xenon arc lamp, which, unless otherwise stated, passed through a 295 nm long-pass cutoff filter. Photolysis in bulk solutions was performed in 10 mm pathlength quartz cuvettes, and photolysis at interfaces was performed in the reaction chamber described in Section 2.3.1.
The lamp power was measured with a power meter optimized between 250 nm and 400 nm, and the power was varied by placing wire mesh in between the lamp and the sample. The photon flux was determined at some lamp powers by nitrite actinometry, as described in Section 3.8.

The decrease in fluorescence intensity from anthracene and benzene, as well as the growth of phenol fluorescence due to nitrite photolysis, was monitored by fluorescence spectroscopy. Kinetics at the air-ice interface were measured using glancing-angle LIF, as described in Section 3.3.2, and kinetics in solution were determined using a commercial fluorimeter, as described in Section 3.3.1.

### 3.7.3 Further Investigations of Anthracene Photolysis

Photolysis for these studies was effected by a 75 W Xenon arc lamp which passed through a 295 nm long-pass cutoff filter prior to reaching the sample. The 355 nm output of a Nd:YAG laser was used to excite the samples, and fluorescence was monitored at 405 nm using LIF or glancing-angle LIF. The experimental geometry and data collection methods are described in Section 3.3.2 and illustrated in Figure 3.2.

Most ice samples were prepared in an atmosphere of air. Photolysis was also carried out under an ambient atmosphere, except when the PAH was introduced from the gas phase in a stream of nitrogen. To determine the effects of oxygen on the photolysis kinetics, reactions were also carried out under atmospheres of pure oxygen and pure nitrogen. For these studies, the reaction chamber was purged with the appropriate gas for 30 minutes prior to introducing the anthracene from the gas phase. For the reactions on ice, N\textsubscript{2} or O\textsubscript{2} was flowed through the chamber during sample freezing as well as during PAH deposition and irradiation.

In addition to ice and liquid water, anthracene photolysis kinetics were measured on liquid and frozen decanol, and on glass microscope slides. Samples on these substrates were prepared in the reaction chamber as described in Section 2.7.2.
3.7.4 Chemicals

All reagents were used as purchased, without further modification. Anthracene, sodium nitrite, and 1-decanol were purchased from Sigma-Aldrich and had stated purities of \( \geq 99\% \). Naphthalene, methanol and concentrated nitric acid were purchased from Caledon and had stated purities of 98\%, 99.8\% and \( \geq 99.9\% \) respectively. Benzene was purchased from ACP and had a stated purity of \( \geq 99.0\% \). Phenol was purchased from ACP and had a stated purity of \( \geq 99\% \). Nitrogen and oxygen gas were purchased from BOC and had stated purities of \( \geq 99.99\% \). Ice samples were prepared from 18 MΩ deionized water.

3.8 Results and Discussion

3.8.1 Development of an In Situ Chemical Actinometer

To determine the photon flux of the lamps used in our photolysis experiments, we developed an in situ chemical actinometry technique, using benzene as a hydroxyl radical trap. Nitrite undergoes photolysis in aqueous solution to form hydroxyl radicals (see for example Ref. 49 and references therein):

\[
NO_2^- \xrightleftharpoons{hν,H^+} NO + OH
\]  

(R3.1)

Benzene and OH react to form phenol with a yield of 0.95.\(^{48}\) We monitored phenol production from this reaction. For this technique, the following reactions are important:

\[
Ox + hν \xrightarrow{J_{OH}} OH
\]  

(R3.2)

\[
OH + B \xrightarrow{k_B} P
\]  

(R3.3)

\[
OH + Ph \xrightarrow{k_P} P
\]  

(R3.4)

where \( Ox \) is the OH-precursor, in this case \( NO_2^- \), \( J_{OH} \) is the photolysis rate constant for OH formation, \( B \) is benzene, \( k_B \) is the second order rate constant for the reaction between benzene and OH, \( P \) is products, \( Ph \) is phenol, and \( k_P \) is the second order rate constant for the reaction between phenol and OH. Since we only used data from short irradiation
times, when phenol concentrations were very low, R3.4 was negligible under our experimental conditions and could be ignored. Reaction 3.3 forms phenol with a 95% yield,\(^{48}\) which leads us to the following expression:

\[
OH + B \xrightarrow{0.95k_B} Ph
\]  
(R3.5)

Since \(k_B\) is large and the initial benzene concentrations were always equal to or greater than initial oxidant concentrations, we expect that \(k_B[OH][B]\) was greater than \(J_{Ox}[Ox]\), and so the steady-state assumption was valid for [OH] under our experimental conditions:

\[
\frac{d[OH]}{dt} = J_{OH}[Ox] - k_B[OH][B] \approx 0
\]  
(3.1)

Rearranging Eq. 3.1 gives us an expression for the steady-state concentration of OH:

\[
[OH]_{ss} = \frac{J_{OH}[Ox]}{k_B[B]}
\]  
(3.2)

The parameter measured in these experiments was \(\frac{d[Ph]}{dt}\). Phenol concentrations were determined from the measured fluorescence intensity using the calibration curve shown in Figure 3.8. Equation 3.3 gives the rate expression for phenol formation in our experiments:

\[
\frac{d[Ph]}{dt} = 0.95k_B[OH][B]
\]  
(3.3)

Substituting Eq. 3.2 into Eq. 3.3 and rearranging the expression gives us \(J_{OH}\):

\[
J_{OH} = \frac{d[Ph]}{dt} (0.95[Ox])^{-1}
\]  
(3.4)

We determined \(J_{OH}\) by plotting the phenol growth rate as a function of nitrite concentration, as illustrated in Figure 3.9. At long irradiation times, phenol can react with OH; to avoid interferences from this reaction, we measured kinetics at short irradiation
times. The slopes of the linear fits to the data give $0.95(J_{OH})$. The photolysis rate constant determined in this manner for nitrite is $(9 \pm 2) \times 10^{-6} \text{ s}^{-1}$. It should be noted that at concentrations above $\sim 4 \times 10^{-5} \text{ mol L}^{-1} \text{ NO}_2^-$, phenol’s growth rate levels off, as illustrated in Figure 3.9b. This does not affect our calculations of $J_{OH}$, as we used $\text{NO}_2^-$ concentrations below this level. It could, however, explain low nitrite photolysis rate constants measured at high nitrite concentrations. This behaviour should be kept in mind for future experiments which use nitrite as an actinometer.

**Figure 3.9.** Dependence of phenol formation rate on nitrite concentration in solution in the presence of $1.2 \times 10^{-3} \text{ mol L}^{-1} \text{ benzene}$. Error bars represent one standard deviation about the mean of at least two trials. The solid trace is a linear fit to the data. Panel (a) shows this at low nitrite concentrations, and (b) shows concentrations up to $10^{-3} \text{ mol L}^{-1}$ nitrite.

We determined $[\text{OH}]_{ss}$ by measuring phenol formation rates as a function of benzene concentration, at a constant nitrite concentration of $2.95 \times 10^{-5} \text{ mol L}^{-1}$. The slope of the linear fit to the data in Figure 3.10 yields $k_B[\text{OH}]_{ss}$. The intercept in Figure 3.10 is zero within the error of the measurements. This suggests that reaction with benzene to form phenol is the major loss process for OH. If other processes were important, we would expect non-linear behaviour at low benzene concentrations, as reaction with benzene would be in competition with some other loss process; it is clear from our data that this is not the case. Dividing the slope by $k_B (= 7.8 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1})$ gives $[\text{OH}]_{ss} = 2.15 \times 10^{-18} \text{ mol L}^{-1}$. This concentration is very low, as expected under steady-state conditions.
As a final test of our technique, we used our measured $J_{OH}$ to calculate the photon flux of the 100 W lamp using the following equation:

$$
J_{OH} = \int_{\lambda}^{\lambda} \sigma(\lambda) \Phi(\lambda) F_\lambda d\lambda
$$

(3.5)

where $\sigma(\lambda)$ is the absorption cross section of nitrite at a given wavelength, $\Phi(\lambda)$ is the quantum yield of OH formation, and $F_\lambda$ is the photon flux. Using absorption cross sections and photolysis quantum yields from the literature, we calculated a photon flux across the wavelength range of absorption of nitrite of $4.45 \times 10^{13}$ photons cm$^{-2}$ s$^{-1}$. Dividing the total photon flux by the wavelength range yields the average photon flux at each wavelength. The photon flux of a new lamp provided by the manufacturer is $1.4 \times 10^{12}$ photons cm$^{-2}$ s$^{-1}$ nm$^{-1}$ in the wavelength range of interest in this study, compared to our predicted value of $3.9 \times 10^{11}$ photons cm$^{-2}$ s$^{-1}$ nm$^{-1}$ based on nitrite actinometry. Given the precision on our rate measurements ($\pm 20\%$), the uncertainties in the literature values of $\sigma$ and $\phi$, and the fact that the lamp was not new, this agreement is quite good.

Figure 3.10. Dependence of phenol formation rate on benzene concentration in the presence of $2.95 \times 10^{-5}$ mol L$^{-1}$ nitrite. The solid trace is a linear fit to the data. Error bars represent one standard deviation about the mean of at least two trials.

### 3.8.2 Photon Flux Dependences of Nitrite, Anthracene, and Benzene

Figure 3.11 shows absorption spectra of nitrite and anthracene in aqueous solution. They absorb over a very similar wavelength range, which suggests that
comparing the photolysis behaviour of the two species as a function of photon flux is valid. Figure 3.12a shows nitrite photolysis rates in aqueous solution, as measured by phenol growth, as a function of lamp power. A linear relationship between the kinetics and lamp power is observed, as expected. Figure 3.12b shows anthracene photolysis rates in aqueous solution, as well as benzene and anthracene photolysis rates at air-ice interfaces, as functions of lamp power. Plateaus in the measured rates are observed for both species on ice and in aqueous solution. We also measured naphthalene photolysis rates in aqueous solution at lamp powers between 0.15 and 1.5 W using the 100 W lamp. The kinetics did not vary with increasing lamp power in this range.

![Absorption spectra](image)

**Figure 3.11.** Absorption spectra of $4 \times 10^{-5}$ mol L$^{-1}$ nitrite (solid red trace) and $2 \times 10^{-7}$ mol L$^{-1}$ anthracene (dashed blue trace) in room-temperature aqueous solution.

To our knowledge, a non-linear photon flux dependence has not previously been reported for direct photolysis reactions. It is known to occur in some photocatalytic surface reactions, as discussed in Ref. 53. A possible explanation for the saturation in the rate in our experiments is that the aromatic compounds could be absorbing as many photons as possible; i.e. at high photon fluxes photons are no longer the limiting reagent, or the initial step of the reaction is no longer rate-limiting. Most studies of photon flux dependence have been performed on inorganic species such as nitrite, which are relatively poor absorbers; anthracene’s maximum absorption cross section in the actinic region is ~360 times higher than that of nitrite. The nonlinearity that we observe may be common in strong absorbers such as aromatic species.
Figure 3.12. (a) Nitrite photolysis rate constant measured as a function of lamp power. Rate constants were determined from the rate of phenol formation. The solid trace is a linear fit to the data. (b) Photolysis rates measured as a function of lamp power for anthracene at air-water interfaces (closed blue circles) and air-ice interfaces (open red triangles), and for benzene at air-ice interfaces (open green squares). The curved traces are hyperbolic fits to the data, and are included to guide the reader’s eye. The vertical arrows indicate photon fluxes at various lamp powers, based on nitrite actinometry; the fluxes are in units of photon cm$^{-2}$ s$^{-1}$. A 75 W Xe arc lamp was used for nitrite and anthracene photolysis, and a 100 W Xe arc lamp was used for benzene photolysis. Error bars represent the standard deviation about the mean of at least three trials, except those at 0 W, which have values of $2.5 \times 10^{-5}$ s$^{-1}$, which is the lowest rate constant we have measured using this technique.
Photolysis rates in the environment are generally predicted based on laboratory measurements: Measured kinetics are scaled from the photon flux of the lamp used in the experiments to that of the sun. This is an appropriate treatment for many species, as the linear dependence of nitrite photolysis rate on lamp power shows. However, our results indicate that this does not hold true for some species, such as anthracene, naphthalene, and benzene. To illustrate, extrapolating the anthracene photolysis rate constant measured at air-ice interfaces in our laboratory at a photon flux of $3 \times 10^{13}$ photon cm$^{-2}$ s$^{-1}$ to the expected photon flux at Summit, Greenland at noon in late June yields an atmospheric lifetime prediction of 1.4 s. This predicted lifetime is approximately factor of 500 shorter than the lifetime predicted from our photon flux dependence. The difference in the predicted lifetimes of anthracene in aqueous solution in Toronto is even greater: A linear extrapolation to our measured kinetics under predicts the lifetime by a factor of 1000.

### 3.8.3 Comparison of Photolysis Kinetics on Solid and Liquid Substrates

Table 3.3 details the observed first order rate constants for anthracene photolysis on liquid water, ice, liquid and solid decanol, and glass microscope slides at lamp powers where the observed kinetics are independent of photon flux. The photolysis rate on ice is over six times greater than that observed at the liquid water surface. The observed rate of reaction on liquid decanol is slightly greater than that on liquid water, and freezing the decanol gives rise to a factor-of-three photolysis rate enhancement.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Attributes</th>
<th>$k_{\text{obs}}$ (s$^{-1}$) $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>deposited from gas (24 $^\circ$C)</td>
<td>$(0.17 \pm 0.03) \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>prepared in solution (24 $^\circ$C)</td>
<td>$(0.17 \pm 0.04) \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>prepared in solution (1 $^\circ$C)</td>
<td>$(0.18 \pm 0.05) \times 10^{-3}$</td>
</tr>
<tr>
<td>Ice</td>
<td>deposited from gas (−16 $^\circ$C)</td>
<td>$(1.06 \pm 0.05) \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>frozen from solution (−16 $^\circ$C to −2 $^\circ$C)</td>
<td>$(1.07 \pm 0.09) \times 10^{-3}$</td>
</tr>
<tr>
<td>Glass</td>
<td>24 $^\circ$C</td>
<td>$(0.13 \pm 0.04) \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>−16 $^\circ$C</td>
<td>$(0.4 \pm 0.1) \times 10^{-3}$</td>
</tr>
<tr>
<td>Decanol</td>
<td>24 $^\circ$C, liquid</td>
<td>$(0.26 \pm 0.05) \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>−8 $^\circ$C, solid</td>
<td>$(0.70 \pm 0.05) \times 10^{-3}$</td>
</tr>
</tbody>
</table>

$^a$ Errors represent one standard deviation about the mean for at least three trials.
The rates of reaction observed on ice and on water are insensitive to the method of sample preparation, the wavelength at which fluorescence is monitored during the reaction, and the surface concentration of anthracene. The photolysis rate of anthracene on glass at room temperature is similar to that on liquid water. At −16 °C, however, the rate measured on glass surfaces increases by close to a factor of three. At this temperature a thin layer of frost was observed on the glass surface, even when dry nitrogen was flowed across the sample.

### 3.8.4 Temperature and Wavelength Dependence

Photolysis kinetics were measured on ice at temperatures ranging from −16 °C to −2 °C, and on water at 1 °C and 24 °C. The observed rate constants on ice were identical within experimental uncertainty at each temperature. Likewise, no temperature dependence was observed for the kinetics at the water surface, as shown in Table 3.3.

The wavelength dependence for the photolysis kinetics of anthracene on ice was measured by substituting various optical filters for the 295 nm filter normally used. The results are displayed in Table 3.4. The decay rate observed using the 295 nm cutoff filter is the same as that seen using a 320 nm filter, or even that seen in the absence of any optical filter. Using a 360 nm cutoff filter reduces the rate of reaction to a value that we can not measure. We estimate an upper limit for the rate constant under these illumination conditions of \(4 \times 10^{-5} \text{s}^{-1}\), based on the slowest rate we have been able to quantify. The observed wavelength dependence correlates reasonably well with anthracene’s absorption spectrum in solution, shown in Figure 2.16.

<table>
<thead>
<tr>
<th>Filter Cutoff</th>
<th>(k_{\text{obs}} \text{(s}^{-1}\text{)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>No filter</td>
<td>((1.3 \pm 0.1) \times 10^{-3})</td>
</tr>
<tr>
<td>295 nm</td>
<td>((1.06 \pm 0.07) \times 10^{-3})</td>
</tr>
<tr>
<td>320 nm</td>
<td>((1.3 \pm 0.3) \times 10^{-3})</td>
</tr>
<tr>
<td>360 nm</td>
<td>(&lt; 4 \pm 10^{-5} ) \text{a}</td>
</tr>
</tbody>
</table>

\text{a Established as an upper limit}
Despite anthracene’s self-association on ice, a red shift in its absorbance spectrum does not appear to enhance its photolysis rate: The observed photolysis rate on glass, where anthracene is also self-associated, is identical to that on water. The observed photolysis rate on frozen decanol is greater than that on liquid decanol, although the emission on both surfaces is that of monomeric anthracene. This suggests that factors other than an increase in reagent concentrations, which is thought to cause rate enhancements in frozen media for bimolecular reactions,\textsuperscript{54} are responsible for our observed rate increases for anthracene on ice. Furthermore, first order photolysis decay kinetics are observed in all instances, also suggestive that an increased anthracene concentration is not responsible for the observed rate increases.

The wavelength dependence of the kinetics for the reaction on ice is consistent with anthracene’s absorption in solution, which suggests that anthracene’s absorption intensity at wavelengths to the red of 360 nm is not greatly enhanced by the change in substrate. It is possible that the magnitude of absorption at wavelengths below 360 nm is enhanced on ice (i.e. anthracene’s absorption cross section is greater) or that the photolysis quantum yield is increased for samples present at the ice surface. For example, Dubowski and Hoffmann\textsuperscript{55} observed a threefold increase in the photolysis quantum yield of 4-nitrophenol in ice compared to that measured in water. Although no reason for this increase was proposed by those authors, such an increase could be more general. This possibility awaits further study.

### 3.8.5 Effect of Surface Polarity

PAH photodegradation rates have been observed to increase with increasing solvent polarity.\textsuperscript{56,57} If there is a large presence of dangling OH bonds at the ice surface, this would increase its polarity compared to that of a liquid water surface,\textsuperscript{58} and these dangling OH groups have in fact been observed spectroscopically.\textsuperscript{59,60} Our experimental and theoretical results from Chapter Two suggest that ice surfaces actually have fewer dangling OH groups than do water surfaces. This is in agreement with other studies: Although high numbers of dangling OH groups are seen in amorphous ice, surface reconstruction due to annealing the surface to form crystalline ice significantly reduces this number.\textsuperscript{60} Under these conditions, the adsorption of N\textsubscript{2} to annealed ice surfaces
becomes similar to adsorption to nonpolar surfaces such as Teflon,\textsuperscript{61} suggesting that annealed ice, such as that used in our experiments, does not present an environment that is more polar than that of liquid water. We have recently used pyrene, a PAH with a polarity-dependent fluorescence spectrum, to compare the polarity of an ice surface with that of the water surface (unpublished data), and the results indicate that the polarities of the two surfaces are in fact very similar. Using this same technique, we have previously observed large differences in polarity between the surfaces of liquid water and organic solvents,\textsuperscript{62,63} even when the latter are only present at monolayer amounts at the water surface.

These observations suggest that increased polarity is not responsible for our observed rate enhancement at the ice surface vs. at the liquid water surface, although it could explain the faster rate observed on ice compared to on frozen decanol. However, a higher surface polarity does not always result in faster photolysis: Anthracene photolysis is faster at the liquid decanol surface than at the liquid water surface, even though decanol is very much less polar a molecule than water.

### 3.8.6 pH Dependence

The photolysis rates of PAHs generally increase with decreasing pH,\textsuperscript{10,64} although anthracene has been observed to react more quickly at a higher pH in water.\textsuperscript{10} Although we did not set out to determine the existence of a pH dependence for anthracene photolysis on ice, we did perform experiments with varying concentrations of nitric acid (see Sections 4.11 and 4.12.1 for a full discussion of these experiments). We did not observe any significant variation in the kinetics in the presence of different nitric acid concentrations up to 3.16 M.

### 3.8.7 Effect of Oxygen

The effect of oxygen on anthracene photolysis kinetics on ice is displayed in Table 3.5. Purging the reaction chamber with oxygen prior to and during photolysis resulted in a factor of three increase in the observed photolysis rate over that measured in air, whereas purging the chamber in the same way with nitrogen resulted in only a very slight increase in the observed rate.
Table 3.5. Effect of oxygen on observed anthracene photolysis rate constants on ice

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>( k_{obs} \times 10^{-3} \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>1.4 ± 0.3</td>
</tr>
<tr>
<td>Air</td>
<td>1.07 ± 0.09</td>
</tr>
<tr>
<td>Oxygen</td>
<td>3.1 ± 0.1</td>
</tr>
</tbody>
</table>

Debate continues regarding the role of molecular oxygen in the photolysis of PAHs. While some researchers have found, based on kinetics studies,\(^ {10} \) that the presence of molecular oxygen is unimportant to the photochemical fate of PAHs in aqueous solutions, others have observed photolysis rates to depend on oxygen concentration.\(^ {65-67} \)

Proposed mechanisms for PAH photolysis in aqueous solutions invoke either direct ionization as the initial reaction step (R3.6),\(^ {66} \) or interaction with oxygen through electron transfer (R3.7) or the direct reaction of the excited triplet state formed by energy transfer to molecular oxygen (R3.8).\(^ {65,68,69} \)

\[
\text{PAH} \xrightarrow{\text{h} \nu} \text{PAH}^+ \xrightarrow{\text{H}_2\text{O}} \text{Products} \quad (\text{R3.6})
\]

\[
\text{PAH} \xrightarrow{\text{h} \nu} [\text{PAH}]^* \xrightarrow{3\text{O}_2} \text{PAH}^* + \text{O}_2^- \xrightarrow{\text{H}_2\text{O}} \text{Products} \quad (\text{R3.7})
\]

\[
\text{PAH} \xrightarrow{\text{h} \nu} [\text{PAH}]^* \xrightarrow{3\text{O}_2 \text{ or } 1\text{O}_2^*} [\text{PAH}]^* + \text{O}_2^* \xrightarrow{3\text{O}_2} \text{Products} \quad (\text{R3.8})
\]

Recently, Fasnacht and Blough\(^ {65} \) determined that anthracene and other PAHs in aqueous solutions do not undergo direct ionization under actinic radiation, so this mechanism can likely be discounted. Both of the other proposed photolysis mechanisms involve molecular oxygen, so it is likely that molecular oxygen is generally important to PAH photodegradation. However, its exact mechanistic role in these reactions, especially in the case of anthracene, remains unclear.

Anthracene photolysis kinetics in water exhibit odd behaviour compared to other PAHs, in that the reaction rate increases both when oxygen concentrations are increased and when they are decreased.\(^ {10,65} \) This is as yet unexplained, and in fact there is not good agreement on the magnitude of the change in reaction rate brought on by varying the ambient oxygen concentration. Going from an air atmosphere to an oxygen atmosphere,
rate increases of 20%, 10 70%, 66 and ~150% 65 have been reported. In experiments where kinetics were measured after purging the system with nitrogen, the rate enhancement was comparable to that obtained by purging the system with oxygen.10,65 Inconsistent results under varying oxygen concentrations have been reported,10 and we have observed this on the water surface as well: We consistently observe a photolysis rate increase in an atmosphere of oxygen, but the rates range from 30% to 110% faster than the rate observed in air.

On ice, we observe a small but reproducible increase in the rate relative to that in air (ca. 20%) when the reaction chamber is purged with nitrogen during freezing and throughout the reaction. Under an oxygen atmosphere we observe a reproducible increase in the reaction rate of a factor of three. It is interesting that on ice we see a much smaller relative rate enhancement under nitrogen than under oxygen, compared to observations in water,10,65 and also that the enhancement due to purging with oxygen is much larger than any seen in water.10,65,66

The enhancement of the rate under both an oxygen and a nitrogen atmosphere suggests that oxygen’s role in anthracene photolysis is somewhat complex. Fasnacht and Blough65 recently proposed that at high oxygen concentrations, PAH radical cations are formed via electron transfer to oxygen due to diffusional quenching of excited singlet state molecules, whereas at low oxygen concentrations the photodegradation occurs primarily by ground state molecular oxygen adding directly to excited triplet-state anthracene. They later suggested70 that PAHs such as pyrene which have long-lived singlet states react primarily through the excited singlet state, whereas compounds with shorter singlet state lifetimes, such as anthracene, react primarily through the triplet state pathway. It is possible that on ice the importance of the singlet-state mechanism is increased for anthracene. This could explain at least some of the difference between the rates observed on ice and on water, since the more energetic singlet state has been seen to be more reactive than the triplet state.70

If the ice surface increases the relative importance of the excited singlet state reaction, it is not due to anthracene’s self-association on the surface or to the fact that the
ice surface is solid. This is evidenced by the slow reaction observed on a glass surface, where anthracene shows efficient self-association. The rate enhancement on frozen decanol shows that this effect is not unique to water ice, and that rate enhancement can occur when anthracene emission indicates that anthracene is present in the monomeric form.

Although the reason for the faster photolysis rates on ice and frozen decanol compared to on glass is not known, it is possible that dissolved molecular oxygen plays a role. If dissolved oxygen interacts more efficiently with PAHs than does gas-phase oxygen, we would expect the reaction on glass to be slower than reactions on ice and frozen decanol, which may contain oxygen in their QLLs. One of our observations supports this idea: On ice, the 20% rate enhancement under a nitrogen atmosphere compared to under air is only observed when the chamber is purged with nitrogen during freezing. No change is observed if nitrogen is introduced to the chamber once the ice is already formed. It is possible that the oxygen content in the ice (or the QLL) influences photolysis kinetics more than that in the overlying atmosphere. This observation could also explain oxygen’s greater effect on ice than in water: Equilibrium partitioning calculations indicate that oxygen partitions more than twice as effectively into water at $-15 \, ^\circ\text{C}$ than water at $25 \, ^\circ\text{C}$.

### 3.9 Conclusions

Anthracene, naphthalene, and benzene show significant enhancements in photolysis rates on ice surfaces compared to those observed on or in water, and compared to those measured in bulk ice samples. These enhancements are insensitive to the means of introducing the PAH to the ice surface, to the method of ice preparation, and to temperature.

Our results indicate that enhancements in the photon flux on ice are not responsible for the faster photolysis rates there. They also suggest that scaling laboratory-
measured photolysis rates based on the output of the sun at the location of interest may not be appropriate for some species.

Parameters such as temperature, polarity, pH, and solid vs. liquid substrate are not responsible for enhanced anthracene photolysis kinetics on ice. Molecular oxygen appears to play an important but complex role in anthracene photolysis; its effects on the kinetics are more pronounced at air-ice interfaces than at air-water interfaces. Self-association of anthracene, and the resulting red-shift in its absorption spectrum, are also not responsible for the observed rate enhancement; conversely, the red-shifts in the absorption spectra of naphthalene and phenol likely are responsible for their enhanced reactivity on ice.

Our results discount a number of possible explanations for the enhanced photolysis rates of aromatic hydrocarbons measured at air-ice interfaces, but they do not tell us what the reason is. Possibilities for the observed enhancements include enhanced absorption cross sections or photolysis quantum yields for aromatics at air-ice interfaces, and altered photolysis mechanisms at air-ice interfaces.
3.10 References


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(54) Pincock, R. E. *Accounts of Chemical Research* 1969, 2, 97.


Chapter 4

Monitoring Bimolecular Reactions at the Air-Ice Interface

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4.1 Introduction

In Chapter Three, we determined that aromatic compounds are more photo-labile at ice surfaces than in bulk ice or in aqueous solution. In this chapter, we investigate bimolecular reactions at ice surfaces. Our results indicate that bimolecular reactions at air-ice interfaces, as well as heterogeneous reactions there, proceed at very different rates than those in aqueous solution or in bulk ice.

Trace species present at atmospheric interfaces can undergo several types of chemical transformation, including unimolecular reactions (such as photolysis), and heterogeneous reactions with gas-phase species. Both types of reactions have been studied extensively, with three primary foci. The first focus has been the nucleation and growth of secondary aerosols. This is a very large and important field of study, but will not be discussed in this work. The second focus has been to understand the manner in which reactions on aerosols can affect the oxidizing capacity of the atmosphere. In polar regions, heterogeneous reactions involving halides can significantly affect the composition of the overlying boundary layer (see for Refs. 1-3 for reviews of this chemistry). The third focus has been on understanding the fate of pollutants adsorbed to various substrates, primarily in urban environments. Snow and ice have only recently begun to be considered as chemical, rather than merely physical, sinks for pollutants.

In this chapter, we investigate several atmospherically relevant bimolecular reactions at air-ice interfaces: Ozonation of bromide and phenanthrene; reactions of anthracene and benzene with photoformed OH; and heterogeneous reactions of gas-phase OH with anthracene and benzene. These reactions can affect the fate of pollutants, and alter atmospheric composition.
In the 1980s, scientists at Barrow, Alaska\textsuperscript{4} and Alert, Nunavut\textsuperscript{5} observed significant depletions of tropospheric ozone during polar spring. Other field measurements\textsuperscript{6} acquired during the same time span showed high atmospheric bromine concentrations which could not be explained by transport. During a major field campaign in 1986, ozone and bromine were sampled together in Alert. A clear anticorrelation between the two species was reported.\textsuperscript{7}

Scheme 4.1. Simplified set of reactions involved in bromine explosions, adapted from Reference 3. The shaded region represents the condensed phase.

Since this discovery, many field campaigns have been mounted in the Arctic and Antarctic to try to understand this observation. (For a complete discussion of this research, see Ref. 3.) While some ozone depletion events can be explained by the transport of air masses depleted in ozone, others are due to local chemical events (see
Ref. 3 for a summary). Specifically, it appears that the majority of chemically-initiated ozone depletion events are caused by so-called bromine explosions.  

Bromine explosions refer to the autocatalytic production of gas-phase bromine in the form of Br$_2$ and BrO initiated by the oxidation of bromide in the snow. The reactions involved in bromine explosions are illustrated in Scheme 4.1. In this cycle, nonreactive bromine (Br$^-$) is converted to (photo)reactive bromine (Br$_2$ or BrO). The initial step of the bromine explosion, in which Br$^-$ is converted either to HOBr or Br$_2$ to form a seed for the autocatalysis, has not been widely studied. It remains unclear how enough Br$^-$ is converted to reactive forms to precipitate catalytic bromine formation.

Several mechanisms for the initial transformation of Br$^-$ to a more reactive form have been proposed and investigated, such as reactions with NO$_x$, OH, and O$_3$. Most reactions studied form HOBr, which can photolyze to form Br$_2$ in the presence of protons, as shown in Scheme 4.1. There is some debate as to whether ice surfaces, and sea ice surfaces in particular, are acidic. Recent calculations suggest they are not. It is possible that Br$_2$ is formed through pathways which do not need acidic environments. The heterogeneous reaction between O$_3$ and Br$^-$ is one such pathway.

The heterogeneous ozonation of halides has recently been shown to occur at aqueous interfaces. The aqueous-phase mechanism forms HOBr, and relies on the presence of excess protons. A possible reaction mechanism for the heterogeneous ozonation which does not require excess protons is:

\[
\begin{align*}
O_3(g) + Br^-(surf) &\rightarrow [O_3 \cdots Br^-](surf) \quad (R4.1) \\
[O_3 \cdots Br^-](surf) &\rightarrow O_3^-(aq) + \frac{1}{2} Br_2(g) \quad (R4.2) \\
O_3^-(aq) &\rightarrow O_2(g) + O^- (aq) \quad (R4.3) \\
O^- (aq) + H_2O &\rightarrow OH^- (aq) + OH(aq) \quad (R4.4) \\
OH(aq) + Br^- (aq) &\rightarrow OH^- (aq) + \frac{1}{2} Br_2(g) \quad (R4.5)
\end{align*}
\]

The overall reaction is:
In this scheme, ozone and bromide form a surface complex (R4.1), which goes on to form molecular bromine via an as-yet unknown mechanism (R4.2). The ozone anion that is formed breaks down to form molecular oxygen and an oxygen anion (R4.3). Then, O\(^-\) reacts with water to generate OH and OH\(^-\) (R4.4). The OH formed in R4.4 can react with another Br\(^-\) to generate OH\(^-\) and a bromine atom (R4.5). This reaction has been observed in our laboratory at air-water interfaces by monitoring changes in pH due to the formation of hydroxide in Reactions 4.4 and 4.5.\(^{13}\) This is a promising initiation reaction for polar bromide explosions because it does not require protons or light; it is possible that Br\(_2\) could build up during the polar winter and be released in the spring to initiate catalytic ozone loss. In this work, we monitored the kinetics of this reaction at air-ice interfaces.

\[
O_3(g) + 2Br^-(surf') + H_2O \rightarrow Br_2(g) + O_2(g) + 2OH^-(aq)
\] (R4.6)

**4.3 Experimental**

Harmine (7-methoxy-1-methyl-9H-pyrido[3,4-b]indole), was used as a pH probe. The protonated form of harmine absorbs to the blue of the neutral form. Figure 4.1 shows excitation spectra of harmine at the surface of a pure ice sample and then on the same surface after the introduction of NH\(_3\) from the gas phase. After introduction of the base, a decrease in absorbance above 320 nm is observed due to an increase in pH at the air-ice interface. This spectral change is similar to that observed in aqueous solution.\(^{13}\) Due to this change in the absorption, an increase in pH results in a decrease in harmine fluorescence intensity from excitation at 322 nm.

The reaction chamber used in this experiment is described in Section 2.3.1. For these experiments, a stainless steel plate covered the chamber floor to prevent oxidation of the copper. Ice samples were prepared by freezing aqueous solutions containing \((1 – 10) \times 10^{-3} \text{ mol L}^{-1}\) NaBr and \(10^{-6} \text{ mol L}^{-1}\) harmine on a stainless steel plate in the reaction chamber. The temperature in the chamber was maintained at \(-20\) °C. Ozone was introduced to the chamber in a stream of oxygen using a variable ozone generator. Ozone
concentrations were monitored by the attenuation of the 254 nm output of a mercury lamp by ozone flowing through a 10 cm pathlength absorption cell prior to entering the reaction chamber; the concentration was \( \sim 8 \times 10^{15} \text{molec cm}^{-3} \) for each experiment. Ice samples were not inverted after freezing for these experiments.

**Figure 4.1.** Excitation spectra of harmine at a pure air-ice interface (solid blue trace), and of the same sample after the deposition of gas-phase ammonia (dashed red trace). The structure of harmine is also shown.

Glancing-angle LIF of harmine was induced by the OPO. Harmine excitation spectra were acquired by monitoring emission and scanning the excitation wavelength in 2 nm intervals between 245 nm and 355 nm. Reaction kinetics were obtained by exciting the sample at 322 nm and monitoring emission at 420 nm.

Harmine (Aldrich, 98%), sodium bromide (ACP, ≥99.0%), ammonium hydroxide (Fisher, reagent grade), and oxygen (BOC, > 99.99%) were used as purchased without further modification. Ice samples were prepared from 18 MΩ deionized water.

### 4.4 Results and Discussion

Figure 4.2 shows excitation spectra of harmine at the surface of a frozen \( 10^2 \text{ mol L}^{-1} \) NaBr aqueous solution before and after ozonation. A decrease in intensity around 320 nm after ozonation is apparent, indicating an increase in pH at the air-ice interface. Figure
4.3 shows harmine fluorescence intensity at 420 nm following excitation at 322 nm as a function of ozonation time. A linear decrease in intensity is observed. Since pH is log[H⁺], the linear fit to these data yields the pseudo first-order rate constant for the reaction.

**Figure 4.2.** Excitation spectra of harmine at the surface of a frozen 10⁻² mol L⁻¹ NaBr solution (solid blue trace) and of the same sample after exposure to 8 × 10¹⁵ molec cm⁻³ gas-phase ozone (dashed red trace).

**Figure 4.3.** Fluorescence intensity of harmine excited at 322 nm and monitored at 420 nm at an air-ice interface during exposure to gas-phase ozone. The arrow indicates the time at which ozone was introduced to the reaction chamber. The straight line is a linear fit to the data during ozone exposure.

Figure 4.4 shows observed rate constants plotted as a function of bromide concentration in the solution prior to freezing. The observed rate constant increases with initial bromide concentration until ~2 × 10⁻³ mol L⁻¹, at which point the rate becomes
independent of concentration. This has also been observed at air-water interfaces; there, the kinetics only become concentration-independent above 1 mol L\(^{-1}\) bromide. The kinetics are well-fit by hyperbolic growth:

\[
k_{\text{obs}} = \frac{A \times [\text{Br}^- (aq)]}{B + [\text{Br}^- (aq)]}
\]  

where \(A\) and \(B\) are constants. The Langmuir—Hinshelwood (L-H) mechanism, which is discussed in more detail in Section 4.8, takes this form, and has been used to describe the heterogeneous ozonation of bromide at air-water interfaces. For the reaction at air-water interfaces, \(B\) describes the partitioning of bromide between the bulk solution and the interface. It is unclear what the significance of \(B\) is for this reaction at air-ice interfaces. Therefore, we hesitate to ascribe the kinetics to a L-H mechanism, but note the independence of the reaction kinetics to initial bromide concentrations at higher concentrations.

Figure 4.4. Observed ozonation rate constants plotted as a function of initial bromide concentrations in the initial unfrozen solution (black circles). Error bars represent the standard deviation about the mean of at least three trials. The red triangle represents the ozonation rate of bromide at the surface of a liquid sodium bromide solution; this value is extrapolated to bromide’s concentration in seawater using Eq. 4.1 based on the \(A\) and \(B\) parameters given in Reference 13.

As shown in Figure 4.4, at low bromide concentrations ozonation occurs more rapidly at air-ice interfaces than at air-water interfaces for identical initial bromide
concentrations; the reaction on a frozen $10^{-3}$ mol L$^{-1}$ bromide solution, which corresponds to the bromide concentration in sea water, is $\sim$60 times faster than the rate at the surface of an aqueous solution of the same concentration as calculated from the parameters to Eq. 4.1 reported in Ref. 13. This rate enhancement on ice could be due to higher bromide concentrations there, since bromide is expelled from the ice matrix during freezing, forming a concentrated brine in at the air-ice interface;$^{18-20}$ this exclusion is discussed in Section 2.4.5.

We calculated a reactive uptake coefficient for ozone based on our observed kinetics. It is given by the following equation:

$$
\gamma = \frac{4k_{obs}}{\sigma_{Br^-} \omega_{O_3}[O_3(g)]}
$$

(4.2)

where $\sigma_{Br^-}$ is the collisional cross-section of bromide, and is given by Eq. 4.3:

$$
\sigma_{Br^-} = \pi R_{Br^-}^2
$$

(4.3)

and $\omega_{O_3}$ is average molecular speed of ozone, and is obtained from Eq. 4.4:

$$
\omega_{O_3} = \left( \frac{8K_BT}{m\pi} \right)^{1/2}
$$

(4.4)

The values of the variables used in these equations are given in Table 4.1.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{Br^-}$</td>
<td>1.96 Å$^{21}$</td>
</tr>
<tr>
<td>$K_B$</td>
<td>$1.38 \times 10^{-23}$ kg m$^2$ s$^{-2}$</td>
</tr>
<tr>
<td>$T$</td>
<td>295 K</td>
</tr>
<tr>
<td>$M$</td>
<td>$7.97 \times 10^{-26}$ kg molec$^{-1}$</td>
</tr>
<tr>
<td>$[O_3(g)]$</td>
<td>$8 \times 10^{21}$ molec m$^{-3}$</td>
</tr>
</tbody>
</table>
Figure 4.5 shows $\gamma$ as a function of initial bromide concentration. Over an order of magnitude of bromide concentrations, $\gamma$ increased by approximately a factor of three. The value at $10^{-2}$ mol L$^{-1}$ NaBr was $(4 \pm 2) \times 10^{-8}$. This is close to the value that has been measured$^{12}$ for the same concentration on ice at $-20$ °C of $\sim 1 \times 10^{-8}$. This small $\gamma$, along with the variation in $\gamma$ with surface composition, assure us that gas-phase diffusion is not rate-limiting.$^{22}$ At seawater bromide concentrations, $\gamma$ is approximately three times smaller.

![Figure 4.5](image.png)

**Figure 4.5.** Reactive uptake coefficient ($\gamma$) for ozone to the surface of frozen sodium bromide solutions at –20 °C as a function of bromide concentrations in solution. Error bars represent the standard deviation about the mean of at least three trials.

### 4.5 Conclusions

The reaction between ozone and bromide that was previously observed at air-water interfaces$^{13}$ also occurs at air-ice interfaces. At bromide concentrations found in seawater, the observed rate constant is a factor of 60 faster on ice than on liquid water. This reaction occurs in the dark, and does not require the presence of excess protons; as has been suggested,$^{15}$ it could be an important initiation step for the catalytic release of active bromine from ice.
Chapter Four: Part Two
Heterogeneous Phenanthrene Ozonation at Air-Ice Interfaces

4.6 Introduction

In Chapter Three, we showed that photolysis kinetics of aromatic compounds were very different at air-ice interfaces compared to in aqueous solution or at air-water interfaces; these differences, at least in the case of anthracene, were not exclusively due to factors such as changes in temperature or reagent concentrations. In Part Two of this chapter, we reported ozonation kinetics of bromide which were much faster on ice than on liquid water surfaces at seawater bromide concentrations. In this case, enhanced bromide concentrations at the ice surface could explain the enhanced reactivity there. Here, we investigate whether phenanthrene ozonation occurs at similar rates at water and ice surfaces.

Although gas-phase ozonation of organic species is generally too slow to be atmospherically relevant, heterogeneous reactions of surface-bound PAHs with oxidizing gases such as ozone could be important loss mechanisms for larger, less volatile PAHs in urban centres. Ozonation kinetics of a range of PAHs have been measured on substrates including soot, organic and inorganic aerosols, water, and organic films. A review of these studies is provided in Ref. In this work, we examine the role of the QLL in the ozonation kinetics of phenanthrene. We show that the difference in rates on ice and on liquid water are due to differences in the local environment rather than to changes in temperature or phenanthrene concentrations. To our knowledge, this work represents the first investigation of a reaction between an organic compound in the QLL and a gas-phase reagent, as well as the first investigation of a temperature dependence for such processes.
4.7 Experimental

The reaction chamber used for experiments at air-ice interfaces is described in Section 2.3.1. Phenanthrene was deposited onto the ice and water surfaces as described in Section 2.3.2. Ozone was introduced to the chamber in the same manner as described in Section 4.3. The temperature within the chamber was maintained at either –11 °C or –30 °C for reactions on ice.

The experimental setup for ozonation experiments on liquid water has been described previously. Briefly, a three-necked round-bottom flask containing ~100 mL of water served as the reaction vessel. All experiments on water were performed at room temperature (22 °C).

Fluorescence was induced by the unfocussed 266 nm output of a frequency-quadrupled Nd:YAG laser (pulse energy ~0.5 mJ) or by the 266 nm or 293 nm output of a Nd:YAG-pumped OPO (pulse energy 0.1 – 1.8 mJ). The laser beam entered and exited the Teflon chamber and the round-bottom flask through quartz windows. The incident angle of the laser was ~87° from the surface normal for experiments performed in the Teflon chamber, and ~80° for experiments performed in the round-bottom flask. Kinetics were obtained by monitoring phenanthrene fluorescence intensity at 348 nm during exposure to gas-phase ozone.

A stream of pure oxygen was introduced into the chamber containing the phenanthrene-dosed ice or water. Fluorescence at 348 nm was monitored for approximately ten minutes to ensure that the intensity was not decreasing due to fluorescence quenching, evaporation, or dissolution. At this time, a known concentration of ozone was introduced into the gas stream, and fluorescence intensity was monitored until the reaction was complete (i.e. until the intensity stopped decreasing).
4.8 Results and Discussion

The time-dependence data of phenanthrene fluorescence intensity during ozonation were fit to Eq. 2.2. The fluorescence decay was well-described by a single-exponential fit in all cases, indicating that the reaction is first order with respect to phenanthrene concentration. To check for the possible involvement of OH (from ozone photolysis, followed by O(^1D) reaction with water vapour), phenanthrene was monitored via excitation at 266 nm and 293 nm in different experiments. Measured ozonation rates were independent of probe wavelength, indicating that the possible production of OH from O_3 photolysis, which is much more efficient at 266 nm than at 293 nm, did not affect our measured kinetics.

Plotting the observed rate constants against gas-phase ozone concentration gives the overall dependence of the reaction rate on gas-phase ozone concentration. This is shown for phenanthrene ozonation on ice and on water in Figure 4.6. The dependence of the rate on the concentration of gas-phase ozone is not linear, but shows an initial increase followed by a saturation in the observed rate at high ozone concentrations. The plots in Figure 4.6 are consistent with a L-H mechanism.\(^{27}\) This mechanism describes a surface process in which one reagent, in this case ozone, is in rapid equilibrium between the gas and condensed phases, and partitions to the condensed phase before undergoing reaction. It takes the following form:

\[
k_{obs} = \frac{A \times [O_3(g)]}{B + [O_3(g)]}
\]  

where \(A\) is a combination of the number of surface sites available to ozone and the second order rate constant for the reaction, \(k^{II}\); and \(B\) is a ratio of the rates of desorption and adsorption of ozone to the ice surface from the gas phase. On a solid surface, \(B\) is the inverse of the gas—surface partition coefficient. Langmuir—Hinshelwood type mechanisms have been observed for heterogeneous ozonation of PAHs on a number of substrates, including soot, inorganic and organic aerosols, water surfaces, and organic films.\(^{26,28-31}\)
Figure 4.6. Observed rate constants for phenanthrene ozonation at the air-ice interface as a function of gas-phase ozone concentration. Error bars represent the standard deviation about the mean of at least three trials. The solid traces are fits to Eq. 4.5. The dashed horizontal line represents the maximum ozonation rate observed at an air-water interface.

The fits to the data on ice are good, indicating that the ozonation of phenanthrene follows a L-H mechanism on this substrate. We were unable to obtain rate constants at low ozone concentrations on water due to the slow reaction rate, and so could not fit the data to a L-H mechanism. However, the rate at the highest ozone concentration on a water surface is identical to that observed previously at an air-decanol interface; this rate constant is indicated by the horizontal line in Figure 4.6. This ozone concentration (≈1 × 10^{16} \text{molec cm}^{-3}) is in the concentration-independent region of the kinetics for other PAHs.\textsuperscript{26,32} It is interesting to note that we have observed similar anthracene ozonation kinetics on water and organic films.\textsuperscript{26,28}

The maximum ozonation rate measured on water and on decanol\textsuperscript{28} was (4 ± 2) × 10^{-4} \text{s}^{-1}, while the maximum rate on ice was an order of magnitude greater: (7 ± 1) × 10^{-3} \text{s}^{-1}. This enhancement on ice is not strictly due to a temperature dependence, as evidenced by the identical kinetics at –10 °C and –30 °C, which suggest that it is the physical nature of the QLL that is altering the observed kinetics as opposed to the temperature difference between the experiments on water and on ice.
It is possible that phenanthrene surface coverage could affect the observed ozonation rates. Higher surface loading, which might be expected at lower temperatures, could alter or mask other temperature effects. Figure 2.21 shows that phenanthrene fluorescence intensity at the ice surface increases linearly after 15 minutes of deposition. As discussed in Mmereki et al.,\textsuperscript{22} this suggests that the experiments reported here were done in the unsaturated regime of phenanthrene surface coverage. However, the emission spectra in Figure 2.15 show that phenanthrene undergoes self-association even at low surface coverages. While we ruled out self-association as a reason for enhanced anthracene photolysis rates on ice (see Section 3.8.3), we cannot rule it out for phenanthrene ozonation based on the existing data.

A recent investigation of heterogeneous ozonation kinetics of fatty acid particles\textsuperscript{33} provides the only other temperature dependence analysis for this type of reaction that we are aware of. Those authors observed a slight positive temperature dependence for the ozonation rates of three fatty acids between 263 and 308 K. It is possible that a similar dependence exists on ice, but that enhanced partitioning of ozone to the ice surface at lower temperatures masks this effect. However, the values that we obtain for the $B$ parameter of the L-H mechanism argue against this: We measure values of $(7 \pm 5) \times 10^{15}$ molec cm$^{-3}$ and $(8 \pm 6) \times 10^{15}$ molec cm$^{-3}$ at $–10$ °C and $–30$ °C respectively. If enhanced ozone partitioning at lower temperatures is responsible for the large rate constants we observe on ice, we would expect to see a lower value for the $B$ parameter at lower temperatures. It is also worth noting that the $B$ parameter extracted from fits of the ozonation kinetics of all PAHs we have studied on water, octanol, and decanol surfaces is approximately $2.1 \times 10^{15}$ molec cm$^{-3}$\textsuperscript{26,28} This indicates that ozone partitions more effectively to room-temperature liquid surfaces than it does to ice, despite the temperature difference.

The results of the present investigation have implications on our understanding of the physical nature of the QLL. Although reports of QLL depth vary greatly,\textsuperscript{34-37} it is generally agreed that a gradient in depth exists in the temperature range of our experiments ($–30$ °C to $–10$ °C).\textsuperscript{34,35,37} While we cannot comment directly on the depth of the QLL based on our results, we can make some inferences regarding the
environment of the QLL based on our kinetics data. The first conclusion we can draw is that the environment presented by the QLL affects phenanthrene’s reactivity toward ozone differently than does a liquid water surface. Kinetic data for heterogeneous ozonation of PAHs on ice likely should not be extrapolated from kinetic data in aqueous solutions or at air-aqueous interfaces.

The lack of temperature dependence for the reaction kinetics on ice also provides us with information regarding the QLL. Specifically, we can conclude that changes in the depth of the QLL between –30 °C and –10 °C do not affect the reactivity of phenanthrene towards ozone. This could mean that at both temperatures the QLL is sufficiently deep to be the only medium in contact with phenanthrene (i.e. the phenanthrene is not in contact with bulk ice); or it could mean that it is the underlying ice substrate, rather than the QLL, that affects the ozonation kinetics. It is also possible that changes in the depth of the QLL are negligibly small in this temperature range. Extending these experiments to lower temperatures might help to determine what is responsible for the identical ozonation kinetics within this temperature range, but with the present results we can conclude that at temperatures relevant to Earth’s surface, changes in temperature will likely not affect phenanthrene ozonation kinetics on ice.

Our kinetic results also yield information about ozone’s interaction with the QLL. As discussed above, ozone partitions more effectively to room temperature water than to ice. This is further evidence that the environment of the QLL is different from that of liquid water: Otherwise, enhanced partitioning of ozone to the surface should be observed at lower temperatures.

In the gas phase, reaction with hydroxyl radicals is the dominant loss process for PAHs: Homogeneous reactions with other oxidizing gases, including ozone, are extremely slow.\textsuperscript{23} A number of studies have shown that heterogeneous reactions of PAHs with oxidizing gases, and especially ozone, can occur much more quickly than the corresponding gas-phase reactions.\textsuperscript{25,26,28-31} The substrate to which the PAH is partitioned has been shown to affect the observed kinetics; a review of some of these results is presented in Kwamena et al.\textsuperscript{25} A large portion of the northern hemisphere experiences ice
coverage for at least part of the year; ozonation of PAHs partitioned to this ice could be important to their fate.

Kwok et al.\textsuperscript{38} report a homogeneous ozonation rate for phenanthrene of $\sim 4 \times 10^{-19}$ cm$^3$ molec$^{-1}$ s$^{-1}$. This translates to an atmospheric lifetime of approximately 22 days, given an ozone mixing ratio of 50 ppb ($1.3 \times 10^{12}$ molec cm$^{-3}$). On the surface of water, we estimate an atmospheric lifetime of approximately 44 days. On ice, the atmospheric lifetime decreases to just under five days. This is not too different from the lifetime of gas phase phenanthrene due to reaction with hydroxyl radicals of just over one day, as reported\textsuperscript{38} for a daytime average OH concentration of $1.6 \times 10^6$ molec.cm$^{-3}$. Based on an air—snow partitioning coefficient of $10^{-1.03}$ m at $-6.8$ °C,\textsuperscript{39} we calculate that roughly 10% of phenanthrene will be partitioned to snow and ice at that temperature. Depending on phenanthrene’s desorption rate from snow and ice, it is possible that heterogeneous ozonation on these media could account for a measurable fraction of phenanthrene loss during the winter, and that snow and ice could be chemical as well as physical sinks for phenanthrene.

Recently, Kwamena et al.\textsuperscript{24} investigated the fates of a suite of PAHs in urban environments using a multicompartmental box model. The loss processes investigated included advection, gas phase oxidation by OH, and heterogeneous ozonation on aerosols and urban grime. Heterogeneous ozonation on urban grime proved to be an important chemical sink for larger PAHs such as pyrene and benzo[\textit{a}]pyrene, which partition much more efficiently to the condensed phase than does phenanthrene. If these PAHs display similar ozonation rate enhancements on ice compared to on organic films as phenanthrene, heterogeneous ozonation on ice would be an extremely important removal process for these compounds during urban winters.

4.9 Conclusions

Phenanthrene ozonation at air-ice interfaces follows a L-H type mechanism, in which ozone partitions to the ice surface before reacting with phenanthrene there. We observed rates at air-ice interfaces which were much faster than those at air-water or air-
decanol interfaces. The enhanced rates on ice were not due to temperature or to enhanced partitioning of ozone to the ice surface; our results suggest that ozone partitions more effectively to a liquid water surface. The enhanced rates are likely due to increased reactivity of phenanthrene toward ozone at the air-ice interface, although the mechanism for this remains unclear.

The enhanced phenanthrene ozonation rates at air-ice interfaces have implications for the fate of aromatic hydrocarbons in winter, especially in urban areas. At atmospherically relevant ozone concentrations of 50 ppb, phenanthrene’s lifetime toward ozonation on ice is predicted to be just under five days, compared to 22 days in the gas phase and 44 days on a liquid water surface. Heterogeneous ozonation of phenanthrene at air-ice interfaces could be an important removal process during the winter.

Chapter Four: Part Three
Indirect Photolysis of Aromatics at Air-Ice Interfaces

4.10 Introduction

Reactions involving hydroxyl radicals are of great interest in environmental chemistry. Hydroxyl radicals react readily with organic pollutants in the atmosphere and in natural waters; it is expected that the same is true in snow and ice (e.g. Ref. 40). If they occur, such reactions would be important both in snow-covered urban centres, where organic pollutants are ubiquitous, and also in remote polar regions, where organic pollutants such as PAHs have been detected in snow and ice. Hydroxyl radical mixing ratios in the air above polar snowpacks can be as high as those in urban centres, due primarily to photochemistry within the snowpack. (See Refs. 2,55 for discussions of the state of knowledge on organics in snow packs.)

The studies that have investigated reactions between aromatic compounds and OH have reported conflicting results. Similar reaction rates for OH with the PAHs phenanthrene, pyrene, and fluoranthene have been reported in water and ice, but
degradation of monochlorophenols in the presence of hydroxyl radicals is reported to occur more slowly in ice compared to in aqueous solution.\textsuperscript{57}

In this work, we performed several experiments to explore the indirect photolysis of aromatic compounds at air-ice interfaces. In Section 4.12.1, we report anthracene photolysis kinetics at air-ice and air-water interfaces in the presence of varying concentrations of the OH-precurors HNO\textsubscript{3} and H\textsubscript{2}O\textsubscript{2}. In Section 4.12.2, we discuss phenol (formed from the reaction of benzene with the OH product of H\textsubscript{2}O\textsubscript{2} photolysis) growth rates in aqueous solution and in ice samples having different specific surface areas. In Section 4.12.3 we follow phenol formation from indirect benzene photolysis in situ in aqueous solution in the presence NO\textsubscript{2}\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, and H\textsubscript{2}O\textsubscript{2}. Finally, in Section 4.12.4, we use glancing-angle LIF to monitor phenol growth from indirect benzene photolysis in situ at air-ice interfaces in the presence of NO\textsubscript{2}\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, and H\textsubscript{2}O\textsubscript{2}. Our results indicate that either the production or the reactivity of hydroxyl radicals is significantly suppressed at air-ice interfaces compared to in bulk ice or aqueous solution.

4.11 Experimental

Anthracene loss kinetics were measured in situ in aqueous solution and at air-ice interfaces using the procedure described in Section 3.3.2. Aqueous solutions containing 10\textsuperscript{−8} to 10\textsuperscript{−7} mol L\textsuperscript{−1} anthracene and varying concentrations of HNO\textsubscript{3} or H\textsubscript{2}O\textsubscript{2} were photolyzed using a 75 W xenon arc lamp which passed through a 295 nm long-pass cutoff filter. Ice samples were prepared either by freezing a solution containing anthracene and one of the oxidants, or by depositing one of or both nitric acid and anthracene to a pure ice surface from the gas phase, as described in Sections 2.3.2 and 2.7.2 respectively.

Benzene reaction kinetics were measured in one of two ways. In one set of experiments, aqueous solutions containing 1.1 \times 10\textsuperscript{−3} mol L\textsuperscript{−1} benzene and 9.9 \times 10\textsuperscript{−4} mol L\textsuperscript{−1} H\textsubscript{2}O\textsubscript{2} were prepared daily. Ice cubes and ice granules were prepared from 3 mL aliquots of solution as described in Section 3.3.1. Photolysis was effected by the 295 nm filtered output of a 75 W xenon arc lamp, and phenol fluorescence was detected with a
fluorimeter, as described in Section 3.3.1. In a second set of experiments, phenol growth was measured in solution and at air-ice interfaces in situ as described in Section 3.3.2. For these experiments, photolysis was effected by the 295 nm filtered output of a 100 W xenon arc lamp. The experimental geometries for the offline experiments are shown in Figure 3.1, and the geometries for the in situ experiments are shown in Figure 3.2.

### 4.12 Results and Discussion

#### 4.12.1 Indirect Anthracene Photolysis in Aqueous Solution and at Air-Ice Interfaces

Table 4.2 compares the dependence of anthracene photolysis rates on the presence of nitric acid and hydrogen peroxide on water and on ice. On water surfaces, the presence of $5 \times 10^{-3}$ mol L$^{-1}$ nitric acid in the bulk increases the rate by an order of magnitude, and unpublished results from this lab show the same increase in photolysis rates in aqueous solutions of nitric acid. On ice, no change in the kinetics is seen when solutions of nitric acid of concentrations up to 3 mol L$^{-1}$ are deposited on the sample surface and frozen. An enhancement in the anthracene loss rate of a factor of five is observed when concentrated nitric acid (15.8 mol L$^{-1}$) is frozen on the ice prior to introducing the anthracene solution. Introducing nitric acid from the gas phase does not increase the observed rate of reaction.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Additional Compound</th>
<th>Concentration</th>
<th>$k_{obs}$ (10$^{-3}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water surface</td>
<td>None</td>
<td>n/a</td>
<td>0.17 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>HNO$_3$</td>
<td>$5 \times 10^{-3}$ mol L$^{-1}$</td>
<td>1.8 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>H$_2$O$_2$</td>
<td>$7.2 \times 10^{-3}$ mol L$^{-1}$ (24°C)</td>
<td>0.73 ± 0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$7.2 \times 10^{-3}$ mol L$^{-1}$ (1°C)</td>
<td>0.90 ± 0.05</td>
</tr>
<tr>
<td>Ice surface</td>
<td>None</td>
<td>n/a</td>
<td>1.06 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>HNO$_3$</td>
<td>$\leq 6.4 \times 10^{17}$ molec (from gas)$^a$</td>
<td>1.1 ± 0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.16 mol L$^{-1}$</td>
<td>1.24 ± 0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.8 mol L$^{-1}$</td>
<td>5.15 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>H$_2$O$_2$</td>
<td>$7.2 \times 10^{-3}$ mol L$^{-1}$</td>
<td>1.03 ± 0.08</td>
</tr>
</tbody>
</table>

$^a$Upper limit based on nitric acid room temperature vapour pressure and volume dispensed onto the ice
The photolysis rate of anthracene was measured on water and on ice in the presence of $7.2 \times 10^{-3}$ mol L$^{-1}$ H$_2$O$_2$, which was either dissolved in the liquid solution or spread across the ice surface prior to introducing anthracene to the sample. The presence of H$_2$O$_2$ increases the observed rate of reaction by a factor of four on the water surface, but does not affect the rate on ice. No significant difference in the photolysis rate on the water surface was observed in the presence of H$_2$O$_2$ when the experiment was performed at 1 °C, versus when it was carried out at room temperature.

4.12.2 Indirect benzene photolysis in aqueous solution and in ice

Figure 4.7 shows phenol fluorescence during irradiation of aqueous samples, ice cubes, and ice granules containing benzene and hydrogen peroxide. At longer irradiation times, phenol formed in the initial reaction can go on to react with OH. To avoid this complication, we determined the initial phenol growth rate by the slope of the linear fit to the concentration vs. time data at short irradiation times. The phenol production rates in aqueous solution and in ice cubes were the same within error ($(4.2 \pm 0.9) \times 10^{-10}$ mol L$^{-1}$ s$^{-1}$ and $(4 \pm 2) \times 10^{-10}$ mol L$^{-1}$ s$^{-1}$ respectively). With ice granules, however, no phenol growth was observed.

Given the sample volumes and radii, we estimate that the surface area-to-volume ratio of the ice granules is approximately six times greater than that of the ice cubes. As we did in Section 3.4.1 for anthracene photolysis, we can calculate the relative phenol formation rates expected in the granules and the cubes. Once again, we use the aqueous rate ($4.2 \times 10^{-10}$ mol L$^{-1}$ s$^{-1}$) to describe the rate in liquid regions within bulk ice, but this time we use a rate constant at air-ice interfaces of zero, based on the lack of phenol formation observed on ice using glancing-angle LIF. This leads us to predict that the measured rate constant in the ice granules will be inversely proportional to the relative increase in surface area. For our samples, that means that the rate in the ice granules should be approximately 6 times lower in the ice granules than in the ice cubes. If this is the case, the expected phenol concentration in the ice granules at the longest time measured, 2700 s, would be approximately $1.9 \times 10^{-7}$ mol L$^{-1}$. This value falls within the error bars for our measured phenol concentrations at this irradiation time.
Figure 4.7. Phenol concentration as a function of irradiation time for samples containing $1 \times 10^{-3}$ mol L$^{-1}$ benzene and $9 \times 10^{-4}$ mol L$^{-1}$ H$_2$O$_2$ in aqueous solution (solid blue circles), in ice cubes (solid green triangles), and in ice granules (open red triangles). The solid traces are linear fits to the data, and error bars represent one standard deviation about the mean for at least three trials.

These results support our hypothesis that reactivity is different at air-ice interfaces than it is in bulk ice. They also strongly suggest that OH is either produced inefficiently at the air-ice interface, or that it reacts inefficiently with any benzene that is present there. Although reduced photon fluxes within ice granules due to scattering would yield the same result, we do not believe that this is responsible for our observations: In Section 3.4.1 we demonstrated that anthracene photolysis is more rapid in ice granules than in ice cubes. Therefore, we are confident that our observations are due to differences in reactivity between OH and benzene at ice surfaces compared to in bulk ice.

4.12.3 In Situ Measurements of Indirect Benzene Photolysis in Aqueous Solution

In Section 3.8.1 we described our development of an in situ chemical actinometer that used benzene as an OH-trap. There, we used nitrite as the OH-precursor. Here we measured phenol growth rates in aqueous solution using the same technique, with NaNO$_2$, HNO$_3$ and H$_2$O$_2$ as OH-precursors. Figure 4.8 shows the growth rate of phenol as a function of OH-precursor concentration. At the concentrations used in this work, the
dependences are linear, indicating simple second order kinetics, as expected from the rate expression \( \frac{d[Ph]}{dt} = k_{rxn}[OH][B] \). Because OH is formed directly from the precursor, we observe linear dependences on the precursor concentration. Using the slope of the linear fits to our data and absorption cross sections and photolysis quantum yields from the literature, we estimated an approximate average photon flux for our lamp over the wavelengths of absorption of each oxidant, as described in Table 4.3. Our calculated photon fluxes using the different OH-precursors match within a factor of three, and in each case match the spectral irradiance of the lamp provided by the manufacturer within an order of magnitude.

**Figure 4.8.** Initial phenol formation rates as a function of concentration of NaNO₂, H₂O₂, and HNO₃ for photolysis in aqueous solutions containing excess benzene. The solid traces are linear fits to the data. Error bars represent one standard deviation about the mean of at least two measurements.

**Table 4.3. Calculated photon fluxes based on measured \( J_{OH} \)**

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Wavelengths (nm)</th>
<th>Total Flux (photon cm⁻² s⁻¹)</th>
<th>Average Flux (photon cm⁻² s⁻¹ nm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>295 – 410</td>
<td>( 4.45 \times 10^{13} )</td>
<td>( 3.87 \times 10^{11} )</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>295 – 330</td>
<td>( 4.99 \times 10^{12} )</td>
<td>( 1.43 \times 10^{11} )</td>
</tr>
<tr>
<td>NO₃</td>
<td>296 – 360</td>
<td>( 1.37 \times 10^{13} )</td>
<td>( 2.14 \times 10^{11} )</td>
</tr>
</tbody>
</table>
4.12.4 In Situ Measurements of Indirect Benzene Photolysis at Air-Ice Interfaces

We monitored phenol growth at air-ice interfaces during the irradiation of frozen samples containing benzene and an OH-precursor. Reagents were either frozen from solution or one or both reagents were introduced from the gas phase. Neither reagent concentrations nor sample preparation methods had any effect on the results. We performed approximately 20 experiments with various OH-precursors and preparation methods. Under no experimental conditions did we observe a growth of intensity at 318 nm. This observation offers strong confirmation that the lack of phenol growth observed in the irradiated ice granules discussed in Section 4.12.2 was due to differences in reactivity at air-ice interfaces compared to in aqueous solution.

4.13 Conclusions

Benzene and anthracene react quickly with photoformed hydroxyl radicals in aqueous solution, but we did not observe these reactions at air-ice interfaces. Benzene was observed to react with OH in low surface area ice cubes at the same rate as in aqueous solution, but no reaction was observed in high surface area ice granules. These results suggest that either the production of OH or its reactivity toward aromatic compounds is significantly suppressed at air-ice interfaces.

Chapter Four: Part Four
Heterogeneous Oxidation of Aromatics at Air-Ice Interfaces by Hydroxyl Radicals

4.14 Introduction

The results from Part Three of this chapter show that benzene and anthracene present at air-ice interfaces do not react to an appreciable extent with OH when OH-precursors are photolyzed in or at the surface of ice. This could be due to one of two
reasons: The photochemical production of OH could be suppressed at air-ice interfaces compared to in bulk ice and aqueous solution; or hydroxyl radicals could be formed, but not react with benzene or anthracene there. To test the reactivity of hydroxyl radicals toward aromatics at air-ice interfaces, we formed OH in the gas phase and monitored the heterogeneous reaction between OH and benzene or anthracene at the surfaces of water and ice.

4.15 Experimental

Aqueous solutions contained either $1.2 \times 10^{-3}$ mol L$^{-1}$ benzene or $9.0 \times 10^{-8}$ mol L$^{-1}$ anthracene. They were placed in a Petri dish inside the reaction chamber. Ice samples containing benzene were frozen from solution as described in Section 2.7.2. Anthracene was deposited onto pure ice surfaces from the gas phase as described in Section 2.7.2. Deposition of anthracene continued for approximately 15 minutes; anthracene fluorescence intensity was monitored during deposition to ensure that its surface coverage remained in the non-saturated (i.e. submonolayer) regime.$^{26,62}$ A stainless steel plate covered the chamber floor during these experiments to prevent oxidation of the copper.

![Figure 4.9. Schematic of the experimental geometry used to photolyze HONO for some experiments.](image)

Hydroxyl radicals were produced from the photolysis of gas-phase HONO. Nitrogen gas was bubbled through a concentrated HCl solution, then passed over glass beads coated with damp NaNO$_2$.$^{63,64}$ The HONO thus formed was immediately
introduced to the chamber through a port in the wall. The HONO was photolyzed in the reaction chamber to form OH, either by the 295 nm-filtered output of a 100 W xenon arc lamp using the geometry described in Section 3.3.2 and illustrated in Figure 3.2, or by the unfiltered output of a 100 W xenon arc lamp, directed into the chamber horizontally just above the sample to avoid illumination of the sample. This configuration is shown in Figure 4.9. Anthracene and phenol emission were detected as described in Section 3.3.2.

4.16 Results and Discussion

Figure 4.10 shows the LIF signal intensity associated with phenol growth at water (blue circles) and ice (red triangles) surfaces as a function of the exposure time to HONO(g). During the initial stage of the experiment, when the HONO in the chamber was not irradiated, no growth of phenol was observed on water or on ice. When the lamp was turned on, the HONO photolyzed to form OH, and an immediate growth of phenol was evident at the water surface. However, no growth was observed on ice in the 8 experiments performed there. We performed this experiment both by irradiating the samples with the filtered \((\lambda > 295 \text{ nm})\) output of the lamp, and by directing the unfiltered lamp’s output just above and parallel to the samples, with no difference in the results.

Figure 4.10. Phenol fluorescence intensity during the exposure of benzene to gas-phase hydroxyl radicals at an air-water (blue circles) and air-ice (red triangles) interface. The chamber was flushed with gas-phase HONO, which was irradiated to form OH at \(t = 10\) min, as indicated by the arrow.
We also measured the degradation rate of anthracene at air-water and air-ice interfaces due to heterogeneous reaction with OH. To avoid loss of anthracene due to direct photolysis, we irradiated the chamber with the output of the unfiltered lamp oriented such that the sample itself was not illuminated, as shown in Fig. 4.9. Figure 4.11 shows anthracene fluorescence intensity as a function of time during exposure to gas-phase OH. While rapid loss is observed at the air-water interface, no change in anthracene’s emission intensity is observed at the air-ice interface.

![Figure 4.11. Anthracene fluorescence intensity at an air-water (blue circles) and air-ice (red triangles) interface as a function of exposure time to gas-phase OH. The solid traces are linear fits to the log-normalized data.](image)

There are several possible explanations for a reduction in reactivity between OH and an organic compound at the air-ice interface. One possibility is that diffusion rates on the ice surface are lower than those in or on water, leading to slower bimolecular reaction rates. However, we might expect to see a noticeable temperature dependence for the reaction if this were the case; we have not observed a temperature dependence in water or on ice for either the indirect photolysis of anthracene (in the presence of H$_2$O$_2$)\(^{62}\) or for the heterogeneous ozonation of phenanthrene.\(^{65}\)

A second possibility is that OH partitions poorly to the ice surface, and is therefore not present in high enough concentrations for us to observe a reaction with benzene, whether the OH is formed in the ice or introduced from the gas phase. We noted in Section 4.8 that ozone partitions up to 75% less effectively to an air-ice interface than
to a liquid water surface. However, despite its less efficient adsorption, ozone reacted much more quickly with phenanthrene on ice than on liquid water; at 50 ppb ozone, phenanthrene’s lifetime toward ozonation would be just under five days on ice, compared to 44 days on water.

It is also possible that hydroxyl radicals recombine quickly to form H₂O₂ or their parent compounds. This recombination process is thought to be a major mechanism of H₂O₂ formation in interstellar ices.⁶⁶,⁶⁷ Although benzene concentrations were in excess of OH by at least an order of magnitude in our samples, it is still possible that OH self-reacted before encountering a benzene molecule. We have previously demonstrated that aromatic compounds self-associate readily at the air-ice interface, even at submonolayer coverages.⁶²,⁶⁵,⁶⁸ They likely exist in “islands” scattered across the surface, rather than as a uniform coating. It is possible that the OH is either formed, or adsorbed to the ice surface, in a region that is not populated by benzene. Since the recombination of OH in ice is thought to occur at close to diffusion-limited rates,⁶⁷ hydroxyl radicals could recombine before encountering a benzene molecule.

In contrast to our observations, a recent study¹¹ reports that gas-phase OH reacts rapidly with bromide at air-ice interfaces. There are two possibilities that could explain the difference in these results. First, it could be that the reactivity of OH on ice is different from that on water for aromatic compounds, but not for small inorganic species such as bromide. In Chapter Two we reported that the QLL appeared to present a solvation environment similar to that of liquid water to small inorganic acids, so it is not unreasonable to hypothesize that the reactivity of such species might be similar at air-ice and air-water interfaces. The second possibility is that the concentrated brine caused by the exclusion of bromide from ice forms a true liquid. In this case, reactions in this brine layer would proceed similarly to reactions in concentrated aqueous bromide solutions, and the QBL would present a reaction medium that is very different from the QLL at the surface of pure ice. The glancing-angle Raman spectra of frozen sodium chloride solutions closely resemble spectra of liquid water surfaces (Figure 2.9); this could indicate that the QBL is a true liquid layer, but it could also simply signal extensive disruption in the hydrogen-bonding network of the QLL. If the QBL is in fact a true
aqueous solution, reactivity of species on sea ice will likely be quite different to that on pure snow and ice.

### 4.17 Conclusions

The results from these experiments do not rule out the possibility that hydroxyl radical formation proceeds at a different rate at air-ice interfaces than in liquid water or bulk ice. They do, however, clearly show that hydroxyl radicals are much less reactive toward benzene and anthracene at air-ice interfaces than at air-water interfaces, whether the hydroxyl radicals are formed in the QLL through the photolysis of $\text{NO}_2^-$, $\text{NO}_3^-$, or $\text{H}_2\text{O}_2$, or introduced from the gas phase.
4.18 References


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Chapter Five:

Conclusions and Future Work
5.1 Conclusions

Ice as a physical sink and as a reaction medium has been widely investigated in the past two decades. However, we still have a poor understanding of the role of ice, and especially of the QLL, as a reaction medium. This gap in our knowledge has made it difficult to form models to predict the fate of atmospheric species in snow and ice. The aim of this thesis was to investigate the role of the QLL in environmentally relevant reactions. Specifically, we wanted to determine whether we could predict the fate of species at air-ice interfaces based on their behaviour in other media such as liquid water. We approached this in two ways: First, by directly investigating the physical characteristics of air-ice and air-water interfaces and by comparing the solvating environments presented by both substrates; and secondly, by measuring reaction kinetics at air-ice interfaces and contrasting those with kinetics measured in aqueous solution or at air-water interfaces.

5.1.1 Investigations of the Physical Properties and Solvating Nature of the Air-Ice Interface

We examined the physical properties of air-ice interfaces using glancing-angle Raman spectroscopy. We compared the extent of hydrogen bonding in bulk water, at air-water interfaces, and at air-ice interfaces. We report that the extent of hydrogen bonding at the air-ice interface is much less than that in bulk ice or liquid water, but greater than that at the surface of liquid water, suggesting that there are fewer dangling OH-groups at air-ice interfaces than at air-water interfaces. We further report that the presence of solutes could alter the structure of the air-ice interface. The presence of halide salts greatly disrupts hydrogen bonding at the air-ice interface, likely due to the formation of a liquid brine. Conversely, the deposition of small inorganic acids from the gas phase enhances hydrogen bonding at the air-ice interface. We attribute this to the formation of hydronium ions, which are superior hydrogen-bond donors than water molecules. The deposition of gas-phase ammonia decreases the extent of hydrogen bonding at the air-ice interface.
We also used glancing-angle LIF of a fluorescing pH probe to monitor changes in pH at air-ice interfaces in the presence of small acids and bases. Changes in the emission spectrum of acridine present at the air-ice interface after the deposition of gas-phase acids indicate acidification of the surface, confirming that acids undergo dissociation at the air-ice interface at temperatures relevant to Earth’s surface. Our results suggest that these small acids dissociated to similar extents at the air-ice interface and in aqueous solution.

We investigated the solvating environment presented by the QLL by monitoring excitation and emission spectra of aromatic species at air-ice and air-water interfaces and in aqueous solution. The spectra of most species on ice indicate self-association. We suggest that aromatics interact less favourably with ice surfaces due to the presence of fewer dangling OH-groups. Molecular dynamics simulations\(^1\) support this hypothesis.

We also monitored uptake kinetics of organic species to water and ice using glancing-angle LIF. Phenanthrene exhibits similar uptake kinetics to water and to ice. The uptake kinetics of monomeric and excimeric naphthalene are well-described by a simple model that includes gas-ice partitioning as well as self-association at the air-ice interface. The deposition of phenanthrene, naphthalene, and acetone to ice surfaces results in a decrease in intensity of the Raman OH-stretch of water, which we used to determine uptake kinetics. The deposition of \(n\)-hexane does not affect the Raman OH-stretch.

The results described above suggest that the QLL presents a distinct environment from liquid water, but that some species, such as small inorganic acids, display similar behaviours in the two media. Other species, such as PAHs, are solvated very differently at air-ice and air-water interfaces.

### 5.1.2 Reaction Kinetics at Air-Ice Interfaces

We studied several unimolecular and bimolecular reactions at air-ice interfaces and compared the kinetics to those in aqueous solution and at air-water interfaces. The direct photolysis of benzene at wavelengths below 295 nm to form phenol showed identical kinetics in aqueous solution and at air-ice interfaces, but all other reactions proceeded at very different rates in the two media.
The direct photolysis of anthracene, naphthalene, and benzene at environmentally relevant wavelengths occurred much more rapidly at air-ice interfaces than in aqueous solution. While the red-shift in the absorbance spectra of naphthalene and benzene could explain the increased rates of these compounds, we determined that the same was not true for anthracene. We also showed that anthracene photolysis within bulk ice is not enhanced to the same extent as at the air-ice interface. We conclude that the observed rate enhancements are not due to increased photon fluxes, changes in temperature, or the state (solid or liquid) of the substrate. We hypothesize that the rate enhancements could be due to increased absorption cross sections or photolysis quantum yields of aromatics at the air-ice interface, or due to photolysis proceeding via a different mechanism there.

We also measured heterogeneous ozonation kinetics of bromide and phenanthrene at air-ice interfaces; each species reacts more quickly there than at water surfaces. The rate enhancement at the air-ice interface for the bromide reaction could be explained by the exclusion of bromide from the ice matrix during freezing. However, since phenanthrene was deposited to the ice surfaces from the gas phase, an alternate explanation must be found for its heightened reactivity on ice.

In a final set of studies, we monitored reaction kinetics of anthracene and benzene with \( \cdot \text{OH} \) formed from the photolysis of \( \text{NO}_3^- \), \( \text{NO}_2^- \), and \( \text{H}_2\text{O}_2 \); both species react quickly in aqueous solution, but no evidence of reaction was observed at the air-ice interface. Analysis of melted ice samples indicated that benzene reacted with \( \cdot \text{OH} \) in bulk ice at a similar rate as in solution, and that the reaction was only suppressed at the air-ice interface. Monitoring anthracene and benzene at air-ice and air-water interfaces in the presence of gas-phase \( \cdot \text{OH} \) showed rapid reactions at air-water interfaces, but no evidence of reactions on ice. We conclude that unlike ozone, hydroxyl radicals appear to be much less reactive toward aromatics at air-ice interfaces compared to in aqueous solution.
5.2 Future Directions

There are many research directions which could be pursued based on the results discussed in this thesis. For example, the glancing-angle Raman spectroscopy probe that we developed has many potential applications, including monitoring chemical reactions on various atmospheric substrates; and numerous reactions could be monitored at the air-ice surface using glancing-angle LIF to provide further information on reaction kinetics there. In this section, though, I will focus on three major research areas that I believe would be of value to the atmospheric community:

1. Investigating the formation and fate of OH at air-ice interfaces;
2. Quantifying pH at air-ice interfaces;
3. Investigating the properties of QBLs;
4. Further investigations of reagent-substrate interactions.

5.2.1 Investigating the Formation and Fate of Hydroxyl Radicals at Air-Ice Interfaces

The results discussed in Parts Three and Four of Chapter Four were quite surprising, and contradicted common assumptions about the behaviour of OH at air-ice interfaces. Our results show that OH is unreactive toward aromatic organics at air-ice interfaces, whether it is formed in solution or introduced from the gas phase. However, our results do not explain why this happens. I believe that investigations addressing this issue would be of great importance. In Section 4.16, we proposed possible reasons for the observed non-reactivity of OH. These included: Lower diffusion rates on ice; poor partitioning of OH to ice; recombination of OH; and interactions with the ice surface. Based on our results, we concluded that the first two possibilities were unlikely to be responsible for our observations.

Several studies\textsuperscript{2-4} have measured OH production rates from the photolysis of precursors such as nitrite, nitrate, and H\textsubscript{2}O\textsubscript{2} in ice; these studies showed similar
production rates in ice as in aqueous solution. However, to the best of my knowledge, OH production rates have never been measured explicitly at the air-ice interface. Given the differences in kinetics that we have observed at air-ice interfaces compared to in bulk ice, I believe that we should be cautious in relating kinetics measured in bulk ice to kinetics expected at air-ice interfaces. This is especially important for reactions that produce volatile species such as OH which can greatly affect the composition of the overlying boundary layer, because snow-air exchange will be most important for OH formed at the air-ice interface. If OH formation rates are different in bulk ice and at the air-ice interface, this will affect our understanding not only of chemistry within snow and ice, but in the overlying atmosphere as well.

I suggest that it would be very worthwhile to measure OH formation rates directly at the air-ice interface, or to measure its release to the gas phase. Gas-phase measurements have been performed at low temperatures and pressures during the photolysis of frozen nitrate solutions, but to my knowledge this has not been done under environmentally relevant conditions.

A second study that I believe would be useful would be to measure reaction rates of OH with a variety of inorganic and organic species at air-ice interfaces to try to understand the factors that affect its reactivity there, and also to help predict the fates of a variety of atmospheric species at air-ice interfaces. I recognize that these studies will present significant technical challenges, but nevertheless I believe that, if they can be done, they could yield very useful information for the atmospheric community.

5.2.2 Quantifying pH at Air-Ice Interfaces

Many atmospherically relevant heterogeneous reactions are pH-dependent. For example, many of the reactions thought to be involved in polar bromine explosions, described in Section 4.2, require acidic conditions. Quantifying pH at air-ice interfaces has so far proved to be an insurmountable challenge, and although many estimations and predictions of pH have been made, there is no consensus on whether the surface of ice is acidic. Our glancing-angle LIF measurements of changes in pH at air-ice interfaces, described in Section 2.4.5, provide a potential first step in quantifying pH at
environmental substrates, including snow and ice. I believe that surface-sensitive spectroscopic techniques could be developed to quantitatively determine pH at air-ice interfaces. This would provide very useful information to the atmospheric community, and would have applications that extend to substrates other than snow and ice where pH is an important unknown, such as mineral dust.

5.2.3 Investigating the Properties of Quasi-Brine Layers

In section 4.16, I raised the possibility that the concentrated brines formed by the exclusion of halide salts from sea ice could be actual liquid. If this is the case, reaction kinetics, especially of aromatic compounds, would likely be very different at frozen halide salt solution surfaces and at pure ice surfaces. Given that both types of ice are very important to atmospheric chemistry, this could be an important issue. To my knowledge, no studies have been performed comparing reaction kinetics in QBLs and QLLs. If QBLs are true aqueous solutions, then reactivity there might be adequately predicted by reactivity in aqueous solution, which would be very beneficial to chemical fate modellers. I suggest that comparing kinetics of various species on pure ice surfaces and on frozen halide salt solutions would be a very useful research direction.

5.2.4 Further Investigations of Reagent-Substrate Interactions

I believe that understanding the way in which atmospheric species interact with ice surfaces is key to predicting their atmospheric fates in snow-covered environments. We have made some strides in this area with the surface-sensitive spectroscopic techniques discussed in Chapter Two, but much more needs to be done. Specifically, I believe that investigating the conformation of reagents deposited onto ice surfaces from the gas phase using techniques such as X-ray spectroscopy could help explain the reactivity of different compounds that has been observed at air-ice interfaces.

5.3 Atmospheric Implications

The ultimate goal of atmospheric chemistry research is to be able to accurately predict the fate of individual species and atmospheric composition as a whole. This necessitates a good understanding of the processes that occur in the relevant media, and
the kinetics at which they do so. I would argue that at this time, our knowledge of chemical reactions in snow and ice is not sufficient to accurately predict the fates of species in or on these substrates. That said, I believe that the research described in this thesis offers information that can help such models now or in the future.

I believe that the most important contribution from the work presented in this thesis is the view of ice as a reaction medium that we have developed. We show that for several reactions involving aromatic compounds, kinetics at air-ice interfaces are different than those in aqueous solution. Further, kinetics are different at air-ice interfaces and in bulk ice. These findings suggest that the way in which some laboratory results are interpreted should be re-evaluated, and that the fate of species in snow and ice could depend to a large extent on whether they are frozen from solution or deposited from the gas phase.

A further finding of this research which could have important ramifications for modelling the fate of organic pollutants such as PAHs both in snow and ice and in liquid water is that some direct photolysis reactions exhibit non-linear photon flux dependences. For strong absorbers such as aromatic compounds, photon flux dependences should be experimentally determined before extrapolating laboratory-measured kinetics to environmental conditions.

The studies discussed in this thesis have provided us with a more in-depth understanding of ice as a reaction medium than previously existed. Based on this work, we can envision ice as a heterogeneous reaction medium that affects reagents differently depending on their location. These results highlight the complexity of the air-ice interface as a reaction medium, and stress the need for further fundamental studies into the physical and chemical nature of the air-ice interface, and into the fate of atmospheric species there.
5.3 References


