Influence of thin liquid films on polar ice chemistry: Implications for Earth and planetary science

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Abstract

The polar snowpack (and sea-ice) plays a major role in affecting overlying boundary layer chemistry and has only recently come to light. Furthermore, the understanding of this system and its importance is steadily growing. Investigations done thus far, nonetheless, examined the subsets of the polar environment as an uncoupled system. Analogous to some materials, the surface of snow/ice exhibits thin liquid layers (e.g., the quasi-liquid layer (QLL) and brine layer (BL)). This paper gives an overview of thin liquid films and illustrations of their function in Earth science. The impact of such films in polar science (i.e., polar snowpack photochemistry) is discussed within the context of how field data has been elucidated through laboratory data and modeling techniques. Specifically, what laboratory and modeling investigations have revealed about the effect of thin liquid layers on constraining field observations and, more importantly, the physicochemical mechanisms that govern the behavior of trace gases within the snowpack (and sea-ice) and how they are released from the polar snowpack. Current and future impacts of these findings are discussed, along with putative implications of the effect of thin liquid films in planetary science.

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1. Introduction

The surface of solids is an area that exhibits traits dissimilar to those of the bulk material. This is primarily due to the fact that atoms (or molecules) at the ice—air interface only encounter bonding forces with other molecules from one side. This imbalance of bonding forces promotes the dislocation of atoms from their original sites, while inducing alterations in their associated force and energy constants, and causing variable disorder on layers below the ice—air delineation.

Faraday (1850a,b) observed “that a particle of water which could retain the liquid state whilst touching ice on only one side, could not retain the liquid if it were touched by ice on both sides.” His observations on pure water ice initiated the concept of thin liquid films existing on solid surfaces, below respective freezing points. Prior to Faraday’s findings, it was known that “two pieces of thawing ice, if put together, adhere and become one.” Yet, mechanism of this refreezing (regelation) process was under debate. Since J. Thompson and
his brother, W. Thompson (or Lord Kelvin), established that pressure lowers the melting point of ice, it was believed that ice regelation was due to a pressure effect. Others suggested that ice refreezing was a result of a temperature gradient, being colder in the interior, compared to the surface. Faraday dispelled both arguments by submerging two pure water ice blocks in a glass jar containing water, all contained in a well-insulated chamber, maintained at 0 °C. The ice, set in place by woolen threads, approached positions of stability due to their buoyancy. After moving the blocks toward each other with slips of wood, Faraday observed that they adhered as soon as their faces touched.

Other substances (i.e., other than water ice), such as solid rare gases, molecular solids, metals, and semiconductors, contain a liquid-like layer on their surfaces (Dash et al., 1995, 2006). The fact that the boundary between the solid and vapor phase is wetted by a thin liquid film causes the free energy of the boundary to be lower than it would be if the thin liquid film were absent (Dash et al., 1995, 2006). In other words, if the state of a system is slightly below the bulk melting temperature to be initially dry, the system could lower its free energy by converting a layer of the solid to liquid. The cost of this conversion involves the free energy change due to melting. If the temperature of the system is near the bulk melting temperature and the layer is thin enough, the cost of the conversion will not be prohibited. Hence, the existence of a thin liquid film at the ice–air interface causes the free energy of the system to be lower than it would be if the thin liquid film were absent (Dash et al., 1995, 2006). Therefore, the physical motivation for surface melting is the reduction of interfacial energy. Thin liquid films should then exist over a finite temperature range on ice surfaces, below the normal melting point of respective ice matrices. The thickness of such films is governed by the competition between the free energy of the ice surface and the energy required to melt a solid layer, where its thickness is present at a state that the free energy of the ice system is at a minimum. Dash et al. (1995, 2006) provide a thorough derivation for the theoretical expressions for the thickness of a thin liquid film as a function of both the ambient and normal melting temperature. These expressions are based on whether dispersion (or van der Waals surface) forces or short range forces are acting at the interface.

Theoretical and experimental analyses have been done on the effect of temperature on the thickness of thin liquid films (Kuroda and Lacmann, 1982; Ohnesorge et al., 1994; Landa et al., 1995; Wettlaufer, 1999; Doppenschmidt and Butt, 2000; Pittenger et al., 2001; Bluhm et al., 2002; Sadtchenko and Ewing, 2002). These studies have all observed an increase in the thickness of the thin liquid films with increasing temperature. The only exception to this observation was reported by Elbaum et al. (1993), who conducted experiments on horizontal facets in the prismatic orientation (10̈0). Still, this study is a contradiction to the Kuroda and Lacmann’s (1982) earlier measurements, which measured the thickness of the thin liquid film and observed a drastic increase in its thickness at ~−10 °C and higher temperatures on horizontal facets in the prismatic orientation of ice. In the uppermost layers of ice samples thin liquid films are almost indistinguishable from their respective liquid phase while transitions to a more crystalline order become apparent within several molecular layers below the surface (1 molecular layer ~ 0.3 nm) (Zhu et al., 1988; Ohnesorge et al., 1994; Landa et al., 1995).

The existence of thin liquid films in and on ice gives it distinct characteristics. For example, the addition of impurities at constant pressure will shift the normal melting of the bulk solid, which is directly dependent on the concentration of the impurity. This inevitably lowers the normal melting point of the ice sample and amplifies the thickness of the premelting layer. Impurities in general are also too large to be molecularly incorporated within the ice lattice during the freezing of aqueous solutions (Takenaka et al., 1996; Rempe1 et al., 2001; Dash et al., 2006). Therefore, the majority of solutes (e.g., NO$^-$, HSO$_4^−$, and SO$_4^{2−}$) are partitioned to the premelting layer and subsurface water channels (or veins) (Mulvaney et al., 1988; Nye, 1989; Fukazawa et al., 1998). The degree of segregation depends on solute concentration and freezing rates (Takenaka et al., 1996).

Before proceeding, we see it fit to qualitatively characterize the distinct nature of various forms of thin liquid films on solid surfaces. What distinguishes various types of thin liquid films on solid surfaces — specifically, what is the difference between the quasi-liquid layer (QLL) (or notably called the liquid-like layer, surface melting layer, or premelting layer) and other premonitory liquid layer modes, such as the brine layer (BL). The sharpness of the bulk melting transition can be broadened and shifted by impurities, dislocations, polycrystallinity, and other forms of disorder. In contrast, premelting is an equilibrium phenomenon of well-ordered crystal surfaces. Surface melting is not a distinct phase change, but is instead a surface aspect of the bulk transition: specifically, a surface phase-transition. Although melting is a first-order phase change, it is initiated with the gradual
development of surface disorder and mobility. As temperatures rise toward the bulk transition temperature, disorder and mobility increase and progress deeper into the solid. The disordered region is a quasi-liquid: that is, when it is microscopically thin, it retains the structure of the underlying solid, but when it thickens, the outer layers become identical to the bulk liquid. In the intermediate zone the liquid-like disorder and fluidity evolve with distance; in some cases the evolution is stepwise in monolayer increments (Phillips, 1989). It is even possible to see that the transition advances as a kind of two-dimensional melting within each layer. And even within this progression, there is a lower-dimensional premelting layer that undergoes its transition (Pengra and Dash, 1992). When the temperature reaches the transition temperature, the transition zone migrates inward, leaving bulk liquid in its wake. The fully developed quasi-liquid thus obtains the width or diffuseness greater than that of the solid–liquid interface. Therefore, for the solid phase of water the QLL pertains only to pure water ice. The addition of solutes induces a freezing-point depression in water solutions below the freezing point of pure water, thus forming a pure liquid (not a quasi-liquid) in equilibrium with ice. Consequently, lowering the temperature (or the freezing) of water solutions containing solutes (of variable concentration), below the melting point of pure water, creates an interfacial- or liquid-layer (in this case—a brine layer) that (at specified temperatures) is in equilibrium with the ice matrix portion. This type of thin liquid layer (i.e., a brine layer) decreases with decreasing temperature as it approaches the solution’s eutectic point, where the entire matrix solidifies. This paper appropriates the term QLL and BL when describing snowpack and sea-ice surfaces, respectively, and denotes that both are forms of thin liquid films.

Thin liquid layers on ice are inimitable aqueous films that exist over a wide range of environments (e.g., from glaciers to polar stratospheric ice clouds). They also exist at Earth’s polar snowpack (Boxe and Saiz-Lopez, 2008) and, depending on ambient pressures and temperatures, possibly at planetary ice and soil-covered regions (Haberle et al., 2001; Lobitz et al., 2001; Richardson and Mischna, 2005; Dash et al., 2006). These layers are bi-directionally involved with their surroundings, considering that they are sensitive to contaminants, crystalline disorder, and temperature. For instance, they govern the: 1) sintering of snowfields; 2) transport of impurities along grain boundaries; 3) shapes of snowflakes and their growth rates, making them important factors in ice sheet dynamics; and 4) transport of electrical charges that power lightning during collisions between ice particles and hail in thunderstorms. Liquid films are catalysts for crystallization, thus facilitating crystal growth. In addition, they remove the nucleation barrier to melting, therefore easing the transformation from solid to liquid.

The polar snowpack is a beacon of both global warming and climate change. Within this context, a multitude of field and laboratory experiments has investigated, throughout the last decade, physicochemical processes that occur in and above the sunlit snowpack and sea-ice, discovering that these locations are two of the most photochemically active environments on Earth. These findings illustrate that snow/ice is a multi-dimensionally complex environment, comprised of thin liquid films (i.e., both at the ice–air interface and within the bulk as liquid veins or channels) and polycrystalline regions within the bulk. Based on laboratory and modeling analyses, this paper gives an overview of the role of thin liquid films in contextualizing field data by explication of physicochemical mechanisms of trace gases within the snowpack and their respective release. It has become clearer that iodine chemistry, intimately linked to NOx chemistry, plays a major role in controlling ozone concentrations in the overlying boundary layer. Iodine forms aerosols and contributes to the transformation of elementary mercury to its reactive form, which detrimental to the polar ecosystems (Saiz-Lopez et al., 2007a,b). Nitrate (NO$_3^-$) contained in the polar snowpack is known to produce NO$_x$ (NO + NO$_2$), which is released to the atmosphere and may also affect ice core records used to derive information about past climate (McCabe et al., 2005; Morin et al., 2008). Furthermore, polar ozone exhibits a significant radiative forcing, linked to iodine and NO$_x$ chemistry (Shindell et al., 2006). Thus, it is imperative to understand the sources of iodine and NO$_x$ in the polar snowpack. This paper discusses the role of thin liquid films in simulating polar iodine and NO$_x$ field data via multiphase modeling techniques. In addition, this paper discusses the possible role that thin liquid films may play on the surfaces of planetary bodies other than Earth.

2. Results and discussion

Honrath et al. (1999) and Jones et al. (2000) initiated investigations of the impact of polar snowpack photochemistry on boundary layer chemistry by their serendipitous reports of elevated NO$_x$ concentrations measured in and above the Arctic and coastal Antarctic
This undoubtedly revived curiosity in re-evaluating the nitrogen cycle over the polar regions. Thereafter, a series of seminal field experiments followed primarily focused on measuring NO\textsubscript{x} in the polar boundary layer (Beine et al., 2003; Cotter et al., 2003; Davis et al., 2004; Dibb et al., 2004; Jones et al., 2007). NO\textsubscript{x} emissions detected in and over the polar snowpack (i.e., at the Arctic and coastal Antarctica) are derived from the photolysis of nitrate (NO\textsubscript{3} \textsuperscript{-}), a major anion present, absorbing at $\lambda \geq 290$ nm. Nitrate photochemistry also produces NO\textsubscript{2} and OH radicals. In this case, the release of OH to the gas phase would be a minor contributor the OH budget in the overlying boundary layer since is produced from non-primary reactions during nitrate photolysis. In addition, NO\textsubscript{2}, as known to occur through the photodecomposition of nitrate in acidic aqueous media (Mark et al., 1996; Mack and Bolton, 1999), may protonate in acidic snow/ice environments to nitrous acid (HNO\textsubscript{2}, pKa $\approx 3.7$ at $-20$ °C (Park and Lee, 1988)), which can be readily released as HONO\textsubscript{(g)}. Similarly, this pathway is likely a minor contributor to OH to the gas phase due to its much higher solubility compared to NO\textsubscript{2}, and kinetic limits, compared to NO\textsubscript{2} photolysis to produce NO (Jacobi and Hilker, 2007). For example, HONO exhibits a solubility constant of $\sim 930$ M atm\textsuperscript{-1}, which is $\sim 3.6 \times 10^4$ higher than NO and NO\textsubscript{2}'s respective solubility constants. The debate still continues as to what mechanism governs the overall release of HONO as its release has been measured from the snowpacks of the Canadian Arctic, Summit, Greenland, and Browning Pass, Antarctica (Zhou et al., 2000; Honrath et al., 2002; Beine et al., 2006). Moreover, a recent laboratory investigation has quantified the release of HONO from nitrate-doped ice at relevant temperatures of the polar regions (Bartels-Rausch and Donaldson, 2007).

Due to its vital role in lower tropospheric ozone polar chemistry, nitrate photochemistry has been the center of attention of a suite of laboratory experiments (Honrath et al., 2000; Dubowski et al., 2001, 2002; Chu and Anastasio, 2003; Boxe et al., 2003, 2005, 2006; Jacobi et al., 2006; Jacobi and Hilker, 2007). These laboratory studies have greatly expounded upon the physicochemical mechanism that governs the release of NO\textsubscript{x} from the polar snowpack. A key part of this process that has been revealed is the influence of premelting layers, most notably the QLL. Honrath et al. (2000) conducted the first experiments (i.e., snow chamber experiments), utilizing nitrate as a solute, and demonstrated that NO\textsubscript{3} photolysis results in the release of NO\textsubscript{3} from snow. More importantly, Honrath et al. (2000) were also the first to suggest that surface disorder may, to some degree, be significant in properly assessing nitrate photochemistry in the snowpack; this suggestion was implied by extrapolation of the aqueous phase nitrate photochemical mechanism (Mark et al., 1996; Mack and Bolton, 1999) to aid in rationalizing their NO\textsubscript{x} measurements. Additional studies revealed more pertinent details of the importance of premelting in snow/ice photochemistry. Dubowski et al. (2001, 2002), by way of isothermal irradiation of nitrate-doped ice pellets, revealed that the quantum yield of NO\textsubscript{2} and NO\textsubscript{2} is approximately similar to their respective quantum yield in nitrate photolysis in the aqueous phase, further supporting the active role of the liquid-like component of snow/ice. Their results further bolstered the existence and impact of the QLL by producing comparable photochemical behavior in nitrate–formate-doped ice samples (formate, HCO\textsubscript{2} \textsuperscript{-}, an efficient OH scavenger) to its aqueous phase. Adding to these findings, Chu and Anastasio (2003) conducted isothermal photolysis temperature-dependent experiments of nitrate-doped ice that showed that the quantum yields of OH in ice pellets and aqueous solutions can be described by the same regression, suggesting that the photolysis of nitrate on ice occurs in a QLL, rather than in bulk ice.

Compared to previous isothermal photochemical studies of nitrate-doped ice matrices (Dubowski et al., 2001, 2002; Chu and Anastasio, 2003), Boxe et al. (2003, 2005) then measured NO and NO\textsubscript{2} released from the ice surface in real-time via temperature-programmed desorption. Both studies showed that although photo-produced NO\textsubscript{x} avoids geminate recombination by escaping from a permeable molecular cage throughout, NO\textsubscript{2} levels are controlled by desorption from the outermost ice layers rather than by NO\textsubscript{3} photolysis rates. Therefore, during temperature-programmed experimental trials, NO\textsubscript{x} produced via photolysis accumulated in the deeper layers bursts when the solid undergoes a sintering transition following the temperature demarcation ($\sim -10$ °C) associated with the onset of the most drastic increase in surface melting (i.e., in these instances, the most drastic increase in the macroscopic dimensions of subsurface interfacial fluids and the QLL at the ice–air interface). Fig. 1 displays this phenomenon very well. Since elementary photochemical events (e.g., photochemical release of NO\textsubscript{x} via nitrate photolysis) occur in a communal fluid phase of molecular dimensions at temperatures far below the KNO\textsubscript{3}/H\textsubscript{2}O ($T_{\text{eutectic}} = -2.88$ °C) and NaNO\textsubscript{3} ($T_{\text{eutectic}} = -18$ °C), it was inferred that premelting layers are likely crucial in contributing to the release of NO\textsubscript{x} even below their...
respecte eutectic temperatures. An even more important finding is that these results implied the existence of sub-eutectic premelting and interfacial layers. Fig. 2 shows an explicit example of the impact of premelting layers on photochemistry in ice media. The existence of the premelting layer appears to cause the known aqueous phase NO2 loss reaction, \(2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + \text{NO}_2 + \text{H}^+\), to contribute notably to the nonlinear production of total released NO2 in photolytic experiments of nitrate-doped ice in individual thermograms, yielding a square root dependence with initial nitrate concentration for the production of total released NO2.

These laboratory experiments have contributed greatly to clarifying the physicochemical mechanisms that may govern the release of NO and NO2 over the polar snowpack, thereby bridging the gap between laboratory, field, and modeling studies. Via FACSIMILE software capabilities Jacobi and Hilker (2007) modeled experimental data obtained from photolysis experiments using artificial snow, containing variable initial concentrations of nitrate and nitrite. Assuming that all reactions took place in the QLL on the surface of ice crystals, they derive a mechanism for the photochemical transformation of nitrate, relevant to the polar snowpack. Jacobi and Hilker (2007) use the correlation derived by Cho et al. (2002), which quantitatively gives the fraction of liquid water in the QLL as a function of temperature and total solute concentration in the QLL. The correlation was used to take into account the concentration effect that may be due to the existence of the QLL in snow/ice, which may increase initial bulk concentrations and reaction rates (Takenaka et al., 1996; Grannas et al., 2007). In Jacobi and Hilker (2007), nitrate and nitrite photolysis rates and NO and NO2 rates of transfer from the snow to the gas phase were adjusted to give an optimum fit to their experimental data.

To bridge the gap even further between laboratory, field, and modeling investigations, pertaining to assessing NOx measurements by way of nitrate photochemistry, a multiphase model CONAIR (Condense Phase to Air Transfer Model) was recently developed (Boxe and Saiz-Lopez, 2008; Saiz-Lopez and Boxe, 2008). Overall, Boxe and Saiz-Lopez (2008) utilize the multiphase model to show that nitrate photochemistry in and on snow/ice surfaces (i.e., the QLL) can account for NOx volume fluxes, concentrations, and NO and NO2 concentration ratios measured just above the Arctic and coastal Antarctic snowpack through multiphase modeling techniques. CONAIR explicitly incorporates the nitrate photochemical reaction mechanism with reaction rates re-quantified for the QLL according to the laboratory-derived enhancement due to the existence of the QLL (Takenaka et al., 1996; Grannas et al., 2007), the concentration effect of solutes (e.g., nitrate and nitrite), and laboratory and model derived photolysis rates for nitrate and nitrite (see Table 1). In addition, by incorporating laboratory-derived parameterizations, Boxe and Saiz-Lopez (2008) show for the first time, using a multiphase model, that NOx measurements measured just above the Arctic and coastal Antarctic snowpack are in general dominated by the secondary photolysis of nitrite (NO2) to produce NO and photoproduced NO2 in the outermost layers of snow/ice is readily released to the gas phase. Fig. 3 displays a schematic describing the reactions that govern the release of NO and NO2 via nitrate photolysis in the QLL. Fig. 4 shows simulated diurnal summer and springtime maximum volume flux profiles of NOx released from nitrate photolysis, which is in general comparable to
analogous measurements done just above the Arctic and coastal Antarctic snowpack.

Similarly, using CON–AIR, recent ground- and satellite-based measurements of IO at coastal Antarctica (Saiz-Lopez et al., 2007a,b) were simulated well by representing boundary layer chemistry coupled to the biological production of iodine from marine algae within and on the underside of Antarctic sea-ice, transport of iodine species through brine channels, and halogen chemistry in the BL at the surface of sea-ice (Saiz-Lopez and Boxe, 2008). The sources of such a large iodine burden in the Antarctic atmosphere were unknown; Saiz-Lopez and Boxe (2008) present the first hypothesis of a possible mechanism to account for this gas phase iodine burden. The study shows that proper parameterization of the BL in CON–AIR is a crucial factor in representing simulating the ground and satellite measurements of IO. This is primarily due to the enhancement of chemical reaction rates occurring in the BL on sea-ice surfaces.

Overall, laboratory and modeling studies have, to a great extent, assisted in understanding the physicochemical mechanisms that govern the behavior and release of trace gases in and from the polar snowpack, respectively. More importantly, they have also yielded greater insight into the role of thin liquid films, such as the QLL in and on snow/ice and the BL in and on sea-ice, that play in governing physicochemical mechanisms of atmospherically relevant trace gases within the polar snowpack and sea-ice. Still, this discussion has been limited to iodine and nitrate chemistry. There are a suite of other species that interact dynamically in the polar atmosphere and the sea-ice and snowpack, where laboratory analysis has been sparse. For

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**Table 1**

QLL reactions and rate constants.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Aqueous rate constants(^a)</th>
<th>QLL rate constants(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NO}_3^- + h\nu \rightarrow \text{NO}_2 + O)</td>
<td>(2.82 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1})</td>
<td>(2.82 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1}/(\text{volumetric}))</td>
</tr>
<tr>
<td>(\text{NO}_3^- + h\nu \rightarrow \text{NO}_2 + O(3P))</td>
<td>(2.00 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1})</td>
<td>(2.00 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1}/(\text{volumetric}))</td>
</tr>
<tr>
<td>(\text{NO}_3^- + h\nu \rightarrow \text{NO} + O)</td>
<td>(6.64 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1})</td>
<td>(6.64 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1}/(\text{volumetric}))</td>
</tr>
<tr>
<td>(\text{O}_2 + O(3P) \rightarrow O_3)</td>
<td>(2.46 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1})</td>
<td>(2.46 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1}/(\text{volumetric}))</td>
</tr>
<tr>
<td>(\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2)</td>
<td>(6.15 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1})</td>
<td>(6.15 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1}/(\text{volumetric}))</td>
</tr>
<tr>
<td>(\text{NO}_3^- + \text{O}(3P) \rightarrow \text{NO}_2 + \text{O}_2)</td>
<td>(3.72 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1})</td>
<td>(3.72 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1}/(\text{volumetric}))</td>
</tr>
<tr>
<td>(\text{NO}_3^- + \text{OH} \rightarrow \text{NO}_2 + \text{OH}^-)</td>
<td>(3.32 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1})</td>
<td>(3.32 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1}/(\text{volumetric}))</td>
</tr>
<tr>
<td>(\text{NO}_2 + \text{NO}_2 + \text{H}_2 \text{O} \rightarrow \text{NO}_2 + \text{NO}_2^- + 2\text{H}^+)</td>
<td>(1.66 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1})</td>
<td>(1.66 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1}/(\text{volumetric}))</td>
</tr>
<tr>
<td>(\text{NO} + \text{NO}_2 + \text{H}_2 \text{O} \rightarrow 2\text{NO}_2 + 2\text{H}^+)</td>
<td>(3.32 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1})</td>
<td>(3.32 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1}/(\text{volumetric}))</td>
</tr>
<tr>
<td>(\text{NO} + \text{OH} \rightarrow \text{NO}_2 + \text{H}^+)</td>
<td>(3.32 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1})</td>
<td>(3.32 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1}/(\text{volumetric}))</td>
</tr>
<tr>
<td>(\text{NO}_2 + \text{OH} \rightarrow \text{NO}_3 + \text{H}^+)</td>
<td>(2.16 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1})</td>
<td>(2.16 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1}/(\text{volumetric}))</td>
</tr>
<tr>
<td>(\text{NO} + \text{NO}_2 \rightarrow \text{N}_2\text{O}_3)</td>
<td>(1.83 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1})</td>
<td>(1.83 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1}/(\text{volumetric}))</td>
</tr>
<tr>
<td>(\text{N}_2\text{O}_3 + \text{H}_2 \text{O} \rightarrow 2\text{NO}_2 + 2\text{H}^+)</td>
<td>(5.3 \times 10^2 \text{ s}^{-1})</td>
<td>(5.3 \times 10^2 \text{ s}^{-1})</td>
</tr>
<tr>
<td>(2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4)</td>
<td>(7.48 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1})</td>
<td>(7.48 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{s}^{-1}/(\text{volumetric}))</td>
</tr>
<tr>
<td>(\text{N}_2\text{O}_4 + \text{H}_2 \text{O} \rightarrow \text{NO}_2 + \text{NO}_2^- + 2\text{H}^+)</td>
<td>(10^3 \text{ s}^{-1})</td>
<td>(10^3 \text{ s}^{-1})</td>
</tr>
</tbody>
</table>

\(^a\) Aqueous phase reaction rate constants were obtained from Mack and Bolton (1999).

\(^b\) QLL rate reaction rate constants were quantified by including the “volumetric” factor (Grannas et al., 2007; Takenaka et al., 1996).

\(^c\) \(J_{\text{NO}_3}\) values were extrapolated from Qiu et al. (2002) and King et al. (2005).

\(^d\) \(J_{\text{NO}_3}\) was extrapolated from Zuo and Deng (1998).

\(^e\) Volumetric \(\sim 4.65 \times 10^{-1}\) (Grannas et al., 2007; Takenaka et al., 1996).

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Fig. 3. Simplified schematic diagram illustrating the primary reactions governing NO\(_x\) release from the QLL to the gas phase from nitrate photochemistry. At QLL depths \(\leq 150\ \mu\text{m}\), NO\(_2\) photolysis does not occur, while at QLL depths \(\geq 150\ \mu\text{m}\) NO\(_2\) photolysis occurs (Boxe and Saiz-Lopez, 2008).
example, what mechanisms govern the release of bromine, chlorine, HNO₃, HO₂NO₂, organic species, etc. from the snowpack? All of these species are inevitably linked to ozone chemistry. What are the partitioning coefficients of such species to the ice lattice and thin liquid films in the polar snowpack? As some reactions are pH dependent, what is the actual pH of the thin liquid films, especially given quantifiable partition coefficients of specified trace gases? Similar questions may also be posed for soil-covered regions on Earth, as they are heterogeneous mediums, consisting predominantly of the soil solution (another thin liquid film mode, where most reactions in soil media occur) encompassing the clay portion or nucleus of individual soil grains. These vital questions will need to be investigated by way of careful laboratory experiments as answering them is necessary for models to better simulate field data.

3. Implications for Earth and planetary science

Furthering the understanding of the role of thin liquid layers on solid surfaces, such as soil and snow/ice surfaces, that play in controlling physicochemical mechanisms of species within such environments is crucial. Such scientific advancements are important on Earth since these environments are receptors of a suite of species, which inevitably are re-released in various forms back to the atmosphere by a range of processes, such as photochemistry and thermal desorption. For instance, Stemmler et al. (2006) showed for the first time that heterogeneous photochemistry is occurring in soil on Earth. Therefore, both the condensed and gas phase regimes are constantly being dynamically altered.

Synonymous to Earth, water ice and soil are abundant on other planetary bodies, such as Mars, Earth’s closest terrestrial analog. Recent findings (Baker, 2001, 2005; Paige, 2005) have pointed toward fact that liquid water once flowed on the Martian surface. Although the atmospheric surface pressure on Mars is too low to permit bulk liquid water as a stable phase on the ground surface, there are periods of time where transient thin liquid films of water can exist at soil-covered and polar regions (Haberle et al., 2001; Lobitz et al., 2001; Richardson and Mischna, 2005). Given these possibilities, laboratory and modeling analyses are needed to address the kinetics such as transient films under analogous Martian conditions. What are the measurable dimensions and transport velocities (if any) of such thin liquid films? What are the energy, nutrient, and water limits for habitability under such extreme conditions? How dynamic is chemistry on and in soil and ice media occur without the existence of thin liquid films? In addition, as observed on Earth, liquid layers (e.g., such as veins and interfacial channels) could possibly be habitats in extreme environments, such as the observed metabolic activity in fluid regions of ice at gigapascal pressures (Sharma et al., 2002) and the existence of microbial communities in glacial ice (Campen et al., 2003). Such scenarios may be pertinent for planetary bodies, such as Mars and even Europa (McKay et al., 1991; Jakosky and Shock, 1998; Chyba, 2000; Chyba and Phillips, 2001). A vast sea of open questions concerning the role of thin liquid layers may play in both Earth and planetary science.

4. Summary and conclusions

An overview was given of the dominate types of thin layer films (e.g., the QLL and BL). Based on thermodynamic constraints, a clear distinction was also made between these two modes of liquid films. In addition, this paper summarizes the influence of thin liquid films in Earth polar chemistry and their implications for planetary science. Although ample scientific advancements have been made via field and laboratory studies of polar science, which have undoubtedly revealed that also advancing the understanding of liquid films within this context is vital. Model investigations aimed at linking field and laboratory studies of polar science by way of including liquid films on snow/ice surfaces in an emerging field. Furthering the understanding of the role of thin liquid films that play in Earth and planetary science will only be achieved through careful field, modeling, and especially laboratory studies.
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