



Photochemistry of Organic and Inorganic Molecules on the Surface of Ice and Snow Crystals

M. R. Hoffmann, A. J. Colussi, M. Guzman and C. Boxe

Environmental Science & Engineering, California Institute of Technology, Pasadena, California 91125 USA (mrh@caltech.edu / Fax: +1-626-395-2940)

With new methods for determining the light absorption by chromophores embedded in packed ice, we have investigated the rates and products of the photodegradation of nitric acid, nitrous acid, nitrate, nitrite, nitroaromatic compounds, and carbonyl compounds on ice surfaces. Our results indicate that photochemical transformations occur within a quasi-liquid layer (QLL), which behaves as a super-cooled solution, on the surface of ice down to -50°C . Analytical techniques that have been employed to study reactions in ice include FTIR, ESR, NMR, MS, TP-LIF, and LIF. The environmental implications of this dynamic chemistry will be discussed relative to ice core data and chemical transformations in ice clouds.

In the case of organic molecules, we have shown that frozen aqueous solutions of pyruvic acid (PA) are readily photolyzed at 302 nm to yield 2-hydroxy-3-butanone and CO_2 . Pyruvic acid photodecomposition rates in water increase with T, but remain constant in the frozen state over a broad temperature range. Experimental results clearly show that pyruvic acid trapped in ice releases CO_2 when exposed to actinic UV radiation. Furthermore, there is strong evidence for formation of a carbene intermediate during the photodecarboxylation of PA excited in its $n \rightarrow \pi^*$ band at 320 nm.

In the case of inorganic molecules, we have examined the photochemical production of gas-phase NO_2 and NO liberated from NO_3^- doped ice crystals at $\lambda \sim 302$ nm was followed kinetically with laser-induced fluorescence (LIF) spectroscopy under isothermal conditions and temperature-programmed desorption (TPD) techniques over the temperature range of $-40 \leq T/^{\circ}\text{C} \leq 5$. NO_2 emission rates show distinct transitions from lower to higher rates of release at three ice sintering transition tem-

peratures of -23, -13 and -8 °C. These observations are consistent with the presence of a QLL at the ice-vapor interfaces and within the ice subsurface at crystal grain boundaries well below the eutectic point temperature (e.g., $T(\text{NaNO}_3/\text{H}_2\text{O})_{\text{eutectic}} = -11.28$ °C).

The QLL characteristics and dimensions have explored by a variety of techniques including FTIR, AFM, and NMR. In the later case, ^{19}F NMR was used to monitor 3-fluorobenzoic acid chemical shifts ($\delta^{19}\text{F}$) as an indirect probe of the nominal pH within the QLL. This technique provides an indirect method for the quantification of pH changes in single electrolyte media during freezing to ice. Downfield chemical shifts were observed for three electrolytes during freezing. These shifts corresponded to a ΔpH ($\text{pH}_{\text{aq}} - \text{pH}_{\text{ice}}$) upon freezing in the QLL ranging from -0.5 to -1.5 pH units (i.e., the QLL is more acidic than the aqueous solution from which the ice was formed).