

# Recommended Laboratory Studies in Support of Planetary Science: Surface Chemistry of Icy Bodies

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## 1. Introduction

The outer Solar System today is populated by ice-rich bodies: comets, Kuiper Belt Objects (KBOs), Centaurs, “primitive” asteroids, and icy planetary satellites. Most outer solar system bodies are covered with ices, predominantly water-ice, although more volatile species can be trapped on (and in) solar system bodies. In the Galilean and Saturnian systems, water ice is the primary geologic component of the surfaces of many moons, and controls the observed geology and chemistry. On Triton, Pluto, and some KBOs, nitrogen ice is an important component. Small admixtures of other volatiles, such as CO<sub>2</sub>, NH<sub>3</sub>, CH<sub>4</sub>, and SO<sub>2</sub> are also present on many bodies, and can substantially modify their chemical properties.

The surfaces of icy planetary bodies are altered by their exposure to a variety of particle and photon sources. The resultant chemistry can be highly variable since it depends on trace impurities delivered to those surfaces, both by endogenic and exogenic processes. As such, chemical processes occurring in ices subjected to energetic processing are important to our understanding of Solar System bodies. Photon and particle bombardment also sputter and desorb material from icy surfaces, weathering the surface and producing tenuous atmospheres. Within the upper layers of icy surfaces, photolysis, radiolysis, and reactions involving free radicals are expected to occur and to influence the survivability of primary biomarkers (e.g., amino acids) as well as the reaction products that may be signatures of biologically important parent molecules. We must have a detailed understanding of the chemistry within these icy environments in order to successfully interpret remote sensing data obtained from spacecraft and ground-based observations, and to maximize the scientific return of future missions.

An increased level of funding for laboratory work in these areas is vitally important in light of current and upcoming missions to the outer Solar System, such as New Horizons, and the Outer Planets flagship missions: the Europa Jupiter System Mission and the Titan Saturn System Mission. The study of icy worlds will be a primary focus of each of these efforts and of planetary science in general in the coming decade.

We identify in this paper several areas where an increased emphasis on laboratory activities would lead to a significant return in scientific results, based on an enhanced understanding of the fundamental surface chemistry of icy bodies.

## 2. Chemical Reactions in Planetary Ices

Temperatures are too low for thermal chemistry to be significant on icy surfaces of the outer Solar System. Instead, reactions are driven by high-energy radiation in the form of protons, electrons, and ions, and by ultraviolet (UV) and vacuum-UV photons. These sources of energy are abundant, and arise from the Sun and the magnetospheres of

the giant planets. An important point to note is that each type of particle and photon radiation will penetrate an icy surface to a characteristic depth, which is highly dependent on the nature and energy of the incoming particle or photon.

In addition to depth-dependent effects of the radiation itself, impact gardening will play a role in determining the makeup of surface and near-subsurface regions. Gault et al. (1974) modeled impact processes in the lunar regolith and concluded that the upper millimeter is a “mixing layer” that is frequently overturned by the micrometeoroid flux that dominates the impactor flux population. For icy bodies, this regolith can extend to deeper levels (Cooper et al., 2001) due to the larger volume of ejecta for volatile materials. This layer will be stirred and exposed at the very surface to external radiation of all kinds resulting in a complex history of multiple chemical processes.

Taken together, radiolytic and impact processes lead to a rich chemistry on the surfaces of icy bodies. The degree of chemical processing will vary in a complex fashion with depth, influenced by the particular mixture of radiation the surface is exposed to, and the surface’s age.

While much laboratory and theoretical work has been undertaken to study the radiation and photochemistry of ices, an *overall* picture of the chemical pathways at work in planetary ices is lacking. Such an overall picture can be built through careful, *quantitative* experiments identifying chemical reactions, and then measuring the production and destruction rates of molecules exposed to appropriate fluxes of particle and photon radiation, reaction rates between radiolytic products in icy matrices, and diffusion rates of species at relevant temperatures. These experiments should be conducted in close conjunction with detailed modeling efforts in order to insure applicability to important Solar System objects and to maximize scientific return. Although related work has been completed in other contexts, the variety of radiolytic and photolytic sources and chemical species present in planetary ices means that much remains to be done. Two examples of areas requiring particular attention are the role of free radicals, including radical ions, and photochemistry.

Free radicals are molecular species that contain an unpaired electron, making them highly reactive. They are commonly produced from the dissociation of molecules due to radiolysis and photolysis. To fully understand the chemical evolution of planetary ices it is necessary to understand the chemical behavior of such radicals in an ice lattice at an appropriate temperature. The experimental methods to detect and quantify radiolytically-produced species *in situ* in ices typically are optical spectroscopic methods, such as infrared and UV-visible spectroscopy. Unfortunately, one of the primary radiation products from irradiated water ice, the hydroxyl radical (OH), is not detectable by such methods due to spectral overlap with strong broad water absorptions. However, the formation of an OH radical can be inferred from reactions with other species, such as combination with a second OH radical to produce hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), or if methane is present the reaction of OH and a methyl radical (CH<sub>3</sub>) to produce methanol (CH<sub>3</sub>OH). However, direct detection of OH in ices is difficult-to-impossible with the commonly-employed laboratory techniques.

In other cases, absorption bands of radical species are often below the detection limit of a certain experimental technique due to either a low intrinsic band strength or a low abundance. However, due to the extreme reactivity of radicals, even low abundances may have a major affect on the chemical evolution of an ice. Other approaches, such as

electron paramagnetic resonance spectroscopy and laser-induced fluorescence spectroscopy, are well-suited to the study of radicals, yet are rarely applied to problems in planetary science. The planetary science community needs to communicate with experts in such laboratory techniques and have them apply their knowledge to the problems that are faced in understanding the chemistry of radicals in ices.

Photochemistry in planetary ices is another area requiring significant additional work. While the photochemistry of ices has been studied for many years (primarily in the context of interstellar ice analogs), the experiments have been conducted primarily with light sources that are not representative of the solar spectrum, and at temperatures far too low for many Solar System bodies. Microwave-excited hydrogen lamps are most commonly used because of their high brightness in the vacuum UV. These lamps emit strongly at 121 and 160 nm, while the Sun's emission is much stronger in the mid- and near-UV regions (200-400 nm) and orders of magnitude stronger in the visible. Wavelengths above 200 nm are not sufficiently energetic to break bonds in most small molecules important in planetary ices, such as H<sub>2</sub>O and CO<sub>2</sub>. However, larger molecules, especially organics, can be effectively photolyzed at these wavelengths. Radical species also often have strong dissociative absorption bands in the visible.

In addition, while water-ice strongly absorbs photons with  $\lambda < 175$  nm, it is highly transparent above 200 nm. Photons with  $\lambda = 175$  nm penetrate only  $\sim 1$  mm before absorption, with this depth decreasing very rapidly with decreasing wavelength. The situation is very different for photons having  $\lambda > 175$  nm as water-ice becomes very transparent and UV photons with sufficient energy to fuel chemistry penetrate more deeply. Orzechowska et al. (2007) showed that these deeply-penetrating, longer-wavelength UV photons rapidly decompose amino acids *throughout the volume of thick ice samples*. Photons with  $\lambda > 175$  nm are an omnipresent energy source that can drive chemical reactions below the mm-thick impact mixing layer where ices remain otherwise undisturbed for long periods. The strong flux of solar near-UV and visible light, coupled with the transparency of water ice to these wavelengths, will have a profound impact on chemistry in the near subsurface of planetary ices.

New photochemical experiments to identify chemical reactions and to determine destruction rates and quantum yields of products are necessary to elucidate the chemical processes described above. These experiments will require tunable sources of near-UV and visible radiation with well-calibrated fluxes. The use of techniques new to the planetary ice community, such as seeded supersonic expansions, may be necessary for the study of organic-molecule photochemistry, as such molecules can be difficult to introduce in the gas phase.

### **3. Sputtering and Desorption**

Radiation impinging on icy bodies also results in sputtering and desorption of surface materials. In many cases, particle radiation is the predominant energy input for these processes. Some of the icy moons of Jupiter and Saturn are embedded in the magnetospheres of these planets, which create highly energetic ions and electrons that bombard the surfaces of the moons. Reviews of the origin and effects of these particles are readily available (Johnson 1999; Madey et al. 2002, Cooper et al., 2001), and so we only summarize the most important points here.

Particle radiation on icy moons in the Solar System comes primarily from the solar wind and from ions accelerated in the magnetospheres of the giant planets. Solar wind

particles are primarily protons with an energy of approximately 1 keV, and an accompanying flow of low-energy electrons. Of the giant planets, the plasma environment of Jupiter is best described. Here proton and electrons are still the dominant particles, but multiply charged oxygen and sulfur ions are present as well, with energies up to 10 keV for the thermal plasma and up to several MeV for the energetic component.

When energetic particles impact an icy surface, a large amount of energy can be deposited. Sputtering of particles arises both collisional interactions, as well as desorption induced by electronic transitions (DIET), where an electronic excitation of the substrate molecule relaxes by transfer into translation away from the surface. Low-energy electrons will produce this type of desorption and high-energy heavy ions produce electronic sputtering. This sputtering leads to tenuous atmospheres around some of the Galilean satellites (Hall et al. 1995), and is partially responsible for the torus of OH radicals around Saturn (Hall et al. 1996). By ejecting particles from the surface, sputtering not only generates an atmosphere, but slowly weathers and modifies the surface of the body itself. These processes are highly energy dependent, and the interaction of high-energy charged particles with surfaces can be difficult to model accurately.

While particle interactions with icy bodies have been studied extensively, the effects of photon radiation on icy bodies are not as well understood. Photons will cause desorption through DIET similarly to low-energy electrons, and the photon energy flux is comparable or greater than the particle flux in certain regions of the Solar System. For instance, the UV-C (4.4 eV to 12.4 eV) energy flux at Jupiter is about twice the energy flux from magnetospheric plasmas (Madey et al. 2002). Desorption induced by photons has many of the same properties as that induced by charged particles. Desorption usually occurs through excitation to an electronic state followed by energy transfer into vibrational modes in a solid (Avouris et al. 1989). Further work is necessary to determine photon desorption yields, especially as a function of wavelength and temperature.

Sputtering from mixed ices is also not well understood. The yields of species as a function of their concentration in an ice matrix, as well as the temperature and energy dependence of the process, needs to be determined. This is especially important for larger organic molecules trapped in ices. Since sputtered molecules may leave a surface with significant velocities, it may be possible to detect them during spacecraft flybys. *This would enable a direct measurement of surface composition.* Thus, additional data on the fragmentation and velocity distribution of larger organic species sputtered from ice is a priority.

#### **4. Nature of the measurements required**

The experiments necessary to explore the phenomena described here require similar methods of investigation. Generally, films of ice are created at cryogenic temperatures on substrates under high or ultrahigh vacuum conditions ( $10^{-8}$  to  $10^{-10}$  torr). These films are interrogated using a variety of analytical techniques. Optical spectroscopy is perhaps the most-utilized technique, with the infrared region from 2 to 20  $\mu\text{m}$  favored for its ability to clearly reveal changes in chemical structure and composition. As well, near-IR studies can provide direct correlations between icy samples and observations of planetary surfaces obtained via remote sensing.

Mass spectrometry is also a workhorse technique, especially for studies involving sputtering and desorption. Mass spectrometry enables a direct analysis of the molecules and fragments released from an irradiated surface, and specialized techniques can provide information on the velocity of the ejected particles.

Like most experiments, there are high initial costs associated with acquisition of the necessary equipment. In addition, the highly quantitative work needed will require a large investment in time. Careful quantitation of the rates, yields, and cross-sections relevant to chemical and physical processes in icy surfaces will rely on numerous repetition and calibration experiments that require many man-hours to complete.

Detailed computational modeling efforts will be needed to maximize the use of the data obtained through experiments. This will lead to a greater understanding of the processes occurring in planetary ices, and is crucial to advancing our understanding of surface composition. Astrobiological investigation will benefit in particular. Search strategies for biomarker compounds in icy environments, such as Europa, require a detailed knowledge of the chemistry that occurs in these environments.

### 5. Recommendations

- Increased funding should be available for experimental efforts that make quantitative measurements of the production and destruction rates of molecules exposed to appropriate fluxes of particle and photon radiation, reaction rates between radiolytic products in icy matrices, and diffusion rates of species at relevant planetary temperatures. In particular, measurements of reactive species, such as radicals, and wavelength-dependent photochemistry and energy-dependent radiation chemistry are needed.
- Detailed theoretical modeling in conjunction with the experimental efforts above should be performed to better explore and apply the new data.
- Measurements of sputtering yields, fragmentation patterns and velocity distributions of sputtered molecules are necessary, and are crucial for planning future missions to icy bodies.
- We also recommend stronger programmatic ties between NASA laboratories and universities to address these problems.

### 6. References

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