

Radiolysis and Photolysis of Icy Satellite Surfaces: Experiments and Theory

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Abstract The transport and exchange of material between bodies in the outer solar system is often facilitated by their exposure to ionizing radiation. With this in mind we review the effects of energetic ions, electrons and UV photons on materials present in the outer solar system. We consider radiolysis, photolysis, and sputtering of low temperature solids. Radiolysis and photolysis are the chemistry that follows the bond breaking and ionization produced by incident radiation, producing, e.g., O₂ and H₂ from irradiated H₂O ice. Sputtering is the ejection of molecules by incident radiation. Both processes are particularly effective on ices in the outer solar system. Materials reviewed include H₂O ice, sulfur-containing compounds

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(such as SO_2 and S_8), carbon-containing compounds (such as CH_4), nitrogen-containing compounds (such as NH_3 and N_2), and mixtures of those compounds. We also review the effects of ionizing radiation on a mixture of N_2 and CH_4 gases, as appropriate to Titan's upper atmosphere, where radiolysis and photolysis produce complex organic compounds (tholins).

Keywords Radiolysis · Photolysis · Sputtering · Tholins · Ices

1 Introduction

This chapter describes the effects of ultraviolet and ionizing radiation on materials in the outer solar system, from the erosion and modification of icy surfaces to the production of aerosols in Titan's atmosphere. Although there have been a number of reviews of radiation effects, we emphasize the signatures in reflectance spectra that indicate radiation-induced modifications. We also describe the importance of radiation in producing gas phase species which can populate the neutral and plasma tori that are so important to inter-satellite exchange processes. The exchange processes mentioned here are described in detail in Krupp et al. (2010, this issue) and Burger et al. (2010, this issue).

When the ionizing radiation consists of energetic ions, electrons and very energetic photons, the processes induced are often referred to as radiolysis, whereas photolysis typically refers to the effect of UV photons. Radiolysis and photolysis may be broadly defined as the chemistry that follows the breakup of molecular bonds. The incident radiation ionizes and fragments the molecules; the resulting radicals can then diffuse and react to form new species in non-equilibrium processes. Such reactions are often followed by the release of energy and sputtering, the ejection of molecules from the surface. Although the studies of radiolysis and photolysis have been of interest since the discovery of radiation sources, particularly as it relates to biology (health physics), the study of the radiation effects in *ices* increased following the experiments of Brown, Lanzerotti and coworkers on radiation processes relevant to the icy bodies in the outer solar system (e.g., Lanzerotti et al. 1978).

The effects seen in laboratory irradiation of low-temperature condensed-gas solids (H_2O , SO_2 , CO_2 , etc.) were often observed on solar system bodies, particularly the icy surfaces of outer planet moons. Reflectance spectra of some water ice surfaces exhibited the presence of common radiolytic products such as trapped H_2O_2 , O_2 and O_3 , and tenuous radiation-induced O_2 atmospheres are common. Sulfur and carbon containing surfaces showed the expected radiation-induced darkening.

Sputtered molecules are often ionized and “picked up” by the local magnetic fields. Since the plasma so formed can diffuse throughout the magnetosphere, material from one body can be implanted in a neighboring body. Sulfur from Io populates the Jovian magnetosphere and may contribute to the sulfur signature on Europa's trailing hemisphere (Lane et al. 1981; Carlson et al. 2009). The description of such processes has led to considerable experimental and modeling efforts both in the planetary science and the radiation effects communities. Using earlier reviews, this effort is summarized here with an emphasis on the implications for exchange processes.

2 Water Ice Radiolysis

Following the discovery of Jovian decametric radiation and the Pioneer mission Jupiter flybys it became clear that the ice-covered moons of Jupiter were imbedded in a relatively intense, by space standards, flux of ions and electrons. This inspired a series of

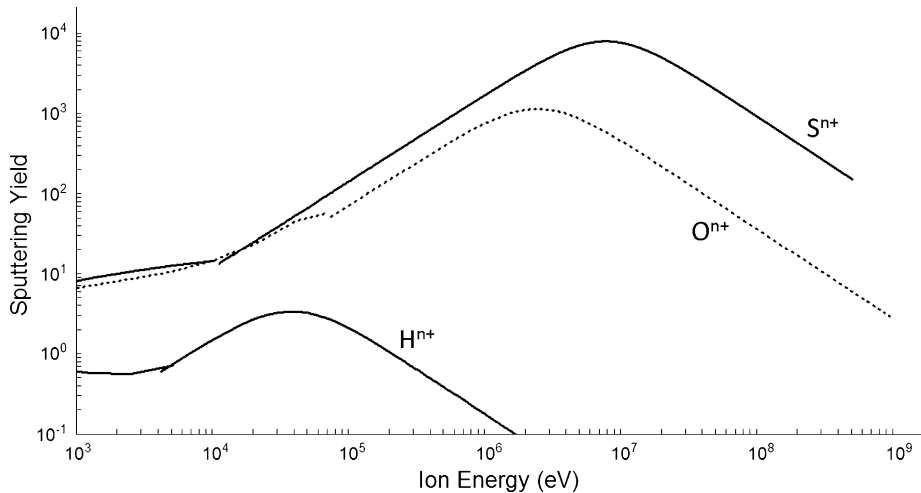


Fig. 1 Water ice sputtering yields (number of equivalent H_2O molecules ejected per incident ion of a given energy) for various ions for $T \lesssim 100$ K. Adapted from Johnson et al. (2009). Below ~ 80 K H_2O dominates the ejecta; with increasing temperature O_2 and H_2 become a large fraction of the ejecta

experiments on energetic plasma ion irradiation of low temperature water ice. *Sputtering*, the ejection of molecules from the surface due to incident radiation, was found to be orders of magnitude larger than predicted (Brown et al. 1978). The incorrect predictions were based on a theory that modeled collisions between molecules (“knock-on collision cascades”) whereas fast ions traveling through a condensed-gas solid, such as H_2O ice, primarily deposit energy as a track of electronic excitations and ionizations. Although there have been a number of reviews of the radiation effects in ice (e.g., Johnson 2010; Baragiola 2003) we describe the principal results as they apply to material transport and as a guide to understanding the subsequent descriptions of more complex ices.

One of the principal measurements relevant to the exchange of materials between outer Solar system bodies is the sputtering yield, the number of molecules ejected per incident ion. Sputtering yields for ions found in the outer planet magnetospheres (H^+ , O^+ and S^+) are given in Fig. 1, which shows semi-empirical fits to a large body of experimental data. Note that the sputtering yield can be as large as $\sim 10^4$ H_2O (for ~ 100 MeV S^+).

The principal sputter products from condensed gases are whole molecules and not radicals, atoms or ions, as is the case for the more extensively studied metallic and ionic solids. At low temperatures water molecules are the dominant sputter product of water ice, but the incident radiation also chemically alters the ice to produce, among other products, molecular hydrogen and oxygen which can dominate the sputtering yield at high temperatures ($T \gtrsim 120$ K). It is now generally agreed that the radiolysis of ice by energetic ions, electrons and solar UV photons produces the oxygen, ozone and peroxide seen at many icy satellites.

Any H_2 formed in ice diffuses and escapes much more efficiently than O_2 at the relevant temperatures in the outer solar system, and, in turn, escapes from the icy moons because of their relatively weak gravitational fields. Therefore the irradiation can preferentially populate the magnetosphere with hydrogen, as is the case at Europa (Lagg et al. 2003; Mauk et al. 2003), leaving behind an oxygen-rich satellite surface (e.g., Johnson et al. 2009).

Extensive laboratory studies of the irradiation of water ice have been carried out using incident electrons, UV photons and a large range of ion energies and types (see Johnson 2010).

In these experiments the ice samples and ejecta are monitored as a function of different radiation doses, incident radiation types, energies and sample temperatures. The sputtering yield is typically monitored via the change in sample thickness (measured by, e.g., microbalance gravimetry) while the identity of the sputter products is determined through mass spectrometry.

Though differing quantitatively, depending on the radiation type and energy, the results are qualitatively the same. Incident ions and electrons, which produce multiple ionizations, promptly eject H_2O so that the sputtering of water molecules is independent of dose (time-integrated number of ions or electrons incident per unit area), but the production of gas phase O_2 starts at zero and grows with fluence, eventually reaching a steady state. The other major product of H_2O irradiation is H_2 , which, though ejected promptly, eventually is lost from ice stoichiometrically in a 2 to 1 ratio with O_2 . The observed O_2 fluence dependence may result from a two-step process: precursor species are created by the incident radiation from which subsequent radiation ejects O_2 . The yield of O_2 produced from vapor deposited ice samples depends on the temperature and radiation dose, but not the dose rate (Reimann et al. 1984; Teolis et al. 2005). The temperature dependence reveals an activation energy; the yields increase with temperature according to the formula: $Y = Y_o + Y_a \exp(-E_a/kT)$, where the activation energy E_a is on the order of 0.05 eV. Y_o is the portion of the sputtering yield that is independent of temperature (primarily due to the ejection of H_2O) and the temperature dependent component Y_a is primarily associated with loss of O_2 and H_2 .

Although laboratory data on the radiolysis and photolysis of ice is now extensive, the chemical pathways are not yet agreed upon. Whereas the principal dissociation process in ice, as in liquid water, is dissociation to form H and OH, the dominant gas phase species ejected from irradiated ice are those with the lowest binding energies (H_2 , O_2 and H_2O). These ejecta are the end result of reactions among the many other species produced; e.g., H_2O_2 , HO_2 and O have all been suggested as precursor species for the formation of O_2 (Laffon et al. 2006). For strongly ionizing particles, such as magnetospheric heavy ions, O_2 itself can be considered a precursor species: radiation-damaged ice traps the radiolytically produced O_2 , which is only released as the ice itself is sputtered away (Teolis et al. 2005, 2009).

Since hydrogen is preferentially lost at the relevant temperatures, oxygen-rich molecules are the principal trace species trapped in the irradiated surface. In addition to the observation of gas-phase oxygen, solid-state O_2 was inferred by the signature of interacting pairs of O_2 molecules in the reflectance spectra of Ganymede (Calvin et al. 1995), Europa and Callisto (Spencer and Calvin 2002). The two signature absorptions for dimer O_2 , at 577.2 nm and 627.5 nm, respectively (Vidal et al. 1997; Cooper et al. 2003b), suggested that the O_2 is locally dense though the band shapes and relative band depths are distorted from solid or liquid O_2 . The presence of O_2 in the solid state at these temperatures is surprising, given O_2 's volatility. Although O_2 can diffuse out of unirradiated H_2O ice in laboratory experiments at relevant planetary temperatures (<150 K), radiolytically-produced O_2 can be trapped in radiation-damaged ice at up to 155 K (e.g., Teolis et al. 2009). The trapping appears to occur in radiation-induced defects that coalesce to form voids in ice (Johnson and Jessor 1997; Loeffler et al. 2006).

Related to the oxygen observations, the Hartley band of O_3 was tentatively identified in the ultraviolet (UV) reflectance spectra of Ganymede and in the icy satellites of Saturn (Noll et al. 1997), although the band shape suggests additional absorbing species may be present. The O_3 is likely formed in the O_2 voids described above (Johnson and Jessor 1997); however, O_3 is not observed on pure ice irradiated in vacuum except when irradiation and H_2O vapor deposition occur simultaneously (Teolis et al. 2006). The O_3 -like feature is superimposed

on a very broad UV absorption shortward of $0.4\ \mu\text{m}$ seen on most of the icy satellites. The broad UV absorption has been attributed to another radiolytically-produced oxidant, H_2O_2 (Carlson et al. 1999a), but may also include absorption by trapped HO_2 and OH (Johnson and Quickenden 1997). Identification of specific radiolytic products in the UV is difficult because the bands are very broad and overlap, but H_2O_2 has been detected via infrared absorption on Europa (e.g. Carlson et al. 2009). H_2O_2 is produced by the principal dissociation product OH in the absence of H (e.g., Laffon et al. 2006).

Although the identifications of the radiolysis and photolysis products (OH , H_2O_2 , O_2 , O_3) are uncertain, the reflectance spectra taken as a whole give a fairly clear picture. The irradiated surfaces of the icy solar system bodies contain trapped molecules that would be expected from radiolysis or photolysis of ice. Consistent with this, oxygen-rich molecules in ice containing trace amounts of sulfur (SO_2 and a sulfate) and carbon (CO_2 and a carbonate) have been identified as well a dark feature consistent with the degradation of organics ice (Hendrix and Johnson 2008) as discussed in later sections of this chapter.

What is most important for the exchange of material between bodies are the radiation-induced chemical processes that eject molecules from the surface. Unfortunately, laboratory data on ejecta energy are sparse to non-existent, so that new results are urgently needed. Reimann et al. (1984) measured the energy spectra of sputtered D_2O for several incident ion energies and Haring et al. (1984) measured the energy spectra of sputtered H_2 and O_2 for several incident ions (Ar^+ , He^+ , H^+). The H_2O energy spectrum is clearly non-thermal and usually fit, for convenience, to a standard sputter distribution $2UE/(E+U)^3$, where E is the sputter product energy, and U is an “effective binding energy” of $0.055\ \text{eV}$ (much less than the actual H_2O binding energy of about $0.45\ \text{eV}$). The spectra of the H_2 and O_2 are primarily thermal, consistent with their diffusion from ice, but also have small high energy tails consistent with non-thermal contributions. When considering escape energies from a regolith, the ejecta energy spectra are also modified by collisions with neighboring grains (Cassidy and Johnson 2005).

3 Sulfur Compound Radiolysis

Water ice is the most abundant compound in the near-surfaces of outer solar system objects, it is the “rock” of the outer solar system, but other compounds are responsible for much of the outer solar system’s character, from the multicolored surface of Io to the dark regions of icy moons that come in a bewildering variety patterns (e.g. Iapetus). The rest of this chapter is devoted to these other compounds, beginning with radiolytic chemistry of sulfur. Sulfur is a common element in the solar system, with a cometary molar abundance relative to H of $\sim 1\%$ (Anders and Grevesse 1989). This is comparable to the relative abundances of nitrogen and silicon ($\sim 4\%$ and 2.5% , respectively), so it is not surprising that sulfur compounds are found in the surfaces and atmospheres of planets, satellites, and comets.

The phase and chemical composition of these sulfur compounds are diverse and related to major planetary features and processes, in part because many sulfur compounds are highly volatile. For example, Venus’s pervasive clouds are composed of sulfuric acid droplets produced from the photolysis of gaseous sulfur dioxide and carbonyl sulfide, while gaseous native sulfur may be present in Venus’s hot lower atmosphere. Volcanoes on Jupiter’s moon Io emit enormous amounts of elemental sulfur and sulfur oxides. Condensed sulfur and sulfur dioxide ice are present on both Io and its neighboring satellite Europa, while the latter also exhibits sulfate compounds, derived perhaps from a subsurface ocean. The outer planets’ atmospheres contain hydrogen sulfide gas and their clouds are thought to contain

hydrosulphides and possibly sulphides that may provide the unknown pigments that color these atmospheres (Coustenis et al. 2010, this issue).

Depending on the particular environment—gaseous or condensed, oxidizing or reducing—different sulfur compounds are found or expected. While numerous radicals and reactive molecules are produced during photon or energetic particle excitation, as in the case of water ice, the most stable and abundant end products will be closed-shell molecules. In the following paragraphs we briefly describe some relevant sulfur compounds and their photolytic and radiolytic chemistry. Summaries of sulfur properties relevant for Io and Europa are given in Carlson et al. (2007, 2009).

The most stable form of elemental or native sulfur is the octahedral molecule S_8 , which is shaped like a puckered or crown-like ring. Sulfur rings (cyclo-S) exist with five to twenty or more sulfur atoms. Small sulfur molecules, S_2 , S_3 and S_4 form chains (catena-S), while molecules with five or more atoms can form chains or rings, with rings generally being more stable. Condensed mixtures of sulfur rings and chains, termed polymeric sulfur, are produced by thermal, photolytic, or radiolytic processes and can exhibit a variety of colors ranging from yellow to red, orange, and black, and even green and purple; Moore (1984) irradiated white, cryogenic, SO_2 with energetic protons and found that irradiation darkened the sample and produced different colors for different sample temperatures. The ultraviolet and visible spectrum can be used to indicate the amount of polymerization and the transient presence of tetrasulfur, S_4 . High-temperature gaseous sulfur contains small rings, chains, and S_2 , S_3 , and S_4 .

As discussed above, radiolysis tends to oxidize icy satellite surfaces through the production and loss of H_2 . Under these conditions, the stable sulfur-containing molecules are expected to be sulfates, sulfur dioxide, and elemental sulfur (as opposed to reducing compounds such as H_2S). In the presence of water, sulfate is likely present as sulfuric acid ($H_2SO_4 + H_2O$ or dissociated into its ions $H_3O^+ + SO_4^{2-}$). The clouds and atmosphere of Venus, for example, contain sulfuric acid, SO_2 , and probable polymeric sulfur.

Irradiation of S_8 grains in H_2O ice produces sulfuric acid (Carlson et al. 2002), similar to the irradiation of sulfur grains in H_2O liquid (DellaGuardia and Johnston 1980; Donaldson and Johnston 1971). It is observed through the presence of its components: the hydronium cation (H_3O^+) and the sulfate anion (SO_4^{2-}). Continued irradiation destroys the previously made sulfate anions to produce SO_2 (Hochanadel et al. 1955), elemental S, and, based on results from irradiated Li_2SO_4 (Sasaki et al. 1978), possibly H_2S . Proton irradiation of SO_2 in H_2O ice also yields sulfuric acid (Moore et al. 2007). When annealed, various hydrates of sulfuric acid ($H_2SO_4 \cdot nH_2O$) are formed. In radiolytic equilibrium, when there is as much sulfuric acid destroyed as that being produced, the proportions of S_n , SO_2 , and H_2SO_4 will become constants that depend on the initial sulfur to water ratio (Carlson et al. 1999, 2002, 2009; Moore et al. 2007). This is called the radiolytic sulfur cycle. Relevant rates are summarized in Johnson et al. (2004). Similar results are obtained by the photolysis of SO_2 in H_2O ice (Schrivver-Mazzuoli et al. 2003).

Relevant exchange processes occur at Europa where sulfur is likely delivered to the water ice surface by two exchange processes: plasma implantation of sulfur ions (ultimately derived from neighboring Io) and sulfate salts from geological processes that deliver briny water from the subsurface ocean. The intense bombardment of electrons and ions transforms these compounds into the S_n , SO_2 , and H_2SO_4 of the radiolytic sulfur cycle, hiding their original identity and complicating interpretation of the surface reflectance spectra (see Chap. X). Implantation of sulfur ions in H_2O ice does not make SO_2 directly, but instead produces H_2SO_4 (Strazzulla et al. 2007). Upon continued irradiation, the H_2SO_4 is decomposed, producing SO_2 (Moore et al. 2007).

If the initial material is from sulfate salts, the presence of the metal cation increases the number of chemical pathways so that metal oxides and hydroxides are possible. If, for example, one started with $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (epsomite), then one expects $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$, MgO , $\text{Mg}(\text{OH})_2$, $\text{MgS} \cdot n\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$, S_μ , and SO_2 (Johnson 2001). The product yields are not well known and more experimental work is needed in this area.

In reducing environments such as the atmospheres of the giant planets, hydrogen sulfide (H_2S) is the dominant form. At about 200 K, ammonia (NH_3) and H_2S condense to form the molecular solid ammonium hydrosulfide (NH_4SH). Ultraviolet photolysis of NH_4SH , which exists as a cloud layer in the giant planet atmospheres, produces ammonium sulfide and ammonium polysulfide, $(\text{NH}_4)_2\text{S}$ and $(\text{NH}_4)_2\text{S}_n$, respectively. H_2S can be photo-dissociated by ultraviolet radiation with wavelengths $\lambda < 0.314 \mu\text{m}$ (Huebner et al. 1992), so photolysis of Jupiter-like mixtures of gaseous H_2S , NH_4 , and H_2 will likely produce similar compounds and perhaps native sulfur and sulfanes (sulfur chains with terminal hydrogen atoms, HS_nH). These compounds could account for some of the red, yellow and brown hues of Jupiter's clouds (Taylor et al. 2004).

4 Carbon Compound Radiolysis

Like sulfur, carbon is an important and abundant compound on the surfaces and in the interiors of many outer solar system bodies. The radiolysis of carbon compounds, however, has added significance in the context of astrobiology. Exchange of radiolytically processed carbon compounds with liquid water in the sub-surface of icy worlds could be critical to their habitability (Hand 2009).

The photolysis and radiolysis of carbon-containing compounds and their mixtures with H_2O have many similarities with sulfur. As with sulfur compounds, irradiation of hydrocarbons tends to darken them. In addition, carbon may undergo a radiolytic cycle analogous to the radiolytic sulfur cycle, with carbonic acid and CO_2 replacing sulfuric acid and SO_2 . Gomis and Strazzulla (2005) demonstrated this by irradiating thin H_2O films on two different complex, refractory organics with a variety of ions and found a buildup of about a monolayer of CO_2 (see also Mennella et al. 2004). Evidence for radiolytic CO_2 production is seen throughout the outer solar system. Hibbitts et al. (2000) suggested that the CO_2 abundance in Callisto's dark terrains follows the bulls-eye pattern of magnetospheric plasma impact, and Grundy et al. (2006) found the same for several of Uranus' moons. The CO_2 is presumed to be in the solid state, which is surprising given its volatility (Sandford and Allamandola 1990). Radiation-induced defects may trap the CO_2 , as discussed for O_2 above.

Irradiation of pure hydrocarbons produces dark, refractory material (e.g., Strazzulla et al. 1995). H_2 is a primary radiation product that easily escapes both solids and gravitational wells, leaving behind polymerized carbon compounds. The simplest example of this is the irradiation of CH_4 (Lanzarotti et al. 1987): cleavage of the H from CH_4 leaves behind the radicals H and CH_3 . CH_3 can combine with an adjacent CH_3 to form C_2H_6 , and the H with another H to produce H_2 . The escape of H_2 and further bond breaking leads to larger polymers (Bennett et al. 2006). The redness of some outer solar system objects might result from the photolysis and radiolysis of small hydrocarbons in icy surfaces (Trilling and Brown 2000). Though the production of refractory organic material in irradiated ices in the laboratory is well documented (see e.g. Khare et al. 1989; Bernstein et al. 1995; Moore and Hudson 1998), the production of dark, refractory organics on the surfaces of icy worlds may, at a minimum, require an initial ice composition of simple organics at relatively

high concentration ($>10\%$ by number abundance). For instance, radiolytically and photolytically processed ices containing only CO_2 and H_2O do not form hydrocarbons as efficiently (Hand et al. 2007).

Experiments at astrophysical temperatures ($\sim 5\text{--}20\text{ K}$) have also shown that formaldehyde (H_2CO) is a minor product during ion and UV irradiation of CO_2 -rich ices (Gerakines et al. 2000; Brucato et al. 1997; Moore et al. 1991). The predominant carbon-bearing products under such conditions were CO and carbonic acid, H_2CO_3 . Similarly, Hand et al. (2007) found carbonic acid and carbon monoxide to be the primary products of electron radiolysis of H_2O and CO_2 ices at temperatures comparable to those found on the icy Jovian and Saturnian moons. Starting with a $\sim 30\%$, by number abundance, of CO_2 in water ice they found that $\sim 97\%$ of the evolved carbon remained as CO_2 or went into CO or H_2CO_3 . No definitive signature of H_2CO , CH_3OH , or even CH_4 was found, though growth of features at 2044 cm^{-1} and 1878 cm^{-1} , may indicate production of the CO_3 radical (Moore et al. 1991).

Figure 2 shows the spectra of CO_2 and H_2O ice at 90 K before and after irradiation by 10 keV electrons with cumulative dose of $\sim 2 \times 10^{21}\text{ eV cm}^{-2}$ (the figure was adapted from Hand et al. 2007). The strong lines that emerged during irradiation are indicated at 2570 , 2141 , 1714 , 1485 , 1380 , and 1298 cm^{-1} . The 2340 cm^{-1} and 2278 cm^{-1} bands show persistence of CO_2 in the irradiated ice and the feature at 2141 cm^{-1} indicates production of CO. The formation of H_2CO_3 is indicated by the combination of the remaining bands (Brucato et al. 1997; Moore and Hudson 1998; Gerakines et al. 2000). Hand et al. concluded that upper limits for H_2CO , CH_3OH , and CH_4 production are $\sim 0.5\%$ by number of the remaining, or observed, CO_2 . For bodies such as Europa, where CO_2 has been observed but where no organics have yet been observed, this has important consequences for geological exchange processes that could bring irradiated surface material to the subsurface ocean, and thus to a possible ecosystem (Chyba 2000). Chyba and Phillips (2002) argued that an ecosystem in a sub-surface ocean on Europa could be powered solely by radiolytically produced H_2O_2 and H_2CO delivered from the surface ice. The astrobiological aspects of exchange processes are considered in greater detail in Raulin et al. (2010, this issue).

5 Nitrogen Compound Radiolysis

NH_3 ice is present, though not common, on the outer planet moons (see summary in Moore et al. 2007). It is more common on trans-Neptunian objects. The reason for this seems to be its volatility and susceptibility to decomposition by radiation. The sputtering yield (number of molecules ejected per incident ion) of pure NH_3 ice is an order of magnitude larger than it is for water ice (Lanzerotti et al. 1984).

The main sputter products are NH_3 , N_2 and H_2 and, as with the sputtering of H_2O , the relative amounts depend on the incident ion used, its energy, and the ice temperature. If ions transfer energy via mainly elastic collisions (knock-on sputtering, as opposed to electronic sputtering), then the principal sputter product is NH_3 . This is the case for the $\sim\text{keV}$ Ar^+ ions used by Haring et al. (1984). However, if the ions have a significant electronic component, like the $\sim\text{MeV}$ ions used by Lanzerotti et al. (1984), then the H_2 and N_2 are the dominant ejecta (Haring et al. 1984). Thus the high sputtering yield observed is likely explained by the rapid decomposition of NH_3 into more volatile species. Infrared transmission studies on the decomposition of NH_3 via ion irradiation (Strazzulla and Palumbo 1998) are consistent with these findings. UV photolysis of NH_3 also produces N_2H_4 and H_2 , as identified by IR spectroscopy (Gerakines et al. 1996). An absorption at 1505 cm^{-1} has been identified as either NH_2 (Gerakines et al. 1996) or NH_4^+ (Moore et al. 2007).

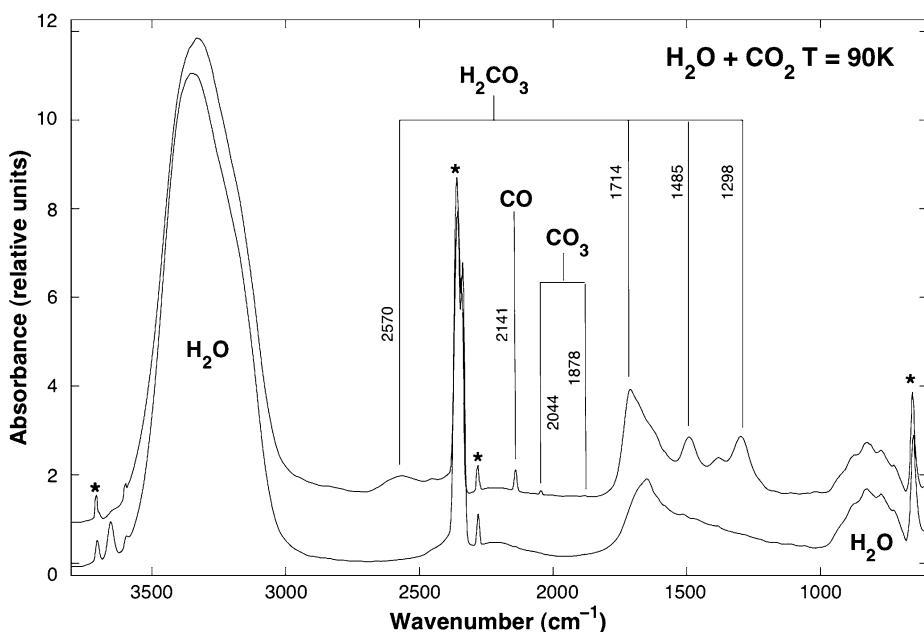


Fig. 2 Electron radiolysis of CO₂ + H₂O ices at 90 K. The film was deposited at 50 K and then warmed to 90 K. The bottom spectrum shows the ice before irradiation while the upper spectrum shows the ice after irradiation. The peaks marked with *asterisks* are CO₂ bands. This figure was reproduced from Hand et al. (2007)

Observed NH₃ is usually identified as a hydrate, a stoichiometric mixture of H₂O and NH₃. The effect of ion irradiation of ammonia-water mixtures has been studied using infrared spectroscopy to monitor the loss of the ammonia absorption feature at either 4523 cm⁻¹ ($\nu_1 + \nu_2$) or 1115 cm⁻¹ (ν_2) (Strazzulla and Palumbo 1998; Loeffler et al. 2006; Moore et al. 2007) and using mass spectroscopy to monitor the composition of the species sputtered during irradiation and thermal desorption (Loeffler et al. 2006). Infrared spectroscopy showed that ammonia radiolytically decomposes faster at 80 K than at 10 K (Strazzulla and Palumbo 1998; Moore et al. 2007); specifically Strazzulla and Palumbo (1998) showed that 30 keV He⁺ ions decreased the ammonia-water ratio from 0.6 to 0.3 at 10 K and from 0.4 to 0.15 at 80 K. Moore et al. (2007) found that ammonia decomposes faster in a matrix of water ice than when it is pure. Loeffler et al. (2006) irradiated a 2:1 H₂O NH₃ mixture with 100 keV protons and found a peak sputtering yield ~ 110 molecules/ion (assuming mass = 17 amu) at a fluence of $\sim 3 \times 10^{15}$ ions/cm², with the yield first increasing and then decreasing with ion dose. This fluence dependence is related to the formation of new species formed in the ice and the destruction of NH₃. Other species detected via infrared spectroscopy, which are estimated to be minor compared to the H₂ and N₂, are NO (20 K; 1871 cm⁻¹) and N₂O (120 K; 2225 cm⁻¹). The sputtered flux ejected from the ammonia-water sample, judging from mass spectrometry, is mainly N₂ and H₂.

N₂ is another volatile solid component of the outer solar system. Neptune's moon Triton, for example, has abundant N₂ ice (Quirico et al. 1999). Gerakines et al. (1996) performed UV photolysis of solid N₂ at 10 K with photons from a hydrogen discharge lamp. After irradiation, they detected a shoulder on top of a stronger CO infrared absorption feature (from background contamination) and tentatively identified it as the N₃ radical. In more recent

experiments, Moore and Hudson (2003) irradiated solid N_2 ice with 0.8 MeV protons and UV photons. However, the N_3 radical (1657 cm^{-1}) was only observed after ion irradiation and not photolysis. Strazzulla et al. (2003) irradiated $N_2:H_2O$ mixtures with 60 keV Ar^{++} at 20 K and found the formation of NO, NO_2 , and N_2O .

Strazzulla et al. (2003) implanted water ice with 15 keV N^+ to see if any new nitrogen species (N_xO_y) would form, just as implantation of S^+ in water ice can produce S-O compounds (see earlier section). After a fluence of 4.2×10^{16} ions/cm², they detected no new species, other than hydrogen peroxide, which could be expected for *any* projectile. In recent unpublished experiments Loeffler and coworkers implanted 100 keV N^+ and N_2^+ into water ice at 80 K and looked for nitrogen species. After irradiating to a fluence of 2×10^{16} ions/cm², they also detected only hydrogen peroxide.

Cottin et al. (2003) performed UV photolysis on pure NH_3 and NH_3 in mixtures of water and nitrogen. Interestingly they found that the destruction of pure NH_3 and NH_3 mixed in water was similar, while the destruction of NH_3 mixed in N_2 actually increased by a factor of seven compared to pure NH_3 . The latter result is intriguing, because the N_2 was transparent to the UV lamp and thus was thought to play no direct role in the radiation chemistry.

Since the transfer of materials between solar system bodies often requires that they be driven into the gas-phase, NH_3 radiolysis and photolysis is of interest as NH_3 might enhance cryovolcanism by suppressing the freezing point of water. The identification of such a process is made difficult by the efficient destruction of NH_3 by plasma and UV photons. Further, unlike sulfur and carbon compounds, but much like H_2O , radiolytic destruction of NH_3 does not produce refractory byproducts. NH_3 has been theorized to play a role in the outgassing of Enceladus (see Sohl et al. 2010, this issue). Although initially difficult to detect (Emery et al. 2005; Verbiscer et al. 2006) its presence has been confirmed (Smith et al. 2008; Waite et al. 2009).

6 Tholins: Photolysis and Radiolysis in Titan's Upper Atmosphere

So far we have discussed the effects of ionizing radiation on ices, as appropriate for the nearly airless moons of the outer solar system, but at Titan it is *gases* that absorb the incident radiation. While ionizing radiation tends to produce gas from solids, it tends to produce solids from the gases of Titan's atmosphere. The transformation from simple molecules (CH_4 , NH_3 , N_2 , CO, CO_2 , H_2O ...) to more complex compounds appears to be a key step in the context of planetary atmosphere evolution. Such transformations may have happened in the reducing atmosphere of the early Earth (Chyba and Sagan 1991; Kobayashi et al. 1998).

Titan's atmosphere consists of mainly N_2 (95% to 98.5% depending on the altitude), CH_4 (5% to 1.5%) and H_2 . As with the solid-state radiolysis described above, the destruction of carbon-hydrogen bonds tends to result in more complex molecules such as HCN, C_2H_2 , C_2H_4 , C_2H_6 . As radiolysis continues, bigger molecules, known as aerosols or, more specifically, "tholins",¹ are formed. These aerosols form a planet-wide haze that gives Titan's atmosphere its characteristic orange colour. This section describes what *in situ* and laboratory studies have revealed about these aerosols.

Sagan and Thompson (1984) made the first estimates of energy deposition in the atmosphere of Titan as a function of altitude. They showed that the short wavelength

¹The name "tholins" proposed by Carl Sagan refers to any *complex organic solid produced from cosmically abundant molecules*.

(<150 nm) solar ultraviolet light is mainly absorbed by N_2 and CH_4 at high altitudes, producing free radicals that initiate chemistry. Wilson and Atreya (2004) correlated the escape of hydrogen produced by photolysis of CH_4 in Titan's upper atmosphere with the formation and precipitation of aerosols. Early work estimated that the aerosols were formed at altitudes of several hundred km, but Cassini's Ion and Neutral Mass Spectrometer INMS team found that aerosol formation begins at much higher altitudes (~1000 km). The observed organic mix strongly implies a series of chemical reactions and physical processes that lead from simple molecules (CH_4 and N_2) to larger, more complex molecules (80 to 350 daltons) to negatively charged massive molecules (~8000 daltons), which are identified as aerosols (Waite et al. 2007).

Besides photolysis, other forms of radiation also contribute to the radiation chemistry of Titan. Titan orbits most of the time within Saturn's magnetosphere, and the magnetospheric plasma can easily dissociate molecules. The magnetosphere is also a source of O atoms which are ultimately derived from Enceladus' outgassing of H_2O (Hartle et al. 2006). The addition of O could affect tholin formation chemistry (e.g., Sittler et al. 2009). When Titan is outside Saturn's magnetosphere, the solar wind and galactic cosmic rays bombard the atmosphere. These penetrating particles ionise species in the lower atmosphere, producing the primary ions N_2^+ and N^+ , and electrons. The nitrogen ions are rapidly converted, by their interaction with CH_4 molecules, into secondary ions and ion clusters. A simplified scheme of these main processes is shown in Fig. 3.

Another external source of energy possibly relevant to Titan is the plasma created during the influx of cometary material. This would have been important in Titan's early history, especially for the contribution of oxygen-bearing molecules to the atmosphere, but in the present day impacts are too infrequent to provide a significant supply of oxygen (Lorenz 1997).

The most accurate information about the properties of aerosols came from direct observation, first in the 1980s flybys of Titan by the Voyager mission, and most recently by the Cassini-Huygens mission (especially the Huygens probe, which descended into Titan's atmosphere in January 2005). Light propagation measurements suggest that the particles are a fractal arrangement of spherical particles (with an average diameter of 0.1 μm) (Tomasko et al. 2005). Huygens probe studies confirmed that the aerosols are solid and have an organic composition. Furthermore, the surface reflectance spectra of Titan (Tomasko et al. 2005) and the surface permittivity measurements (Fulchignoni et al. 2005) suggest that the aerosols coat the landing site surface. Despite these observations, our knowledge of the composition and structure of Titan's haze particles is limited. This is why it is necessary to use laboratory simulations of Titan's chemistry to study the processes that occur in this environment.

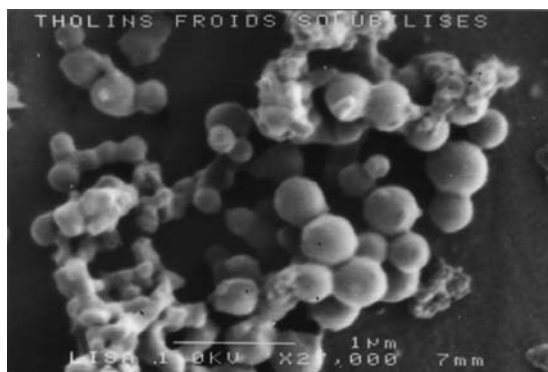
7 Laboratory Work

Analogues of Titan's tholin aerosols can, in principle, be synthesized in the laboratory to study their physical and chemical properties (Sagan and Khare 1979). A variety of experimental conditions have been used to synthesize tholins (e.g., Coll et al. 1999; Imanaka et al. 2004 and references therein). Differences between experiments include the radiation source (UV photons or plasma produced from electrical discharge), gas composition, temperature, and pressure. Figure 4 shows a laboratory-synthesized tholin aerosol.

Tholins are usually generated from N_2/CH_4 gas mixtures, the two major components of Titan's atmosphere. In experiments, the ratio of CH_4 to N_2 is usually varied from 2 to 50%. These variations do not affect the hydrogen content of the tholins, but seriously affect their

A complementary way to study the structure is pyrolysis coupled with gas chromatography mass spectrometry (GC-MS) to identify the fragments produced by thermal degradation. Compounds such as aliphatic hydrocarbons (propane, heptane, propene, butene, pentene...), nitriles (hydrogen cyanide, acetonitrile, propanenitrile, isobutanenitrile, crotonitrile...) and aromatics (benzene, pyrrole, toluene, imidazole, xylene, pyridine, pyrazine, benzonitrile, triazine) have been identified using this technique (Ehrenfreund et al. 1995; Khare et al. 1984; Coll et al. 1999). The main evolved products are unsaturated hydrocarbons, nitriles and

Fig. 4 Electron microscope view of a tholin aerosol analogue synthesized in a laboratory (Coll et al. 1999)



monoaromatic species including N-containing aromatics. However, it is important to note that a significant refractory fraction remains after pyrolysis, and thus remains undetected by the GC-MS. Further, some of the species detected could be formed *during* pyrolysis.

Trainer et al. (2004) provided additional information on the molecular composition of tholins using aerosol mass spectrometry, which flash vaporizes the aerosols after measuring their size. They identified PAHs (polycyclic aromatic hydrocarbons, with a maximum of 4 rings) and alkylated PAHs when high CH_4/N_2 ratios were used in the initial gas mixtures, and, when CH_4/N_2 was less than 0.5%, aliphatic structures, demonstrating that the aerosol-forming chemical pathways (aromatic versus aliphatic) are sensitive to the CH_4/N_2 ratio in the initial mixture.

Overall, tholin analogue experiments have produced two families of tholins. First, the family produced with *photochemistry* is characterized by low N content, organic polymers, aliphatic unsaturated chains and low or no aromatic content. Second, the family of tholins produced by electrical-discharge *plasma* is characterized by higher N content, organic oligomers, aromatic structures including N-heterocycles and aliphatic chains.

Aerosols in the lower atmosphere might interact with liquid water in episodic surface pools produced by cometary impact or by cryovolcanism. Somogyi et al. (2006) exposed tholins produced by AC plasma to hot liquid water with dissolved ammonia. They concluded that laboratory tholins are reactive enough with the water/ammonia mixture to generate oxidized solid material. If the aerosols of Titan's environment are from the same chemical family as Somogyi's tholins, they can be considered a potential starting material for several synthetic processes that can provide organic compounds of pre-biotic interest (Fig. 5).

Other simulations investigated acidic hydrolysis of plasma-generated tholins (Khare et al. 1986; Nguyen et al. 2007), hydrolysis at neutral pH (Raulin et al. 2007) and at low temperature (Neish et al. 2009). They produced amino-acids, such as glycine, β -alanine and aspartic acid, and urea. Such water-tholin interactions might not be possible, however: Tran et al. (2003) showed that photolytically-produced tholins are not soluble in most solvents, and McKay (1996) and Coll et al. (1999) concluded that plasma-produced tholins have very low solubility in liquid hydrocarbons (which have been detected on Titan's surface).

8 Conclusion

Radiation-induced processing of materials is an ubiquitous feature at outer solar system bodies. The satellites of the outer solar system are exposed to intense ionizing radiation over

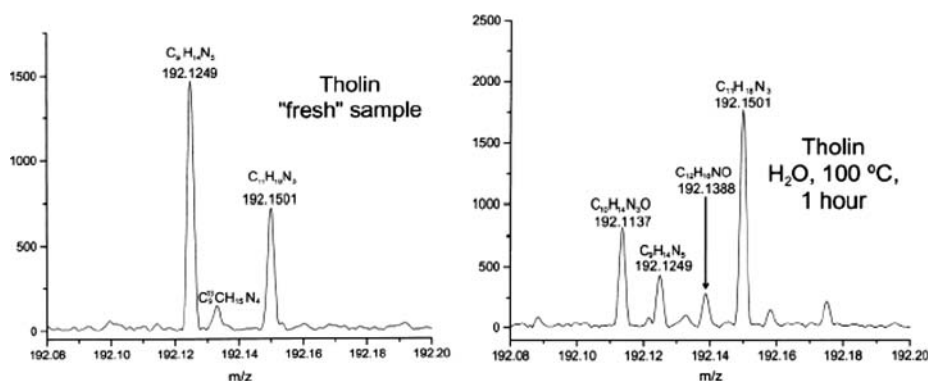


Fig. 5 Mass spectrum of a tholin (*left*). Mass spectrum after one hour of reaction with water (*right*). This investigation shows the integration of O atoms into the tholin ($C_{12}H_{14}N_3O$ on the left and $C_{12}H_{18}NO$ on the right). Hydrolysis reactions occur with rate constants of $2\text{--}10\text{ hour}^{-1}$ at room temperature. Adapted from Somogyi et al. (2006)

geologically long periods of time, producing volatiles from the solids and solid particulates from gases. Ions, electrons, and, to a lesser extent, UV photons, erode and chemically alter satellite surfaces. Although the affected layer is small ($<$ a few meters, the gardened layer), it is this layer that is sensed remotely. Therefore, inferring bulk properties from surface properties requires observers to understand the effects of radiolysis and photolysis. For instance, NH_3 reaching Enceladus' surface will be quickly converted to N_2 and H_2 by magnetospheric plasma and solar UV photons. Similarly, a definitive interpretation of the source of the sulfur on Europa has not been possible because material from the two proposed sources, the neighbouring moon Io or the sub-surface ocean, is radiolytically processed in a relatively short time period into materials that are spectroscopically similar. Radiolysis does more than just complicate planetary science, though. It is responsible for some of the exchange processes described in this issue. Materials driven into the gas phase can be ionized and transported by plasma diffusion to neighbouring bodies.

As discussed above, the effects of radiation of materials of interest in the outer solar system are primarily determined in the laboratory and then applied to the observations. However, there have been counter examples, as in the HST detection of solid-state oxygen trapped in irradiated ice before it was observed in the laboratory. Although analytic and computer models have been useful for extrapolating and interpreting laboratory data, there is a dearth of quantitative models. Even a problem as relatively simple as the sputtering of pure H_2O has not been accurately simulated. Therefore, for the foreseeable future, our understanding of the space weathering of outer solar system surfaces will rely heavily on extrapolations from experimental data.

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