# Sputtering of ices in the outer solar system

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Exploration of the outer solar system has led to studies in a new area of physics: electronically induced sputtering of low-temperature, condensed-gas solids (ices). Many of the icy bodies in the outer solar system were found to be bombarded by relatively intense fluxes of ions and electrons, causing both changes in their optical reflectance and ejection (sputtering) of molecules from their surfaces. The small cohesive energies of the condensed-gas solids afford relatively large sputtering rates from the electronic excitations produced in the solid by fast ions and electrons. Such sputtering produces an ambient gas about an icy body, often the source of the local plasma. This colloquium outlines the physics of the sputtering of ices and its relevance to several outer-solar-system phenomena: the sputter-produced plasma trapped in Saturn's magnetosphere; the  $O<sub>2</sub>$  atmosphere on Europa; and optical absorption features such as  $SO_2$  in the surface of Europa and  $O_2$  and, possibly,  $O_3$  in the surface of Ganymede.

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# I. INTRODUCTION

An exciting period of exploration of the outer solar system has been opened up by spacecraft, by orbiting telescopes, and by remarkably improved ground-based observations. These studies have revolutionized our understanding of this region of space, revealing worlds very different from ours, some of which are bizarre. Because of the low surface temperatures, typically <120 K, the ''rock'' of outer-solar-system bodies is water ice. That is, excluding the four giant planets, it is the structural and thermal properties of ice that determine the geology of the surfaces of many of the small objects from Jupiter's orbit and beyond (Burns and Matthews, 1986). Other more volatile molecular species, such as  $N_2$ ,  $O_2$ ,  $CO$ ,  $CO_2$ ,  $NH_3$ , and  $CH_4$ , form atmospheres and polar ices, or can cause the surface to be active. An interesting exception is Io, a moon of Jupiter, which does not have water ice. Owing to its tidal interaction with Jupiter, Io is volcanically active and has been desiccated, losing all of its water and other light volatiles. Because of this, frozen  $SO_2$ , a familiar, heavy volcanic gas on earth, covers Io's surface (Burns and Matthews, 1986; Spencer and Schneider, 1995).

Since most small outer-solar-system bodies, with the exception of Titan, have either no atmospheres or tenuous ones at best, their icy surfaces are exposed to the solar ultraviolet radiation and to the local plasma. These irradiations can alter such surfaces physically and chemically (Johnson, 1990). Since the Pioneer and Voyager spacecraft found that both Jupiter and Saturn had surprisingly intense plasmas (Fig. 1) trapped in their giant magnetic fields (Dessler, 1983), questions arose about the effect of the plasma bombardment on their icy moons.

Therefore, following the Pioneer encounters with Jupiter and in preparation for the 1979 Voyager encounters, W. L. Brown, L. J. Lanzerotti, and colleagues at



FIG. 1. Plasma flux vs ion energy near Dione, a moon of Saturn, obtained by the Voyager spacecraft. Dotted and dashed lines are extrapolations of Plasma Science Instrument data. Squares are Low Energy Charged Particle Detector data, presumed to be mostly  $O<sup>+</sup>$ . Solid line is a possible extrapolation (from Shi *et al.*, 1995). Inset: The overall plasma flow direction is determined by the magnetic field ''rotating'' with Saturn. The moon's inner hemisphere always faces Saturn (Burns and Matthews, 1986), so that the lower-energy plasma (small gyro radius) primarily bombards the trailing hemisphere of the moon.



FIG. 2. (a) Calculated stopping power  $(dE/dx)$  for O<sup>+</sup> in H<sub>2</sub>O shown as a sum of two components: nuclear-elastic (knock-on) collisions  $(dE/dx)$ <sub>n</sub>, and electronic excitation and ionizations  $(dE/dx)$ <sub>e</sub> (from Zeigler *et al.*, 1985). (b) Summary of data for the sputtering yield for incident H<sup>+</sup> and O<sup>+</sup> on low-temperature ( $\leq 80$  K) water ice, plotted vs the ion energy (from Shi *et al.*, 1995).

AT&T Bell Labs, carried out a series of experiments to measure the ejection of molecules induced by energetic ion impact on ice (Brown *et al.*, 1978; Lanzerotti *et al.*, 1978). Their discovery, that the sputtering of lowtemperature ice by fast, light ions is determined by the electronic excitations produced in the ice, rather than by knock-on collisions of the ions with water molecules, initiated a new area of physics, the study of electronic sputtering of low-temperature condensed-gas solids (ices).

The study of sputtering in refractory materials has a long history, as sputtering is a tool for producing a vapor from a low-vapor-pressure solid (Sigmund, 1993). Therefore the application of this standard sputtering process to ices is first discussed, followed by a description of electronic sputtering of ices. Finally, the relevance of sputtering to recent observations of icy bodies in the outer solar system is described. For a more extended description, see Johnson (1990, 1996).

# II. SPUTTERING AND DESORPTION

A fast ion penetrating a solid gradually loses energy to the atoms that make up the solid. The average rate of energy transfer is represented by *dE*/*dx*, the energy loss per unit path length of the ion in the solid, called the "stopping power" of the material. Since the ion's energy is transferred by nuclear-elastic (knock-on) collisions and by electronic excitations and ionizations of the atoms in the material, it is seen in Fig. 2(a) that  $(dE/dx) \approx (dE/dx)_n + (dE/dx)_e$ .

A measure of the sputtering of a solid is the yield *Y*, the number of molecules ejected per incident ion. Since both knock-on collisions and electronic excitations can cause sputtering of an ice, *Y* can also be written as a sum of two components:  $Y \approx Y_n + Y_e$ . In metals and other refractory materials knock-on collisions are the dominant cause of sputtering at all ion energies, so that  $Y \approx Y_n$ . For ices, on the other hand, the electronic component  $Y_e$  is seen to be dominant at ion energies where the electronic stopping power dominates the knock-on stopping [Fig. 2(b)]. Before considering electronic sputtering, we describe knock-on sputtering.

# A. Knock-on sputtering

When an incident ion strikes an atom in a solid, setting it in motion, the recoiling atom will quickly collide with another atom in the solid. This sequence of collisions produces a cascade of ''recoil'' atoms. In the bulk, the recoils knocked out of their sites form defects, but at the surface they are ejected (sputtered) from the solid.

Based on the above,  $Y_n$  is determined by the number of recoils set in motion near the surface, which is proportional to  $(dE/dx)_{n}$ .  $Y_{n}$  also depends inversely on *U*, the average binding energy of the atoms to the surface, also called the sublimation energy. Therefore

$$
Y_n \approx c \left[ l (dE/dx)_n / U \right]^p, \tag{1}
$$

where *l* is the mean spacing of the molecules, *c* is a proportionality constant, and *p* will be discussed below. We note that the term in brackets is dimensionless. Equation (1) makes it clear that knock-on sputtering is much more efficient in ices than in metals, since the values of *U* can be an order of magnitude smaller in ices (Johnson and Schou, 1993). The sputtering of ices can also be more efficient because the deposited energy can produce chemical reactions, which are discussed shortly.

For fast, light ions,  $(dE/dx)$ <sup>n</sup> is small, and the spatial distribution of recoils is sparse. Therefore, the sputtering yield is proportional to the probability of producing a recoil at the surface. This implies that  $p=1$  in Eq. (1) above some threshold ion energy. Since the recoils collide primarily with ''thermal'' atoms in the solid, their energy spectrum varies as  $E^{-2}$ , where *E* is the recoil energy. This spectrum comes from a linearized particletransport equation (Robinson, 1965).

At high  $(dE/dx)$ <sub>n</sub> the density of atoms and molecules set in motion increases, so that recoil atoms collide with other recoils, leading to nonlinear energy transport. The recoil energy spectrum can now be approximated by a Maxwell-Boltzmann energy distribution, and  $p \approx 2-3$  in Eq. (1). For very heavy incident ions or cluster ion impacts, the penetration depth is small and the geometry of the energized region changes. In this case the yield depends roughly on the ion energy  $E_i$ , i.e.,  $Y_n \approx c(E_i/U)^p$ , with *p* near unity. A similar result is found in the study of meteorite impacts on surfaces. The transfer of energy results in crater formation, spallation, cluster ejection, and vaporization.

In the nonlinear regime, approximate models of sputtering have been made by separately considering either the random motion (''thermal-spike'' models) or the coordinated motion (''hydrodynamic'' models) (Johnson *et al.*, 1989). However, a good theoretical description of particle transport at high  $(dE/dx)$ <sub>n</sub> is lacking. In addition, considerable effort is still needed to describe the ejection of intact molecules versus fragments (Johnson and Sundqvist, 1992), to treat the induced chemical reactions, and to describe the internal state distributions of the molecular ejecta, all interesting problems in nonequilibrium thermodynamics.

#### B. Electronic sputtering

Electronic sputtering is closely related to the study of photon- and electron-stimulated desorption of gases adsorbed on surfaces. Whereas workers in that field had concentrated on the easily detected ions ejected from a surface, Brown *et al.* (1978, 1982) showed that several  $MeV H<sup>+</sup>$  and  $He<sup>+</sup>$  ions eject many more neutral molecules than ions. This implied that the ejected neutrals, not the ions, were indicative of the dominant pathways for electronic "relaxation" in such solids.

As with knock-on sputtering described above, there can be an enormous variation in the excitation density  $(dE/dx)_{e}$ , depending on the type and energy of the incident ion. For example,  $1$ -MeV  $H^+$  produces on the average  $\sim 0.3$  excitations or ionizations per molecular layer of ice penetrated, whereas a 1-MeV  $O<sup>+</sup>$  produces on the average  $\sim$ 10 excitations/layer, forming a cylindrically excited region with a mean radius  $\sim$ 1 nm. Electronic sputtering at high excitation densities has been used in samples of condensed biomolecules to eject whole biomolecules into the gas phase (Håkannson, 1993).

To account for the large range of excitation densities, the electronic sputtering yield is also written in the form used in Eq.  $(1)$ ,

$$
Y_e \approx c \left[ l f (dE/dx)_e / U \right]^p. \tag{2}
$$

Here  $[f(dE/dx)_e]$  replaces  $(dE/dx)_n$ ; *f* indicates the fraction of the deposited electronic energy converted into energetic atomic motion (Johnson and Brown, 1982). If, at low  $(dE/dx)_{e}$ , an individual excitation can lead to ejection of an atom or a molecule from the surface, then the electronic sputtering process is related to photon-stimulated desorption, and *p*=1. For much larger  $(dE/dx)_{e}$ , one has  $p>1$ , since interactions between excited molecules occur in addition to the nonlinear energy transport discussed above. The principal new problems in electronic sputtering of solids are the conversion of electronic energy into atomic motion and the calculation of *f*.

The energy deposited electronically in a solid can lead to energetic atomic motion by a number of nonradiative relaxation processes (Johnson and Schou, 1993). As was the case for knock-on sputtering, electronic sputtering is a surface manifestation of defect production in insulators.

In the ices of interest here, about half of the energy deposited by a light, fast ion  $[low (dE/dx)_e]$  goes into the production of electron-hole pairs, and the other half into electronic and vibrational excitation of the molecules. In the other extreme, a highly ionizing particle [large  $(dE/dx)_{e}$ ] produces a transient, high-temperature plasma around its path through the solid. This region, called the track core, has a radius roughly proportional to the ion velocity, but its evolution is not well understood theoretically (Watson and Tombrello, 1985). In fact, sputtering has proved to be a useful probe of the transient ''temperature'' in the track core (Johnson and Sundqvist, 1992). In addition, the energetic secondary electrons emitted radially from the track core produce a much larger region of lower excitation density, which is important in fast-ion irradiation of biological materials and polymers.

If the density of energy deposited along the ion's path remains sufficiently high for a long enough time, it can heat the lattice leading to transient sublimation, called ''thermal spike'' sputtering (Johnson *et al.*, 1989). If the ionization produced in the track core results in a transient repulsive force between the holes sufficient to energize the atoms in the solid, the process is referred to as a ''Coulomb explosion.'' These models have also been used to describe permanent ion track production in solids (Fleischer *et al.*, 1975; Trautman *et al.* 1993), a process closely related to electronic sputtering (Haff, 1976). Ion track identification has been used for particle detection in both nuclear physics and space science. For instance, tracks produced by solar flare ions have served to determine exposure ages for lunar grains collected during the Apollo missions (Taylor, 1982), and for interplanetary grains ejected from comets and collected in the earth's upper atmosphere (Bradley, 1994).

Above some threshold excitation density, the exponent  $p$  in Eq. (2) is roughly equal to 2 for either the Coulomb-explosion or thermal-spike mechanisms (Johnson and Schou, 1993). In Fig. 3, at the higher displayed values of  $(dE/dx)_{e}$ , a quadratic dependence is in fact seen for sputtering of low-temperature ices. At these excitation densities, *f* is about 0.1–0.2, and the ejecta is dominated by whole molecules. At higher excitation densities, *f* is found to increase, indicating a more efficient conversion of electronic excitation into energetic atomic motion (Johnson and Brown, 1982).



FIG. 3. Straight-line fits to sputtering of ices at low temperatures ( $\leq 20$  K) by fast H<sup>+</sup> and  $He<sup>+</sup>$  ( $\approx$ 50 keV/u). Dashed line is an extrapolation (from Johnson, 1990).

At the lowest excitation densities in Fig. 3, the yields for  $N_2$  and  $O_2$  exhibit a *linear* dependence on  $(dE/dx)_{e}$ , indicating that individual excitations lead to sputtering (Johnson *et al.*, 1991). In contrast to these materials, the yield for low-temperature  $S_8$  varies steeply at low  $(dE/dx)$ <sub>e</sub> (Torrisi *et al.*, 1988), and that for H<sub>2</sub>O or CO is quadratic down to the lowest  $(dE/dx)$ <sub>e</sub> shown. It is interesting that at higher temperatures ( $\approx 80-100$  K), a yield linear in  $(dE/dx)$ <sub>e</sub> is found for water ice (Brown *et al.*, 1980).

The excitations initially produced, or formed on electron-hole recombination, can relax energetically and produce the well-known luminescence spectra (see, for example, Johnson and Schou, 1993). Energy release can occur by a transition to a state having a repulsive interaction with a neighbor, as in gas-phase dissociative recombination, e.g.,  $N_2^+ + e \rightarrow N + N +$ kinetic energy. Of course, all of the excitation energy eventually decays to heat, defect formation, secondary electron emission, or luminescence. But it is the repulsive interactions produced by closely spaced holes or excited molecules, by electron-hole recombination, or by excited-moleculelattice interactions, that energize atoms or molecules sufficiently to cause electronic sputtering. Therefore, carefully contrived experiments can lead to a description of the excited-state interactions in such materials. Not surprisingly, the greatest progress in describing the sequence of events following the production of a track of excitations has been made for rare-gas solids. For such solids the relation of sputtering by ions, electrons, and photons, to secondary electron ejection and to luminescence, is roughly understood at the atomic level (Johnson and Schou, 1993; Grosjean *et al.*, 1995). For the molecular ices, which are important in the outer solar system, chemistry adds an additional level of complexity, so that a molecular level understanding of sputtering has not yet been obtained.

## C. Chemical sputtering

Late effects, which occur after the initial dissipation of the track energy and which depend on the ambient temperature (Pirronello *et al.*, 1982), can also lead to sputtering of ices. The term ''chemical sputtering'' served initially for the sputtering of refractory materials by protons and other ions that react on implantation into the solid (Roth, 1983). For example, low doses of protons sputter refractory materials inefficiently; the implanted H atoms, however, can form new chemical bonds. Therefore, with increasing proton dose new species, such as  $H_2$  and  $H_2O$ , are ejected from silicates; similarly,  $O^+$  and  $H^+$  incident on graphite produce CO and CH<sub>4</sub>.

For low-temperature ices and organic materials in the outer solar system, all incident ions leave a trail of broken bonds and trapped radicals. When the temperature is increased, either directly, or transiently in a thermal spike, or the density of radicals is increased, reactions are initiated. Brown *et al.* (1980) found the sputtering yield of water ice by several-MeV  $He^+$  and  $H^+$  to increase with increasing ambient temperature beyond 80– 100 K. From the mass spectra of the ejecta produced by several-MeV He<sup>+</sup>, the increase in the yield appeared to correlate with increased emission of  $H_2$  and  $O_2$  (Brown *et al.*, 1982; Bar Nun *et al.*, 1985). Such molecules must be formed in the ice and then sputtered.

The observation of ejected  $H_2$  and  $O_2$  is due to their low binding energy in ice. Known radiolytic products such as OH,  $H_2O_2$ , and  $HO_2$  do not contribute significantly to sputtering, as they are bound much more strongly to ice. For  $NH_3$  ice,  $H_2$  and  $N_2$  are seen in the ejecta, and for  $CO<sub>2</sub>$  ice,  $CO$  and  $O<sub>2</sub>$  are seen (Haring *et al.*, 1984), in addition to the parent molecules  $NH<sub>3</sub>$ and  $CO<sub>2</sub>$ . For methane, primarily  $H<sub>2</sub>$  is seen, since loss of H results in *cross linking* between carbon atoms. Cross linking efficiently converts a volatile solid into a refractory organic material, as observed in the reflectance spectra of outer-solar-system objects (Calcagno *et al.*, 1985; Lanzerotti *et al.*, 1987).

Chemical effects have been found recently in the photodesorption of water ice (Westley *et al.*, 1994). At low temperatures ( $\leq 80$  K) individual Lyman- $\alpha$  photons do not desorb water molecules. After an ''incubation'' dose, a sufficient radical density accumulates to create new relaxation pathways which lead to  $H_2O$  ejection on a photon-by-photon basis. The incubation dose is, not surprisingly, temperature dependent.

### III. APPLICATION TO SOLAR SYSTEM OBJECTS

The samples collected during the Apollo missions show the lunar surface to be modified by the incident solar-wind ions ( $\sim$ 1 keV/u H<sup>+</sup> and He<sup>++</sup>) and by energetic solar particles (Taylor, 1982). This aspect of planetary physics has recently been revived by the remarkable observation of Na and K atmospheres around Mercury and the Moon (Potter and Morgan, 1985, 1988). Such atmospheres are initiated by the sputtering of these relatively volatile species from rocky surfaces. The sodium atmosphere has been seen to extend to  $\sim$  5 lunar radii from the moon's surface (Flynn and Mendillo, 1993), providing an impressive manifestation of sputtering. However, the sputter flux at the moon produced by the solar wind is only  $\sim 10^7$  atoms/cm<sup>2</sup> s (Johnson and Baragiola, 1991). On the other hand, the Jovian magnetospheric plasma ions, which bombard the surface of the moon Europa, produce a sputter flux of  $\sim$ 2×10<sup>10</sup> molecules/cm<sup>2</sup> s, more than 3 orders of magnitude larger (Johnson, 1990). Although both of these fluxes are much smaller than typical laboratory sputtering rates, their exposure times are very long, producing a significant effect on a surface.

The application of laboratory data to the erosion of small objects in space exposed to either ultraviolet photons or to a plasma is straightforward. For instance, the icy main rings of Saturn are a *transient* feature of the planet ( $\sim$ 10<sup>8</sup> yr), since erosion by collisions, by plasma ions, by solar photons, and by micrometeorites leads to ejection of molecules, primarily into Saturn's atmosphere.

Of considerable current interest is an extended ring of micron-sized ice particles around Saturn called the E-ring, lying outside the main rings in the region where the plasma trapped in Saturn's magnetosphere is relatively intense (Fig. 1). Cheng and Lanzerotti (1978) first suggested that these particles might be eroded by sputtering. The sputtering rates calculated using recent laboratory data (Shi *et al.*, 1995) place an upper limit on the survival of the charged ice grains in the E ring of about 1000 years. The E ring appears to have as its source the moon Enceladus (Burns and Matthews, 1986). Therefore either the ring is debris from a relatively recent massive impact on Enceladus, or there is a continuous source of material from volcanic activity on Enceladus produced by  $NH<sub>3</sub>$  in its surface (Kargel, 1992).

Sputtering of the E-ring grains and of the surfaces of Saturn's icy moons (Enceladus, Tethys, Dione and Rhea) is the source of a low-density but giant toroidal cloud of neutral water molecules and water-molecule products (Fig. 4). Quite remarkably, its OH content was recently detected using the Hubble Space Telescope (Shemansky *et al.*, 1993). These neutral molecules, produced by plasma-ion sputtering, are eventually ionized (Eviatar and Richardson, 1992), supplying fresh ions to the magnetosphere. This feedback process maintains the plasma in the inner Saturnian magnetosphere shown in Fig. 1.

The application of sputtering data to large objects is more interesting owing to the mass selectivity created by the gravitational field. That is, for moons which do not have a significant atmosphere, the energized atoms or molecules must overcome not only the binding energy to the solid but also the gravitational attraction in order to escape into space (Johnson, 1990). Measurements of the energy spectra of the ejected molecules are, therefore, extremely useful.

The  $H_2$ ,  $O_2$ , and  $H_2O$  sputtered from an icy moon each has a characteristic distribution of speeds. Even for a large moon like Europa, most of the  $H_2$  produced can escape directly, but, depending on the incident ion, only  $\sim$ 10–25 % of the H<sub>2</sub>O and  $\sim$ 5–15 % of the O<sub>2</sub> can escape (Johnson *et al.*, 1983). Any  $H_2O$  that does not escape will recondense because of the low surface temperatures, but this is not the case for  $O_2$ . Even in the polar regions the temperatures allow solid  $O<sub>2</sub>$  to have a significant vapor pressure. Therefore the  $O_2$  molecules produced by plasma bombardment are repeatedly adsorbed and thermally desorbed, until they are lost by dissociation, or by ionization and sweeping by the rotating magnetosphere (see Fig. 1). Since the loss processes



are also determined by the plasma flux, the amount of gas-phase and adsorbed  $O_2$  is self-limiting.

Based on the laboratory measurements, the amount of gas-phase  $Q_2$  on Europa was predicted to be very small,  $\sim$ 2×10<sup>15</sup> mol/cm<sup>2</sup> averaged over the surface (Johnson *et al.*, 1982), equivalent to a couple of monolayers of  $O<sub>2</sub>$  if condensed. Much larger quantities of  $O<sub>2</sub>$ are transiently absorbed on the surface, particularly in the cold polar regions. Quite remarkably, the gas-phase component of  $O_2$  was recently detected by Space Telescope observations of the excited O atoms produced by dissociation (Hall *et al.*, 1995). This confirmation that sputtering and mass selectivity are occurring (Ip, 1996), may also imply that the surface has a larger D/H ratio than expected from the initial solar abundances of H and D (Johnson, 1990).

Because the moons of interest around Jupiter and Saturn orbit with the same face always toward the planet, the plasma trapped in the rotating magnetosphere preferentially bombards the hemisphere that trails the moon's orbital motion (see Fig. 1). This has resulted in hemispherical differences in the optical reflectance (Burns and Matthews, 1986). Taking the ratio of the reflectance of the trailing hemisphere to that of the leading hemisphere, one can extract subtle absorption features. One of the first confirmations that plasma-surface interactions cause changes in reflectance was the observation of an SO absorption band at 280 nm on Europa's trailing hemisphere (Lane *et al.*, 1981). Such a band is produced by incident S<sup>+</sup> (Sack *et al.*, 1992). The sulfur comes initially from the surface of the neighboring moon Io, then is ionized and accelerated in the rotating magnetosphere, and finally is implanted into Europa's surface. Material involved in sputtering is thus transported from one moon to another!

At the neighboring icy moon Ganymede, gas-phase  $O<sub>2</sub>$  is also expected. In addition, the apparent polar caps are most likely produced by plasma erosion of the surface (Johnson, 1985). Recently, a subtle feature in the reflectance spectra of Ganymede's trailing hemisphere has been assigned to an absorption band seen in *solid* or

FIG. 4. Calculation of the neutral cloud around Saturn produced by sputtering of the icy moons (E–Enceladus, T–Tethys, D–Dione, R–Rhea) and of the E-ring grains (E ring extends from Enceladus to Rhea), and by micrometeorite impacts on the main rings. Contours of equal neutral densities (total of  $H<sub>2</sub>O$ , OH, and O) given in powers of ten (from Pospieszalska and Johnson, 1991). Note: recent values for micrometeoriteimpact contribution are lower than those used here (Ip, 1995), but satellite and E-ring source rates are larger (Shi *et al.*, 1995); density near Tethys is still somewhat smaller than deduced from Space Telescope observation (Shemansky *et al.*, 1993).

high-pressure  $O_2$  (Calvin *et al.*, 1996). Since the average equatorial surface temperatures of Ganymede exceed those of Europa, the observed  $O_2$  is apparently produced by plasma impact and then trapped in the large voids formed in the ice by the plasma irradiation. This process resembles He bubble formation in the walls of nuclear reactors caused by  $\alpha$ -particle irradiation. More recently, Space Telescope observations revealed that the surface also contains another absorption feature associated with the plasma bombardment, which has tentatively been identified with  $O_3$  (Noll *et al.*, 1996).

If a large moon has a significant, gravitationally bound atmosphere, penetrated only by very energetic ions, sputtering can add trace species to the atmosphere. This occurs on Io, a moon of Jupiter, and possibly on Triton, a moon of Neptune. Both Io and Triton have atmospheres supplied by gases venting from the interior, and by sublimation of materials more volatile than water ice. On Io, sputtering adds the observed Na to the  $SO<sub>2</sub>$  atmosphere (Spencer and Schneider, 1995), and penetrating ions modify the sulfur-containing ices, producing darkened polar regions (Johnson, 1990). On Triton, the plasma converts  $CH<sub>4</sub>$  into organic material (Thompson *et al.*, 1989) and NH<sub>3</sub> into  $N_2$  (Johnson, 1996). Such processes may also occur on Pluto (Strazzulla *et al.*, 1984; Johnson, 1989) and on its moon Charon.

## IV. SUMMARY

Following the discovery that icy objects in the outer solar system are exposed to relatively intense fluxes of ions and electrons, laboratory measurements were made on the sputtering of ices. Such measurements have shown that the sputtering rates are large and that sputtering is produced by the electronic energy deposited by incident ions, electrons, and ultraviolet photons. This data has been applied to determine the supply rate for a toroidal cloud in the Saturnian magnetosphere containing neutral molecules which are products of sputtering of the icy moons and the E-ring grains (Fig. 4). Ionization of these neutrals is then the source of the local plasma.

Based on laboratory measurements which showed that sputtering of a low-temperature ice directly produced  $O_2$ , the ice-covered moon Europa was predicted to have an extremely tenuous  $O_2$  atmosphere. This was recently observed using the Hubble Space Telescope. Similarly, Europa's surface has implanted S ions derived from Io, and the neighboring moon, Ganymede, appears to have  $O_2$  and  $O_3$  formed and trapped in the radiationproduced defects and voids in its icy surface. Therefore, sputtering can result in dramatic and subtle alterations of both the optical reflectance and the ambient gas and plasma environment of icy bodies.

A new wave of exploration is under way. The Galileo spacecraft will have arrived at Jupiter shortly before this article appears, the Cassini spacecraft will arrive at Saturn at the beginning of the century, and the Europeanled Rossetta mission is expected to put a lander on a comet early in the next century. These missions, together with continuing Hubble Space Telescope observations, should yield a wealth of new data on the surfaces of icy bodies in the outer solar system. Therefore, more laboratory studies and a more detailed understanding of plasma interactions with icy surfaces will be needed to interpret the expected data.

#### ACKNOWLEDGMENTS

This work was supported by NASA's Planetary Geology and Geophysics Program and by the Astronomy Program of the NSF.

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