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Laboratory studies of radiation effects in water ice in the outer solar system

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Abstract

We present new experimental results on radiolysis of water ice below 140 K induced by 150-eV electrons and 100-keV ions, obtained to understand processes occurring in the outer solar system and interstellar space. The experimental methods discussed are low-energy electron-energy-loss spectroscopy (EELS) and Fourier-transform-infrared (FTIR) spectroscopy. The phenomena studied are the formation and trapping of radiation products, in particular H_2O_2, and radiation-induced amorphization of crystalline ice.

Keywords: Ice radiolysis; Amorphization; Sputtering; Hydrogen peroxide (H_2O_2); Hydroperoxyl radical (HO_2); Electron-energy-loss spectroscopy (EELS)

1. Introduction

The most common occurrence of radiolysis of water is in space, where low-temperature water ice—in objects ranging from interstellar dust to comets and icy satellites—is subject to irradiation by high-energy ultraviolet light and atomic particles. Most of what we know about the surfaces of those icy bodies derives from studies of the reflected solar light (reflectance spectra). The sampled depth (optical skin) varies between a few microns or less in the mid-infrared and vacuum ultraviolet to centimeter in the visible due to scattering from mixed minerals and impurities. The impacts by energetic particles in this layer alter the reflectance due to radiolysis, which includes the creation of new chemical species, the ejection of molecules and atoms from the surface (desorption or sputtering), and the generation of lattice defects (Johnson, 1998; Baragiola, 2003b). The temperatures of interest are from 30 to 160 K; in this range, the growth temperature of the ice is the main factor determining its crystallographic phase (Sceats and Rice, 1982; Baragiola, 2003a). Condensation below 190 K but above ~135 K, leads to cubic crystalline ice (Ic), which transforms into hexagonal ice above 160−200 K. Icy deposits grown on substrates colder than ~130 K are amorphous; this phase (Ia) is metastable and converts to Ic at a rate that depends on temperature. Crystallization of Ia is observed above 125 K in laboratory time scales.

A crucial characteristic of Ia grown from the vapor phase is its microporosity, which may affect radiolysis because radiation products may be trapped in pores, and because porous ice in space will absorb other gases that may affect the radiolytic processes. For growth below 60 K, the micropores in the bulk of the ice are connected

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to the surface; above about 60 K, there is no connection of the micropores to the surface and gas adsorption capacity drops dramatically (Baragiola, 2003a).

2. Radiolysis and its consequences

Many molecular mechanisms have been proposed to explain radiolysis of ice based on detailed information from studies in the gas and liquid phases (Ferradini and Jay-Gerin, 1999). A main aspect in the radiolysis of ice is an enhanced cage effect due to the rigidity of the lattice, which results in lower radiation yields (Spinks and Woods, 1990; Johnson and Quickenden, 1997). Understanding is difficult because possible reactions involve a large number of species such as electrons, and H, OH, O, H_2, O_2, HO_2 and H_2O_2 that can be neutral or charged, and in the ground or excited states. The time-dependent population of such species is in turn a function of the linear energy transfer (LET) of the projectile. There are no measurements at the short time scale of molecular rearrangements that follow the initial energy deposition events; therefore, most of the information must be inferred from the molecular products left on the solid at long time scales. There is, however, a window into short time events that may give understanding to primary radiation processes. This is sputtering, the removal of molecules from the ice during irradiation (Baragiola et al., 2003). Sputtering can be considered a truncation, caused by the ice surface, of the cascade of atomic motions initiated by the primary excitation or ionization event. This truncation extends over the whole range of times since the primary event, and thus offers information not available by other methods, such as the kinetic energy distribution of the sputtered radiation products (H_2O, H_2 and O_2). Thus, sputtering is an alternative method to study radiolysis; for the specific case of ice, the interested reader may find useful a recent review by Baragiola et al. (2003).

To understand remote sensing of astronomical icy objects, a direct comparison can often be made with laboratory reflectance experiments. A weak absorption in the ultraviolet below about 300 nm appears in irradiated ice (Sack et al., 1991), a likely signal of H_2O_2 and possibly other radiation products. A complement to these measurements is electron-energy-loss spectroscopy (EELS), which yields information closely related to optical absorption (Wilson et al., 2001). One can maximize the surface sensitivity by choosing an optimum electron energy, around 100 eV, where the stopping power of the electrons is largest (Luo et al., 1991). Using the same ultrahigh vacuum methods described by Wilson et al. (2001), we explored the ability of EELS to detect radiation damage produced by high fluences of electrons. Ice was grown by passing H_2O vapor through a capillary array onto a Mo substrate cooled by liquid nitrogen, conditions known to lead to formation of the amorphous phase (Sack and Baragiola, 1993). Electrons were incident at 40° to the surface normal; backscattered electrons emitted at an angle of 137° to the incident beam were energy analyzed with an energy resolution of 1 eV. Other details can be found in Wilson et al. (2001). Fig. 1 shows the ratio of EELS spectra of radiolyzed vs. virgin ice at 100 K, taken with 150-eV electrons at normal incidence. The energy losses in the band-gap region are evidence of the formation of molecules that absorb energy in this region (Ghormley and Hochanadel, 1971), consistent with the observation of H_2 and O_2 desorbed from ice by low-energy electrons (e.g., Kimmel et al., 1994; Sieger et al., 1998). The huge fluences required to produce detectable changes demonstrate the small efficiency of damage by electrons, compared to ions, also evident in sputtering. These new EELS findings look promising for characterizing ion and UV-photon-induced radiolysis.

More useful for studies of radiolysis is photon absorption in the infrared, as shown by the studies of Gerakines et al. (1996), who followed the population of OH, HO_2 and H_2O_2 from their weak infrared absorption bands, as a function of fluence of Lyman-α photons on ice. We are using FTIR spectroscopy to study the formation of hydrogen peroxide by fast ions under ultrahigh vacuum conditions to understand the presence of this molecule on the Jovian satellite Europa (Carlson et al., 1999). Thin water ice films were grown by depositing high-purity water vapor onto a cold gold mirror (Westley et al., 1998). The gold substrate is one of the electrodes of a quartz-crystal microbalance used to

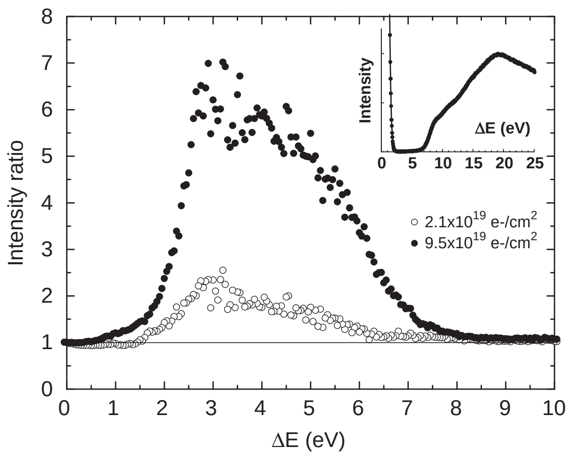

Fig. 1. Ratio of electron-energy-loss (EEL) spectra of amorphous ice at 100 K irradiated with 150-eV electrons to the indicated fluences, to the EEL spectrum of undamaged ice, showed in the inset. The energy losses in the band-gap region (<9 eV) are evidence of the formation of radiolytic products that absorb in that energy window.

measure accurately the amount of water deposited per unit area. The infrared spectra were obtained in specular conditions for an angle of incidence of 45°, using a Thermo-Nicolet Nexus 670 FTIR spectrometer at a resolution of $2\,cm^{-1}$, using external mirror optics. The spectra were ratioed to the spectrum obtained with the bare gold mirror, and then converted to optical depth.

Fig. 2 shows results of irradiation of Ia at 80 K with 100-keV protons at normal incidence on the OH-stretch region of the infrared spectrum. The thickness of the film was chosen to be 1.9 μm, slightly larger than the maximum range of the ions. The H_2O_2 band, which is seen here and also in the experiments of Gomis et al. (2004) with 30-keV ions, was not detectable for 800-keV protons on pure ice at this temperature (Moore and Hudson, 2000). We attribute the difference to the well-known strong dependence of formation of peroxide on LET, which is 2.5–2.9 times smaller for 800-keV H^+ ions than for 30–100-keV H^+ ions. An additional effect at 800 keV is the dilution of the energy deposition due to the larger range of distant collisions in the excitation track created by the ions. This agrees with the well-known dependence of molecular yield on LET and the drop of the yields with velocity, at constant LET (Meesungnoen et al., 2002). The likely reason for this behavior is that, in dense excitation tracks, nearby OH can combine to form H_2O_2 rather than recombine back with their H dissociation partners. In this context, it is important to note that the sputtering yield (molecules ejected/incident ion) is proportional to the square of the LET of the projectile ions near the surface, indicating

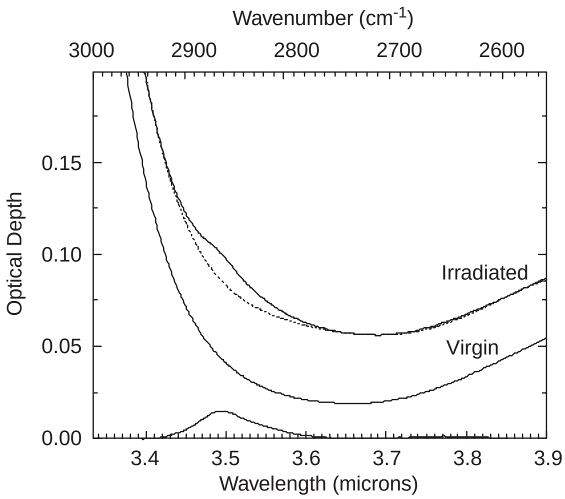

Fig. 2. Infrared absorbance of a 5.07×10^{18} molecules/cm^2 (~2 μm) film of amorphous ice grown at 80 K before and after irradiation at normal incidence and 80 K with 100-keV H^+ ions to a fluence of 2.7×10^{15} ions/cm^2. The absorbance due to H_2O_2 is shown after subtraction of the baseline shown as a dashed line.

the importance of double events (Baragiola et al., 2003). Weak sputtering by single events also occurs, as exemplified by photodesorption with Lyman-α radiation (Westley et al., 1995a, b). A detailed analysis of the experiments will be presented in a future publication.

The observations using infrared spectroscopy complement our previous mass spectrometry studies that revealed the presence of O_2 and H_2O_2 radiation products in the gas evolved when heating radiolyzed ice (Bahr et al., 2001). These studies showed that radiolytic O_2 trapped in the ice is not produced in sufficient quantities to explain the astronomical observations of solid O_2 on the Jovian satellite Ganymede. Atmospheric O_2, produced by sputtering (Reimann et al., 1984; Bar-Nun et al., 1985; Westley et al., 1995b; Sieger et al., 1998; Baragiola et al., 2002; Orlando and Sieger, 2003) or photodissociation of sputtered or sublimated H_2O molecules can condense on bright, very cold surface patches (Baragiola and Bahr, 1998; Baragiola et al., 1999) or exist in the form of an atmospheric haze (Vidal et al., 1997).

3. Radiation-induced amorphization of crystalline ice

Electron diffraction has been used to show that crystalline ice can be rendered amorphous below 70 K by irradiation with high-energy electrons (Dubochet and Lepault, 1984) and 110–400-nm UV light (Kouchi and Kuroda, 1990). Differences in infrared spectra between amorphous and crystalline phases have been used to study amorphization by energetic ions (Strazzulla et al., 1992, Hudson and Moore, 1992) and UV light (Leto and Baratta, 2003). We have used FTIR spectroscopy of the water OH-stretch band to study amorphization of crystalline ice (grown at 150 K) by 100-keV Ar^+ ions at normal incidence using the same setup as for the H_2O_2 formation experiments described above. Here again the thickness of the film was chosen to be slightly larger than the maximum range of the ions, 0.373 μm for the H^+ impact experiments. The temperature was 70 K to simulate amorphization of crystalline ice on Europa, a phase that may be produced by melting ice in tectonic processes or in meteorite impact. The Ar^+ ions should simulate well 100-keV S^+ ions that abound in the Jovian magnetosphere. Important to notice in the changes of the OH-stretch band in Fig. 3 are the remarkably low fluences needed to alter the ice, about ~6 orders of magnitude smaller than those needed to produce changes in EELS using low-energy electrons. It is also notable that the effect of ion irradiation depends strongly on the position within the band and, while the shape of the infrared band evolves towards that of Ia upon irradiation, significant differences remain. Further discussion will appear in a future article.

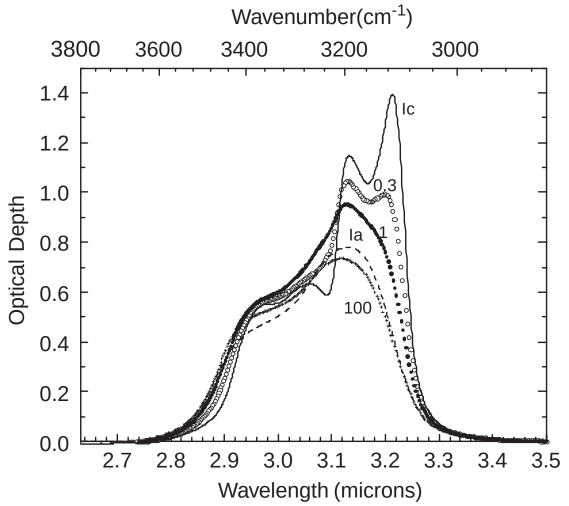

Fig. 3. OH stretch band measured at 70 K for a 1.02×10^{18} molecules/cm^2 crystalline ice film grown at 150 K and irradiated at 70 K by 100-keV Ar^+ ions at normal incidence. Ic—unirradiated crystalline (cubic) ice. The spectra with symbols show Ic irradiated to different fluences indicated by the numbers adjacent to the curves, in units of 10^{13} ions/cm^2. The dashed curve labeled Ia is the spectrum of amorphous ice grown at 20 K and taken to 75 K.

4. Conclusions

Sputtering, electron-energy-loss spectroscopy and infrared spectroscopy, which are rarely considered in the radiolysis literature, can be used in laboratory to obtain insight on radiation processes in ice and to help the interpretation of astronomical observations of icy surfaces in the outer solar system. In the future, it is envisioned that these techniques will produce a wealth of information from the detailed analysis of the spectra, once it becomes possible to couple the measurements with theoretical modeling.

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