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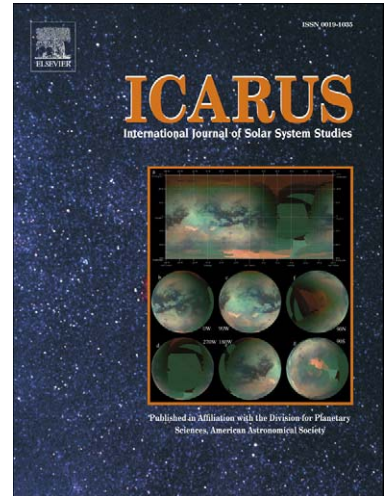
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Hydrate Sulfuric Acid after Sulfur Implantation in Water IceG. STRAZZULLA¹, G.A. BARATTA¹, G. LETO¹, O. GOMIS²

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ABSTRACT

For many years an ongoing research program performed at our laboratory has had the aim to investigate the implantation of reactive ions in ices relevant to planetology by using IR spectroscopy. We present new results obtained by implanting 200 keV sulfur ions into water ice at 80K. We have looked at the formation of sulfur-bearing molecules such as sulfuric acid, sulfur dioxide and hydrogen sulfide. We find that hydrated sulfuric acid is formed with high yield (0.65 ± 0.1 molecules/ion). An upper limit to the production yield of SO_2 ($Y \leq 0.025$ molecules/ion) has been estimated; no hydrogen sulfide has been detected. The formation of hydrogen peroxide is confirmed. Ozone is not detected. The results are discussed relevant to the inquiry on the radiolytic sulfur cycle considered responsible for the formation of sulfur-bearing molecules on the surfaces of the Galilean satellites. We demonstrate that sulfur implantation efficiently forms hydrated sulfuric acid whose observed abundance is explained as caused by an exogenic process. It is more difficult to say if the observed sulfur dioxide is quantitatively supported by only sulfur implantation; additional experimental studies are necessary along with direct observations, especially at UV wavelengths such as those that could be performed by instruments on board Hubble Space Telescope or by the forthcoming World Space Observatory (WSO/UV).

Key Words: Radiation chemistry; Surfaces, satellites; Ices

I. INTRODUCTION

Solid surfaces containing ices are found both in the interstellar medium on silicatic or carbonaceous grain mantles (e.g., Whittet and Tielens, 1997; Pendleton and Chiar, 1997; Sandford et al., 1997; Mennella et al., 2006) and in/on many objects in the Solar System (e.g., Schmitt et al., 1998). In space, these icy targets are continuously bombarded by energetic ions from solar wind and flares, planetary magnetospheres, stellar winds and galactic cosmic rays. When an energetic ion collides with an icy target produces physico-chemical modifications in the latter. Original and newly produced molecules can be ejected (sputtered) or remain in the target (chemical alteration), and the structure of the target can be changed. The study of those effects is based on laboratory experiments on ice irradiation carried out under physical conditions as close as possible to the astrophysical ones. (e.g., Johnson, 1998; Strazzulla, 1998; Moore et al., 2001; Strazzulla et al., 2001; Baragiola et al., 2003; Johnson et al., 2004).

In our laboratory an ongoing research program consists of the study of the implantation of reactive ions (S in the present paper) to verify if and when new molecules that contain the projectile can be synthesized. In fact, when the penetration depth of the incoming (reactive) ions is lower than the thickness of the target, these ions are stopped (implanted) into the ice. Ions penetrating an icy target deposit energy by elastic (nuclear) and by inelastic (electronic) interactions (Johnson 1990). Each incoming ion, having energies between 10 keV and 100 keV, breaks about 10^3 – 10^4 chemical bonds producing fragments and/or radicals that can then react to synthesize new molecules. As an example, the presence of H₂O₂ on Europa (Carlson et al., 1999a) has been attributed to radiolysis processes occurring on the icy surface of the satellite (Carlson et al., 1999a, Moore and Hudson 2000; Gomis et al. 2004). In addition to the radiolytic effects induced by un-reactive species, only reactive ions have a chance of synthesizing species that contain the projectile with a maximum yield of one molecule per incoming ion (e.g. Strazzulla et al. 2003).

Strazzulla et al. (2003) presented results on C implantation into water ice to study the production of CO₂. They have shown that, although a relevant quantity of carbon dioxide can be synthesized by C implantation into water ice on the Galilean moons, this is not the dominant formation mechanism of the CO₂ molecule. In a subsequent work, Gomis and Strazzulla (2005) presented laboratory results on experiments of irradiation of water ice deposited on top of carbonaceous materials. Those authors found that CO₂ is produced efficiently after irradiation. Their results show that radiolysis of mixtures of frost water and carbonaceous compounds could account for the quantity of CO₂ ice present on the surfaces of the Galilean satellites. Similar experiments have been recently performed with thin films (much thinner than the penetration depth of bombarding ions) of water ice deposited on top of sulfurous solid materials. In this way all of the ions travel the ice and penetrate the sulfurous substrate. The purpose was to see if sulfur dioxide molecules can be formed at the interface. The result was negative: sulfur dioxide is not formed in detectable quantity (Gomis and Strazzulla 2006).

Implantation experiments such as those presented here are well suited for scenarios where the ice thickness is much greater than the penetration depth of the incoming ion bombarding the icy target; in particular, for the case of the Solar System, ices on planetary surfaces, comets, etc. As a consequence, it is possible to detect, on planetary surfaces, species which are not native of the surface itself but synthesized by implantation of incoming reactive ions. As an example, sulfur ions, originating at Io, are trapped in the Jovian plasma and can be implanted into the surfaces of the icy satellites (Lane *et al.* 1981). S implantation has been thought to produce SO₂ trapped in the ice (Lane et al., 1981; Noll et al.,

1995, 1997; McCord et al., 1997). However Sack *et al.* (1992) showed that the UV absorption feature seen in the laboratory for sulfur ion implantation differs somewhat from that in the Lane *et al.* (1981) observations. Based on experiments of electron irradiation of sulfur grains in ice, some authors correlated the possible presence of hydrated sulfuric acid on Europa with a radiolytic sulfur cycle (Carlson *et al.* 1999b; Carlson *et al.* 2002). Again it has been suggested (Johnson et al. 2004) that when sulfur is a minor species in ice, as occurs in the case of implantation, the induced chemistry is similar to that of irradiation of sulfur grains in ice. Thus experiments of sulfur implantation are relevant to clarify the induced chemical pathway and establish if the suggested exogenic source can quantitatively explain the sulfur-bearing molecules observed on Europa.

In this paper we present new results obtained by implanting 200 keV sulfur ions in water ice at a temperature of 80 K. Experiments have been also done at lower temperatures (20 K) obtaining results essentially identical to those here presented. As noted by an anonymous referee Europa's diurnal temperature cycle near the equator goes from about 75-78 K in the pre-dawn terminator to around 130-135 K shortly after local noon. For Ganymede and Callisto, their hot temperatures are even warmer than Europa and their cold temperatures will be again in the 75 to 90 K range. This temperature range begins where OH radicals have limited to no mobility in the cold water ice to wide-ranging mobility in the 130 K range. In future experiments we plan to study sulfur implantation in warmer ice (100-150 K).

II. EXPERIMENTAL APPARATUS

The experimental apparatus has been described many times (e.g. Strazzulla *et al.* 2001). A vacuum ($P \approx 10^{-7}$ mbar) chamber is faced, through KBr windows, to an IR spectrophotometer (Bruker Equinox 55) that enables acquiring spectra over a wide wavelength range. Here we present spectra in the 1400-1000 cm^{-1} (7.1-10 μm) range acquired with a resolution of 1 cm^{-1} . Water ice is accreted by vapor deposition on a KBr substrate in contact with a cold finger (10-300 K) and irradiated by 200 keV sulfur ions. Ions are obtained from a 200 kV ion implanter (Danfysik 1080-200) and beam currents are maintained lower than a few micro-ampere cm^{-2} to avoid macroscopic heating of the target. The substrate plane forms an angle of 45 degrees with the IR beam and the ion beam (these latter being mutually perpendicular) so that spectra can be taken without tilting the sample. With such geometry the ion beam sweeps the target to obtain uniform irradiation and produces an elliptical spot with an area of 1 cm^2 (semi-axis 0.5 and 0.64 cm) i.e. larger than the area sounded by the IR beam passing through a circular (radius 2mm) hole on the cold finger. Before deposition liquid water has been purified by many cycles of freeze-pump-thaw that assure the lack of contaminant gases (mainly O_2).

The residual gas pressure is $\approx 10^{-7}$ mbar. In blank experiments we stay at low T (16 or 80 K) for hours to measure what contaminant is deposited on the target. The only contaminant we are able to detect is water ice that is deposited at a rate of about 0.1 nm/min. Typically the experiments are conducted within a couple of hours and an extra deposition of about 10 nanometers of water ice is expected. Blank experiments demonstrate also that, with an un-reactive Ar^+ beam on the substrate and currents significantly higher than that commonly used for implantation, we can clean the substrate from spurious deposit of water ice accumulated during all of the previous steps of the experiment (i.e. before deposition of the chosen species). Once the substrate is clean and the background IR spectrum is acquired, we begin to deposit water. With the beam on the water ice target the pressure near by the target increases depending on the ion beam current, typically from 1-1.5 $\times 10^{-7}$ mbar to 2-4 $\times 10^{-7}$ mbar, because of the species released from the target.

Here we present implantation experiments, i.e. the thickness of the deposited water ice layers is greater than penetration depth of incoming ions. 200 keV S^+ ions penetrate about 300 nm in water ice (assuming an ice density of 1 gr/cm³ this correspond to about 8×10^{17} H₂O-molecules cm⁻²) as we calculated using the TRIM program (Transport of Ions in Matter; e.g., Ziegler et al. 1996). In our experiments we deposited about 2250 nm (6×10^{18} H₂O-molecules cm⁻²). In some experiments we continued the water deposition also during ion implantation to obtain thicker samples having sulfur atoms implanted in a wider range of ice depths.

The results presented below have been obtained at 80 K, a temperature appropriate to simulate possible effects occurring on the surface of Jovian moons. After implantation, we warmed-up the samples and obtained spectra at progressively higher temperatures.

III. RESULTS

One of the effects of ion irradiation is the destruction of molecules of the target whose fragments recombine. In the case of water ice most of the fragments recombine to form water again, some have a chance to form species originally not present. The abundance of a given species in the target can be evaluated by measuring the integrated area (cm⁻¹ in an optical depth scale) of an IR band and by knowing the integrated absorbance of that band (cm molecule⁻¹). In this way it is possible to measure the column density (molecules cm⁻²) of a given species.

We have in fact searched for SO₂ and H₂S after sulfur (200 keV) implantation in water ice. In Fig. 1 we show the infrared spectra, in the range 1410-990 cm⁻¹ (7.09-10.1 μm), of frozen (80 K) water before and after implantation with 200 keV S^+ ions (3.2×10^{16} ions cm⁻²). It is clear the appearance of a new broad band centered at about 1100 cm⁻¹ (9.09 μm) that we discuss below. We searched for the formation of SO₂, by looking at its most intense bands at about 1340 cm⁻¹ (7.46 μm; asymmetric stretch, ν_3) and 1150 cm⁻¹ (8.69 μm; symmetric stretch, ν_1). The spectra of frozen SO₂ deposited at three different thicknesses (8×10^{16} , 8×10^{15} , 8×10^{14} , molecules cm⁻²) are also shown in Fig. 1. The column densities have been obtained for the two spectra with the highest thickness, by measuring the integrated areas of the two bands and by using the integrated absorbances: 3.2×10^{-17} cm molecule⁻¹, for the 1340 cm⁻¹ (7.46 μm) band and 0.4×10^{-17} cm molecule⁻¹ for the 1150 cm⁻¹ (8.69 μm) band (Sandford et al., 1991). The spectrum of frozen SO₂ with the lowest thickness (8×10^{14} , molecules cm⁻²) has been theoretically calculated by scaling those obtained at higher thicknesses. No SO₂ bands appear in the spectra of frozen water after S implantation. By considering the noise in the spectrum of the S implanted water ice film and for comparison with the SO₂ spectra at different column densities, we estimate an upper limit to the production of sulfur dioxide of $Y \leq 0.025$ molecules/implanted ion. An anonymous referee noted that a slight absorption centered at 1335-1340 cm⁻¹ appears in the post-implant spectrum shown in Fig. 1. We have in fact calculated the area of that band that gives the upper limit of $Y = 0.025$ molecules/implanted ion.

Inset here Figure 1

We searched also for the formation of H₂S. Its most intense band is at about 2550 cm⁻¹ (3.92 μm; symmetric and asymmetric S-H stretches) with an integrated absorbance of 2.9×10^{-17} cm molecule⁻¹ (Smith 1991). In Fig. 2 we show the infrared spectra, in the range 3100-2400 cm⁻¹ (3.23- 4.17 μm), of

frozen (80 K) water ice before and after sulfur implantation. For comparison we show also the spectrum of frozen H₂S (7.9×10^{17} molecule cm⁻²). We do not detect H₂S after sulfur implantation in water ice. From the same figure it is possible to notice the formation of a broad feature at about 2850 cm⁻¹ (3.51 μm) easily attributed to hydrogen peroxide that easily forms after (reactive or unreactive) ion bombardment of water ice (Moore and Hudson 2000, Gomis et al. 2004, Loeffler et al. 2006).

Let us now discuss the origin of the newly formed broad band centered at about 1100 cm⁻¹ (9.09 μm). It is very likely due to a sulfate (see e.g., Moore et al., 1984), in particular we believe it is due to sulfuric acid (H₂SO₄) for the reasons described in the next.

Inset here Figure 2

The chemistry of irradiated water starts with the dissociation to H+OH. A plethora of neutral, excited and ionized species are also formed: H, H₂, O, O₂, H₂O, HO₂, H₂O₂ (e.g. Baragiola *et al.* 2003). In the present case of sulfur implantation, sulfur dioxide might be formed by direct addition of S to O₂ that is one of the products of water radiolysis or by:



This reaction is however rather complicated since the formation of HO₂ requires at least three reactions (e.g. Petrik et al. 2006).

Similarly hydrogen sulfide might be formed by direct addition of S to H₂ (that however seems to be rather complicated being the amount of molecular hydrogen presumably low) or by:



Although we do not know the reaction rates of (1) and (2) however, for the reason given above, it is not surprising that SO₂ and H₂S are not observed in our experiments.

Irradiation of water-sulfur dioxide mixtures easily produces hydrated sulfuric acid as predicted by Carlson et al. (1999b) and experimentally demonstrated by Moore et al. (2002). In this light we have investigated the origin of the broad band centered at about 1100 cm⁻¹ (9.09 μm). By using the temperature and composition dependent optical constants of H₂SO₄ in water (Niedziela et al. 1999, <http://chemistry.che.depaul.edu/rniedzie/research/OCDB/SAW/SAW.htm>), we have calculated synthetic spectra of sulfuric acid hydrate. In the theoretical calculations we considered a fixed thickness (1.7 μm) of water ice that is equal to the thickness of the water ice film grown before implantation. At a fixed depth of 0.2 μm (comparable with the penetration depth of 200 keV sulfur ions) we added to the water ice, a layer constituted by a sulfuric acid hydrate mixture. In the computations we considered different mixtures, having different H₂SO₄ concentration, with variable thickness. The best solution was found for a layer of sulfuric acid hydrate whose thickness is of 0.1 μm constituted by 32%wt of sulfuric acid. We used, among the available optical constants, those corresponding to that mixture at 210 K (the lowest available temperature). Results are shown in Fig. 3 where the spectrum of as deposited water ice at 80 K (dashed line) is shown along with the spectrum corresponding to the ratio among the spectrum obtained after implantation of 3.2×10^{16} 200 keV sulfur ions and the original one (dot line). For comparison, the spectrum given by the ratio between the synthetic spectrum of the sulfuric acid hydrate-water ice layer complex described before and the synthetic spectrum of a pure 1.7 μm thick water ice film, is also shown (full line). The presence of HSO₄⁻ and SO₄²⁻ (the products of the dissociation of sulfuric acid in water) is evident along with that of H₂O₂. The assignment of the two

bands at about 3400 and 3200 cm^{-1} to H_3O^+ is made on the basis of the results by Lund Myhre *et al.* (2003). However, as noted by the referees, the radiation chemistry initiated by the impinging S^+ forms many species which includes the formation of protons and electrons. These will migrate and trap in the vicinity of defects in ice and give rise to optical signatures which are not necessarily the same as the optical signatures associated with freezing a “dissolved” (sulfuric) acid. We have also made a rough estimate of the production yield of equivalent sulfuric acid molecules formed per impinging S ion which appears to be a quite high value of $Y = 0.65 \pm 0.1$.

Inset here Figure 3

IV. APPLICATIONS TO ICY SATELLITES

Near IR observations made by instruments on board of the Galileo spacecraft confirmed that on Callisto, and Ganymede water ice is the dominant species but absorption features attributed to C-H, H_2O_2 , S-H, SO_2 , CO_2 , and CN have been reported (McCord *et al.* 1997, 1998). On Europa water ice is also the dominant species with traces of a hydrate compound, H_2O_2 , SO_2 , and CO_2 . A still open question is to understand if those species are native from the satellites or are synthesized by exogenic processes such as ion irradiation. Implantation experiments such as those here presented would contribute to understand if the atomic components of the observed molecular species are native or come from outside as reactive energetic ions implanted in the surfaces. It is important to note that the spectral features observed in this experiment are not in the region sampled by the NIMS spectrometer. In addition, as pointed out recently in the literature (Orlando *et al.* 2005) there are many solvated ion structures which can give rise to perturbed spectral features which can complicate the chemical identity of the “contaminants” within the ice matrix. Among the simplest are protons and Na^+ ions. There is also quite a bit of compelling evidence that indicates that there is a source term for Na which is not easily explained by a completely exogenic source term for sulfuric acid (Johnson *et al.* 2002).

Experiments of implantation of reactive ions are not so numerous and consequently their applications have been little discussed. A noteworthy exception is the case of SO_2 . It has been detected, by space UV observations, on Europa and Callisto (Lane *et al.* 1981; Lane and Domingue 1997; Noll *et al.* 1995, 1997) and it has been interpreted as possibly formed by magnetospheric sulfur implanted in water ice (Lane *et al.* 1981, Sack *et al.* 1992).

Carlson *et al.* (1999b) evaluated the amount of sulfur bearing species possibly present in the observable Europa surface layers (about 200 micrometers thick). They suggest three sulfur bearing species: polymerized sulfur, SO_2 (about $2 \times 10^{17}/\text{cm}^2$) and hydrated sulfuric acid H_2SO_4 (about $3 \times 10^{19}/\text{cm}^2$).

The fluxes of sulfur (keV-MeV) ions at the surfaces of the Galilean moons have been reported by Cooper *et al.* (2001). Johnson *et al.* (2004) reviewed the global fluxes of some atoms at Europa, the minimum and maximum values for sulfur are reported in the first column of Table 1. We use those values, and the formation yields measured in the present work, to evaluate the times necessary to produce the inferred amount of sulfur dioxide and hydrated sulfuric acid. The results are reported in the second and third column of Table 1 respectively. We see that the observed quantity of hydrated sulfuric acid can be formed by implantation of sulfur on time scales of the order of 10^4 years. This is of the same order estimated by Carlson *et al.* (1999b) for the production due to radiolysis of sulfur dioxide in

water. In fact radiolysis of SO_2 forms SO_3 (Moore 1984, Gomis and Strazzulla 2006) that in water, rapidly produces H_2SO_4 .

Inset here Table 1

Johnson et. al. (2004) outlined that to discriminate between exogenic and endogenic sources it is possible to use measurements of the spatial distribution of total sulfur, which is given by the distribution of the sulfur hydrate since $[\text{H}_2\text{SO}_4] \gg [\text{S}_x] > [\text{SO}_2] > [\text{H}_2\text{S}]$. In fact Johnson et. al. (2004) evidenced that the global distribution of hydrate shows a trailing side enhancement that is suggestive of the plasma implantation distribution. This is also true for the sulphur dioxide UV signature. The results of this paper confirm that, quantitatively, sulfur implantation can produce the observed amount of H_2SO_4 . It is also interesting to note the absence of H_2S in our experiments, and the fact that the polymer-like sulfur residues that are obtained after photolysis and radiolysis of sulfur bearing species (e.g. Lebofsky and Fegley 1976; Strazzulla et al. 1993), well reproduce the Europa observed reflectance spectrum (Carlson et al. 1999b Fig. 2).

More difficult is to say if the observed sulfur dioxide is quantitatively justified by sulfur implantation, in fact we have been able to find only an upper limit to its production yield. The question of its origin remains still open and needs further investigation both in the lab and from space observations. Particularly useful would be experiments and observations in the UV spectral range. In fact the suggestion of the presence of sulfur dioxide on the Europa and Callisto surface has been made by the observation of an UV band at $0.28 \mu\text{m}$ originally made by the International Ultraviolet Explorer (IUE; Lane et al. 1981; Lane and Domingue 1997). By the way the absorbance of that band is several order of magnitude greater than the absorbance of the IR band at $4.07 \mu\text{m}$ as we have verified in unpublished experiments. IUE observations have been confirmed by the UV instrument on board of the Hubble Space Telescope (Noll et al. 1995, 1997). Further observations are however necessary and could be performed by the World Space Observatory (WSO/UV), an international collaboration to build a UV (100-310 nm) 1.7m telescope with capabilities which are presently, in the long term future unavailable to the world-wide astronomical community (<http://www.oact.inaf.it/wso/index.htm>).

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Table 1. Fluxes of sulfur ions (after Johnson et al. 2004) at Europa and times necessary to produce the amount of sulfur dioxide and hydrated sulfuric acid observed on the satellite.

Average flux of S-ions ($\text{cm}^{-2} \text{s}^{-1}$) at Europa (global)	Minimum time (years) to produce 2×10^{17} SO_2 molecules cm^{-2}	Time (years) to produce 3×10^{19} H_2SO_4 molecules cm^{-2}
Min 0.2×10^8	1.2×10^4	7.3×10^4
Max 1.4×10^8	1.8×10^3	1.0×10^4

FIGURE CAPTIONS

Figure 1. Infrared spectra, in the range $1410\text{-}990\text{ cm}^{-1}$ ($7.09\text{-}10.1\text{ }\mu\text{m}$), of frozen (80 K) water before and after implantation with 200 keV S^+ ions (3.2×10^{16} ions cm^{-2}). The spectra of frozen SO_2 deposited at three different thicknesses are also shown

Figure 2. Infrared spectra, in the range $3100\text{-}2400\text{ cm}^{-1}$ ($3.23\text{-}4.17\text{ }\mu\text{m}$), of frozen (80 K) H_2S and water ice before and after sulfur implantation.

Figure 3. The spectrum of as deposited water ice at 80 K (dashed line) is shown along with the spectrum corresponding to the ratio among the spectrum obtained after implantation of 3.2×10^{16} 200 keV sulfur ions and the original one (dot line). For comparison the synthetic spectrum of sulfuric acid hydrate (32%wt, 210 K) is also shown (full line). See the text for details.

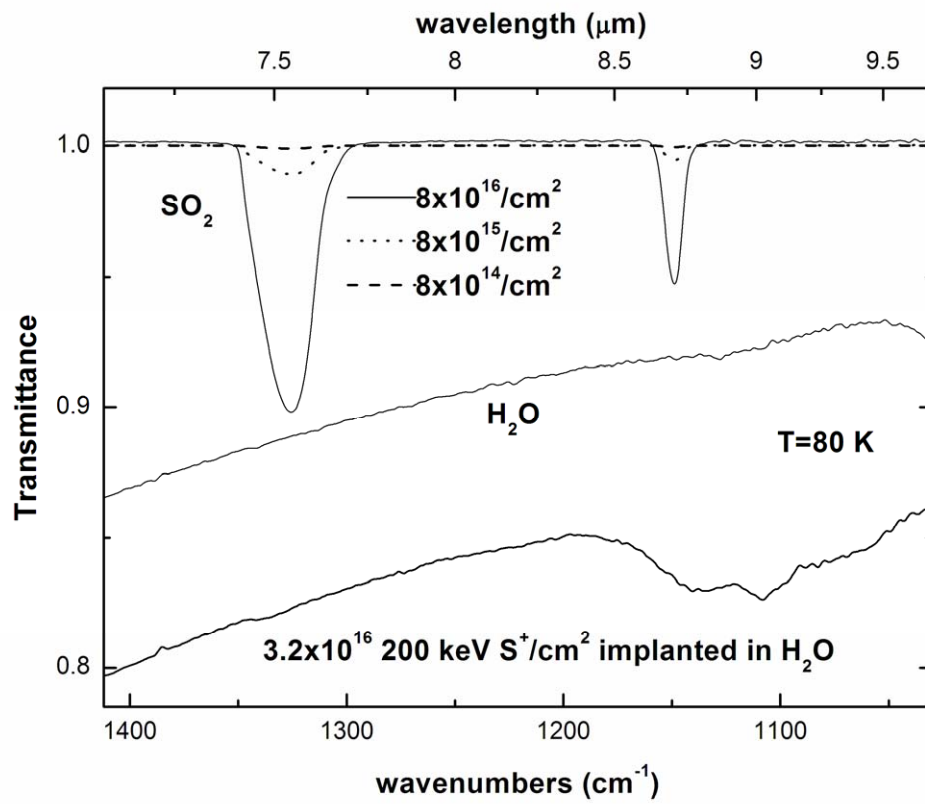


Fig. 1

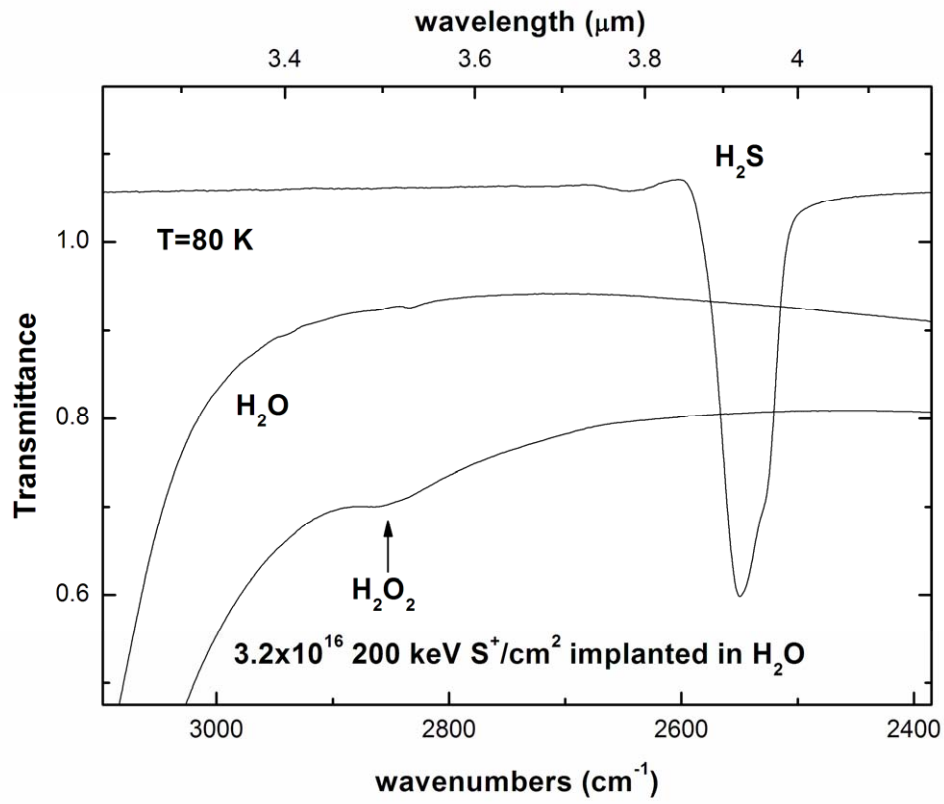


Fig. 2

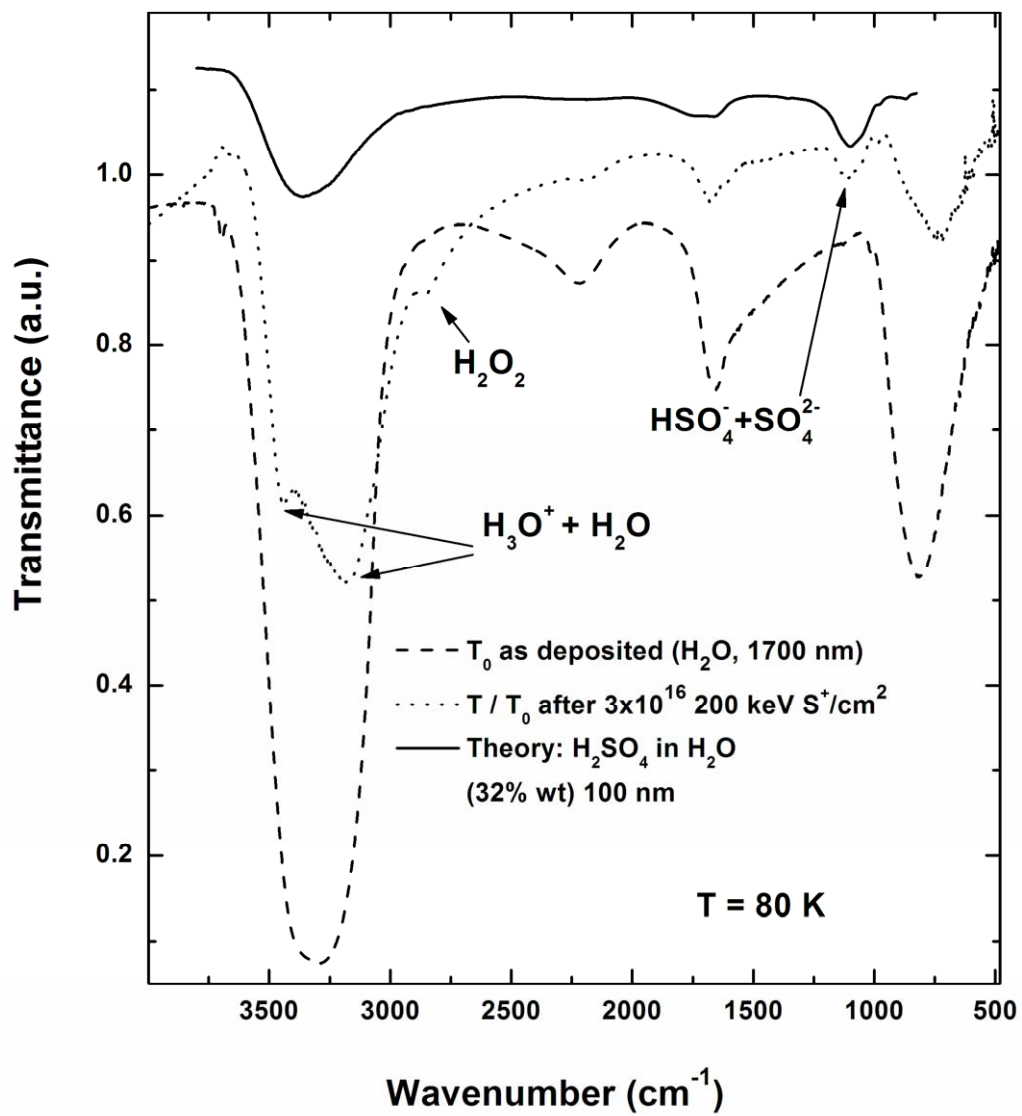


Fig. 3