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Sputtering of Sulfur by Kiloelectronvolt Ions: Application to the Magnetospheric Plasma Interaction with Io

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Measurements of total yields, temperature dependences, mass spectra, and energy spectra of molecules sputtered from condensed sulfur (S₂) at low temperatures by keV ions are reported and results are given for Jovian plasma ion bombardment of Io. A change in the reflectance of the sulfur, which can be removed by annealing, is produced by the most penetrating ions and may be connected with the darker, colder polar regions on Io. The measured sputtering yields are much lower than those estimated earlier for room temperature sulfur films but are comparable to previous measurements of keV ion sputtering of SO₂ at low temperatures. The corrected mass spectrum indicates that ~66% of the total yield corresponds to S₂ ejection while only 5% and 16% correspond to S and S₃, respectively. Therefore, ions reach the surface of Io and its atmosphere will have a non-negligible sulfur component of primarily S₂. The ejection of S and S₂ is temperature independent for temperatures characteristic of most of the surface of Io. The energy spectrum for S has an approximate \(1/E^2\) dependence at high ejection energies, whereas S₂ and S₃ fall off more rapidly. Assuming 50% coverage of both sulfur and SO₂ and a thin atmosphere (e.g., nightside and polar region) the direct sputter injection of sulfur atoms and molecules into the Jovian plasma torus and the indirect injection due to coronal processes are estimated. These injection rates for sulfur are compared to those for SO₂ showing that injection from sulfur deposits contributes 13% to the total mass injection rate of \(\sim 2-3 \times 10^{29}\) amu/sec.


I. INTRODUCTION

The surface of Io is generally agreed upon as the source of the surprisingly dense Jovian magnetospheric plasma (Matson et al. 1974, Haff et al. 1981, Cheng 1982). Originally ejected as neutrals and subsequently ionized, these new magnetospheric plasma ions will in turn bombard the surface and/or atmosphere of Io, ejecting, either directly or indirectly, additional material. This process, therefore, couples the composition of the magnetospheric plasma with the composition of the surface material of the satellite. Such a connection should allow one to infer information about surface composition from magnetospheric plasma content and vice versa.

Although the surface composition of Io is not established completely, it is known to have condensed SO₂ (Smythe et al. 1979, Fanale et al. 1979) associated with volcanic activity (Morabito et al. 1979, Smith et al. 1979, Johnson et al. 1979, McEwen and Soderblom 1983). This volatile species has thus been the center of attention as the sole source of neutral material (Cheng 1982, Boring et al. 1983, Johnson et al. 1984a) for the predominantly sulfur and oxygen plasma (Sullivan and Siscoe 1983) and for Io’s tenuous atmosphere (Kumar 1984). Besides trace species such as the alkali metals, which are observed as neutral clouds (Brown 1974, Trafton 1975), the other often discussed surface constituent is some form of condensed sulfur (Sagan...
which is also associated with the volcanic activity on Io (McEwen and Soderblom 1983). Sulfur has received considerably less attention as a plasma source because of its lower volatility (Haff et al. 1981). Although the ratio of sulfur to oxygen ions generally accepted can now be explained with an SO$_2$ source alone (Shemansky 1986), there has been considerable speculation on the contribution due to surface sulfur.

Recently Linker et al. (1985) and Moreno et al. (1985) have attempted to explain the observed radial profiles of the ion density and ion partitioning by introducing a separate source of neutral sulfur ejected by plasma ion bombardment as a free parameter. However, the only data available at the time of their calculation on the sputtering of sulfur were room temperature yields for 30–300 keV He$^+$ (Fink et al. 1984) which have since been shown to grossly overestimate the actual yield (Torrisi et al. 1985). In any case the measurements were done at ion energies and target temperatures that are not characteristic of the surface of Io.

This paper presents measurements of the sputter ejection of sulfur atoms and molecules from condensed sulfur films by keV H$^+$, He$^+$, N$^+$, Ne$^+$, Ar$^+$, Kr$^+$, and Xe$^+$ in a sample temperature range appropriate for most of Io and discusses their relevance to Io. Because the experimental ion energies are somewhat higher than the corotating energy of the plasma ions and the ions conveniently accelerated differ from those that dominate the torus, we use the measured yield data for these ions to determine the physical mechanism of sputter ejection. We recognize, though, that the actual plasma ions (S ions and O ions) will make new bonds with the target producing chemical sputtering also. Once the physical mechanism is determined we can then extrapolate the surface ejection rates appropriate for the range of energies of plasma ions which could have access to the surface and estimate the maximum effect chemical sputtering could have. The sulfur species which are ejected can add to an atmosphere, redistribute mass across the surface, or escape directly if the atmospheric density is low. In order to be able to calculate the amount of sulfur and the molecular species participating in these processes, mass and energy spectra of the predominant ejected species are also measured. These data are compared with the data for the sputtering of condensed SO$_2$ in order to estimate the relative contributions of sulfur and SO$_2$ to the formation of a neutral atmospheric corona on Io and the direct and indirect injection rate to the torus (Johnson et al. 1984a, Sieveka and Johnson 1985, 1986). Therefore the results presented should be useful as our knowledge of the plasma satellite interaction improves, particularly the knowledge of those ions which might reach the surface of Io.

II. EXPERIMENT

The sulfur targets were formed by evaporating sulfur pieces (AESARS, 1–4 mm sulfur pieces, 99.9995% pure) onto either Ni or Zn substrates in a vacuum evaporator. The target substrates were ~0.1 mm thick, positioned 4 cm above the Mo evaporating boat, and maintained near room temperature. The temperature of the evaporating sulfur was not measured directly. Instead the Mo boat was warmed until the sulfur pieces began to slowly melt, indicating that the temperature of the sulfur during evaporation was about 120°C. A typical evaporation lasted 7–10 min when using 7 pieces of sulfur. A rough value of the thickness of the film was determined by the difference in weight of the substrate before and after evaporation, on a balance accurate to ±10$^{-5}$ g. Films of the order of ~5 $\mu$m thick were used for the total sputter yield measurements and thicker films, ~20 $\mu$m, were used for the mass and energy spectra determinations. These films were then mounted in a high vacuum target chamber and cooled to low temperatures. Before cooling the sulfur films were a pale yellow, whereas when cooled to 15°K they were snowy white in color. Under these conditions of
formation the stable form of sulfur is orthorhombic \( \alpha \)-sulfur composed of weakly bound \( S_8 \) rings (Meyer 1976, Fink et al. 1984, Steudel et al. 1986).

Measurements of the mass spectra and the energy spectra of ejected neutrals were done using a quadrupole mass spectrometer (QMS). The QMS was at 45° with respect to the beam direction. For all QMS measurements the beam was incident at 45° whereas the absolute yields were done at normal incidence. Typical current densities used were \( \leq 5 \) \( \mu \)A/cm\(^2\) (3 \( \times \) 10\(^{13}\) ions/cm\(^2\)/sec). The details of the QMS measurements and analysis are given by Chrisey et al. (1987).

The yield measurements were performed on a Ni substrate which had 1 microcurie of Po-210 electrochemically deposited on the center. Once the sulfur was deposited the energy loss of the 5.305 MeV alpha particle emitted by the Po-210 could be measured with a silicon barrier charged particle detector and a film thickness calculated. The sputtering yield could then be determined by measuring a change in film thickness for a given amount of integrated beam current. (See the paper by Chrisey et al. (1987) for further details on this technique.)

III. EXPERIMENTAL RESULTS AND COMPARISONS TO \( \text{SO}_2 \)

A. Mass Spectrometry of Ejected Neutrals

The percentage of the total amount of sulfur sputtered as neutral \( S_2 \), \( S_3 \), and \( S_4 \) when an ion bombards sulfur at 15°K is 5, 66, 16, and less than 13%, respectively. This measurement was performed for incident 34 keV \( \text{N}^+ \), \( \text{Ne}^+ \), \( \text{Ar}^+ \), \( \text{Kr}^+ \), and \( \text{Xe}^+ \). The relative amounts of each sulfur species ejected were very nearly the same for each incident ion. The total amount of sulfur ejected was different and the fraction of larger species increased somewhat for the heavier ions. These relative yields have been corrected (Chrisey et al. 1987) for various instrumental effects and sensitivities such as the fragmentation of \( S_2 \) to \( S_8 \) by the 80 eV electrons used to ionize the sputtered neutrals in the QMS.

It is seen that ejection of sulfur takes place predominantly as \( S_2 \) with smaller amounts of \( S_3 \) and \( S_4 \). Also the amount of sulfur ejected in each of these forms is much greater than that due to \( S_8 \), the dominant species evaporated from rhombic sulfur at higher temperatures (Berkowitz and Chupka 1964). Although it has been argued as to the extent and particular allotrope of elemental sulfur on Io (Hammel et al. 1985, Young 1984, Sagan 1979), it is the authors' position that this will not have an effect on present results since the energy density deposited is large compared to individual bond strengths or structure differences for various sulfur allotropes or polymers. This idea is clearly exemplified by the mass spectrometry results in that a target of \( S_8 \) molecules sputters as small fragments of the initial target.

The corresponding mass spectrometry results for keV \( \text{Ne}^+ \) and \( \text{Ar}^+ \) incident on \( \text{SO}_2 \) at low temperatures showed that it sputters predominantly as whole \( \text{SO}_2 \) molecules of mass 64 (Boring et al. 1983, 1984). Masses 32, 48, and 80 were also detected and could be \( \text{O}_2 \) or \( S \), \( \text{SO} \) or \( \text{O}_3 \), and \( \text{SO}_3 \) or \( \text{S}_2\text{O} \) respectively. Although a detailed analysis of the relative contributions to the total yield was not performed it was estimated that masses 48 and 80 only amounted to a few percent. At higher temperatures, like those characteristic of the surface of Io, the production of mass 32 (probably \( \text{O}_2 \)) was found to increase dramatically.

B. Chemical Changes Observed in the Target

It is widely recognized that, even at low doses and low temperatures, plasma-ion bombardment can permanently alter the chemical state, composition, and surface concentration of molecules in an initially pure target like \( \text{SO}_2 \) (Johnson et al. 1984b). \( \text{SO}_3 \) has been observed by Moore (1984), using IR spectrometry, as the primary molecule synthesized in \( \text{SO}_2 \) films irradiated with 1 MeV protons. Polymeric \( \text{SO}_3 \) was also identified by Moore (1984) as being synthesized in the \( \text{SO}_2 \) ice at low tempera-
**TABLE 1**

<table>
<thead>
<tr>
<th>Energy (keV) ion → target</th>
<th>$\alpha$</th>
<th>$n^1 (dE/dx)_e$ (eV \cdot Å$^2$)</th>
<th>$n^1 (dE/dx)_n$ (eV \cdot Å$^2$)</th>
<th>Yields SO$_2$/ion (S/ion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 Ar$^+$ → SO$_2$</td>
<td>—</td>
<td>2930</td>
<td>540</td>
<td>170</td>
</tr>
<tr>
<td>30 Ar$^+$ → SO$_2$</td>
<td>—</td>
<td>2920</td>
<td>760</td>
<td>180</td>
</tr>
<tr>
<td>45 Ar$^+$ → SO$_2$</td>
<td>—</td>
<td>2800</td>
<td>930</td>
<td>210</td>
</tr>
<tr>
<td>45 Ne$^+$ → SO$_2$</td>
<td>—</td>
<td>960</td>
<td>900</td>
<td>90</td>
</tr>
<tr>
<td>10$^5$ He$^+$ → S$_8$</td>
<td>—</td>
<td>$&lt;1$</td>
<td>680</td>
<td>10.5</td>
</tr>
<tr>
<td>33 H$^+$ → S$_8$</td>
<td>—</td>
<td>1</td>
<td>177</td>
<td>.8</td>
</tr>
<tr>
<td>49 H$^+$ → S$_8$</td>
<td>—</td>
<td>$&lt;1$</td>
<td>216</td>
<td>1.3</td>
</tr>
<tr>
<td>10 He$^+$ → S$_8$</td>
<td>.66</td>
<td>22</td>
<td>98</td>
<td>2.4</td>
</tr>
<tr>
<td>20 He$^+$ → S$_8$</td>
<td>.66</td>
<td>16</td>
<td>138</td>
<td>1.9</td>
</tr>
<tr>
<td>34 He$^+$ → S$_8$</td>
<td>.66</td>
<td>12</td>
<td>180</td>
<td>2.6</td>
</tr>
<tr>
<td>34 N$^+$ → S$_8$</td>
<td>.37</td>
<td>217</td>
<td>293</td>
<td>25</td>
</tr>
<tr>
<td>34 Ne$^+$ → S$_8$</td>
<td>.32</td>
<td>438</td>
<td>323</td>
<td>29</td>
</tr>
<tr>
<td>34 Ar$^+$ → S$_8$</td>
<td>.24</td>
<td>1232</td>
<td>344</td>
<td>92</td>
</tr>
<tr>
<td>63 Ar$^+$ → S$_8$</td>
<td>.24</td>
<td>1151</td>
<td>468</td>
<td>89</td>
</tr>
<tr>
<td>19 Kr$^+$ → S$_8$</td>
<td>.20</td>
<td>2514</td>
<td>267</td>
<td>92</td>
</tr>
<tr>
<td>34 Kr$^+$ → S$_8$</td>
<td>.20</td>
<td>2781</td>
<td>357</td>
<td>110</td>
</tr>
<tr>
<td>44 Kr$^+$ → S$_8$</td>
<td>.20</td>
<td>2870</td>
<td>407</td>
<td>120</td>
</tr>
<tr>
<td>14 Xe$^+$ → S$_8$</td>
<td>.18</td>
<td>2970</td>
<td>225</td>
<td>126</td>
</tr>
<tr>
<td>34 Xe$^+$ → S$_8$</td>
<td>.18</td>
<td>3790</td>
<td>351</td>
<td>167</td>
</tr>
<tr>
<td>54 Xe$^+$ → S$_8$</td>
<td>.18</td>
<td>4167</td>
<td>442</td>
<td>201</td>
</tr>
<tr>
<td>.52 S$^+$ → SO$_2$</td>
<td>—</td>
<td>1180</td>
<td>100</td>
<td>59$^{b}$ —</td>
</tr>
<tr>
<td>.52 S$^+$ → S$_8$</td>
<td>.26</td>
<td>440</td>
<td>40</td>
<td>26$^{b}$</td>
</tr>
<tr>
<td>.26 O$^+$ → SO$_2$</td>
<td>—</td>
<td>540</td>
<td>70</td>
<td>49$^{b}$ —</td>
</tr>
<tr>
<td>.26 O$^+$ → S$_8$</td>
<td>.35</td>
<td>180</td>
<td>30</td>
<td>14$^{b}$</td>
</tr>
</tbody>
</table>

$^a$ Absolute yields for ions incident on sulfur and sulfur dioxide targets at low temperatures. The values for $\alpha$ were taken from an empirical fit to experimental data by Sigmund (1981) and correspond to $M_2 = 32$. The yield for sulfur is given in terms of the equivalent number of sulfur atoms ejected per incident ion. The keV electronic stopping power is calculated from Lindhard and Scharff (1961), the MeV electronic stopping power is from Ziegler (1977), and the nuclear energy loss is from Ziegler (1984). These stopping powers have been divided by the number density $n$ so as to represent them as effective stopping cross sections per sulfur atom or SO$_2$ molecule.

$^b$ Corotating ion values determined by extrapolation as described in text.

...
QMS by 45 keV Ar⁺ bombardment was small at first and reached a steady state in about $10^{14}$ ions/cm² (Johnson et al. 1984a). The gradual rise in the mass 80 signal was interpreted as the initial ions producing new species with latter ions ejecting them. Such results indicate that a fresh SO₂ ice sputters nonstoichiometrically at first. The chemical alterations occur in a time (Johnson et al. 1984a) that is short compared with the volcanic resurfacing rate (Johnson et al. 1979, Johnson and Soderblom 1982).

A similar dependence on fluence in the species ejected might be expected for the radiation synthesized products of sputtered sulfur, but the relative yield measurement did not indicate any such dependence. The only qualitative evidence that the material was being modified was the observed color change of the material in the beam spot over very large fluences ($\sim 6 \times 10^{17}$ ions/cm²). The change of the color from white to a light brown occurred more quickly and more dramatically for lighter ions which deposit proportionately more electronic energy than the heavier ones (see Table I) and have larger penetration depths. The darkening is presumably due to the production and trapping (at 15°K) of smaller sulfur fragments (Meyer 1977, Young 1984). The low temperature at which the present measurements were performed should be noted though, since at higher temperatures recombination is known to occur (Young 1984). In fact, warming the sulfur target to $\sim 170°K$ removed some of the brown color and at $\sim 200°K$ most of the color was removed. Therefore the observations of a color change of S₈ by ion bombardment could be very important in explaining the observed darker color at the poles. This is a region probably unprotected by an atmosphere (Thomas 1986), hence it is exposed to all ions, and is a region in which the annealing does not occur efficiently.

C. Yield Measurements and Extrapolations

In Table I, a summary of the low temperature sputtering yield measurements for ions incident on S₈ and SO₂ films is given. Values of the electronic and nuclear stopping power ((dE/dx)ₑ and (dE/dx)ₙ) for each ion-target pair are given for comparison. The value for 1 MeV He⁺ $\rightarrow$ S₈ is from Torrisi et al. (1985) and the values for SO₂ sputtering are from Boring et al. (1983, 1984) and Johnson et al. (1984a). Also shown are the extrapolated yield values expected for corotating ions. The extrapolated yield values were obtained as described below by assuming the total yield ($Yₜ$) is the sum of a nuclear (collisional) yield ($Yₙ$) and an electronic yield ($Yₑ$). This method has recently been applied to the sputtering of frozen xenon (Stevanoic et al. 1984) and H₂O ice (Bar-Nun et al. 1985, Chrisey et al. 1986).

To obtain the above separation of the yield into nuclear and electronic parts we begin by assuming that the total yield as measured for 33 and 49 keV H⁺ is due entirely to electronic excitations ($Yₜ \approx Yₑ$) because the predominant mode of energy loss for these ions is through electronic excitations, as shown in Table I. Furthermore it is also assumed that the yield is proportional to the square of the electronic energy loss rate (i.e., $Yₑ = K(n^{-1} dE/dx)^2$ where $n$ is the target number density). This was found to be the case for H₂O (Brown et al. 1982), CO (Brown et al. 1984), SO₂ (Lanzerotti et al. 1982), and Xe (Stevanovic et al. 1984). We obtain a proportionality constant $K = 2.33 \times 10^{-5}$ S atoms/ion/(eV·Å²). The quadratic dependence with this proportionality constant is also consistent with the present keV H⁺ yield and the MeV He⁺ yield value, as shown in Fig. 1. The line in Fig. 1 indicates a quadratic dependence on $n^{-1}(dE/dx)_e$. Therefore using $K$, we can now estimate the electronic contribution ($Yₑ$) to the yield expected for other incident ions and energies such as those in Table I.

The nuclear component of the sputtering yield for monatomic solids in the linear cascade regime is described accurately by Sigmund (1969, 1981) as being proportional to the surface damage function, $F_D(0)$, divided by the surface binding energy $U$, $Yₙ$
Fig. 1. The total yield, $Y_T$, versus $n^{-1}(dE/dx)_e$ for incident ions that deposit energy mostly by electronic excitation (i.e., $Y_T \approx Y_e$). The line indicates a quadratic dependence on $n^{-1}(dE/dx)_e$.

$$Y_T \propto \left[n^{-1}(dE/dx)_e\right]^2$$

$= 0.042 \cdot F_D(0)/U$ (atoms/ion/Å²). $F_D(0)$ is generally written as $\alpha n^{-1}(dE/dx)_e$ where $\alpha$ corrects for the fraction of the energy deposited near the surface which does not contribute to sputtering. The difficulty in applying Sigmund's formula for monatomic targets to a molecular target is apparent in the mass spectrometry results where it was seen that $S_8$ sputters predominately as $S$, $S_2$, and $S_3$. Therefore three species instead of one comprise the principle ejecta each with their own unknown surface binding energy $U$. In order to investigate the dependence of the yield on $F_D(0)$, to deduce a mean surface binding energy, and finally to extrapolate $Y_n$ to corotating ions we present in Fig. 2 a plot of $Y_n = Y_T - Y_e$ versus $F_D(0)$. The line corresponds to a linear dependence and a binding energy of 0.19 eV per sulfur atom. Additional evidence supporting the linear cascade description of the nuclear sputtering mechanism was given in the mass spectrometry section where it was stated that the relative mass spectrum was independent of the ion used for ions which deposit mostly nuclear energy. Only the total amount of sputtered material changed and that varies linearly with $F_D(0)$ as shown in Fig. 2.

The arrows in Fig. 2 indicate the nuclear yield that would be expected from 520 eV S ions and 260 eV O ions, the corotating ion impact energies at Io. The values of $Y_n$ at these points in Fig. 2 are 26 and 14 S atoms per ion, respectively. At this point if we assume each implanted O ion could remove, at most, one additional S atom by means of chemical sputtering, this would only change the O ion yield by 7% and the average yield per plasma ion by 3%. Since the magnitude of this maximum correction is within the uncertainty of our extrapolated values for physical sputtering, we ignore this possible chemical sputtering contribution. Using existing experimental data (Lanzerotti et al. 1982, Boring et al. 1984, Johnson et al. 1984a), a similar extrapolation was carried out for the sputtering of SO$_2$ and it produced yields of 59 and 49 SO$_2$ molecules per ion for corotating S ions and O ions, respectively. Therefore our experimental measurements show that the sputtering yield of corotating O and S ions is due almost entirely to a mechanism of elas-
tic collisions of the incident ions with the molecules of the solid and only for the higher velocity plasma component will the electronic contribution be important. Estimates of the two contributions to the yield ($Y_e$ and $Y_n$) can now be obtained for most ions of interest in the Io plasma torus using Figs. 1 and 2.

The sputter ejection of S and $S_2$ versus temperature was measured with the QMS, and we found that for temperatures characteristic of the majority of Io's surface, $T < 180^\circ$K, the sputter yield is temperature independent. However, care must be taken in making such measurements as we found that an increase in our beam flux from 3 to $5 \times 10^{13}$ ions/cm$^2$/sec gave a strong temperature dependence for $T > 150^\circ$K. For $SO_2$, a temperature dependence of the sputtering yield was observed and associated with the formation of new molecular species, in particular mass 32, similar to that found in D$_2$O (Reimann et al. 1984, Chrisey et al. 1986).

At higher temperatures sputter enhanced sublimation should occur in sulfur giving increases in the yield (Johnson et al. 1984a). This is not a gross beam heating effect but rather it is enhanced sublimation on a per particle basis about the track of the ion and, hence, will also occur at the lower bombardment rates associated with space plasmas. Therefore, quite large sputter yields can be attained at higher temperatures as shown for sulfur by Nash (1986). This result could have implications for the injection rate from the sputtering of hot spots ($T \sim 200$–$400^\circ$K) and their correlation with certain features of the plasma torus (McEwen et al. 1985). The yields of Fink et al. (1984) were known to be due to gross beam heating (D. B. Nash, private communications, Torrisi et al. 1985) and, hence, do not apply to space plasmas.

D. Energy Distributions of Sputtered Neutrals

Figure 3 gives the energy distribution of ejected particles. These spectra, taken with

![Figure 2](image-url)  
**Fig. 2.** The nuclear yield $Y_n = Y_f - Y_e$ versus $F_D(0)$. The values of $\alpha$ for each ion target combination at normal incidence were taken from an empirical fit to experimental measurements using $M_2$ equal to 32 and $M_i$ equal to the mass of the incident ion (Sigmund 1981). Using Sigmund's sputtering yield formula, $Y_n = 0.042 F_D(0)/U$, the line corresponds to a binding energy of 0.19 eV per sulfur atom. The arrows, located at the surface energy deposition that would be expected for 520 eV S ions and 260 eV O ions, S being larger than O, indicate a $Y_n$ of 26 and 14, respectively.
44 keV Ar⁺, have been normalized arbitrarily. The ejection of S is seen to exhibit a $1/E^2$ falloff at high energies which is characteristic of a linear cascade (collisional) sputtering mechanism, whereas S₂ and S₃ are seen to fall off more rapidly. Possible explanations of this falloff can be found elsewhere (Chrisey et al. 1987). The energy spectra in Fig. (3) can be thought of as a few energetically ejected particles and a much larger group of quasi-thermal particles ($E \approx 0.1$ eV). At higher surface temperatures the yields should eventually become dominated by a Maxwellian associated with the surface temperature.

E. Angle of Incidence and Surface Effects

It is found that for keV light ions on heavy metals (Bay and Bohdansky 1979, Andersen and Bay 1981) and for MeV light ions on condensed gases (Brown et al. 1984, Ollerhead et al. 1980) the angular dependence of the sputter yield is faster than $(\cos \Theta)^{-1}$ for $\Theta < 60°–80°$ where $\Theta$ is the angle between the incident ion and the surface normal. For larger angles, $\Theta > 60°–80°$, the yield passes through a maximum and then decreases due to a rapid increase in the reflection coefficient of incident ions. Andersen and Bay (1981) caution that angular dependence results may be influenced by surface topography, i.e., at glancing angles a larger fraction of the yield is due to the direct knock-off of surface atoms. Hapke (1986) and Matson and Nash (1983) have pointed out that the surfaces of objects in space are likely to be extremely rough, fairy-castle-like surfaces, unlike the laboratory surfaces generally examined. Evidence for this for the outer solar system satellites is the pronounced opposition effects (e.g., Brown and Cruikshank 1983). Here we point out, first, that Io is resurfaced at a rate that is high compared to many objects in the outer solar system (Matson and Nash 1983) and the resurfacing process is, to an extent, replicated in the laboratory (e.g., vapor deposition and melts). In addition, in all of the laboratory measurements on volatile samples which are efficiently sputtered we find the production of rough, pitted surfaces after long-term bombardment (Johnson et al. 1985,
Johnson 1985). Nash (1986), for example, has shown that even sublimation of sulfur in a vacuum produces rough, fairy castle surfaces. In spite of these roughening effects and the coloration change observed with fluence, our yields did not noticeably decrease with fluence or exposure time in the vacuum. Therefore, unlike the application of data on the sputtering of metals to describe the sputtering of rocky surfaces, the sputtering of large-yield, insulating solids may reflect the long-term space-plasma bombardment of such surfaces rather well, unless geological processes in the top micron of the surface are both very fast compared to sputter alterations and very different from the laboratory deposition process. In applying our measurements to the trailing hemisphere of Io we have generally ignored the angular enhancement (Sieveka and Johnson 1982, 1985) in order to approximately account for any possible surface roughness effects. Based on a recent simulation additional reductions may not be warranted (P. K. Haff, private communication).

IV. APPLICATION TO THE IO TORUS SUPPLY

It is seen in Table I that the low temperature sputtering yields of sulfur are comparable to the sputtering yields of the much more volatile SO$_2$ at low temperatures. This means that any description of the plasma interaction which allows ions to reach the surface of Io must include sulfur sputtering as well as SO$_2$ sputtering assuming the sulfur coverage on the surface is also comparable. At the high temperatures, when the trailing hemisphere is the day side, the SO$_2$ yields can increase considerably over the sulfur yields due to their temperature dependence (Lanzerotti et al. 1982). However, on the night side and in the polar regions sulfur sputtering contributes a nonnegligible amount. In addition, as pointed out by Linker et al. (1985), the sulfur deposits may predominantly occur in certain regions on Io (e.g., Jovian-facing hemisphere). The average erosion rate of a fresh sulfur deposit from our measurements is found to be about $2 \times 10^{-4}$ cm/year as compared to $10 \times 10^{-4}$ cm/year for an SO$_2$ deposit, but both of these estimates are much lower than the volcanic resurfacing rate (Johnson and Soderblom 1982). Therefore, fresh deposits are generally being sputtered.

An analytic fit to the normalized energy spectra presented here is used in Table II to determine, in the absence of an atmosphere, the direct escape fraction of sputtered sulfur. It is seen from Table II that the escape fractions determined for S$_1$ and S$_2$ are larger than that for SO$_2$. Thus the contribution of sulfur to direct injection is increased somewhat. The results in Table II show that including sulfur sputtering on a surface which is 50% sulfur and 50% SO$_2$ gives a net direct torus injection rate ($\sim 7 \times 10^{28}$ amu/sec) which cannot quite account for the required plasma supply rates ($\sim 10^{29}$ to $10^{30}$ amu/sec). Sulfur accounts for 20% of the direct mass ejection in this model.

The sputtered particles which do not directly escape form a neutral corona of ballistic particles (e.g., Watson 1982) from which secondary processes can eject particles. Sieveka and Johnson (1985, 1986) calculated this for a surface-sputtered SO$_2$ corona. Using their results, which ignore the enhancement at higher temperatures, the inclusion of coronal processes increases the net ejection rate significantly. The exact amount depends on the contribution from plasma electron ionization in the corona. Table II also presents the injection rates due to coronal processes based on the recent calculations of McGrath and Johnson (1987) for sulfur using the present data. A comparison of the targets for both material injection processes shows sulfur contributing a small amount ($\sim 13\%$) to the total mass injection. In terms of only sulfur injection and not mass injection this amount increases by about a factor of 2 since half of the SO$_2$ mass injection is due to oxygen injection. (A small increase in this amount is
TABLE II

<table>
<thead>
<tr>
<th>Target</th>
<th>Species</th>
<th>Escape fraction</th>
<th>Escape energy (eV)</th>
<th>Direct injection (10^28 amu/sec)</th>
<th>Coronal injection (10^29 amu/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_6</td>
<td>S</td>
<td>0.066</td>
<td>1.1</td>
<td>0.2</td>
<td>0.1–0.2</td>
</tr>
<tr>
<td>S_8</td>
<td>S_2</td>
<td>0.049</td>
<td>2.2</td>
<td>1.1</td>
<td>1.1–1.2</td>
</tr>
<tr>
<td>S_8</td>
<td>S_3</td>
<td>0.008</td>
<td>3.3</td>
<td>0.1</td>
<td>0.3–0.5</td>
</tr>
<tr>
<td>SO_2</td>
<td>SO_2</td>
<td>0.03</td>
<td>2.2</td>
<td>5.4</td>
<td>10–20</td>
</tr>
</tbody>
</table>

*The net ejection rates of S, S_2, S_3, and SO_2 from Io. The net injection rate into the torus is (2πR_Io^2ΦeF_coverage/F_w exh MW) where Φ is the mean yield for a plasma assumed to be made up equally of oxygen and sulfur ions (Φ ~ 20 for sulfur and ~54 for SO_2 from Table I), Φ ~ 10^9 ions/cm^2/sec, F_ex is the gravitational escape fraction, determined from an analytical fit to the energy spectra in Fig. 3, F_coverage is the fraction of the surface covered by that target (assuming equal coverage F_coverage = .5), F_sp is the percentage of the total yield sputtered as that species, and MW is the molecular weight in amu (MW = 32 for sulfur and 64 for SO_2). Note a factor of ½ has been included to approximate the effects of surface roughness. The upper and lower limits on the coronal injection are obtained by including and ignoring the plasma electron ionization contribution (McGrath and Johnson 1986).*

suspected since, as stated before, SO_2 sputters nonstoichiometrically. The sum of both direct and indirect injection rates for sulfur and SO_2 sputtering gives a rate (~2 to 3 x 10^29 amu/sec). This rate is larger than the lower limit on the plasma supply rate but still below that rate generally thought to be most reasonable (~10^30 amu/sec). Changes in the surface coverage to more complete SO_2 coverage increases the net mass injection (Sieveka and Johnson 1986), but, of course, modifies the sulfur to oxygen ratio.

If the larger required supply rate (~10^30 amu/sec) is correct, then the deficit in the net supply by direct surface sputtering and from the surface-sputtered corona has generally led to the conclusion that ejection occurs from an atmospheric vapor having an exobase above the surface (Haff et al. 1981, Kumar 1984, Cheng 1984). If this is a sublimed atmosphere then it will clearly be dominated by SO_2 giving the usual result, more O than S supplied to the torus. If photodissociation and diffusion operate, then the O to S ratio is increased further (e.g., Kumar 1984), although a way around this has been suggested (Hunten 1985). A number of authors have discussed possible sputter contributions to the atmosphere. That is, at reasonable atmospheric densities a significant fraction of the ions might reach the surface (McGrath and Johnson 1987). At the corotation energy the ions have a mean penetration depth ~3 x 10^{15} SO_2/cm^2, which is more than the mean exospheric column density of SO_2, and they have a distribution in ranges of an equivalent size. Further, there is a broad distribution in the energies of the incident ions (Baggenal 1985) so that some ions will reach the surface under most circumstances. It is, therefore, likely that the composition of the atmosphere is affected by the ion sputtering rates (Summers et al. 1983, Lanzerotti and Brown 1983). Therefore, ion bombardment produces a vapor of surface material having a composition different from a sublimed vapor and a mean temperature higher than the surface temperature.

Matson et al. (1974) pointed out that sputtered particles ionized within Io's disk (by charge exchange or electron impact) can reimpact the surface if the magnetic...
field penetrates close to the surface. Under such conditions Sieveka and Johnson (1985) have shown that the large sputtering rates and rapid ionization times imply that the sputtered column density of atmospheric gases will approach the projected range of the freshly created and accelerated ions, thereby producing a sputter-limited atmosphere of the type initially suggested in the description of the sputtering of icy satellites (Lanzerotti et al. 1979, Johnson et al. 1981). Based on the present experiments, this supply rate would be from an atmosphere having a considerable contribution from sulfur in the form of $S_2$. If sulfur and $SO_2$ are equally available on the surface, then about $\frac{1}{3}$ of the S atoms (as S, $S_2$, $S_3$, or $SO_2$) in the sputtered component of the atmosphere are due to sulfur sputtering. The production of such an atmosphere, therefore, should be considered when describing the similarities in the amount of sulfur and oxygen in the plasma torus.

V. SUMMARY

We have presented accurate measurements of the yields, mass spectra, and energy spectra of ejected sulfur from vapor deposits of sulfur at temperatures and ion energies relevant to the plasma interaction with the surface of Io. These are integrated into a semiempirical model which allows extrapolation to most ion energies and ion types of interest for the Jovian magnetospheric interaction with Io. These results are compared to our previous measurements of the sputtering of condensed $SO_2$. In both cases the predominantly ejected species is mass 64. Sulfur and oxygen ions bombarding low temperature sulfur at 57 km/sec give yields of 26 and 14 S atoms (predominantly as $S_2$) versus 59 and 49 $SO_2$ molecules, respectively. Whereas the $SO_2$ sputtering showed a fluence dependence and a temperature dependence indicative of chemical activity induced by the ions, the sulfur sputtering only showed a color change with fluence and no clear fluence dependence or temperature dependence up to 180$^\circ$K. The color change occurred faster and more dramatically for the lighter ions and was suggestive of fragmentation of $S_8$.

The contribution of sulfur to direct gravitational ejection from the surface of Io was less than that for $SO_2$ due to its lower yield. We have also calculated the net injection from a sputter-induced corona assuming 50% coverage each of sulfur and $SO_2$. Including this and assuming the full corotating ion bombardment flux, the total supply rate is approximately $2 \times 3 \times 10^{29}$ amu/sec which is the lower limit on the required supply rate but smaller than what is considered to be the most reasonable value under the bombardment conditions assumed. Allowing reimpact of neutrals ionized in the disk would increase this estimate.

The above results can be used to evaluate ejection on the night side and in the polar region where less than an exospheric component of atmosphere is likely to be present. In the limit in which more than an exosphere exists, but the ions still reach the surface, the ejection energies of the sputter products are not important but the yields can be used directly to estimate the fractional contribution of sulfur to the atmosphere by sputtering. The darker colors of Io’s surface in the polar region may suggest that the magnetospheric ions do reach the surface producing an alteration in the reflectance, as observed in the laboratory, which is not annealed rapidly in these regions. The results presented here indicate that although the huge sputtering rates in sulfur presented earlier are irrelevant, sputtering of sulfur from the surface should be included as a small but nonnegligible contribution to the atmospheric and torus sulfur at Io.

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