

LABORATORY STUDIES OF THE INTERACTION OF IONS WITH CONDENSED
GASES: PLANETARY APPLICATIONS

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INTRODUCTION

The work described in this paper is concerned with laboratory studies of the processes that produce the ejection of molecules from the surfaces of condensed gas solids, the change in the chemistry of the surface materials, and the relationship of these results to processes occurring in the solar system. Included is a discussion of the experimental techniques employed in making these laboratory measurements.

In the solar system as one goes away from the sun the temperature of the surfaces of solid bodies decreases, such that many of the surfaces in the outer solar system are composed of substances that are gases at earth temperatures. This means that the binding energy of the molecules that form these solids tends to become smaller as one goes out in the solar system. Since these surfaces are frequently exposed to some form of radiation one has the possibility that these volatile substances can be ejected by the radiation to form an atmosphere in the vicinity of the body. The bodies of principal interest in this context are planetary satellites and rings, as well as comets and asteroids. The relevant radiation that causes ejection from these objects are ions, electrons and photons. In some instances, such as when a comet comes close to the sun, the net radiation flux is large enough to cause the temperature of a large fraction of the surface to become great enough that evaporation of the surface materials occurs. This removal of surface material by increased temperature is reasonably well understood and will not be considered here. Rather, we will concentrate on the ejection of surface molecules as a result of exposure to energetic ions, electrons and photons, where the ejection rate is proportional to the incident radiation flux. This implies that each incident particle produces an effect that is independent of the others. In some situations it is useful to speak of a transient increase in the temperature of the solid in the vicinity of the incident particle. The

process of the ejection of surface material as a result of incident radiation is called sputtering (or desorption) if the ejection rate is proportional to the incident flux.

Particles (ions, electrons, photons) deposit their energy in a solid in two forms: (1) Kinetic energy of motion of the atoms of the solid (nuclear deposition) and (2) Excitation of the electronic structure of the atoms/molecules of the solid (electronic deposition). Since the ejection of atoms/molecules from the surface of the solid is a result of their having attained a larger than average kinetic energy, it is easy to see how nuclear deposition leads to ejection. In the case of electronic excitation, however, it is necessary that the electronic disturbance lead to repulsion between neighboring particles and subsequent ejection of one or more particles from the surface. In the case of incident electrons and photons there is only an electronic contribution to the ejection, whereas for ions there can be both an electronic and a nuclear contribution, with the latter dominating for heavy ions.

When the solid under consideration has molecules composed of several different kinds of atoms there is the possibility of significant chemical change initiated by the incident radiation, even at the low temperatures of the condensed gas solids. Both the nuclear and electronic energy deposition can result in the breaking of chemical bonds, resulting in various molecular fragments. These fragments can diffuse and combine to form new chemical species, some of which may be volatile enough to leave the solid of their own accord while others may be ejected by subsequent radiation. The net result of all of this activity is that the chemical nature of the solid, along with its physical characteristics, may be permanently altered by the radiation, and various particles are ejected from its surface, both molecules of the original material and the new ones that have been produced by the radiation. Among the characteristics of the surface that are changed are its ability to reflect light and the rate at which it is eroded by subsequent radiation. An example is the bombardment of CH_4 by ions or electrons. The primary ejected species is H_2 , resulting in a decreasing H to C ratio (Fig. 1). Eventually the material becomes rather carbon-like, very different from the original clear condensed gas solid. The tendency toward a carbonaceous material is accompanied by an increase in the average binding energy of particles on the surface, with a corresponding decrease in the probability of their ejection.

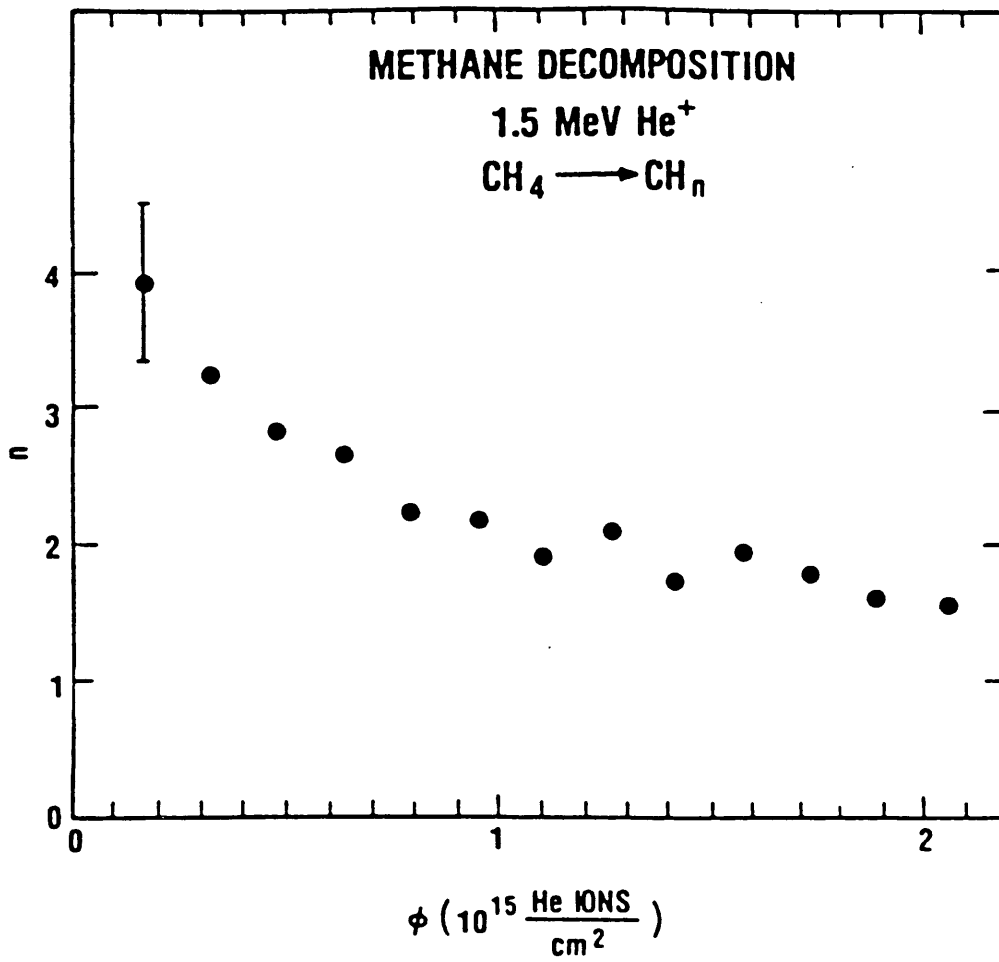


Fig. 1 Hydrogen-carbon ratio vs. fluence for methane bombardment by 1.5 MeV He⁺ ions

Processes such as this may well have altered the surfaces of solar system bodies that were originally hydrocarbons but which as a result of radiation bombardment became much like carbon with a corresponding decrease in ability to reflect sunlight.

As implied in the previous discussion the principal factor in determining whether an atom or molecule is ejected from a surface is how strongly it is bound. We have also seen that chemical activity produces new species, some more strongly and some more weakly bound than the molecules of the original material. The ejection rate is, of course, also strongly affected by the density of energy deposited at the surface by the incident particle.

Experimental Techniques

We concentrate here on positive ions and electrons as incident particles and condensed gas solids as targets. The experimental systems described here are at the University of Virginia for keV measurements and Bell Labs for MeV measurements, and the results described later are from these two labs. Electrons with energies in the keV range are produced simply with an electron gun, consisting of a filament, an accelerating voltage and suitable focussing. Ions in the keV range require a little more equipment, including an ion source, an analyzing magnet and suitable pumping to maintain a low pressure at the target. Ions with energies in the MeV range are usually produced by using a van de Graaf accelerator. Condensed gas targets can be produced by deposition of the gas or vapor onto a cold substrate. Temperatures of $\sim 15\text{K}$ will allow one to condense any material except He, H_2 and Ne. Temperatures in this range can be obtained using liquid He, but more conveniently with a closed cycle helium refrigerator.

In studying the ejection of atoms and molecules from the surface of the solid one is primarily interested in three quantities: (1) The absolute rate at which the ejection takes place, usually stated as the sputtering yield $Y =$ particles ejected per incident ion. (2) The mass spectrum of ejected particles and (3) The energy spectrum of each of these masses. A typical apparatus for making these measurements is shown in Fig. 2. In this system the ion beam is incident on a condensed gas target. In making measurements of the absolute sputtering yield it is necessary to be able to measure the beam current accurately. This is aided with a flow-through Faraday cup before the target. One also desires to have the pressure at the target as low as

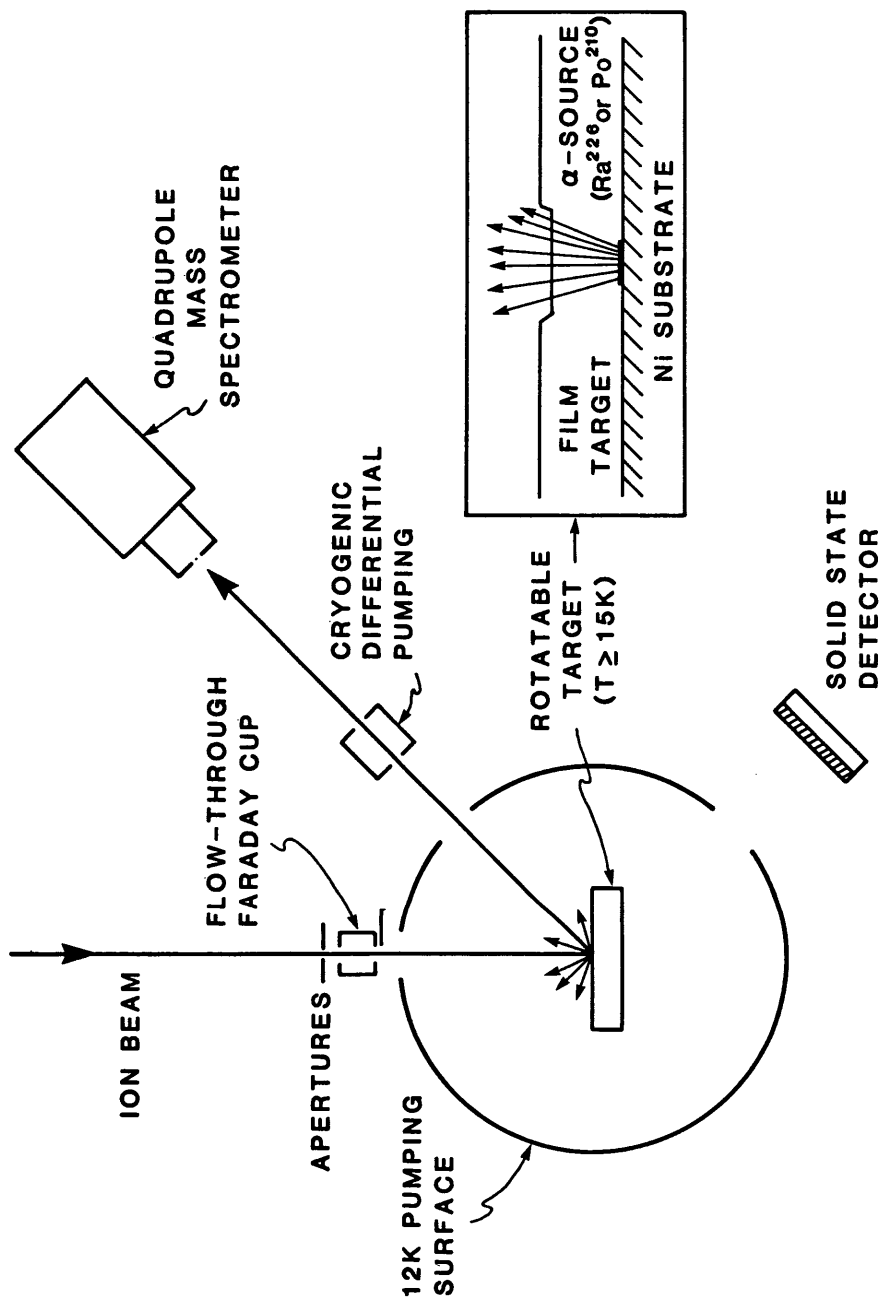


Fig. 2 Experimental system for investigating the sputtering of condensed gas solids

possible. This is accomplished by having the target surrounded by a copper cylinder maintained at a temperature of 12K, which serves to cryopump the target region, maintaining a pressure at the target of $\sim 10^{-10}$ Torr. The mass spectrum of ejected neutral particles is observed with a quadrupole mass spectrometer located in a separate vacuum chamber. Ionization of the neutral particles is by an electron-emitting filament just before the quadrupole. The kinetic energy spectrum of ejected particles is measured by pulsing the ion beam and observing the time spectrum of particles arriving at the quadrupole. Since the distance from target to detector and the mass of the particle are known one can then obtain the energy spectrum of each of the ejected species. In these time-of-flight measurements it is essential that the detected particles come directly from the target. This means that the detector chamber must be well isolated from the target chamber in a vacuum sense so that a pressure rise in the target chamber is not detected in the detector chamber. This is accomplished by having cryogenic differential pumping between the two chambers. In order to determine the total absolute yield of ejected particles one needs a method of determining changes in the thickness of the target as it is eroded by the ion beam. In this system this is accomplished by having an alpha source (R_a^{220} or P_o^{210}) deposited on the substrate that the target film is grown on. After the film is grown the alphas pass through it and their energy is a measure of the film thickness. These alphas are detected and their energy analyzed with a surface barrier solid state detector and a multichannel analyzer.

Since the character of the irradiated condensed gas solid is altered by the radiation it is important to be able to study these changes in the species present in the target. An experimental system capable of monitoring the atomic composition of the target is shown in Fig. 3. In this case the incident beam is composed of incident MeV H^+ or He^+ ions. These ions can be used for sputtering the film, but they can also be used for analyzing the atoms present in the target by Rutherford backscattering of these ions (usually He^+). A small fraction of the incident ions are scattered through an angle near 180° . The energy of these ions is determined only by the mass of the scattering atom and the amount of material through which the ion has passed. One can thus measure the proportion of the various atoms present in the target as a function of the amount of radiation. The incident ions that produce the radiation effect being studied may well be different from those

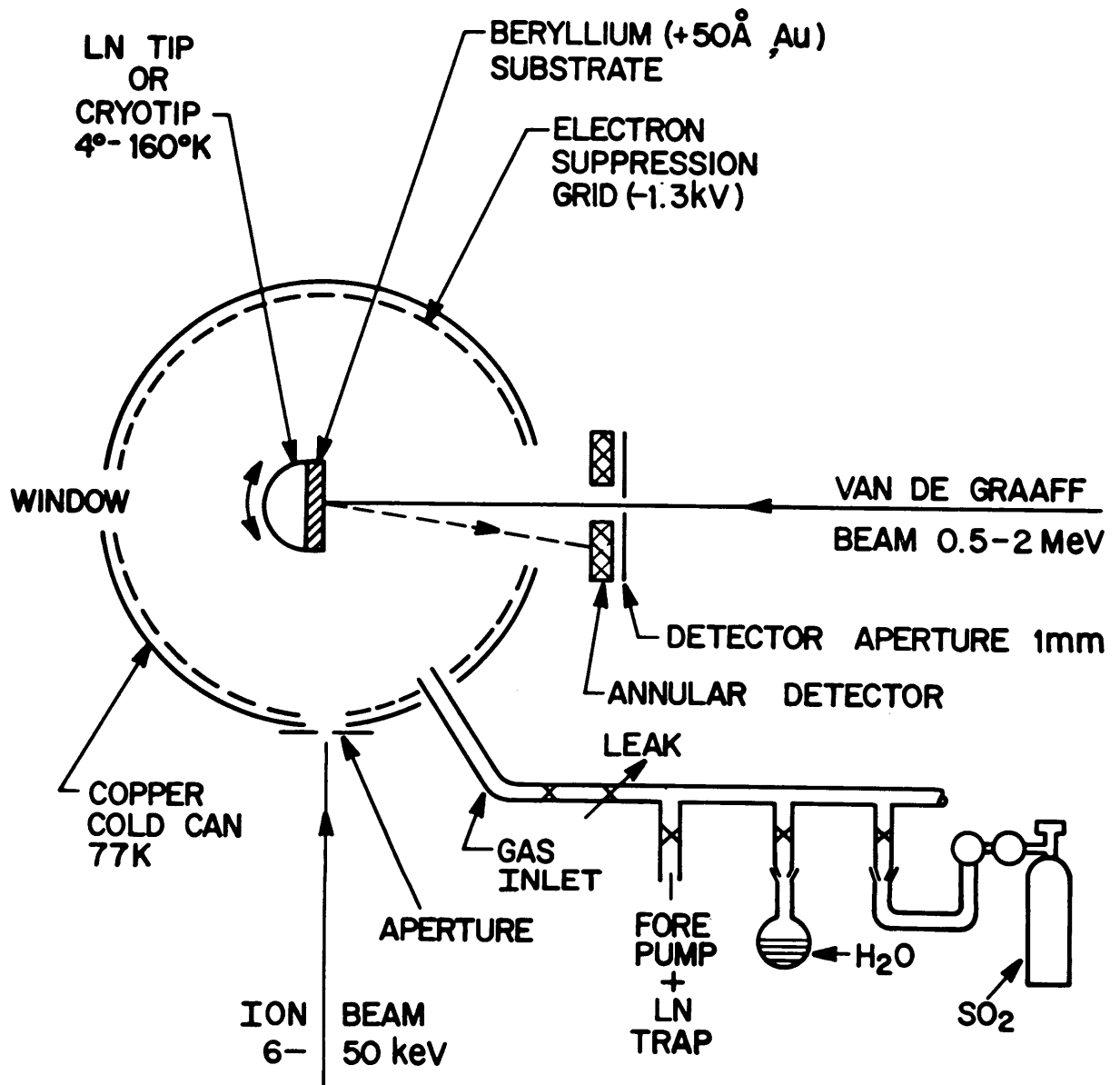


Fig. 3 Experimental configuration for Rutherford backscattering analysis

used in backscattering analysis. The technique gives no information on the molecular character of the target material, but it may also be used to measure the thickness of the target film in much the same manner as the alpha particle method described above.

Information about the molecular character of the solid may be obtained by a number of methods including SIMS, warming the irradiated condensed gas target and looking at the mass spectrum of what comes off, but we concentrate here on information that can be obtained by probing it with photons. The most useful wavelength ranges are in the infrared and ultraviolet. The configuration can utilize either the spectrum of photons transmitted through a thin film or those reflected from its surface region. Shown in Fig. 4 is an experimental system for studying in transmission the absorption of IR photons by a condensed gas target. The target is formed onto a cold KRR substrate with subsequent bombardment by an ion beam. One is principally looking for new absorbing molecular species formed as a result of the bonds broken by the incident particles. An arrangement for studying the reflectance of UV light by solid H₂O is shown in Fig. 5. The light from a high pressure Xe arc is incident on an ice target and the reflected spectrum is observed with a VUV-visible monochrometer. A spectrum is taken before ion bombardment and compared to that after bombardment. In addition to the changes in the molecular structure of the target caused by the breaking of chemical bonds by the ions, one can also expect absorption by new species that are created by the implantation of the ions into the target.

Representative Results

The key statements from the above discussion of the sputtering of condensed gas solids are that: (1) Incident ions and electrons can break chemical bonds, producing fragments. (2) The fragments can diffuse and combine to form new species. and (3) The character of the solid is permanently altered by these processes and particles are ejected from its surface, both the molecules of the original solid and the new species. In this section we present the results of measurements that indicate these features. In Fig. 6 we show the results of the bombardment of D₂O ice (D₂O is chosen over H₂O for reasons of lower background) by 1.5 MeV He⁺ ions, where the energy deposition is predominantly electronic. The principal detected species are D₂O, D₂ and O₂, indicating the presence of new species created by the incident ions. In

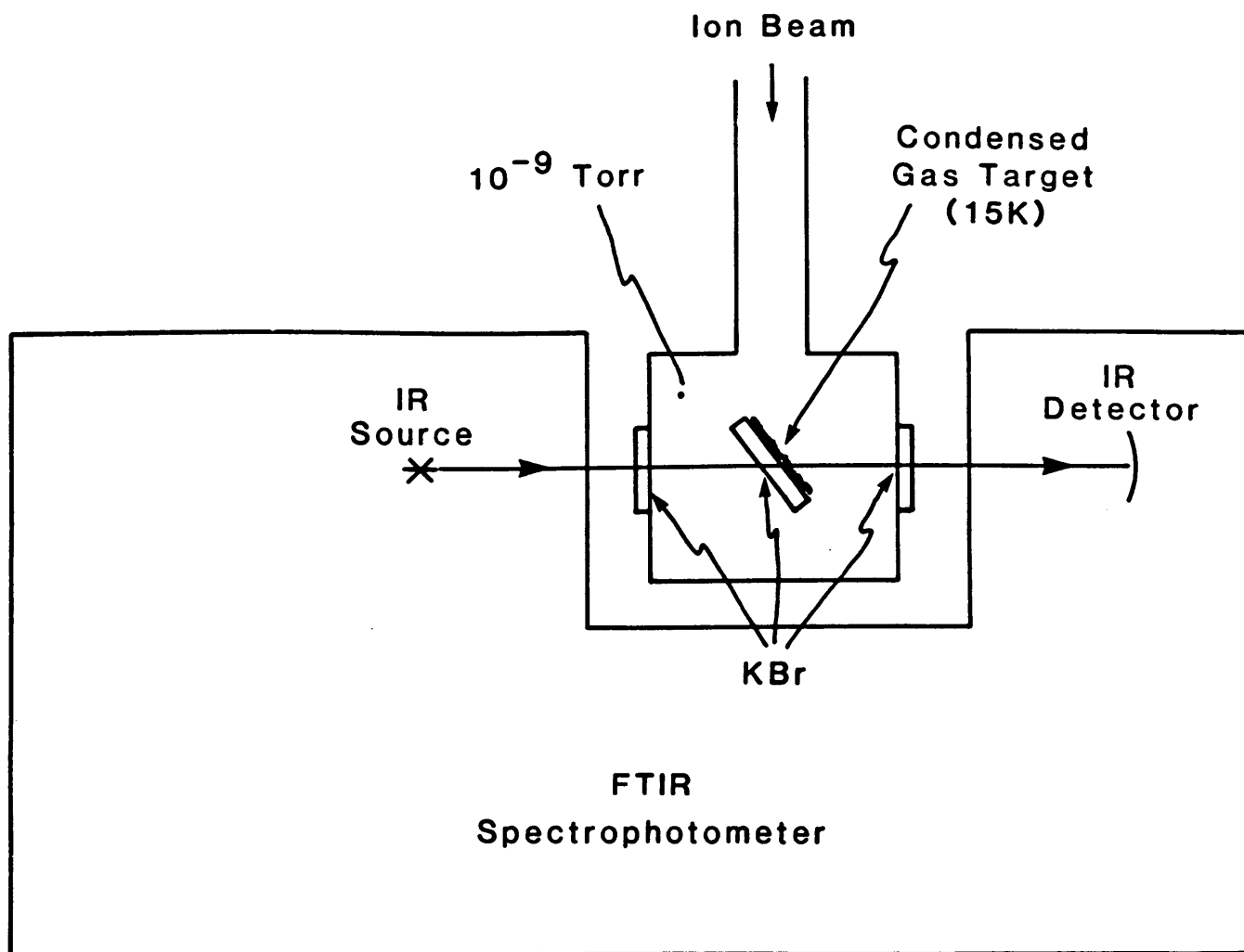


Fig. 4 Apparatus for infrared transmission studies of ion-bombarded condensed gas targets

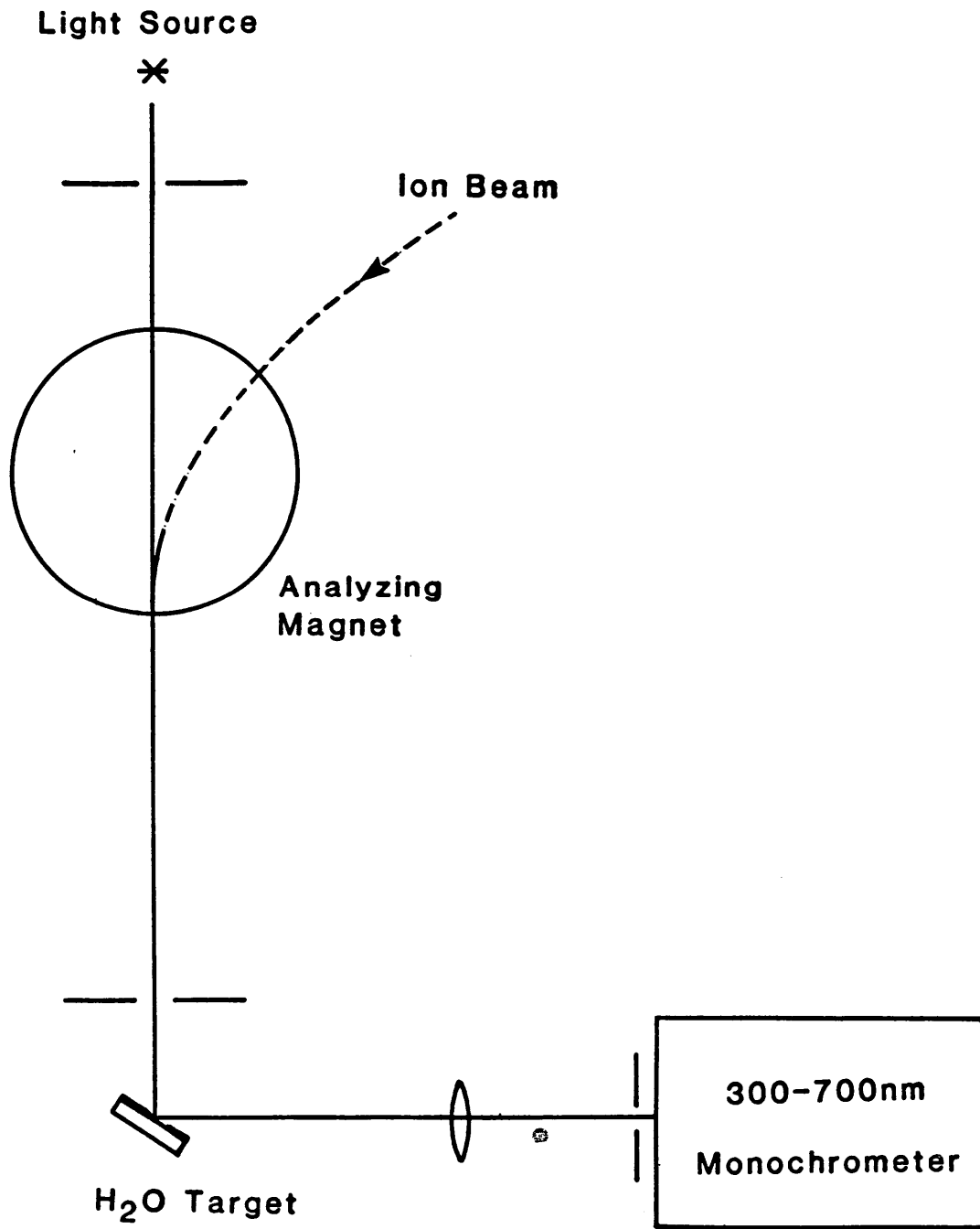


Fig. 5 Experimental system for reflectance studies of ice

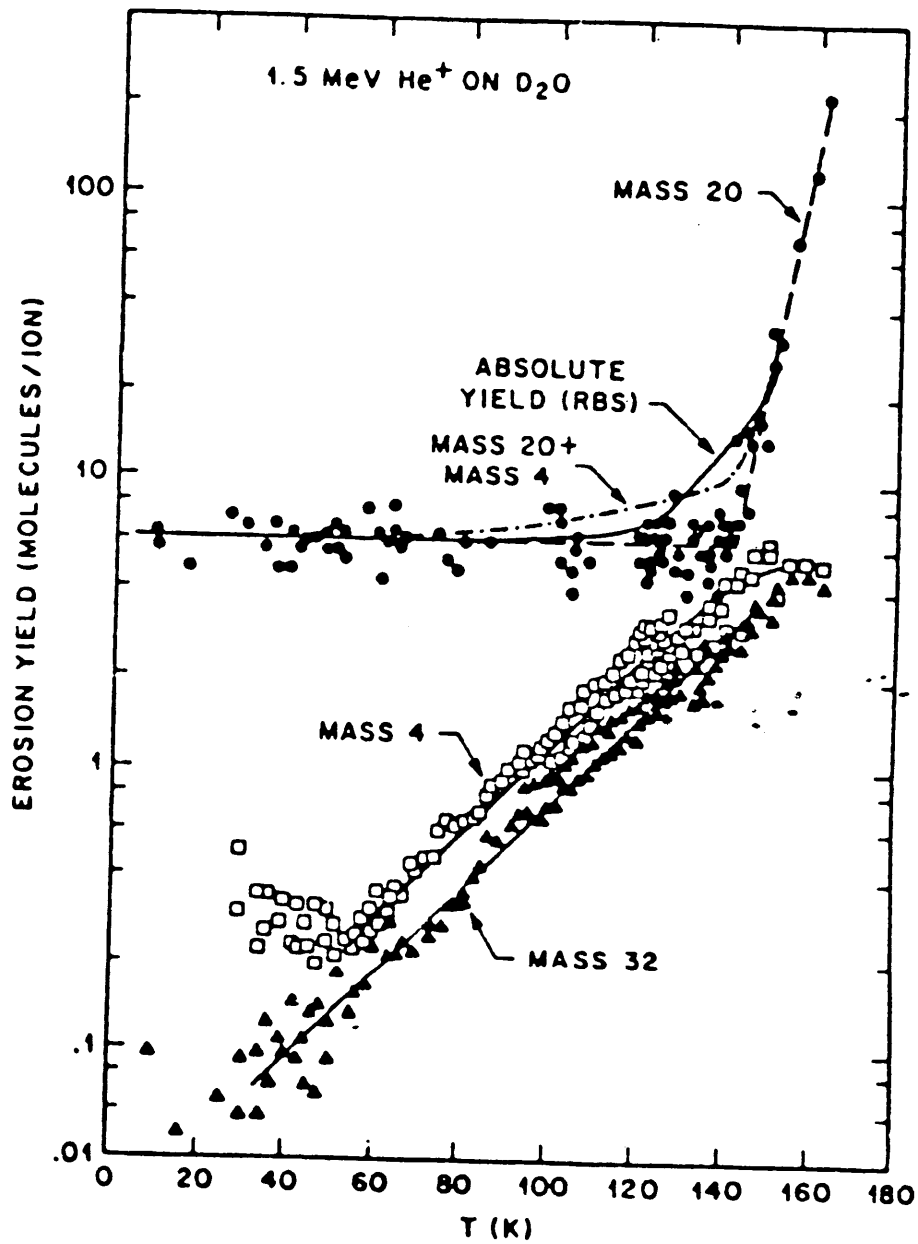


Fig. 6 Temperature dependence of the ejection of D₂O, D and O₂ from solid D₂O.

Fig. 6 we plot the yield of ejected particles as a function of target temperature, as measured by a mass spectrometer. It is seen that in the temperature range 50 - 140K the yield of D_2O is independent of temperature, while the yield of D_2 and O_2 is dependent on temperature over the entire range. This is as expected since D_2 and O_2 are created species which depend on diffusion for their production. Evidence of the production of new species is also shown in Fig. 7 for D_2O where the mass spectrometer signal for D_2O , D_2 and O_2 is displayed as a function of beam fluence (or time after the beam is turned on). One sees that the D_2O signal (mass 20) rises rapidly to a constant value while the O_2 signal (mass 32) rises slowly, indicating the finite time required to produce a significant amount of this new species. The D_2 signal (mass 4) seems to have a more complicated structure with both a rapid and a slow component. The behavior of targets with different possible product species is shown in Fig. 8, where the total sputtering yield is plotted vs. temperature for Ar, CO_2 , SO_2 and H_2O . The curve for Ar is the simplest since there are no new chemical species produced. The yield is constant up to a temperature just under where one expects significant sublimation, followed by a rapid rise, probably due to local heating of the target in the vicinity of the track of the incident particle. The H_2O and SO_2 targets show a behavior similar to each other - a region of constant yield followed by a slow rise when the diffusion and ejection of new species becomes comparable to the ejection of the parent species. The CO_2 target exhibits the most complex behavior with two distinct steps, corresponding to the sudden production of new species at the corresponding temperatures.

Satellites of Jupiter and Saturn

The general information discussed above is useful for considering the contributions to atmospheres and plasmas in the environment of planetary bodies. For a specific situation we consider how information of the type presented here applies to two of the Jovian satellites - Io and Europa, and the icy Saturnian satellites.

Io

The surface of Io is composed largely of sulfur-containing compounds, elemental sulfur and SO_2 . In the absence of a thick atmosphere (e.g. night side and poles) the surface of Io is continually bombarded by ions of the

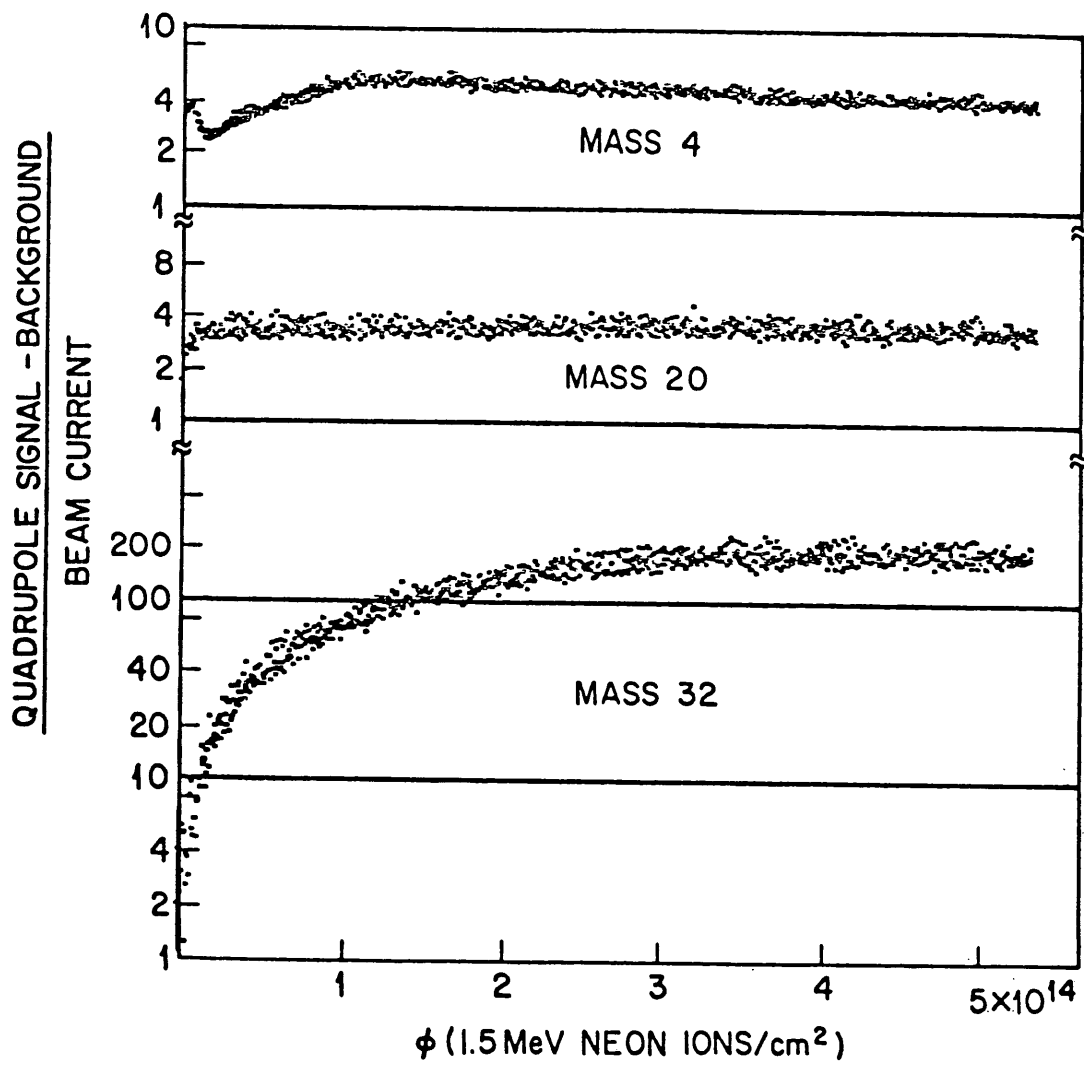


Fig. 7 Transients in the ejection of D_2O , D_2 and O_2O

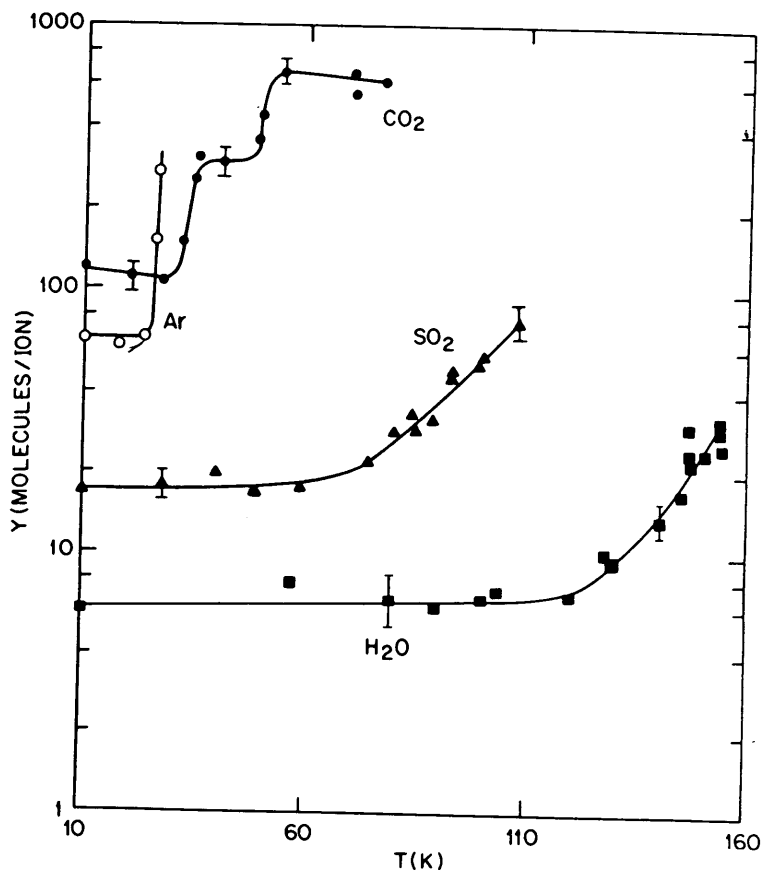


Fig. 8 Temperature dependence of the sputtering of Ar, CO₂, SO₂ and D₂O

plasma torus trapped in Jupiter's magnetosphere. We are thus interested in the rate at which particles are ejected from the surface and their subsequent history. One important factor in the ejection is the energy spectrum of ejected species, since this determines the fraction of ejected particles that escape the gravitational field of the satellite. The ones that do not escape will probably pass in a ballistic trajectory and be redeposited on the surface. The ones that do escape are bound in Jupiter's gravitational field until they are ionized by solar photons or electrons, at which time they become part of the plasma torus around Jupiter, with the likelihood that they will later contribute to the erosion of the surfaces of the satellites embedded in this torus.

For the case of sulfur on the surface of Io we consider first the mass spectrum of ejected particles. Shown in Fig. 9 is a spectrum obtained in the laboratory for the erosion of sulfur by keV ions. Solid sulfur is composed of S_8 rings, but one sees that very few of the ejected species are S_8 , with the ejecta being predominantly S_2 . This is because it is difficult to have ejecting impulses applied to the whole S_8 ring, whereas S_2 is a particularly stable small fragment of sulfur. Evidence for particles altering the surface and producing fragments may be the dark poles of Io. An example of the energy spectrum of ejected sulfur species is shown in Fig. 10. At the higher ejection energies it is seen that for the small fragments S_1 and S_2 the behavior goes as E^{-2} , which is typical of collision cascade sputtering. For the larger species the curve drops more rapidly, indicating the difficulty of ejecting a large fragment as a result of an energetic impulse in the solid. Similar energy spectra have been obtained for the sputtering of SO_2 by keV ions, allowing one to assess the relative importance of those particles that escape the gravitational field of Io and those that become redeposited on the surface.

A problem of major interest to atmospheric scientists is the source of Na observed in the atmosphere of Io. We have recently measured the ejection of Na from Na_2S and combined that with our sulfur results to help understand Na_2S_x (i.e. any combination of sodium and sulfur on Io). We find that sodium is ejected primarily in the form Na, NaS, and Na_2S . Therefore, both atomic and molecular forms should be observed. Using our measured energy spectra we find we can produce a sodium atom line-of-sight column density with a profile like that observed. Because of the recent observation of H_2S in this system

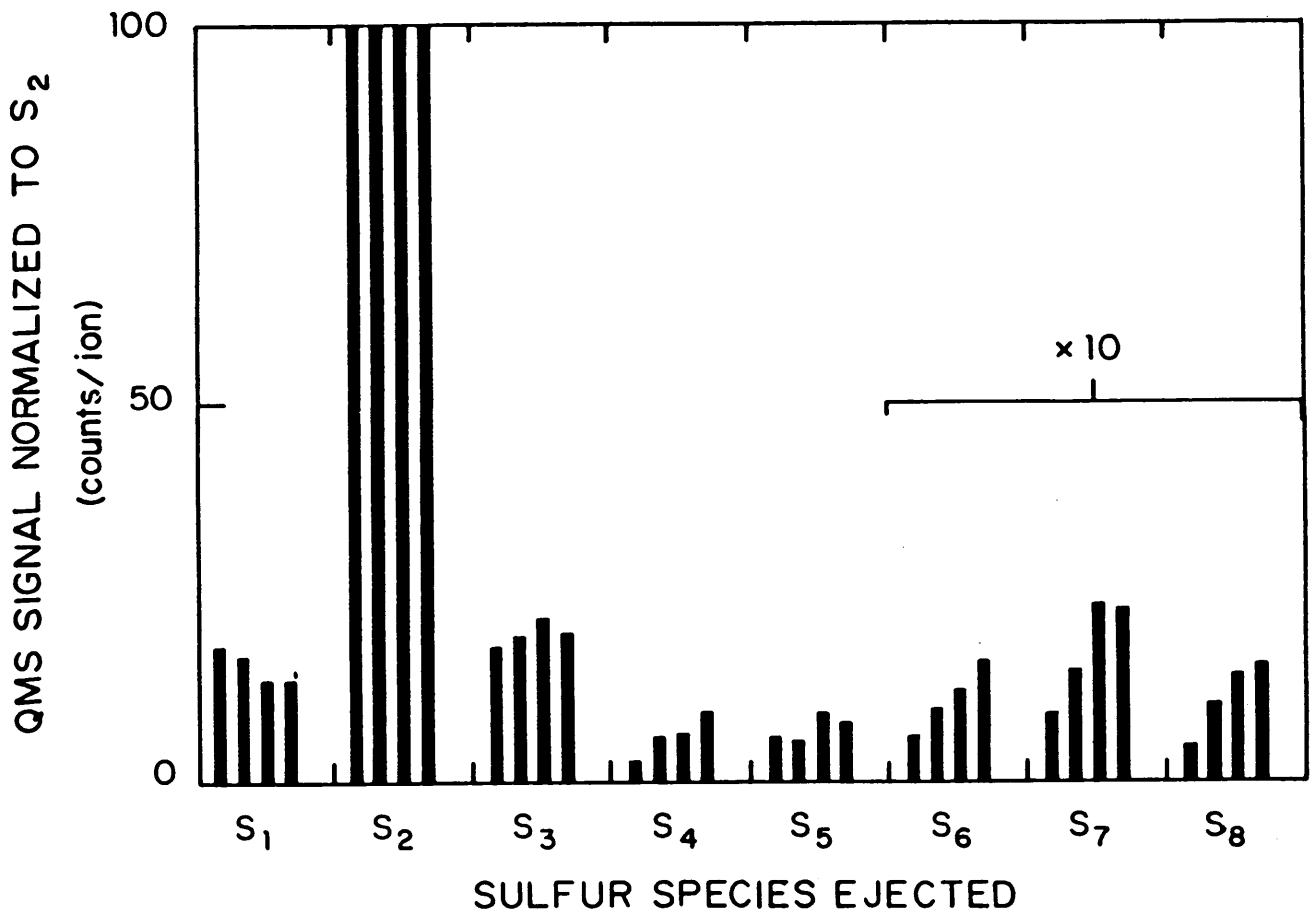


Fig. 9 Mass spectrum of particles ejected from sulfur by keV ions

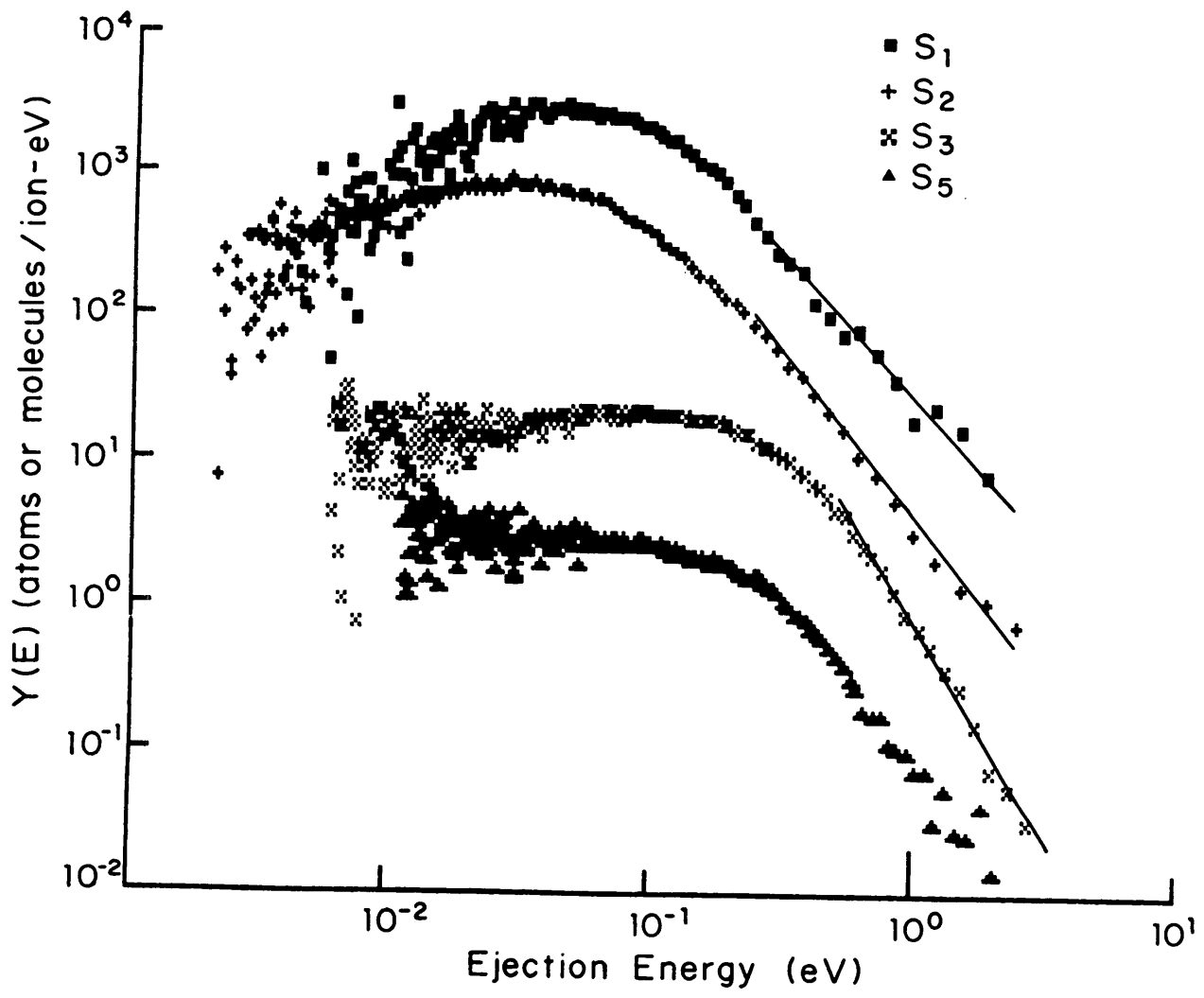


Fig. 10 Energy spectrum for several masses ejected from solid sulfur

we will shortly be studying the yield of H_2S from sulfur bombarded by protons.

Europa

The surface of Europa is largely solid H_2O and much of the information about its composition is obtained by looking at the spectrum of reflected sunlight, particularly in the UV region. Compared to pure ice, one observes in the Europa spectrum a rather strong absorption in the wavelength range 200-500nm. It has been suggested that this may be due to S-O bonds in the solid that result from S^+ implantation into H_2O from the ions in the Jovian magnetosphere. We have explored this hypothesis in the laboratory by observing the reflectance of solid H_2O in the UV, both before ion bombardment and after bombardment by various ions. Shown in Fig. 11 is the ratio of a spectrum taken after bombardment by SO_2^+ ions to that before bombardment for a temperature of 20K. It is seen that there is in fact a strong absorption feature at the lower wavelengths. In order to test whether this was due to S implantation or some more general interaction of the ions with the target we repeated the experiment with Ar^+ ions. The resulting spectrum was substantially the same as for SO_2^+ ions, indicating that the absorbing species was probably a result of bond breaking in the H_2O target rather than being due to an implanted species. When the experiments were repeated at 120K, a temperature more representative of Europa, the absorption feature was absent for all incident ions, indicating that the low temperature was necessary to preserve the absorbing species. This leaves open the question of what does produce the absorption on Europa. One thing that must be kept in mind with regard to the above laboratory results is that the range of the ions in the solid is ~ 20 nm, meaning that only a thin layer contains implanted ions and that these may produce an absorption much too weak to be observed. It is possible that on Europa the implantation of S^+ takes place over a long time, along with simultaneous redeposition of ejected H_2O onto the surface, resulting in a surface region that contains many sulfur atoms to a depth that is large compared to the penetration depth of the light that is reflected.

Icy Saturnian Satellites

From Mimas to Rhea a plasma containing H^+ and O^+ has been identified. Of particular interest here is the heavy species whose source must be the icy satellites. That is, plasma ions bombard the surface and sputter H_2O (H_2 +

Reflectance Spectra SO₂⁺ on H₂O (20K)

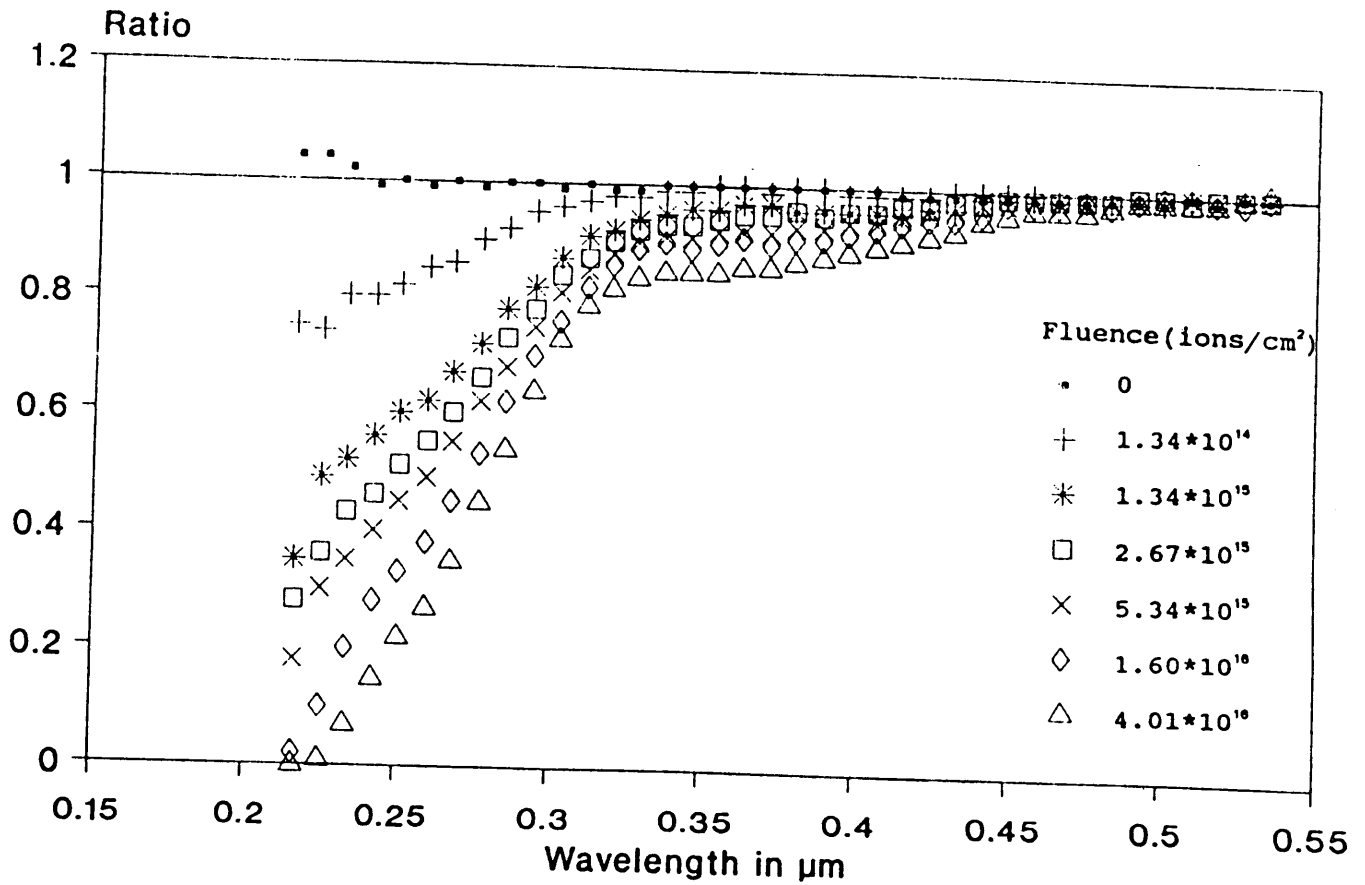


Fig. 11 Reflectance spectrum for SO₂⁺ bombardment of H₂O

O₂) which based on our laboratory measurements easily escape the gravitational fields of the small satellites. These molecules reside in the gravitational field of Saturn orbiting at a speed close to that of the parent satellite, as determined by our ejected particle energy spectra. Eventually the molecules are ionized (by electrons or UV photons) producing the observed plasma. We therefore, have been able to take our laboratory measurements and calculate the source rate of ions in the inner magnetosphere. As the electron temperatures inside the orbit of Enceladus are low, the plasma may contain molecular ions, the detection of which by Cassini would be an exciting test of these ideas. These satellites also have reflectance spectra which are not those of pure H₂O and we are at present working on sorting out the role of bombardment vs. that of contaminants in the solid.

As an example of the use of laboratory data to calculate atmospheric densities we show in Fig. 12 the density contours in the vicinity of the Saturnian satellites, as calculated from the ejection rate and energy distribution of particles ejected from these satellites.

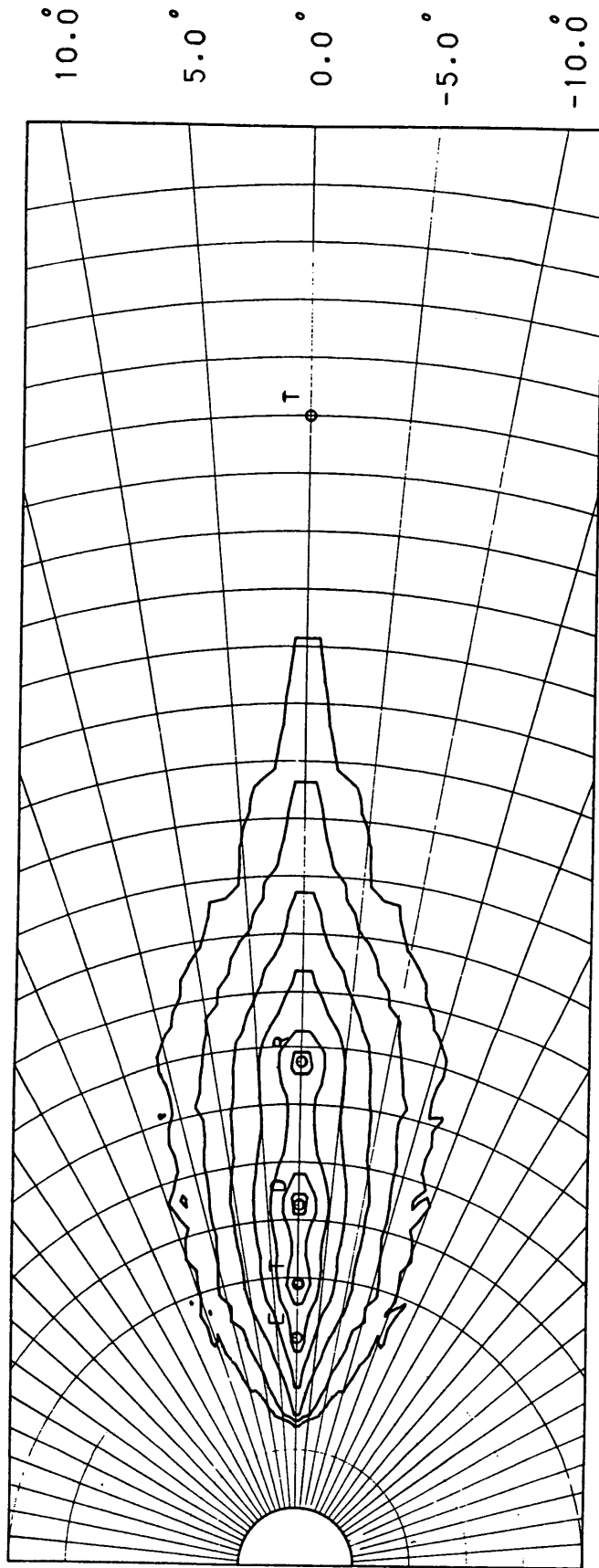


Fig. 12 Density contours near the Saturnian satellites as calculated from ejected energy spectra from the satellite surfaces. The outermost contour is 10^{-1} part/cm³, the next are $10^{-0.5}$, 10^0 , etc.