ION-INDUCED MOLECULAR EJECTION FROM D₂O ICE


Department of Nuclear Engineering and Engineering Physics, University of Virginia *, Charlottesville, Virginia 22901, USA

and

W.L. BROWN, K.J. MARCANTONIO and W.M. AUGUSTYNIAK

AT&T Bell Laboratories, Murray Hill, New Jersey 07974, USA

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Studies of molecules ejected from water ice by fast ions provide insight into the electronic relaxation processes and subsequent chemistry occurring in ice at very low temperatures. The ion-induced ejection of D₂O, D₂, and O₂ molecules from thin films of D₂O ice has been measured as a function of the fluence of incident MeV ions at temperatures between 10 and 140 K. For a given beam current, the O₂ yield exhibits initial transients which are slow compared with the prompt ejection of D₂O. We interpret these results as due to the build-up of O₂ in the films following fragmentation of D₂O molecules by incident ions. The fragments re-form into new molecular species which diffuse to and escape from the surface, aided by subsequent bombardment. The D₂ transient has a prompt component, which we postulate is due to rapid formation during electronic recombination near the surface. A slow component of the D₂ transient is also observed, which may arise through a two-step process similar to that of O₂. Time-of-flight energy spectra of the ejected D₂O molecules have also been measured. Incident ion masses and energies range from those for which nuclear elastic energy deposition dominates (50 keV argon) to those for which electronic energy deposition dominates (1.5 MeV helium). The spectra cannot be described by models typically employed for the sputtering of metals. For instance, the spectra do not have maxima characteristic of the sublimation energy of the solid. In addition, the sputtering yield in the high energy part of the ejection spectrum of D₂O is too large to arise from nuclear elastic energy deposition. It must result instead from relatively energetic non-radiative relaxation of electronic excitation. For incident MeV ions that deposit their energy predominantly in electronic excitation, the low energy part of the D₂O ejection spectrum is greatly enhanced, indicative of a weakly antibinding region formed along an incident particle track. Enhanced ion yields are also found in the collision cascade region which are attributed to electronic processes.

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1. Introduction

The sputtering of dielectric materials by incident fast ions and electrons has become increasingly important for understanding the very fast electronic relaxation processes occurring in insulators [1]. When the material is a condensed gas solid, the sputtering process takes on further importance because of the relevance of the results to planetary and space science [2].

In this article, we present new results on the ejection of D₂O, O₂ and D₂ molecules from D₂O ice by incident ions. Earlier, we had reported that the total loss of material from water ice, expressed as a sputtering yield, was determined for MeV incident ions by the electronic excitation and ionization produced in the material and not by the nuclear elastic collision processes responsible for sputtering in metals [3]. We also had shown the sputtering yield from water ice to be temperature independent at temperatures below ~ 100 K, but to be strongly temperature dependent at higher temperatures [4]. Subsequently we measured the masses of the sputtered products [5] and detected significant signals for masses 32 (O₂), 20 (D₂O) and 4 (D₂). The temperature dependence of the total yield, as well as that of the individual masses, suggested that molecular transport and formation processes, occurring in response to the production of broken bonds by the incident ion, played an important role in determining the yields at higher temperatures.

Here we present data on the fluence (radiation flux × time) dependence of the ejection of D₂O, D₂, and O₂ as a freshly deposited film is bombarded. We also present energy spectra derived for ejected D₂O from time-of-flight data. Both the fluence dependence and the energy spectra give insight into the nature of the erosion and the chemical transformations occurring in this molecular solid. The fluence dependence of the ejection of O₂ and D₂ suggests a strongly temperature dependent build-up of these species in D₂O films during initial bombardment. The low energy (< 0.3 eV) part of energy spectra of ejected D₂O molecules from ice films is qualitatively different depending upon whether ejection results solely from electronic excitation (by incident MeV He ions) or includes nuclear momentum transfer (by incident 50 keV Ar ions).

2. Experimental method

The ice layers used in the measurements to be reported here were formed by condensation from the gas phase on a substrate cooled to temperatures < 25 K. The layers were typically between 0.1 and 1 μm in thickness. Ion beams from a 60 keV accelerator at the University of Virginia or a 3.75 MeV Van de Graaff at Bell Laboratories bombarded these films. The experimental set-ups are essentially the same and a schematic diagram is shown in fig. 1. The beam current densities used were such that the phenomena being studied were
produced by individual ions penetrating the films and not by collective heating [3].

Neutral molecules ejected from the films were measured in quadrupole mass spectrometers. To reduce the surface contamination of the ice and to reduce the background in the quadrupole mass spectrometers, the target chambers were maintained at ultra high vacuum by cryogenic pumping. To further improve the signal-to-background ratios, D$_2$O rather than H$_2$O ice was used because the background at mass 20 is much less than at mass 18. (We have measured the absolute sputtering yield of D$_2$O and find it to be about 10% less than the sputtering yield of H$_2$O. This difference is comparable to the uncertainties of the measurements, but a lower yield for D$_2$O than for H$_2$O might be expected because of the larger mass of D$_2$O. The temperature dependence of the total yield for D$_2$O is the same as that for H$_2$O [4].) Neutral molecules are ionized in an electron ionizer at the entrance to the quadrupole mass selector. An electron multiplier detector following the quadrupole is positioned off the axis of the quadrupole to minimize the detection of photons or high energy scattered beam particles coming from the target. The low energy ions leaving the quadrupole are directed onto the electron multiplier by a small

![Diagram](image_url)

Fig. 1. Schematic of the experimental set-up. Incident ions either DC or pulsed and from either a 60 keV or a 3.75 MeV accelerator bombard an ice film. An electron bombardment ionizer and quadrupole mass spectrometer measure the neutral particles ejected from the film.
transverse electric field. We have chosen to focus attention on the neutral molecules because they are the dominant species ejected from the films. Ions are also ejected but are not detected with the biasing arrangement of our electron ionizer. They comprise less than one percent of the ejected particles.

Two types of experiments are reported. In the first, freshly deposited ice was bombarded with ions. The current output of the mass spectrometer was sampled periodically by a computer system, typically over time intervals of 10–50 ms. This experimental mode was used to examine early transients in the ejection of molecular species from the ice.

The second type of experiment determined energy spectra of ejected molecules by measuring their time-of-flight distributions. The pseudo-random beam pulsing method [6] was used. The Bell flight path was 7 cm, with a typical time/channel of 16 μs in a 127-channel pseudo-random sequence. The University of Virginia flight path was 59.5 cm with a typical time/channel of 50 μs in a 127-channel pseudo-random sequence. In these experiments pulses due to individual ions arriving at the detector of the quadrupole were selected with a fast discriminator and stored in time bins in a multi-scaler over many cycles of the pseudo-random sequence. Time spectra were extracted by cross-correlation between the beam pulsing pattern and the time pattern stored in the multiscaler. These time spectra were then converted to velocity or energy spectra. It should be pointed out that if there is an appreciable delay between the arrival of the incident ion pulse on the target and the ejection of the sputtered molecules from the surface, for instance due to diffusion or chemical reaction times, a time spectrum at the detector is not a true time-of-flight spectrum, and such data will not directly yield an energy spectrum.

3. Mass transients in fresh films

The principal molecular species found when D₂O is bombarded with fast ions are masses 20 (D₂O), 4 (D₂) and 32 (O₂). The relative importance of the yields of D₂ and O₂ is strongly temperature dependent [5]. Initial bombardment of a freshly grown ice film produces transients in the molecular release, as illustrated in fig. 2 for these three species when D₂O is bombarded by 1.5 MeV neon ions at 10 K. The different masses display very different behavior. In fig. 2a the D₂O yield rises sharply when the beam is turned on and is essentially independent of fluence. Fig. 2b for D₂ shows an initial sharp spike followed by a rise and then a very slow decay with increasing fluence. Fig. 2c for O₂ shows a gradual rise in yield (starting at essentially zero when the beam is first turned on) towards a steady-state value. Fig. 2d is the beam current density on the target. For high fluences the yield of all species eventually decreases as the film is eroded away. The maximum values of the D₂ and O₂ yield in fluence curves such as those of fig. 2 increase with initial film
thickness, indicating that molecules formed deep in the film are contributing to
the ejection. The yield of D₂O is thickness independent in these measurements,
as reported previously for RBS measurements of total sputtering yield [4]. The

Fig. 2. Mass transients in a fresh ice (D₂O) film bombarded with 1.5 MeV Ne⁺ ions. Transients
are shown for masses 20 (a), 4 (b) and 32 (c) as a function of the fluence of incident ions. Part (d)
of the figure is the beam current density which was interrupted twice between the start and finish
of the experiment; note the two points at zero current at fluences approximately 1.7 and 3.4×10¹⁴
ions/cm².
decrease in $D_2$ in fig. 2b is due to film thinning. The slower (in fluence) $O_2$ transient build-up also begins to decrease, but only at higher fluences when the film thinning dominates the $O_2$ build-up. During the mass transients, any

Fig. 3: Temperature dependence of the slope of the mass 32 transient. Two slopes can be identified in the temperature range $\sim 80$–$100$ K, see inset.
off–on sequence in the ion beam results in an immediate return of the yield to a value equal to that before the beam was turned off. Two off–on sequences are evident in the data of fig. 2. The beam current goes to zero; the mass signals drop toward background and immediately return when the beam is restored. This behavior indicates that there has been an irreversible change in the composition of the film due to the bombardment.

The transients presented in fig. 2 are transients in fluence. If a lower beam current is used, the transient is slower in time but not in fluence. At higher temperatures the mass 32 transient is not a simple saturating exponential, but tends to exhibit two quite different slopes, as indicated in the inset of fig. 3. Two straight lines have been fitted to these transients; their slopes are plotted as a function of inverse temperature in fig. 3. The process associated with slope 2 only becomes measurable between 80 and 100 K. Lines corresponding to activation energies of \( \sim 0.05 \) and 0.07 eV have been drawn through the slope values. Though the points exhibit some scatter, the results indicate that thermally activated processes are dominant in the formation and loss of \( \text{O}_2 \).

4. Energy spectra of ejected molecules

Raw time spectra \( s(t) \) from \( \text{D}_2\text{O} \) bombarded at low temperatures by 1.5 MeV and 50 keV Ar ions are shown in fig. 4. These are the direct results of cross-correlations of multi-scaler data with the pseudo-random time pattern of the ion beam (section 2). At very long times, the spectra approach the background (no beam) counting rate. Subtracting the asymptotic value of the data at long times from the signal at each point, an adjusted spectrum can be obtained. Finally, the ionizer of the quadrupole mass spectroemter has an efficiency that is proportional to the time a molecule spends in the ionizer volume. Consequently, we divide the data in each channel by the corresponding time of the channel to correct for the molecule's velocity and obtain the true time-spectra, \( s(t) \).

To convert the time spectra \( s(t) \) to energy spectra \( s(E) \), we set \( s(E) \propto t^3s(t) \) where \( t \) is related to \( E \) by \( E = \frac{1}{2} MD^2(t)^{-2} \); \( M \) is the mass of the ejected molecule and \( D \) is the flight distance from the target to the ionizer of the quadrupole mass spectrometer. For ejected \( \text{D}_2\text{O} \), we believe there is no delayed ejection due to thermally activated diffusion, since the energy spectra are unchanged over a temperature range of 10 to 130 K.

Energy spectra are presented in fig. 5 for incident beams of 1.5 MeV \( \text{He}^+ \), 1.5 MeV \( \text{Ar}^+ \), and 50 keV \( \text{Ar}^+ \). Whereas electronic excitation and ionization are the overwhelmingly dominant modes of energy loss for 1.5 MeV \( \text{He}^+ \) in ice, nuclear collisional energy loss is the predominant mode for 50 keV \( \text{Ar}^+ \), and 1.5 MeV \( \text{Ar}^- \) is intermediate between these; see table 1. Energy spectra for 1.5 MeV \( \text{Ne}^+ \) are similar to those for 1.5 MeV \( \text{Ar}^+ \).
Table 1

<table>
<thead>
<tr>
<th>Ion and energy (MeV)</th>
<th>Electronic stopping cross section $n^{-1}(dE/dx)$ ($10^{-15}$ eV cm$^2$)</th>
<th>Nuclear stopping cross section $n^{-1}(dE/dx)$ ($10^{-15}$ eV cm$^2$)</th>
<th>Measured total yield $E &gt; 0.52$ eV</th>
<th>Measured spectral yield $E &gt; 0.52$ eV</th>
<th>Yield$^a$</th>
<th>Calculated with zero binding energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>He$^-$ (1.5)</td>
<td>59.3</td>
<td>0.051</td>
<td>6.5$^c$</td>
<td>0.047</td>
<td>0.306</td>
<td>0.014</td>
</tr>
<tr>
<td>Ne$^+$ (1.5)</td>
<td>226.4</td>
<td>4.1</td>
<td>600$^d$</td>
<td>0.108</td>
<td>65</td>
<td>1.2</td>
</tr>
<tr>
<td>Ar$^{+}$ (1.5)</td>
<td>214</td>
<td>19.9</td>
<td>$&gt; 10^3$</td>
<td>0.12</td>
<td>120</td>
<td>6.1</td>
</tr>
<tr>
<td>Ar$^{+}$ (0.05)</td>
<td>39</td>
<td>127</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Product of two preceding columns.

$^b$ We use $Y = (3/2 \pi^2) \alpha S_n / \sigma E_0$ for cascade sputtering of molecules with energy greater than $E_0$ and zero binding energy [22]. We also use $\sigma = (\text{molecules density})^{-2/3}$ and $\alpha = 1$.

$^c$ See fig. 3, ref. [3].

$^d$ Estimated 1.5 MeV Ne$^+$ yield as same as that for 1.5 MeV O$^+$.

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Fig. 4. Time-of-flight spectra of neutral mass 20 molecules deduced by pseudo-random beam pulsing and cross-correlation techniques. Results for 1.5 MeV and 50 keV Ar$^+$ ions are shown.
5. Discussion

Water and water ice are generally very stable against decomposition into H$_2$ and O$_2$ by gamma ray or electron radiation [7,9]. In contrast, fast ions, which deposit significantly higher energy densities along individual particle tracks, have been found to produce decomposition with a yield of approximately 0.15 O$_2$ molecules per 100 eV deposited [7]. This yield was obtained by irradiating ice at low temperatures and then melting the sample to collect the O$_2$ produced. In contrast to this, the experiments reported here, and those reported earlier [5,8], measure O$_2$ released from the D$_2$O ice at low bombardment temperatures without subsequent heating. A bulk yield of 0.15O$_2$/100 eV deposited suggests that for each 1.5 MeV He$^+$ ion that traverses a 1000 Å water ice film, of the order of 25 O$_2$ molecules are produced. This is more than we have estimated are released in our thin film experiments [5] unless the temperature is close to that for rapid vacuum sublimation of ice (140 K). We presume that radicals, such as H(D) and OH(OD), are also formed (and

Fig. 5. Energy spectra of neutral mass 20 molecules deduced from time-of-flight spectra such as those of fig. 4. Results for 1.5 MeV He$^+$, 1.5 MeV Ar$^+$ and 50 keV Ar$^+$ are shown. The high energy ends of the spectra are very similar.
ejected [8]). Their sputtering yields should be much less than those for species with saturated bonds such as H$_2$(D$_2$) and O$_2$ which once formed have lower binding energies and hence higher diffusion coefficients in the ice matrix.

With this as background the difference in the fluence dependence of the D$_2$O, D$_2$, and O$_2$ yields can be understood. The D$_2$O is present initially and thus can be sputtered immediately. The D$_2$ transient has two components: a prompt component indicated by the immediate rise of the signal from zero, and a more slowly increasing component indicated by the rise to a maximum in fig. 2b. We postulate that the fast component is due to rapid formation of D$_2$ on electronic recombination in the surface region and that the slow component is due to a chemical formation process throughout the thickness of the film with diffusion to the surface and sputtering by later arriving ions. At temperatures > 80 K these two processes appear to merge, presumably because the rate of diffusion to the surface increases. Note, as D$_2$ leaves the ice, fragments of D$_2$O are less likely to re-form D$_2$O and more likely to form O$_2$. Thus, loss of D$_2$ also contributes to a rising O$_2$ yield.

The O$_2$ transient is relatively slow. We postulate that a two step process is involved: one ion breaks bonds in a track; species diffuse, react, and form O$_2$. Subsequent ions sputter O$_2$ molecules which are present in the near surface region as a result of the earlier step. This continues until the cylindrical regions around individual tracks overlap and the creation and destruction of O$_2$ and its precursors come into balance. At temperatures above about 80 K a continuing increase in the O$_2$ yield is observed at high fluences (slope 2 in fig. 3). The increase with increasing fluence persists until the thickness of the film is significantly reduced. The temperature dependence is consistent with the observation [7,9] of the gradual disappearance of paramagnetic centers (presumably due to loss of radicals and formation of O$_2$ and D$_2$O) as ice is warmed up from 77 K to 150 K.

The two slopes in the transient O$_2$ build-up seem to represent two different processes through which O$_2$ is formed. They have similar activation energies but very different pre-exponential factors. We suggest that the first slope (at lower fluences) is associated with the formation of O$_2$ in the track of an individual ion, in those regions of the track where the local density of ionization is high enough to produce free radicals close enough together so they can interact. As the ice is bombarded to higher fluences, radicals formed from different tracks may interact to produce O$_2$, hence the second slope. At low temperatures the fluence at which the transition from slope 1 to slope 2 is observed (\( \sim 10^{14} \text{ ions/cm}^2 \)), is reasonable for the overlap of \( \sim 10 \text{ Å} \) diameter regions of ionization produced by individual incident ions. In neither case does O$_2$ escape from the ice unless the ion beam is present. The beam may sputter O$_2$ that is formed near or has diffused to the surface. Alternatively the beam may act to enhance the diffusion of O$_2$ to the surface which acts as a sink.

The energy spectra shown in fig. 5 are roughly characterized by an \( E^{-2} \)
energy dependence at energies above 0.05 eV. They are also characterized by a component at low energies that increases with an increasing ratio of \((dE/dX)_e/(dE/dx)_n\). The \(E^{-2}\) dependence at high energy would appear to be consistent with collision cascade sputtering, produced by the nuclear elastic energy loss [10]. A spectrum with the shape \(E/(E + U)^3\) is expected in this case, where \(U\) is the surface binding energy. There are numerical inconsistencies with this conclusion, however, as indicated in table 1. Column 5 of this table gives the fraction of the ejected D₂O particle which have energies in excess of 0.52 eV (the normal sublimation energy of water ice). These values were obtained by integration of curves such as those in fig. 5. Column 4 of table 1 gives total sputtering yield values deduced from Rutherford back-scattering measurements as discussed, for example, in ref. [3]. The products of the values in columns 4 and 5 are given in column 6 which is then the absolute yield of D₂O particles with energies > 0.52 eV. These are to be compared with the entries in column 7 which are calculated yields for ejected molecules with energies > 0.52 eV using the model for sputtering of metals [10]. The experimental values in all cases are much larger than the calculated values although the calculated values have been maximized by reducing the binding energy \(U\) to zero. Further, we used cross-sections for molecule/molecule (rather than atom/atom) scattering in the collision cascade [11].

We conclude from the discrepancy between columns 6 and 7 of table 1 that additional sputtering processes must be contributing to the high energy part of the spectra of fig. 5, and that these must arise from electronic excitation rather than elastic nuclear collisions. These events appear to result in mini-cascades having a high-energy dependence close to \(E^{-2}\) over a limited range of ejected molecule energies. Such events may be repulsive recombination [12,1], or the Coulomb repulsion resulting from neighboring ionized sites [1] or multiple ionization [13]. The results in fig. 5 clearly indicate that the energy spectrum is not characteristic of the cylindrical thermal spike model, which decays at least as fast as \(E^{-3}\) at high energies [14]. However, a dependence close to \(E^{-2}\) can be produced by a small diameter spherical thermal spike at the surface [15] and by Coulomb repulsion between neighbors with variable separations [1]. In fact, since the more energetic particles are ejected from the first layer, the high energy part of the energy spectra is determined by the repulsive interaction.

The dependence of the low energy parts of the spectra of fig. 5 on the electronic energy deposition is also interesting. Even for 50 keV Ar⁺ incident on D₂O the maximum in the spectrum is well below that expected for the collision cascade model [10] or the cylindrical thermal spike sputtering model [1] using the normal (0.5 eV) binding energy. It is quite remarkable, however, how closely the 50 keV data can be fit by the Thompson energy spectrum [10,11] \(E/(E + U)^3\) with \(U \sim 0.055\) eV, a value nearly 10 times smaller than the sublimation energy of ice. The Thompson model which leads to this energy spectrum was developed for a solid composed of identical atoms having a
planar surface potential. For molecular solids such as water ice which have atoms with very different masses, internal vibrational states, and small binding energies, it should not be surprising that the spectral maximum does not occur at simply half the static binding energy. This is particularly so since those collisions in the surface region which are energetic enough to eject a molecule will also efficiently excite vibrational states, and vibrational relaxation can result in molecular ejection in such materials [1]. Roosendaal et al. [16] have suggested that for very large sputtering yields, where many molecules are simultaneously in motion, the effective surface binding changes. However, their assumption of a planar surface potential is unreasonable when the yields are very large. A breakdown in the planar condition would also clearly change the low energy portion of the energy spectrum.

For the 1.5 MeV particles, for which electronic energy deposition is dominant, (compare columns 2 and 3 of table 1), the spectra at low energies do not at all resemble a Boltzmann-like distribution of the type found for the erosion of alkali halides by electrons [17]. In fact, the spectra do not rise to a maximum as would be expected for any process in which the molecules are escaping from a surface with a static, planar binding potential. Furthermore, since the total sputtering yield for incident 1.5 MeV He$^+$ is less than 10 (table 1), surface binding modifications associated with large yields are not applicable. Nakayama and Itoh [18] found a very similar energy spectrum for laser ejection of zinc atoms from ZnO. The low energy dependence goes roughly as $E^{-1/2}$ for both our He$^+$ sputtering of ice and their laser sputtering of ZnO. This energy dependence persists out to energies of about 0.06 eV in the former and about 0.4 eV in the latter experiments, a reflection of the very different cohesive energies of the two materials.

The occurrence of an increasing yield with decreasing ejected molecule energy down to energies well below the sublimation energy would seem to imply that the energetic events discussed earlier take place in a milieu in which the surface binding energy becomes small or the surface becomes anti-binding. This situation can occur in a number of ways. Because the sublimation energy of D$_2$O is much smaller than even the lowest electronic excited states, the overall binding along the track is certain to be changed if the excited states are closely spaced, as pointed out by Watson and Tombrello [19]. The nature of this change, however, may be quite complex as locally excited molecules can interact either attractively or repulsively with neighbors [12]. On the other hand, when the ionized sites are closely spaced along the track the residual repulsive force, even in the presence of considering screening, may easily result in a reduced binding or an anti-binding region in a material such as ice. This would require that the region remain anti-binding for times of the order of $3 \times 10^{-12}$ s for the ejection of the molecules with the lowest energies shown in fig. (5). This is consistent with estimates of the time required for the electrons to transfer energy to phonons [1,16,19,20]. Therefore, one has the picture of the
charged particle temporarily creating a weakly anti-binding region in which energetic events occur, such as repulsive recombination or repulsion between two ionized neighbors, in addition to those events produced by the nuclear elastic energy loss. In this scenario the water molecules do not necessarily leave from the surface region as separate neutral molecules. Indeed, the ejection of molecular ion clusters which neutralize near the surface and relax dissociatively [12] could result in energy spectra such as those observed. This type of process has been discussed in connection with sputtering of large organic molecules [21]. We do not have energy spectra at very low electronic excitation densities where the average spacing between excited states is large [22]. Based on the above discussion, it is important to see if the energy spectra change in this region.

6. Conclusions

The measurements presented here describe the chemical reactivity induced in D$_2$O films in the vicinity of an energetic ion track even at very low temperatures. Earlier we had reported, that there was no fluence dependence in the erosion of ice by fast ions [3]. Here we confirm this to be the case for ejected D$_2$O but not for the O$_2$ which at low temperatures accounts for a very small fraction of the total loss of material [5]. We have shown that the ejection of O$_2$ builds up from essentially zero as the ion fluence increases. The effect of increasing temperature is to increase the slope of the O$_2$ transient with fluence. This occurs in addition to an overall increase in the O$_2$ yield with increasing temperature, as reported earlier [5]. In general, the transient build-up is comprised of two very different slopes which have similar activation energies but very different pre-exponential factors. We associate the two build-ups with different modes of formation of O$_2$ in the ice.

The measured energy spectra presented here cannot be described by models generally employed to describe the ejection of atoms or molecules upon charged particle bombardment. Further, the ejection of material by very energetic particles, such as 1.5 MeV He$^+$, Ne$^+$ and Ar$^+$, gives a clear demonstration that a relatively energetic electronic relaxation process occurs in the material. That is, a significant component of molecules is ejected with escape energies on the order of or larger than the normal surface binding energy ($\sim 0.52$ eV). We have shown that the ejection of such molecules cannot be associated with nuclear collision cascade ejection even if the binding energy in that model is reduced to zero. These energy spectra are quite similar to those of laser ejection of ZnO in which electronic excitations and ionizations are the only effects produced. The observed low-energy dependence of these spectra would seem to indicate that a repulsive (anti-binding) region persists near the surface for times sufficient to eject molecules either individually or in clusters which subsequently decay.
References

    (1982) 1;
    a repeated sequence of beam on and off intervals with an approximately random distribution
    of interval lengths is used to induce ejection. The arrival times of ejected particles detected at
    the end of a flight path are cross correlated with the beam sequence to deduce the distribution
    of time delays between excitation and arrival. The pseudo-random method has a duty factor
    of almost one half. This is in contrast to the low duty factor of conventional time-of-flight in
    which short excitation pulses are repeated only after all particles stimulated by an individual
    pulse have had time to be detected. In cases of relatively low signal-to-background, the
    pseudo-random method greatly accelerates the data taking process.
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    are incorrect.)
    1951.