Production of oxygen by electronically induced dissociations in ice

R. E. Johnson
Engineering Physics, Thornton Hall B103, University of Virginia, Charlottesville, VA 22904

P. D. Cooper and T. I. Quickenden
Chemistry M313, School of Biomedical and Chemical Sciences, The University of Western Australia, 35 Stirling Highway, Crawley, Western Australia 6009, Australia

G. A. Grieves
School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

T. M. Orlando
School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

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A solid-state chemical model is given for the production of O$_2$ by electronic excitation of ice, a process that occurs on icy bodies in the outer solar system. Based on a review of the relevant available laboratory data, we propose that a trapped oxygen atom-water complex is the principal precursor for the formation of molecular oxygen in low-temperature ice at low fluences. Oxygen formation then occurs through direct excitation of this complex or by its reaction with a freshly produced, nonthermal O from another excitation event. We describe a model for the latter process that includes competition with precursor destruction and the effect of sample structure. This allows us to put the ultraviolet photon, low-energy electron, and fast-ion experiments on a common footing for the first time. The formation of the trapped oxygen atom precursor is favored by the preferential loss of molecular hydrogen and is quenched by reactions with mobile H. The presence of impurity scavengers can limit the trapping of O, leading to the formation of oxygen-rich molecules in ice. Rate equations that include these reactions are given and integrated to obtain an analytic approximation for describing the experimental results on the production and loss of molecular oxygen from ice samples. In the proposed model, the loss rate varies, roughly, inversely with solid-state defect density at low temperatures, leading to a yield that increases with increasing temperature as observed. Cross sections obtained from fits of the model to laboratory data are evaluated in light of the proposed solid-state chemistry. © 2005 American Institute of Physics.

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I. INTRODUCTION

Oxygen has been detected in the very thin atmospheres on the icy moons of Jupiter, and peroxide and oxygen-rich molecules have been observed as trapped species in their icy surfaces. The observed O$_2$ is primarily a product of the decomposition of ice by energetic ions and electrons trapped in the Jovian magnetosphere. More recently molecular oxygen ions have been detected over the rings of Saturn suggesting of an oxygen ring atmosphere produced by ultraviolet (UV) photons incident on an ice sample. Our goal is to characterize the primary physical and chemical pathways for the nonthermal production of oxygen in low-temperature ice. Quite remarkably, a quantitative model for this was not available in spite of laboratory studies that have been carried out since the 1950s. Thus, we give a model for the chemical pathways at low doses that differs from those models typically suggested to be dominant in water. We show that the model is consistent with available data and suggest critical experimental tests.

Following a brief review of the space observations, we summarize the principal results of the considerable laboratory data on the radiolysis and photolysis of ice in order to motivate the model. We then describe the generalized rate equations for a chemical kinetic model for production of molecular oxygen in ice. In this model, trapping at defects and percolation from depth play important roles. These equations are then integrated over the depth of penetration of the radiation-induced production of O$_2$ from ice. We then use these results as a guide in describing the physical and chemical processes leading to the formation of molecular oxygen by energetic charged particles (e.g., ions), electrons, and ultraviolet (UV) photons incident on an ice sample. Our goal is to characterize the primary physical and chemical pathways for the nonthermal production of oxygen in low-temperature ice. Quite remarkably, a quantitative model for this was not available in spite of laboratory studies that have been carried out since the 1950s. Thus, we give a model for the chemical pathways at low doses that differs from those models typically suggested to be dominant in water. We show that the model is consistent with available data and suggest critical experimental tests.
radiation and simplified to obtain an approximate analytic expression for the yield of molecular oxygen from ice that can be tested experimentally. This expression also reduces to the precursor model of Sieger et al. and Orlando and Sieger. Fits of the model to the available data are used to extract primary dissociation and reaction cross sections and to show the commonality of the results for photon, electron, and fast-ion-induced chemistry. We also show that hydrogen peroxide (H$_2$O$_2$) or the superoxide (HO$_2$) are not necessary precursors for oxygen production from a fresh ice sample, although they likely become important at higher doses and on annealing of the irradiated samples.

II. SUMMARY OF SPACE OBSERVATIONS AND LABORATORY STUDIES

Gas-phase oxygen has been observed to be associated with the icy bodies in the Jovian and Saturnian systems as discussed. In addition, two well-known transitions for interacting pairs of O$_2$ molecules at 577.2 and 627.5 nm were observed in the reflectance spectra of Jupiter’s moons Ganymede and Europa. These bands are associated with the O$_2$ dimer, suggesting that molecular oxygen is locally dense, likely as an inclusion in the icy surface. Finally, the Hartley band of O$_3$ has been tentatively identified in the UV absorption spectra of certain icy satellites. Although the band shape suggests that additional absorbing species are present, O$_3$ trapped within the ice surface is consistent with the presence of trapped oxygen inclusions exposed to radiation. This feature is superimposed on a broad UV absorption extending from about 0.4 μm to shorter wavelengths and attributed to another radiolytically produced oxidant, H$_2$O$_2$, which was also identified in the infrared (IR). Consistent with the above, oxygen-rich molecules appear to be produced by the radiation processing of ice containing sulfur (SO$_2$ and a sulfate) and carbon (CO$_2$ and a carbonate). Below we summarize the laboratory data bases showing a few of the principal results.

Although impurities are known to affect luminescence in ice, the production of O$_2$ by photolysis was inferred via luminescence from thick samples of ice formed from purified water. In most other studies, the radiation-induced production of O$_2$ from ice is detected in the gas phase by a quadrupole mass spectrometer (QMS) either after warming or during irradiation as an outgassed species. In the latter experiments, the production efficiency is given as a yield, the number of O$_2$ produced during irradiation of the sample per electron, ion, or photon incident. This is a quantity we will calculate below. In such studies, the O$_2$ that remains trapped in the ice is typically not measured.

Though some early radiolysis experiments were likely affected by impurities, the ion- and electron-beam results presented in this paper were carried out in ultrahigh vacuum (UHV) with very pure ice samples. Though the techniques have been described in detail, we present a brief description of the most relevant facts concerning the low-energy electron experiments. Briefly, an UHV chamber (base pressure of 1 × 10$^{-10}$ Torr) was equipped with a pulsed low-energy (5–250 eV) electron gun, a cryogenically cooled sample holder, and a QMS. The electron beam has a maximum time-averaged current density of $\sim$10$^{14}$ electrons/cm$^2$·s and a typical beam spot size of $\sim$1.5 mm. The maximum total dose used in the experiments reported here is $\sim$10$^{15}$ electrons/cm$^2$ which was achieved using pulsed irradiation over a 100 s interval. The typical pulse width was 100 μs and the frequency used was 1000 Hz. The current density per pulse never exceeded $\sim$10$^{10}$ electrons/cm$^2$ pulse. This is an effective impingement rate of one low-energy electron per 10$^5$ surface molecules. Even after limited photon excitation and secondary scattering, the subsequent heating of the surface during our pulsed electron-beam dosing condition is negligible. Since there is a secondary-emission yield from ice and holes at the surface are not all neutralized by recombination, measurable surface charging occurs rapidly. A quasisteady state is reached at doses as low as $\sim$10$^{13}$ electrons/cm$^2$, and then the surface charge changes very slowly. Therefore, charging cannot account for the principal fluence dependence observed for the O$_2$ yield.

Ice thin films were grown after several freeze-pump-thaw cycles by controlled vapor deposition on either Pt(111) or graphite substrates. Note that oxygen was never observed/present in the absence of radiation. The substrates were heated resistively which allowed for temperature control from 80 to 500 K. The substrate temperature was monitored with a thermocouple and a computer-controlled feedback system drove the temperature ramp at a rate of 8 K/min. Porous amorphous solid water (PASW) samples were deposited at 80 K with a directional doser oriented approximately 70° from normal incidence. Nonporous amorphous solid water (ASW) samples were dosed between 110–120 K at normal incidence and crystalline ice (CI) samples were deposited between 150 and 155 K. Film thickness is estimated to be between 50–100 ML by comparison to published temperature-programmed desorption data.

The principal dissociation processes in ice lead to H, OH, H$_2$, and O, but the principal species that escape from an irradiated ice sample are those that have the lowest binding energies to ice: H$_2$, O$_2$, and H$_2$O. That is, surface binding and reactive pathways act as filters for the ejecta. Therefore, gas-phase O$_2$ coming from an irradiated sample in a vacuum can be readily detected although decomposition of bulk ice is inefficient.

At low doses the O$_2$ yield was found to increase linearly with dose until saturation occurs. This dependence has been seen in a number of experiments and is shown in Figs. 1(a) and 1(b) for a fast heavy ion and low-energy electrons. These yields have also been shown to be temperature dependent by a number of laboratories using several types of incident radiation. As an example, this is shown at saturation for incident 1.5 MeV Ne$^+$ and low-energy electrons in Figs. 2(a) and 2(b). For temperatures < ~ 140 K, the yield of O$_2$ and D$_2$ produced from vapor-deposited ice samples at low radiation doses decreases with decreasing temperature. It has been shown repeatedly, over most of the temperature range studied, that the measured yields depend on the total dose and not the dose rate, although this has not been tested at the higher temperatures shown in Figs. 1 and 2. Also seen in Fig. 2(b) is a clear drop in the yield for temperatures above...
150 K. This drop has been shown to be related to the amorphous to cubic phase transition which is manifested by the small shoulder on the leading edge of the thermal desorption yield of molecular water.3 There is also a shoulder prominent in the D2 yield at 170 K that is due to reactive scattering in the gas phase.

The O2 yields have also been shown to depend on the sample formation temperature and crystal state,3 indicating that structure and defects can affect the O2 yield. An O2 production “threshold” of \(-5.3 \text{ eV}\) was suggested by the photolysis experiments of Mattich et al.17 In the UHV experiments a threshold of \(-6.5 \text{ eV}\) was found using low-energy electrons2,3 with a similar threshold for O\(_3\) and H\(_2\) productions.20

As seen in Fig. 1(a), D2 is promptly ejected from D\(_2\)O ice whereas O2 is not. However, after an incubation dose, the O2 yield and D2 yields in steady state are correlated,21,22 as indicated in Figs. 2(a) and 2(b). In this way the stochiometry of the surface layer is only slightly altered.23

The temperature dependencies for the yield of O2 from ice have been repeatedly interpreted in terms of effective activation energies. At temperatures \(40–120 \text{ K}\), these were found to be relatively small \(0.03 \text{ eV}\) Fig. 2(a). Such energies are equivalent in size to activation energies for mobility of protons or hydrogen in ice and for structural rearrangements. Finally, for thin samples and penetrating radiation, percolation of oxygen from depth can occur so that the yields are found to depend on the sample thickness. Since the measured yields were also shown to depend on the excitation density, sample formation, and temperature, comparisons between experiments have proven to be difficult.

Hydrogen peroxide and related species formed by incident radiation are not readily ejected into the gas phase, but can be detected via absorption bands as trapped species in an irradiated ice sample.24–26 Hydrogen peroxide forms via the principal dissociation product, OH, and the production yields correlate with H\(_2\) formation.4 Hydrogen peroxide and/or HO\(_2\) have been suggested3 as potential precursor species for the
formation of $O_2$. However, the fluence dependence observed in the QMS experiments suggests that $O_2$ can be formed by a process that does not involve these species, as described below. In addition, recent matrix isolation studies indicate that trapped O can be converted to hydrogen peroxide and hydrogen peroxide converted into trapped $O$ by incident radiation (i.e., $H_2O\rightarrow H_2O_2; H_2O_2+h\nu\rightarrow H_2O+O$). In the model below, trapped O is the principal species considered for formation of $O_2$ at low doses. At higher doses, the conversion of hydrogen peroxide to trapped O can provide additional channels for $O_2$ formation that may involve pairs of $H_2O$ or $H_2O_2$. Although on a planetary surface the high-dose results may be more relevant, here we are primarily interested in the new channel occurring at relatively low doses in order to interpret a number of recent laboratory results. Below we construct a chemical kinetic model of the production of $O_2$ and then use this model to interpret a number of experiments.

### III. MODEL FOR FORMATION OF $O_2$

The yield of $O_2$ from ice at low temperature increases linearly with radiation fluence (flux $\times$ time or dose) at the low fluences as indicated in Fig. 1 and is independent of beam flux. Quite remarkably, this is the case both for low-energy electrons that make a single excitation for each impact and fast ions that make a density of excitations along their path through the solid. At low temperatures, if the beam is turned off and later turned back on, the measured yield returns to the value it had before the beam was turned off indicating that a stable chemical alteration occurred. Therefore, either the ice is chemically altered before the incident radiation produces $O_2$, or $O_2$ is produced and trapped in the solid and then caused to escape by the subsequent radiation. Whereas the former is the case for the low-energy electrons, both processes occur for penetrating radiation. It is the preferential loss of hydrogen [e.g., Fig. 1(a)] from an irradiated ice that enhances the likelihood of forming oxygen-rich precursors and the subsequent production of molecular oxygen. Therefore, we consider the chemical precursors and the production of $O_2$ during the irradiation of ice.

The analytic model used by Seiger et al. to fit their electron data is first reviewed. This is followed by the more detailed chemical kinetic model for the radiation processing of ice at the low fluences shown in Fig. 1. This model is then used to obtain cross sections from the available laboratory data.

#### A. Analytic precursor model

In describing their electron irradiation experiments, Seiger et al. separated the temperature-dependent precursor formation step from the temperature-independent $O_2$ production step. The column density of a precursor species $N_p$ formed in ice by incident radiation was calculated using cross sections for production $\sigma_p$ and destruction $\sigma$ of the precursor. $O_2$ is then formed by direct or indirect electronic excitation of this precursor described by the cross section $\sigma_{O_2}$. The model is described by a pair of simple rate equations, one for $N_p$ and one for the production rate of oxygen $dN_{O_2}/dt$.

$$dN_{p}/dt = \sigma_p \phi N - \sigma \phi N_p,$$  \hspace{1cm} (1)

$$dN_{O_2}/dt = \sigma_{O_2} \phi N_p.$$  \hspace{1cm} (2)

Here $\phi$ is the radiation flux and $N$ is the column density of $H_2O$ from which the incident radiation can produce and eject $O_2$. For low-energy electrons, $N$ is a few monolayers ($\sim 3 \times 10^{15} H_2O/cm^2$) but $N$ is much larger for energetic ions. Here we write the destruction cross section as $\sigma = \sigma_p + \sigma_{O_2}$ where $\sigma_p$ accounts for precursor destruction processes other than the formation of $O_2$.

Solving Eq. (1) assuming $N$ is nearly constant, the fraction of precursors $c_p$ in the penetrated column after time $t$ is

$$c_p = N_p/N = [\sigma_p/\sigma] [1 - \exp(-\sigma \Phi)].$$  \hspace{1cm} (3)

Here $\Phi = [\sigma \phi] t$ is the fluence (flux $\times$ time), the number of particles (photons, electrons, or ions) incident on the surface per unit area. Using $c_p$ in Eq. (2), the $O_2$ yield $Y$ at any fluence can be written in terms of the yield at steady state, $Y_\infty$.

$$Y = [dN_{O_2}/dt]/\phi = \sigma_{O_2} c_p N = Y_\infty [1 - \exp(-\sigma \Phi)].$$  \hspace{1cm} (4a)

$$Y_\infty = [\sigma_p \sigma_{O_2}/\sigma] N.$$  \hspace{1cm} (4b)

Accounting for the destruction of water molecules in the initial column, $N$, changes the result in Eq. (4) only slightly. Photolysis experiments suggest that the number of dissociated water molecules in steady state is $\sim 10\%$ of the irradiated column.

The form in Eq. (4a) gave excellent fits to the incident electron data, as seen in Fig. 1(b). In order to extract both $\sigma_p$ and $\sigma_{O_2}$ from these fits to the yield versus fluence data, it was also assumed that the production of $O_2$ is the principal precursor destruction process, i.e., $\sigma = \sigma_{O_2}$ and $\sigma_p = 0$. However, other precursor destruction processes can dominate $\sigma$, especially for penetrating radiation, as discussed below.

In the above model the precursor is formed in a single excitation event in a fresh ice sample. For low-energy ionizing radiation, hydrogen peroxide, a suggested precursor, is formed as a product of two dissociation events in ice, i.e., $2H_2O \rightarrow 2H+2OH \rightarrow H_2+H_2O_2$. If it were the principal precursor, the form for the yield in Eq. (4a) could be roughly recovered. However, there would be an offset due to the two-step precursor formation process, i.e., $Y \approx Y_\infty [1 - \exp(-\sigma \Phi - \Delta)]$, where $\Delta$ is determined by the peroxide formation and destruction processes. This would also be the case if our proposed precursor was formed in any other process that required two excitation events, such as $H_2O \rightarrow H+OH \rightarrow H+H+O$. Since no obvious offset at low fluences was observed, we consider a precursor formed by a single energy absorption event.

#### B. Trap density and trapped O

In Eqs. (1) and (2), the density of trapping sites $n_t$ is not explicitly included. However, trapping sites and porosity have been shown to be important for ice chemistry.
Although the density of defects, voids, and interfaces decrease as the temperature of the ice increases, the efficiency of production of \( O_2 \) is the opposite, increasing with increasing \( T \) for \( T < \sim 140 \) K.

We propose that trapped oxygen atoms are the principal precursor at low fluences. \( O_2 \) is then formed by the reaction of \( O \) (or OH) with this precursor or by electronic excitation of the precursor complex. Here we describe the kinetics of the production of \( O_2 \) by O-atom reactive scattering. This is similar to the production of \( CO_2 \) in a \( CO/H_2O \) ice mixture.\(^{31}\) A paper describing the role of direct and indirect electronic excitations of the precursor is the subject of a separate paper.\(^{22}\)

Following dissociation to \( H_2+O \), which is given by the absorption cross section \( \sigma_p^O \), \( H_2 \) is lost from the ice samples at the temperatures above \( \sim 40 \) K. The \( O \) produced by ions or electrons can be in the ground-state or in the excited singlet and triplet states. However, the UV absorption below the band gap can only produce excited singlet states. These can quench in the ice matrix releasing energy but eventually trap. The newly formed \( O \) produces an oxygen-water molecule complex, \( O \cdot \cdot (H_2O)_n \), which we refer to in the following as trapped \( O \). \( O \) occurs according to the reaction rate \( k_{O,\sigma} \) and we propose this as a precursor to the formation of \( O_2 \). This precursor might produce \( O_2 \) on excitation,\(^{22}\) but here we suggest that a subsequent radiation absorption can again produce a nonthermal \( O \) via \( H_2+O \) (\( \sigma'_p \)). The nonthermal \( O \) can react with \( O \) within some reaction radius resulting in the formation of \( O_2 \) [\( O+O \rightarrow O_2 \)] described by \( k_{O,\sigma} \). These two excitation events give a net production of two \( H_2 \) and an \( O_2 \).

The principal dissociation channel (\( H_2O \rightarrow H+OH \)), described by \( \sigma_p^O \), produces a mobile \( H \). It can also react with \( O \), described by \( k_{H,\sigma} \), removing trapped \( O \). Nonthermal \( H \) and \( O \) can also be removed by other reactants \( R \) [e.g., \( R+H \rightarrow RH(k_{H,R}n_R) \), \( R+O \rightarrow RO(k_{O,R}n_R) \), where \( R \) can be a radiation product, such as \( OH \), or a contaminant in the ice]. Reaction of a newly formed, mobile and electronically excited OH with \( O \) might also produce \( O_2 \), a process that needs to be tested experimentally. We ignore this in the model and also initially ignore the conversion of trapped \( O \) to hydrogen peroxide by an electronic excitation.\(^{4}\)

The principal reaction pathways considered for oxygen are

\[ \frac{dn_O}{dt} = k_{O,O}n_ON_0R_{O,R}. \]  

Here \( n_i \) is the density of species \( i \) in the irradiated volume and \( n_i \) is the density of trapping sites. As in Eq. (2), \( O_2 \) destruction processes are ignored in Eq. (6d), since for low-energy electrons the newly produced \( O_2 \) can escape from the excited near surface layers. For penetrating radiation this changes and \( O_2 \) that did not escape can, in principle, be dissociated by a subsequent excitation event. In addition, if direct excitation of the precursor can produce \( O_2 \), then the term \([k_{O,O}n_O]n_0 \) in Eqs. (6a), (6b), and (6d) is replaced by a term like \( \sigma_p^O(n_0) \). The above equations act in parallel with the equations for formation of \( OH \) and hydrogen peroxide described elsewhere.\(^{4}\)

Integrating the above equations over the depth of escape of \( O_2 \) from an irradiated sample, the analytic precursor model of Seiger et al.\(^{2} \) is recovered.\(^{4} \) Therefore, \( \sigma_p^O, \sigma'_p, \sigma_{O_2} \) and \( \sigma \) can now be determined in terms of the rate constants and primary dissociation cross sections.

C. Trapped versus newly produced species

In the solid state the role of defects is critical. Defects are produced by sample formation at low-temperatures and, for penetrating radiation, defects/damage sites are produced by the irradiation itself. Since the newly produced species from an excitation event trap in times short compared to the time scale of the incident particle fluxes typically used, a steady-state background of nonthermal \( O \) does not accumulate. Therefore, the above equations can be solved simultaneously. That is, there are trapped \( O \) and freshly produced \( O \) that rapidly react or trap. If the density of traps is large, then the quantities \( n_H \) and \( n_0 \) averaged over the bombardment rate, are roughly time independent: \( \frac{dn_O}{dt} \sim 0 \) and \( \frac{dn_H}{dt} \sim 0 \). Therefore, only species trapped at defects, pores, or grain surfaces are assumed to be present before a subsequent impact. This is consistent with the lack of a dependence of the \( O_2 \) yield on the incident beam flux at those temperatures that have been tested for dose rate effects: \(<120 \) K. Solving Eqs. (6a) and (6c) for \( n_0 \) and \( n_H \), which describe the transiently mobile \( O \) and \( H \), and substituting, Eqs. (6b) and (6d) reduce to the rate equations Eqs. (1) and (2) with \( O \), as the precursor.

Since the density of trapped \( O \) is small compared with the density of sites at which \( H \) can react, then from Eq. (6c) \( n_H \sim [\sigma_p^O(n_0)k_{H,H}n_R]t^{1/4} \). For a low radiation flux \( \phi \), the average value of \( n_H \) is small. The \( O_2 \) yield \( Y_\phi \) is equal to \([ \frac{dn_O}{dt} ]\Delta x / \phi \) with \( \Delta x \) being the \( O_2 \) escape depth. The yield can now be written in the form given in Eq. (4a) with an analytic expression for the steady-state yield \( Y_\phi \).

\[ Y_\phi[(\sigma_p^O)n_0] = 1 + [(q-1)^2 + 8q]^0.5 \delta/4 \delta, \]

\[ q = \frac{k_{O,\sigma}n_0}{[k_{O,H}n_H](\sigma'_p n_0)k_{O,\sigma}} \]

\[ \delta = 0.5\left[1 + n_H/(n_0 + n_R)\right]. \]  

We further note that for large \( n_i \) and small \( \phi, q \) can be large. Assuming that \( q \gg 1 \) and that \( n_i \gg n_R \), then Eq. (7) becomes
Y_{o} \rightarrow \left[ \sigma_{d}^{2}N / d = \left( \sigma_{d}^{2} \sigma_{d} \right) \right] n \xi, \tag{8}

\xi = \left[ \left( k_{O_{2},H.} / k_{H,O,k_{O_{2}}} \right) \right] n_{R} / n_{T}

Here the factor \( \xi \) accounts for the competing reactions. The result in Eq. (8) is based on the fact that the production of H is more efficient than the production of O (i.e., \( \sigma_{d} > \sigma_{o} \)) so that the destruction of the precursor, O_2, by reaction with H is more efficient than the reaction with mobile O to form O_2.

Comparing Eq. (8) with the expression for \( Y_{o} \) in Eq. (4b), we can write \( \sigma_{d} \sim \sigma_{d} \), \( \sigma_{o} \sim \sigma_{o} \), and \( \sigma_{o} \sim \sigma_{o} \). Since mobile H and O affect both the numerator and denominator of \( \xi \), writing \( k_{i} = [\sigma_{i} \nu] \) where the \( \sigma_{i} \) is an interaction cross section (square of an interaction length) and \( \nu_{i} \) the mean speed of the mobile species, the ratio \( \xi = \left( \sigma_{o} \sigma_{o} / \sigma_{o} \sigma_{o} \right) \) \times \( n_{T} / n_{T} \) is the ratio of interaction cross sections times the density of reaction sites to density of traps ratio. That is, the precursor destruction rate is proportional to the quenching of O by H, which occurs in competition with the loss of mobile H by other reactions including recombination to form H_2O.

Saturation, the reaction sites are primarily dissociation products.

It is seen from Eq. (8) that the steady-state yield \( Y_{o} \) depends inversely on the density of traps \( n_{T} \). That is, when the trap density is high, O_2 formation requires that a newly formed O find a trapped O before it becomes trapped or reacts with impurities or other reaction products. Therefore, the observed increase in the O_2 yield with increasing \( T \) at low doses is related to the change in the trapping density \( n_{T} \), with increasing temperature of the ice sample. In this model, the small activation energy measured (Fig. 2) is related to the reorientation of defects leading to a reduction in trap density. As the sample formation temperature increases and the density of traps in the bulk decreases, the surface and grain interfaces eventually become the dominant traps.\(^{22,32}\)

Radiation-induced defects/damage become important trapping sites for penetrating radiation and thus increases of dose can affect the production of molecular oxygen. In addition, O_2 production can increase in the presence of oxygen-rich impurities, such as CO_2 or SO_2, since their dissociation can also provide mobile O. Such species also act as hydrogen scavengers\(^{26}\) affecting the destruction of O_2.

### IV. COMPARISON OF MODEL TO DATA

The model above is strongly suggested by the available laboratory data on the radiolysis and photolysis of ice. Here we obtain estimates of \( \sigma_{d} \) and \( \sigma \) such as those given in Table I for a few such experiments. We first consider the data for photolysis by \( \sim 10 \) eV photons. We then consider the parameters from the fit to the low-energy electron data and obtain parameters for the energetic ion data.

#### A. UV photolysis

The results of Gerakines \textit{et al.}\(^{25}\) confirm that H_2O_2 forms in ice from two OH after a buildup of trapped OH. They monitored the band associated with H_2O–HO_2,\(^{33}\) in which the HO is bound to water with \( \sim 0.24 \) eV. Since they monitored a subset of the trapped OH seen in earlier experi-

<table>
<thead>
<tr>
<th>Radiation</th>
<th>( E ) (eV)</th>
<th>( T ) (K)</th>
<th>( \sigma ) \times 10^{16} \text{ cm}^{2}</th>
<th>( \sigma_{o} ) \times 10^{16} \text{ cm}^{2}</th>
<th>( E_{a} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( e^{+} )</td>
<td>30–100</td>
<td>50–120</td>
<td>0.8–3</td>
<td>–1</td>
<td>0.02–0.03</td>
</tr>
<tr>
<td>( h^{+} )</td>
<td>( \sim 10 )</td>
<td>( \sim 10 )</td>
<td>0.1–1</td>
<td>0.09</td>
<td>0.03</td>
</tr>
<tr>
<td>( \text{He}^{+} )</td>
<td>( 10^{6} )</td>
<td>40–140</td>
<td>–10</td>
<td>0.03</td>
<td>( 1.5 \times 10^{6} )</td>
</tr>
</tbody>
</table>

\(^{24}\) Seigler \textit{et al.}, 1998 (Ref. 2); \( \text{precursor formation} \left( 0.5 \sim 2.0 \right) \times 10^{18} \text{ cm}^{-2} \) \( \left( 30 \sim 100 \right) \text{ eV} \) proportional to \( \left( E_{a} \right) \), \( E_{a} = 10 \) eV, \( N \sim 10^{17} \text{ cm}^{2} \).

\(^{25}\) Watanabe \textit{et al.}, 2000 (Ref. 29); \( \text{saturation of yield} \left( D_{2}O \rightarrow 5 \times 10^{-19} \text{ cm}^{2} \right) \).

\(^{26}\) Westley \textit{et al.}, 1995 (Ref. 34); \( E_{a} \) based on D_2O yields, \( \sigma \) based on lowest fluence.

\(^{27}\) Brown \textit{et al.}, 1982 (Ref. 39); based on lowest fluence.

\(^{28}\) Reimann \textit{et al.}, 1984 (Ref. 21); \( \sigma_{a} \) based on \( \left( dE/dx \right) /W=92 \times 10^{-19} \text{ eV} / 26 \text{ eV} \).

#### B. Low-energy electrons

For the low-energy electron data, Sieger \textit{et al.}\(^{2,3}\) reported an O_2 production cross section of \( \sim 2 \times 10^{18} \text{ cm}^{2} \) for 100 eV incident electron energy. This is of the order of the electron impact ionization cross section for H_2O, consistent with mobile H or mobile protons as the principal destructive agents.

The O_2 yield versus fluence in these experiments was reasonably well fit by the expression in Eqs. (4). Over a narrow range of \( T \), Sieger \textit{et al.}\(^{2}\) find \( Y_{o}(T) \sim Y_{o}^{+}(\sim E_{a}/kT) \) with an activation energy \( E_{a} \sim 0.02–0.03 \) eV consistent with other estimates of an activation energy. Assuming that in the low-energy electron experiments

\( \text{Table I. Parameters for sample data. } \sigma_{i} \text{ is of the order of } 10^{15} \text{ cm}^{2} \).
Production of oxygen by electronically induced dissociations in ice


N is about 3 ML (\textasciitilde 3 \times 10^{15} \text{H}_{2}O/cm^2), the measured \(Y_{\infty}\) gives \([\sigma_{p} \sigma_{O}/\sigma] = (0.5 - 2.0) \times 10^{-18} \text{cm}^2\) over the electron impact energy range of 30–100 eV. At 110–120 K, this ratio was found to be proportional to \(E - E_{o}\) and \(E > E_{o} \sim 10 \text{eV}\), again assuming fixed \(N\). Using the sizes of \(\sigma\) and \(Y_{\infty}\) then one obtains \([\sigma_{p} \sigma_{O}/\sigma] \sim (0.2 - 6) \times 10^{-34} \text{cm}^2\). This size is consistent with both \(\sigma_{p}\) and \(\sigma_{O}\) being described by events of the type \(\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}(\sigma')\). That is, they are consistent with \(\sigma\) being formed for \(\sim 10\%\) of the radiation-induced dissociation events \((\sigma' \sim 0.1 \sigma_{p})\).

The cross section for production of \(O\) may depend on the availability of dangling bonds at interfaces, in pores, or at defects, as suggested by a number of authors. However, the defect and trap densities are critical, as shown here. The role of defects is consistent with the low activation energy and differences observed in the electron-induced yield for initially crystalline and amorphous ice. At relatively high \(T\), the density of initially formed traps becomes small and the mobility of defects is high, so that the sample surface or grain interfaces are the principal trapping sites. For this reason, it is important to determine if the yield for \(T\) greater than \(\sim 140 \text{K}\) depends on the incident flux \(\phi\), i.e., the dose rate. Pulsed radiolysis experiments in thick ice, in which the transients are studied rather than the steady-state yields, are required.

C. Incident ions: Escape from depth

Even though the shower of secondary electrons produced in a solid by a fast incident ion can result in multiple excitations locally, the yield versus fluence for \(O_2\) production also varies linearly with fluence at low fluences. \(T\) for low \(T\), this yield is also independent of dose rate at low-dose rates suggesting \(O_2\) formation via a chemical precursor. The \(O_2\) yield versus fluence in Fig. 1(a) for incident ions at low doses can also be roughly fit by the expressions in Eq. (4). However, the fit is not as good as it is for the low-energy electrons suggesting other effects are important. In addition, \(Y_{\infty}\) vs \(T\) was shown to have two “plateaus:” one for very low doses and one at higher doses with activation energies in the range \(\sim 0.02 - 0.07 \text{eV}\). These differences indicate that additional precursors can be formed in the ion track and that the ion penetration and escape depth for a newly produced \(O_2\) are important. That is, the quantity \(N\) in Eq. (1) is the “depth” from which \(O_2\) formed below the surface can percolate to the surface and escape. Ignoring these differences and fitting the data for the incident 1.5 MeV \(\text{Ne}^+\) at 10 K, one obtains \(\sigma = 60 \times 10^{-16} \text{cm}^2\). This is comparable to size of the molecular destruction cross section, \(\sigma_{d} = 30 \times 10^{-16} \text{cm}^2\) by these ions (Table I).

At saturation (steady state) a single new event leading to an \(O\) can lead to the production \(O_2\) from the steady-state density of trapped precursors in the model proposed here. Therefore, allowing for changes in sample structure, the yield at saturation should be nearly linear in the excitation cross section. This is the case for the low-energy electrons, and it was initially assumed to be the case for the fast ions. However, Baragiola et al. showed that for a temperature at which decomposition dominates the sputtering of ice, the steady-state yield \((Y_{ss})\) is proportional to the square of the electronic energy deposition per unit path length in the solid. If the production and destruction cross sections in \(Y_{ss}\) also varies as \((dE/dx)^{1/2}\). Therefore, we propose that the quantity \(N\) in \(Y_{ss}\) also varies with \((dE/dx)^{1/2}\). That is, the density \(\sim \text{from which O}_2\) can be mobilized to escape depends on the excitation density \((dE/dx)^{1/2}\). This is consistent with the observation that the \(O_2\) yield depends on thickness for samples thinner than the ion penetration depth. Based on the proposed model, a description of the percolation depth for escape, \(N\), is required to compare the yields for penetrating radiation with those for nonpenetrating radiation. Since the defects/damage produced by the ions can affect both the density of traps and the percolation of \(O_2\), the low-energy electron and UV photon experiments provide better tests of the chemistry for molecular oxygen production.

V. SUMMARY

The exciting observations of thin oxygen atmospheres and oxidants trapped in the icy surfaces on outer solar system bodies have lead to increased interest by chemists in the radiation-induced production of oxygen in ice. Although this is a process that has been studied for a half century, quite remarkably, no quantitative model existed. In this paper we first summarized the principal results of those experiments and then give a solid-state chemical model for the production of \(O_2\) in ice at low doses. The model is consistent with the available data for formation of oxygen due to electronic excitations in ice produced by fast ions, low-energy electrons, and UV photons at low temperatures.

In our model, trapped oxygen atoms are the dominant precursor to the formation of molecular oxygen at low radiation doses. The proposed rate equations are integrated to obtain an analytic model for the fluence and temperature dependences of the \(O_2\) yield. In deriving the analytic model from the rate equations, the competition between the formation and destruction processes is accounted for. The role of trapping sites and escape from depth for penetrating radiation are also accounted for. These are both affected by the thermal and radiation histories of the sample. This has allowed us to put low-dose data for incident photons, electrons, and energetic ions on the same basis for the first time.

The proposed model suggests measurements that are needed to describe the chemical state of the irradiated ice and to interpret new laboratory data. For instance, the proposed precursor, trapped \(O\), may be detectable. In addition, much more data are needed on the production of oxygen by UV photons, especially as this process is thought to produce the oxygen atmosphere recently observed over Saturn’s rings. Studies of possible dose rate effects above \(\sim 140 \text{K}\) are needed to test the limit of applicability of the trapped precursor model. Studies of the effect of impurities, such as carbon and sulfur species, are needed as these can compete with defect sites to scavenge \(O\). Scavenging by impurities is known to affect the radiolytic yields. This could have been a problem in the earlier experiments but, quite remarkably, more recent results, using ultrahigh vacuum and the vapor
deposition of purified water samples, give similar results. Scavenging by impurities is also of considerable astrophysical interest and has been suggested to be consistent with the observation of primarily oxygen-rich carbon and sulfur species on the icy satellites. It has also been suggested that the direct production of H$_2$ and the production of the precursor will be enhanced at the ice surface or at an internal surface in a porous sample. Therefore, the correlation of the formation temperature and radiation damage with the defect density and the formation of trapped O need to be studied in detail. Finally, it is also important to describe quantitatively the relationship between H$_2$ loss and the competition between O$_2$ and H$_2$O$_2$ formations over a range of temperatures and fluences. Such experiments are in progress and the model above will provide a framework for interpreting new data. More importantly, this model can now be used to apply the presently available laboratory data to understanding the observations of molecular oxygen on icy bodies in the outer solar system, an exciting new aspect in planetary science.

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