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O atom production in water ice: Implications for O_2 formation on icy satellites

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[1] We have found that O atoms are a primary product in the irradiation of water-ice with 0.8 MeV protons. This observation has implications in understanding the chemical reactions that occur to produce molecular oxygen (O_2) in such laboratory ices, as well as ices found on the surfaces of Ganymede and Europa, and the ice particles present in Saturn's rings. We estimate that in irradiated water-ice, O_2 can be formed at a lower limit of 0.07% by number relative to water and is in agreement with observations of the icy Jovian satellites.

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1. Introduction

[2] There have been several recent laboratory investigations of the formation of molecular oxygen (O_2) from irradiated water ice [*Orlando and Sieger*, 2003; *Petrik et al.*, 2006; *Teolis et al.*, 2006; *Teolis et al.*, 2009]. This area of research is of particular interest in the formation of O_2 on the surface of the icy Galilean satellites [*Calvin et al.*, 1996; *Calvin and Spencer*, 1997; *Spencer and Calvin*, 2002; *Spencer et al.*, 1995] and also an O_2 atmosphere associated with Saturn's rings [*Johnson et al.*, 2006; *Tokar et al.*, 2005]. In both cases, O_2 is postulated to form from the radiolytic and/or photolytic destruction of H_2O molecules in the ices of these objects.

[3] Despite ongoing efforts from various research groups, there is still a void in our understanding of the chemical processes that form O_2 molecules in irradiated water ice. The problem is not helped by the weak electronic and vibrational transitions of O_2 that make detecting solid-phase O_2 by optical spectroscopic methods difficult. Consequently, the detection of O_2 is commonly performed by quadrupole mass spectrometry of molecules sputtered during the irradiation process or later released in temperature-programmed desorption experiments.

[4] A good review of the field can be found in the work by *Johnson et al.* [2003]. Here we shall present a brief summary of the literature published since then and at the same time describe each O_2 production model. The focus will be on the chemical steps involved rather than the kinetics of each model. Details of our experiments will then be given.

[5] The papers by *Johnson et al.* [2003], *Orlando and Sieger* [2003], and *Sieger et al.* [1998] culminated in the publication of *Johnson et al.* [2005] with what shall be referred to here as the J(2005) model. This model proposes that O_2 is produced from the decomposition of H_2O to H_2 and O atoms.

$$H_2O + \text{energy} \rightarrow H_2 + O \tag{1}$$

The O atoms are trapped in the form of a stable precursor, possibly an $H_2O \cdot O$ complex, before a second excitation produces H_2 and O_2.

$$H_2O \cdot O \rightarrow H_2 + O_2 \tag{2}$$

Alternatively, a nonthermal O atom from a secondary dissociation may form O_2.

$$H_2O \cdot O + O \rightarrow H_2O + O_2 \tag{3}$$

[6] An alternative model proposed by *Petrik et al.* [2006], and which shall be referred to here as the P(2006) model, proposes that the stable precursor is HO_2 and that more steps are required than are used in the J(2005) model. First, H_2O is dissociated into H and OH.

$$H_2O + \text{energy} \rightarrow H + OH \tag{4}$$

Next, the OH, which is formed within the sample, migrates to the surface of the ice. Multiple OHs then react to form H_2O_2 and subsequently HO_2.

$$OH + OH \rightarrow H_2O_2 \tag{5}$$

$$H_2O_2 + OH \rightarrow HO_2 + H_2O \tag{6}$$

The hydroperoxy radical (HO_2) is then dissociated by an energetic excitation to form O_2.

$$HO_2 + \text{energy} \rightarrow H + O_2 \tag{7}$$

[7] Recently, *Teolis et al.* [2009] have published an alternative model based upon experiments in which ices are

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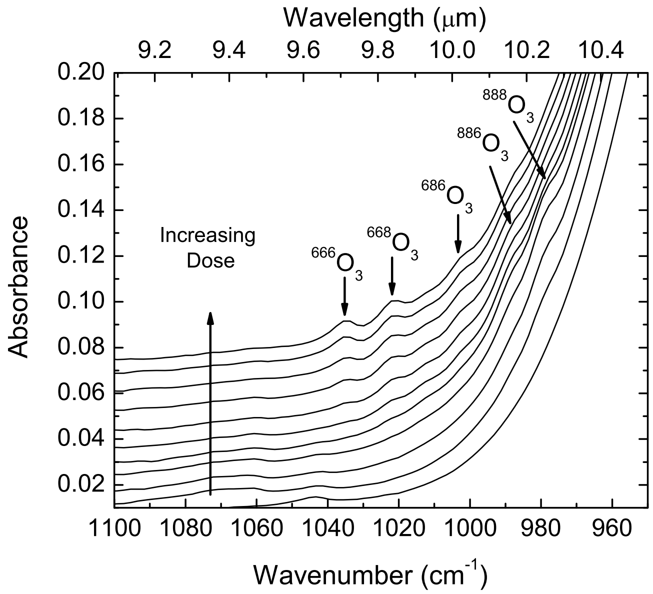

Figure 1. The evolution of absorption bands of ozone isotopologues produced in an $H_2^{16}O$ + $^{18}O_2$ ice sample irradiated with increasing doses of 0.8 MeV protons. Irradiation doses from bottom to top are 0, 0.3, 0.6, 1.2, 2.5, 3.7, 4.9, 6.1, 7.4, 8.6, and 9.8 eV/16-amu.

irradiated by 100 keV Ar^+ ions and then subsequently sputtered by lower-energy ions. These workers proposed that OH is produced via the primary dissociation step of water (equation (4)) and can then follow one of two paths to produce O_2. First, the OH may react with H_2O_2 as in equation (6), and then a further reaction with HO_2 produces O_2 as in equation (8).

$$HO_2 + OH \rightarrow H_2O + O_2 \tag{8}$$

This is designated as T(2009)a. Alternatively, an OH produced by water dissociation may be further dissociated by another impacting ion X:

$$X + OH \rightarrow OH^* \rightarrow O + H \tag{9}$$

This is designated T(2009)b. All three models predict very specific but different atomic and/or molecular intermediates, yet in the experiments from which these models are constructed, the researchers never actually identified any of the chemical intermediates.

[8] The direct detection of radiolytically produced O atom in an ice sample poses many experimental challenges. A recent study identified O atoms in near-edge X-ray absorption spectra of X-ray irradiated ices [*Laffon et al.*, 2006], however it is unknown whether O atoms are produced directly from H_2O or from secondary reactions. Other evidence for the production of O atoms in ice in the literature is found in the detection of Herzberg emission lines of O_2 in UV-irradiated water ice [*Matich et al.*, 1993]. The authors reasoned that the O_2 was formed from O atom recombination, although other reactions not involving O atoms were possible. Again, however, the mechanism of producing O atoms is unclear. Here we present new laboratory results on the observation of O atom production in H_2O ice using the detection of isotopologues of ozone in irradiated H_2O + $^{18}O_2$ thin-film samples. We propose that the O atoms we measure come from the direct dissociation of H_2O as in equation (1).

2. Experimental

[9] The experimental details are similar to those described earlier [*Cooper et al.*, 2006, 2008]. In brief, we prepared gaseous mixtures of $H_2^{16}O$ + $^{18}O_2$ (6:1) in a vacuum manifold. Millipore water was freeze-pump-thaw cycled multiple times to remove dissolved atmospheric gases. The $^{18}O_2$ (Isotec; purity of >97%) was used without further purification. Blank experiments on irradiated pure $^{18}O_2$ produced $^{18}O_3$ and no other detectable scrambled isotopes. The H_2O + $^{18}O_2$ gaseous mixtures were then deposited onto an aluminum mirror precooled to 10 K by a closed-cycle helium refrigerator. The samples were then warmed to 80 K at ~2 K/min. The 80 K irradiation temperature was chosen to approximate ice temperatures on the Galilean satellites. An increase in the vacuum-chamber's base pressure when the preirradiated ice was warmed to ~30 K indicated that some of the O_2 sublimed out of the sample. This observation is consistent with previous work [*Loeffler et al.*, 2006]. Owing to the sublimation of some of the O_2, the exact H_2O/O_2 ratio in the irradiated ice is unknown. The samples were then irradiated at 80 K with 0.8 MeV protons generated by a Van de Graaff accelerator. The ion beam was focused to match the sample mirror size of 25 mm in diameter. At the typical ice-film thickness of ~3–5 μm, the 0.8 MeV protons penetrated the ice fully. We utilized this to determine the fluence (H^+/cm^2) by measuring the current produced when the protons hit the aluminum mirror. IR spectra were measured using a Nicolet 6700 Nexus spectrometer at 4 cm^{-1} spectral resolution. The IR beam size is focused on the sample in our reflectance setup and is much smaller than that of the ion beam. As is the case with all of the experiments performed in this laboratory, reduction of the thickness of the ice due to sputtering of the sample is not significant.

3. Results and Discussion

3.1. Chemical Reactions

[10] Figure 1 shows spectra of a $H_2^{16}O$ + $^{18}O_2$ sample before and after irradiation. As the dose increased, two broad but shallow absorption bands appeared at 980 and 990 cm^{-1} associated with the formation of the 888 and 886 isotopologues, where 8 represents an ^{18}O atom and 6 represents a ^{16}O atom. For clarity, the spectra are shown in Figure 2 with the broad water absorption band removed. The 888 is produced from residually trapped $^{18}O_2$ molecules that were nearest neighbors. The irradiation of pure $^{18}O_2$ did not yield any measurable ozone isotopes containing ^{16}O, and there was no measurable amount of CO_2 atmospheric contaminant in our sample, so the ^{16}O atom in the 886 must have been produced from H_2O. This was the first ozone mixed isotopologue observed as the dose increased, and it is thought to be due to the first reaction step shown in Figure 3, i.e., the combination of a radiolytically produced ^{16}O atom from water with $^{18}O_2$ that was trapped in the ice. The 888 isotopologue was gradually destroyed (as shown in

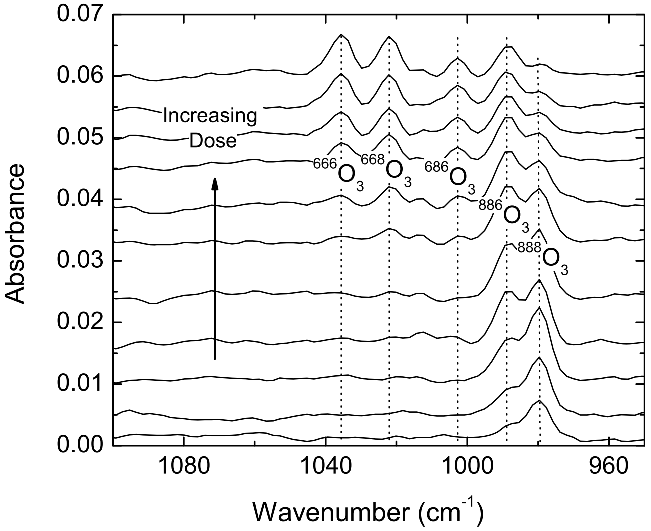

Figure 2. The spectra from Figure 1 with the strong broad water absorption band removed for clarity. Irradiation doses from bottom to top are 0.3, 0.6, 1.2, 2.5, 3.7, 4.9, 6.1, 7.4, 8.6, and 9.8 eV/16-amu.

Figure 2) with increasing dose by the replacement of ^{18}O by radiolytically produced ^{16}O to form 886.

[11] We considered the possibility that the source of ^{16}O in these experiments could be ^{16}OH formed in the radiolytic destruction of H_2O. An ozone molecule containing a ^{16}O atom could then be produced by the following reactions.

$$^{16}\mathrm{OH} + {}^{18}\mathrm{O}_2 \rightarrow \mathrm{H}^{16}\mathrm{O}^{18}\mathrm{O}^{18}\mathrm{O} \rightarrow \mathrm{H} + {}^{16}\mathrm{O}^{18}\mathrm{O}^{18}\mathrm{O} \tag{10}$$

However, calculations [*Varandas*, 2002; *Yu and Varandas*, 2001] show that reaction (10) probably does not occur to any great extent because the energy of the HO_3 intermediate is only marginally below that of OH + O_2 on the ground-state HO_3 potential energy surface. These workers have shown that the O + HO_2 and H + O_3 states are accessible in the gas phase when the reacting O_2 and OH are in highly excited vibrational states. These excited states are likely to be very rapidly quenched in the cold ices discussed in the present work. Additionally, we have recently shown that HO_3 produced in irradiated ices [*Cooper et al.*, 2006] is probably formed from H-addition to O_3.

[12] Radiolytic dissociation from a stable HO_3 precursor (reactions (11a)–(11c)) could also be possible.

$$\mathrm{HO}_3 + \mathrm{energy} \rightarrow \mathrm{H} + \mathrm{O}_3 \tag{11a}$$

$$\mathrm{HO}_3 + \mathrm{energy} \rightarrow \mathrm{O} + \mathrm{HO}_2 \tag{11b}$$

$$\mathrm{HO}_3 + \mathrm{energy} \rightarrow \mathrm{OH} + \mathrm{O}_2 \tag{11c}$$

However, from the potential energy surface [*Varandas*, 2002], reaction (11c) would be expected to dominate owing to the small difference in potential energy. Reaction (11a) would be the least significant due to the largest difference in potential energy of reactants and products. In addition, the HO_3 abundance in irradiated H_2O + O_2 ices at 80 K is small compared with the amount at 10 K [*Cooper et al.*, 2006].

[13] Once the 886 ozone species is produced, further reactions can occur (Figure 3). Other radiolytic ^{16}O atoms originating from radiolyzed water may add to either end of the 886 molecule and displace an O atom from the opposite end. For example, a ^{16}O atom may then react with the 886 isotopologue to form either the 686 or 866 species that are observed at 1003 and 1022 cm^{-1}, respectively. The 866 can then form 686 or 666, and the 686 may form 866 which can feed back into the former reaction channel. The 666 isotopologue is observed at 1035 cm^{-1}. The positions of these isotopologues are summarized in Table 1. This reaction mechanism is diagrammatically shown in Figure 3.

[14] Assuming that oxygen atoms cannot add in between two end-member O atoms in an ozone molecule, the 868 isotopologue would need to form from the reaction between an 886 or 686 molecule and an ^{18}O atom. These reactions could occur if an 886 or 686 molecule and $^{18}O_2$ were nearest neighbors and the $^{18}O_2$ were dissociated to produce an ^{18}O atom. However, the absence of the 868 (~1016 cm^{-1}) isotopologue in the sample indicates that ^{18}O is irreversibly lost to the water lattice once it is displaced. This suggests that the amount of ^{16}O produced radiolytically from H_2O must dominate the amount of ^{18}O in the sample produced from the residually trapped $^{18}O_2$. The lack of 868 also validates the reaction mechanism shown in Figure 3. We have also included in Figure 3 the possibility that 86 and 66 molecular oxygen, formed from one or two isotope exchanges, respectively, or from the dissociation of ozone isotopologues, can potentially react with ^{16}O.

[15] In our experiments on pure H_2O, we see no infrared evidence of ^{16}O atom production via the formation of molecular oxygen, because the oxygen absorption band is very weak. Ozone is also not produced in any detectable quantity because the amount of O_2, the precursor needed for O_3 production, is too small. However, when $^{18}O_2$ is added to pure water, as described above, it acts as a trap for ^{16}O atoms via the formation of ozone isotopologues that can be detected spectroscopically.

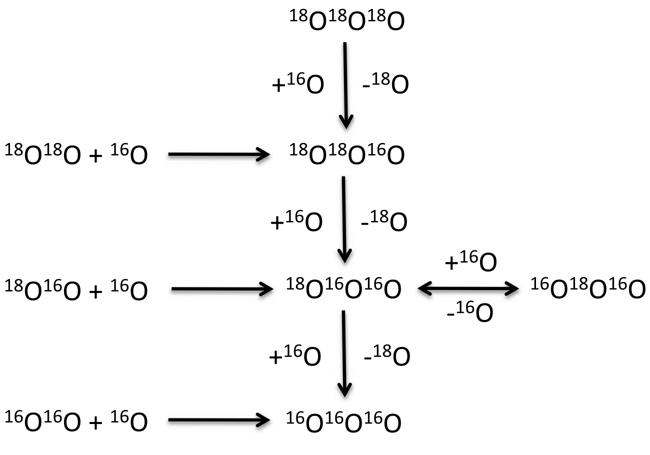

Figure 3. The chemical pathway for the formation of each ozone isotopologue. This model assumes that ^{16}O only reacts with one end of an O_3 isotopologue and results in the loss of an O atom from the opposite end.

Table 1. IR Band Positions (cm^{-1}) for the ν_3 Vibration of Ozone Isotopologues in the Gas Phase [*Schriver-Mazzuoli et al.*, 1996] and in the Present Work in Water Ice

	$^{18}O^{18}O^{18}O$	$^{18}O^{18}O^{16}O$	$^{16}O^{18}O^{16}O$	$^{18}O^{16}O^{18}O$	$^{18}O^{16}O^{16}O$	$^{16}O^{16}O^{16}O$
Gas phase	984.8	993.9	1008.5	1019.4	1028.1	1042.1
In ice (this work)	980	990	1003	–	1022	1035

3.2. Oxygen Abundance

[16] Using a band strength of 1.4×10^{-17} cm molecule^{-1} [*Smith et al.*, 1985] for the ν_3 absorption of O_3, and assuming that it is the same for all isotopologues, we have calculated that there are 0.14% ^{16}O atoms produced by number relative to H_2O (Table 2) at the highest dose of 9.8 eV/16-amu molecule. This has been estimated by first calculating the percentage of each O_3 isotopologue by number from their respective measured column densities and the thickness of the ice sample. The percentage abundance of each isotopologue is then multiplied by the number of ^{16}O atoms it contains to get the percentage abundance of ^{16}O atoms. These values are then summed to produce the total percentage abundance of ^{16}O atoms. It should be noted that it is well known in the literature [*Teolis et al.*, 2007] that interference effects can distort band shapes and consequently estimates of column density of species in ices in reflectance measurements. However, because the band depths for the isotopologues are of similar magnitude, covering a small wavelength region of the spectrum, and are measured from the same ice sample, the relative band depths of each isotopologue are a good estimate for the relative abundance for each isotopologue. There may, however, be an error in the absolute column density due to these interference effects [*Teolis et al.*, 2007].

[17] In pure water ice, without the presence of $^{18}O_2$ to trap ^{16}O atoms as an ozone isotopologue, it could be argued that the highly reactive ^{16}O atom may react with water or another water radiation fragment (such as H or OH) before ever encountering a second radiolytically produced ^{16}O atom. The lifetime of a single ^{16}O atom surrounded by H_2O in an ice lattice is unknown, but it may be stabilized via forming a complex with H_2O [*Khriachtchev et al.*, 2000]. However, if the ozone isotopologues produced in the present work were dissociated and the ^{16}O atoms were to reform exclusively as $^{16}O_2$, then there would be 0.07% $^{16}O_2$ by number relative to H_2O. This small amount of O_2 in pure water is far below the detection limits of our spectrometer, but using the O_3 tracer molecule, we can detect ^{16}O atoms that could otherwise form O_2. In these experiments, the presence of O_2 cannot be shown, but what can be shown is that there are enough ^{16}O atoms produced directly from the radiolysis of water ice that potentially can account for the estimated astronomical O_2 abundances.

Table 2. Percentage Abundance of Ozone Isotopologues and the Equivalent Percentage Abundance of ^{16}O Atoms in Irradiated $H_2^{16}O$ + $^{18}O_2$ Ice at 80 K After a Dose of 9.8 eV/16-amu Molecule[a]

	Ozone Isotopologues			
	666	668	686	886
% abundance	0.024%	0.024%	0.006%	0.009%
% abundance of ^{16}O atoms	0.072%	0.048%	0.012%	0.009%
Total % abundance of ^{16}O atoms	0.14%			

[a] Percentage abundances are calculated as a fraction of the total number of molecules present. Ozone column densities were measured by band area measurement. The total number of molecules in the ice was calculated from a laser interference method of film thickness.

[18] We note that these abundance estimates are calculated at the highest radiation dose of 9.8 eV/16-amu molecule used in the present experiments. At this dose, ^{16}O atom production does not appear to be at steady state (Figure 4), i.e., the yield of O atoms has not reached a point where the O atom abundance does not change with increasing dose. However, determining whether the O atom production is at steady state is impossible in these experiments because we cannot measure all of the O atoms. We can only observe the O atoms that are present as an ozone isotopologue. Previous experiments from our laboratory [*Cooper et al.*, 2008] have shown that in H_2O + $^{16}O_2$ ices that O_3 production reaches steady state by ~5 eV/16-amu molecule.

[19] It is common in radiation chemistry to present production rates as a yield, *G*, the number of molecules produced per 100 eV of energy absorbed. As we cannot measure all O atoms produced, we calculate an average *G* over the entire dose. An effective $G_{H+}(^{16}O)$ was estimated from a plot of the number of ^{16}O atoms measured in ozone isotopologues as a function of radiation dose (Figure 4). The *G*-value was then calculated as follows:

$$G = 100 \times \frac{N(\text{molecules cm}^{-2})}{E(\text{eV cm}^{-2})} \tag{12}$$

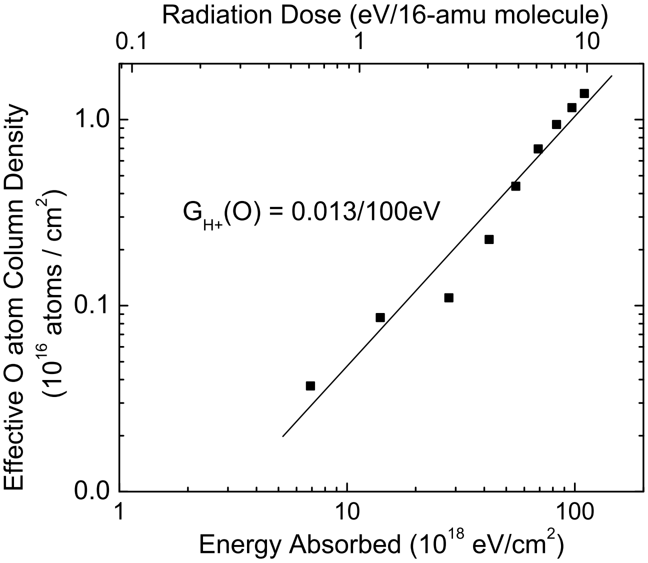

Figure 4. The dose dependent ^{16}O atom production (measured as an ozone isotopologue) at 80 K in an H_2O + $^{18}O_2$ ice sample irradiated with 0.8 MeV protons.

where N is the column density of the O atoms, and E is the energy deposited in the ice and is calculated from the product of ion flux, stopping power, density of ice, and thickness of ice.

[20] Using equation (12) and the data from Figure 4, $G_{H+}(^{16}O) = 0.013$. Again, however, this value represents a lower limit due to the O atoms that cannot be directly measured in this experiment and is only an effective G value as we are actually not measuring ^{16}O atoms directly, but indirectly in the form of ozone isotopologues.

[21] Estimates of the O_2 abundance on Ganymede range from 0.1–1.0% [*Calvin et al.*, 1996] to 1.4–4.2% [*Hand et al.*, 2006]. While our percentage abundance is lower than these estimates, our value represents a lower limit estimate that is in good agreement with the planetary observations. In these laboratory experiments, we cannot account for the ^{16}O atoms that remain trapped in the ice and do not react or the $^{16}O_2$ that is formed but is present at a level below our detection limits because of the extremely weak fundamental vibration, and also the $^{16}O_2$ formed that is sputtered or desorbed out of the sample. In addition, other trapping mechanisms, such as clathrates [*Hand et al.*, 2006] or simultaneous irradiation and deposition [*Teolis et al.*, 2006], may increase the amount of O_2 trapped in an icy satellite.

[22] In terms of modeling the radiation processes that produce O_2 in pure H_2O, we have found that O atoms produced in these experiments, support the J(2005) model. Although it does not by any means conclusively prove the model is correct, it does provide added support via the observation that O atoms can be produced directly from H_2O molecules. The chemistry presented in the P(2006) and T(2009)a models that include the formation of HO_2 and then subsequent dissociation or reaction respectively to O_2 may also be correct. In fact, this paper does not discredit the validity of these authors' work. Rather, the results presented herein simply show that O atoms are produced in radiolytic dissociative events in water ice.

[23] The chemistry of the T(2009)b model is in essence similar to the model proposed in this paper, with the difference being that we propose direct production of O atoms from the dissociation of H_2O whereas *Teolis et al.* [2009] propose production of O atoms from the dissociation of OH. Although similar, the small difference is significant as the T(2009)b model relies upon stable trapping of OH to allow subsequent dissociation to O. This could occur at low temperatures (below 30–40 K), but is probably not a dominant process at temperatures of 80 K or higher, as OH is well known to be mobile [*Johnson and Quickenden*, 1997] and will react soon after its formation. This is supported by observations of chemical reactions within thermally processed ices [*Cooper et al.*, 2008; *Loeffler et al.*, 2006] that appear to be the result of high OH reactivity at 80 K or higher.

[24] Further research is needed to produce a robust and accurate model for the formation of O_2 in irradiated pure water ice, but we have shown here that O atoms produced directly from water may play a part. The actual mechanism will likely require a multi-instrument approach to detect all the intermediate species and reactions. In addition, further laboratory work needs to be performed to understand the trapping mechanism of O_2 on icy satellites.

[25] Nevertheless, we have shown that O atoms are produced directly from H_2O molecules in an H_2O ice. If these O atoms recombine to form O_2 in similarly irradiated water ice, a lower abundance limit of 0.07% by number relative to water could result. This value agrees with the observed O_2 abundance on Ganymede [*Calvin et al.*, 1996; *Hand et al.*, 2006].

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