On Simulating the Proton-irradiation of $O_2$ and $H_2O$ Ices Using Astrochemical-type Models, with Implications for Bulk Reactivity

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Abstract

Many current astrochemical models explicitly consider the species that comprise the bulk of interstellar dust grain ice mantles separately from those in the top few monolayers. Bombardment of these ices by ionizing radiation—whether in the form of cosmic rays, stellar winds, or radionuclide emission—represents an astrochemically viable means of driving a rich chemistry even in the bulk of the ice mantle, now supported by a large body of work in laboratory astrophysics. In this study, using an existing rate-equation-based astrochemical code modified to include a method of considering radiation chemistry recently developed by us, we attempted to simulate two such studies in which (a) pure $O_2$ ice at 5 K and (b) pure $H_2O$ ice at 16 K and 77 K, were bombarded by keV $H^+$ ions. Our aims were twofold: (1) to test the capability of our newly developed method to replicate the results of ice-irradiation experiments, and (2) to determine how bulk chemistry in such a well-constrained system is best handled using the same gas-grain codes that are used to model the interstellar medium. We found that our modified astrochemical model was able to reproduce both the abundance of $O_3$ in the 5 K pure $O_2$ ice, as well as both the abundance of $H_2O_2$ in the 16 K water ice and the previously noted decrease of hydrogen peroxide at higher temperatures. However, these results require the assumption that radicals and other reactive species produced via radiolysis react quickly and non-diffusively with neighbors in the ice.

Key words: astrochemistry – cosmic rays – molecular processes

1. Introduction

The upcoming launch of the James Webb Space Telescope (JWST) promises to usher in a new astrochemical “ice age” by allowing for the collection of an unprecedented amount of data regarding species frozen onto dust grains in the interstellar medium (ISM). Astrochemical models will surely figure prominently in both interpreting these data as well as in informing future observing proposals. This opportunity, however, requires models that are up to the task and unfortunately significant uncertainties remain regarding the chemistry of dust grains and dust grain ice mantles (Cuppen et al. 2017)—a situation that has given it the dubious reputation of “the last refuge of the scoundrel” (Charnley et al. 1992).

Currently, it is a common practice in modern astrochemical codes to distinguish between species in the top few monolayers of dust grain ice mantles (the selvedge), and those underneath, in the interior (the bulk), though there exists considerable disagreement as to whether, or to what degree, such bulk species are chemically active (Cuppen et al. 2017). The hypothesis that chemistry within the ice mantle is less significant than that in the selvedge rests on the following three main lines of reasoning:

(a) species in the bulk are more tightly bound;
(b) a richer chemistry is possible in the selvedge, given the constant exchange of species with the surrounding gas; and

(c) photoprocesses, which further drive chemical reactions, are more efficient in the topmost monolayers.

An implicit assumption behind (a) is that reactions in the bulk occur largely via thermal diffusion, as on surfaces, and thus reaction rates will be low or negligible for species with high binding energies in cold environments. However, some previous experimental studies strongly suggest that reactions in the bulk can occur quickly among neighboring species without the need for diffusion (Baragiola et al. 1999; Bennett & Kaiser 2005; Abplanalp et al. 2016; Chiesa et al. 2018). Similarly, just as selvedge chemistry is stimulated via photoprocesses and interactions with the gas—as noted in (b) and (c)—so too have experiments shown that bombardment by energetic ions, which penetrate solids much more efficiently than photons (Spinks & Woods 1990; Gerakines et al. 2001), causes physicochemical changes that drive a rich chemistry within the ice at low temperatures. This radiation chemistry is quite relevant to the ISM, since ices there are continually bombarded by energetic particles of one kind or another, though typically in the form of cosmic rays (Indriolo & McCall 2013; Rothard et al. 2017), stellar winds (Hudson & Moore 2001; Maday et al. 2002), or radionuclide emission (Cleeves et al. 2013).

Thus, the processing of dust grain ice mantles by ionizing radiation is a very real phenomenon and the fact that such interactions can lead to the formation of astrochemically interesting, even prebiotic, species makes radiation chemistry very promising from a modeling standpoint (Kaiser & Roessler 1997; Holtom et al. 2005; Hudson et al. 2008;...
Abplanalp et al. 2016). Until recently, though, the variety and complexity of the underlying microscopic processes have hindered attempts to add radiation-chemical reactions to astrochemical codes (Abplanalp et al. 2016; Shingledecker et al. 2018).

These processes result from collisions between an incoming particle (the primary ion) and species in the target material. Following the formalism of Bohr (1913), it is customary to divide such collisions into two categories, namely those in which energy is transferred to target nuclei (elastic) or electrons (inelastic). One can therefore express the energy loss per unit path length of the primary ion—called the stopping power—as follows:

\[
\frac{dE}{dx} \approx n(S_n + S_e),
\]

where \( n \) is the density of the target (\( \text{cm}^{-3} \)) and \( S_n \) and \( S_e \) are, respectively, the so-called nuclear/elastic and electronic/inelastic stopping cross sections (\( \text{eV-cm}^2 \)). Inelastic collisions, in turn, can further be divided into those in which target species are ionized or excited. Such ionizations result in the formation of so-called “secondary electrons,” which typically have energies under 50 eV and can themselves ionize or excite target species, thereby further propagating the physicochemical effects initiated by the primary ion (Johnson 1990; Spinks & Woods 1990).

Recently, in Shingledecker & Herbst (2018, hereafter, SH), we introduced a method for treating radiation-chemical processes that is simple enough to include in existing astrochemical models, while simultaneously preserving salient features inferred from experimental data. This method was later added to the astrochemical-type Nautilus v1.1 code (Ruaud et al. 2016) and used by us to determine what effects, if any, these new processes would have on cold core models (Shingledecker et al. 2018). Preliminary results from that study indicated that cosmic-ray-induced reactions could indeed result in enhanced abundances for a number of species, including methyl formate and ethanol, and allowed us to include novel reactions such as insertions (Bergner et al. 2017; Bergantini et al. 2018). However, given the uncertainties sometimes involved in comparing the results of astrochemical models with observations of interstellar environments—particularly in cases where grain-surface chemistry is involved—questions lingered regarding how well astrochemical models were actually simulating irradiation chemistry.

To that end, we have carried out simulations of two different ice irradiation experiments using an existing astrochemical-type code (Vasyunin et al. 2017), modified to include the SH method for treating radiation chemistry. Specifically, we have modeled the bombardment of a 5 K pure \( \text{O}_2 \) ice by 100 keV protons as described in Baragiola et al. (1999), as well as that of a pure water ice at both 16 and 77 K by 200 keV protons, as reported in Gomis et al. (2004a). Doing so has afforded us the opportunity not only to compare how well our simulations replicate the experimental data, but also to directly gauge how well our models perform more generally with handling reactions in bulk ice over a range of temperatures. By thus testing our approaches to ice chemistry in well-constrained experimental systems, confidence can be increased in the results of models of much less well-constrained interstellar environments.

The paper is organized as follows. In Section 2 we discuss details of both the model and chemical network used in this work. In Section 3 our major results are described and their significance is discussed. Finally, our conclusions and suggestions for future work are presented in Section 4.

2. Model and Network

The basis of this work is the MONACO code, described in Vasyunin et al. (2017), which uses a rate-equation approach for reactions in the gas phase and the so-called “modified rate-equation” method for reactions on and in dust grain ice mantles (Garrod 2008; Garrod et al. 2009). As in Vasyunin & Herbst (2013) we assume the selvedge, a term for the altered layers near the top of the mantle, is comprised of the top four monolayers of the ice (Vasyunin & Herbst 2013).

We have modified the code to account for irradiation-chemical reactions on and in ice using the SH method, the foundation of which is the assumption that one of the following outcomes is possible upon collision between an energetic particle, the primary ion or a secondary electron, and some target species, \( A \):

\[
A \rightarrow A^+ + e^-; \quad (P1)
\]

\[
A \rightarrow A^+ + e^- \rightarrow A^* \rightarrow B + C; \quad (P2)
\]

\[
A \rightarrow A^*; \quad (P3)
\]

\[
A \rightarrow A^*; \quad (P4)
\]

where the curly arrow indicates a collision. In processes (P1) and (P2), \( A \) is ionized, though with fast charge recombination leading to the formation of suprathermal dissociation products, designated with an asterisk, assumed to occur in (P2). Processes (P3) and (P4) represent collisions in which a suprathermal product is electronically excited directly into some higher state, which in the case of (P3) is assumed to lead to the formation of thermal products. The efficiencies of (P1)–(P4) are characterized by radiochemical yields, called \( G \)-values, which give the number of molecules created (or destroyed) per 100 eV transferred from bombarding particles to the system (Dewhurst et al. 1952; Spinks & Woods 1990). A full list of the radiolysis processes used here is given in Table 3 of Appendix A. The yields given there were arrived at through a two-step process where initial values were estimated using the SH method and subsequently adjusted to improve agreement with the experimental data. It should be noted that following Shingledecker et al. (2018), we assume the rate of process (P1) is zero, i.e., that all charged species produced in the bulk via ionization are quickly neutralized.

First-order rate coefficients for each radiolysis process are calculated using

\[
k_{\text{rad}} = \left( \frac{G}{100 \text{ eV}} \right) S_e \phi,
\]

with \( \phi \) being the radiation flux and \( S_e \) being the previously described inelastic/electronic stopping cross section. In this work, we assume the flux to be \( 1.0 \times 10^{11} \text{ H}^+ \text{ cm}^{-2} \text{ s}^{-1} \), and use the stopping cross sections given in Table 1.

We assume that, in the bulk, suprathermal species produced via radiolysis rapidly undergo either (a) reaction with a neighbor, or (b) are quenched by the surrounding material. Rate coefficients for the reaction between \( A \) and \( B \)—where
Table 1

| Parameter | Value | Source |
|-----------|-------|--------|
| Temperature | 5 K | Baragiola et al. (1999) |
| Density | 5.7 × 10^{22} cm^{-3} | Horl & Kohlbeck (1982) |
| H+ Energy | 100 keV | Baragiola et al. (1999) |
| S_e | 4.6 × 10^{-14} eV cm^2 | Baragiola et al. (1999) |

Table 2

| Species | E_D (K) | Source |
|---------|---------|--------|
| O | 1660^a | He et al. (2015) |
| O_2 | 1040^b | Minissale et al. (2013) |
| O_3 | 930 | Jing et al. (2012) |
| O_4 | 1833 | Jing et al. (2012) |
| H | 450 | Garrod & Herbst (2006) |
| (Thrower et al. 2011; Marchione et al. 2016) | | |
| OH | 2850 | Garrod & Herbst (2006) |
| H_2O | 5700 | Garrod & Herbst (2006) |
| HO_2 | 4510 | E_D^O + E_D^{OH} |
| H_2O_2 | 5700 | E_D^{OH} + E_D^{O2H} |

Notes. Diffusion barriers in the selvedge were assumed to be 0.5 × E_D, while those in the bulk were assumed to be 0.7 × E_D.

^a Used in models (a) and (b).

^b Used in model (c).

As an example of how the above equations are utilized in our code, consider the time-dependent abundance of B'. Assuming B' is produced via the radiolysis of A as in (P2) and destroyed both via quenching and reaction with some other bulk species, X, then the rate of change in the number of B' as a function of time can be described by

\[
\frac{d N_{B'}}{dt} = k_{rad} N_A - \nu_0^A N_{B'} - k_{fast} N_X N_{B'},
\]

where the reaction between B' and X is, as with all suprathermal species here, assumed to occur barrierlessly.

In order to gauge how well astrochemical models are able to reproduce bulk chemistry, we have run the following three sets of simulations for each experiment considered here using the parameters listed in Table 1:

(a) a set of models in which thermal radicals and atomic oxygen were assumed to react non-diffusively with neighboring species in the ice with rate coefficients calculated using Equation (3);

(b) a set of models in which all bulk rate coefficients were calculated using the standard diffusive formula (Hasegawa et al. 1992) along with diffusion barriers obtained from the desorption energies listed in Table 2 and no tunneling under diffusion barriers for any species;

(c) a set of models similar to (b) but with tunneling through diffusion barriers allowed for H, H_2, and O.

For the third set of simulations, we treat tunneling under diffusion barriers by H and H_2 using the standard formalism in Hasegawa et al. (1992) with a barrier width of 1.0 Å. For atomic oxygen, following results from Minissale et al. (2013), we use a desorption energy of 1040 K and a barrier width of 0.7 Å. In all simulations, H and H_2 were assumed to tunnel through reaction barriers (Tielsch & Hagen 1982). The competition mechanism for systems with chemical activation energies (Chang et al. 2007; Herbst & Millar 2008) is used here in all models only for reactions on the surface.

For the chemical network, we used the reactions listed in Table 4 of Appendix B, as well as the neutral–neutral oxygen reactions listed in Table 7 of Shingledecker et al. (2017). In cases where we have been unable to find values for activation energies, we have assumed a barrier of 10^4 K, except for radical–radical reactions, which were assumed to be barrierless. For every thermal reaction of the type given in Table 4, we included variants involving one suprathermal reactant. To illustrate this point, for every reaction of the form A + B \rightarrow products, we include the following suprathermal variants:

\[
A^b + B \rightarrow \text{products},
\]

\[
A + B^b \rightarrow \text{products}.
\]
3. Results and Discussion

In order to examine how well astrochemical models using the SH method are capable of reproducing experimental data, as well as to determine the accuracy of bulk chemistry in such codes, we have simulated the ice-irradiation systems described in two previous radiation-chemical studies discussed above; the results of these simulations are described below.

3.1. H$^+$ Bombardment of Pure O$_2$ Ice

In this system, the only radical used is atomic oxygen, which can be thermal or suprathermal. We first simulated the irradiation of a pure O$_2$ ice at 5 K by 100 keV H$^+$, following the study by Baragiola et al. (1999), which was previously modeled using the much more detailed Monte Carlo code, CIRIS (Shingledecker et al. 2017). An irradiated O$_2$ ice is, in many respects, an ideal system for testing simulations of radiation chemistry, given the limited number of possible neutral species, i.e., O, O$_2$, and O$_3$. However, in the Monte Carlo code even this seemingly simple system required a network of $\sim$50 reactions or processes and involved a level of detail beyond the practical capabilities of rate equation-based astrochemical codes, such as explicitly calculating the tracks of incident ions and secondary electrons or following each ice species on a hop-by-hop basis.

Despite these limitations though, as shown in Figure 1(a), even our simplified approach is capable of reasonably reproducing the concentration of O$_3$ as a function of fluence. Here, fluence—the product of the H$^+$ flux and irradiation time—represents the number of ions that have bombarded the ice per cm$^2$. As can be seen in Figure 1, the best results were obtained in model (a), where thermal atomic oxygen is assumed to react non-diffusively in the bulk, yielding excellent agreement between calculated and experimental abundances in the steady state regime. An analogous assumption was made in our previous Monte Carlo simulations using CIRIS, with similarly good results (Shingledecker et al. 2017). The slight underprediction of O$_3$ at fluences under $\sim$10$^{13}$ H$^+$ cm$^{-2}$ is likely due to additional processes—such as dissociative electron attachment (DEA)—which are also driven by energetic ion bombardment but not currently considered in this simplified treatment of radiolysis (Arumainayagam et al. 2010). Also noticeable in Figure 1(a) is the fact that atomic oxygen abundances remained low throughout the simulation, despite their continuous production from the dissociation of O$_2$, and to a lesser degree, O$_3$. 

![Figure 1. Results from simulations of an irradiated pure O$_2$ ice using (a) a fast bulk reaction of O, (b) standard bulk rate coefficients based on thermal hopping, and (c) O atom tunneling.](image-url)
Comparison with Figure 1 reveals that model (b), using standard Langmuir–Hinshelwood rate coefficients, is the least accurate. There, though the modeled O$_3$ abundance is only a factor of a few lower than the experimental values, an unrealistically large abundance of atomic oxygen is predicted, contrary to what has been suggested by previous studies (Gerakines et al. 1996; Baragiola et al. 1999; Bennett & Kaiser 2005). This buildup is caused by the very slow rates of thermal diffusion reactions at 5 K, given the high atomic oxygen desorption energy of 1660 K (He et al. 2015).

In order to determine the possible effects of quantum tunneling by atomic oxygen through diffusion barriers, as suggested by Minissale et al. (2013), we ran further simulations using their best-fit results of a barrier width of 0.7 Å and a desorption energy of 1040 K (assuming $E_o = 0.5E_D$). Tunneling for H and H$_2$ is treated using the method of Hasegawa et al. (1992), in which a barrier width of 1 Å is assumed. Comparison of the results of this model, shown in Figures 1(c), with (b) reveals that though agreement between the calculated and experimental ozone abundances is improved, the abundance of atomic oxygen remains too high.

The results of these three models demonstrate that the best agreement with experimental data—both the measured O$_3$ abundance as well as the inferred low O abundance—is obtained when atomic oxygen is assumed to react quickly in the bulk. We note, however, that the predicted atomic oxygen abundances in model (a) may in fact be somewhat too low, based on the observation by Bennett & Kaiser (2005) of an IR feature associated with an [O$_3$...O] complex, though no estimate of the atomic oxygen abundance (or an upper limit) was derived. In such irradiated ices, it is likely that some fraction of the oxygen atoms cannot react quickly, either due to trapping by O$_3$ or steric effects, in which case their abundance would indeed be greater than that predicted in our models. These effects could be accounted for in the method used here by decreasing the value of the pre-exponential frequency, $\nu_0$, thereby increasing the abundance of O. Here, we use the characteristic vibrational frequency given in Equation (4) (which typically has a value on the order of $10^{12}$ s$^{-1}$) as a rough approximation, though in fact the value of this parameter can be as low as $10^{-3}$ s$^{-1}$ (Theulé et al. 2013), and rate...

**Figure 2.** Calculated abundances of H$_2$O$_2$ vs. proton fluence from simulations of a pure H$_2$O ice bombarded by 200 keV H$^+$ assuming (a) fast bulk reactions of radicals and atomic oxygen, (b) only thermal bulk diffusion, and (c) diffusion barrier tunneling for H, H$_2$, and O. Approximate steady-state hydrogen peroxide abundances from Gomis et al. (2004a) at both 16 K and 77 K are represented by the solid, and line-filled boxes, respectively.
coefficients obtained using (4) should probably be interpreted as upper limits.

3.2. H⁺ Bombardment of Pure H₂O Ice

We next simulated the irradiation of a pure H₂O ice by 200 keV H⁺ at both 16 and 77 K using the three different bulk chemistry schemes described in Section 2. Here, in addition to atomic oxygen, we further assume that all radicals in our network—H, OH, and HO₂—react quickly in model (a). This system, though substantially more complex than O₂, is of greater astronomical interest, given the ubiquity of water ice in planetary bodies (Carlson et al. 2009; Altwegg et al. 2015) as well as interstellar dust grain ice mantles (Gibb et al. 2004).

Shown in Figure 2 are both our calculated H₂O₂ abundances vs proton fluence as well as the approximate steady-state experimental values from Gomis et al. (2004a) relative to H₂O of ~1.0% at 16 K and 0.25% at 77 K. As with the pure O₂ ice, model (a) once again provides the best agreement with experimental data and notably is the only one of the three to predict a drop in hydrogen peroxide abundance at higher temperatures. Moore & Hudson (2000), who first detected this trend, speculated that it was due to the reaction

\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2. \] (R3)

We find that, in agreement with Moore & Hudson (2000), reaction (R3) is indeed behind the drop in H₂O₂ abundance at ~80 K, because even though it is assumed that radicals such as OH react quickly, (R3) only becomes competitive at 77 K due to the 755.3 K barrier (Ginovska et al. 2007). In models (b) and (c) the effect of reaction (R3) is reduced by the slow diffusion rates of OH and H₂O₂. As can be seen in Figure 3, without the assumption that radicals react quickly in the bulk, OH in particular becomes quite abundant in the ice, even at 77 K.

The increase in hydrogen peroxide abundance at 77 K in models (b) and (c) is due to the following reactions:

\[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2, \] (R4)

\[ \text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2, \] (R5)

where here, the higher rate of H₂O₂ formation is due to the increased mobility of the reactants. Enabling quantum tunneling through diffusion barriers, as in model (c), further speeds up the rate of reaction (R5), as well as the formation of the
Table 3
Radiolysis Reactions, Branching Fractions, and Yields (G-values) Used in This Work

| Process                                      | \( f_0 \) | G-value* | Type |
|----------------------------------------------|----------|----------|------|
| \( \text{H}_2\text{O} \rightarrow \text{OH}^+ + \text{H}^+ \) | 0.9      | \( 2.57 \times 10^{-4} \) | I    |
| \( \text{H}_2\text{O} \rightarrow \text{O}^+ + \text{H}_2^* \) | 0.1      | \( 2.57 \times 10^{-4} \) | I    |
| \( \text{H}_2\text{O} \rightarrow \text{OH} + \text{H} \)    | 0.9      | \( 1.58 \times 10^{-4} \) | II   |
| \( \text{H}_2\text{O} \rightarrow \text{O} + \text{H}_2 \)    | 0.1      | \( 1.58 \times 10^{-4} \) | II   |
| \( \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^* \)    | 1.0      | \( 1.58 \times 10^{-4} \) | III  |
| \( \text{O}_2 \rightarrow \text{O}^+ + \text{O}^+ \) | 1.0      | \( 6.81 \times 10^{0} \)  | I    |
| \( \text{O}_2 \rightarrow \text{O} + \text{O} \)    | 1.0      | \( 2.91 \times 10^{0} \)  | II   |
| \( \text{O}_2 \rightarrow \text{O}_2^* \) | 1.0      | \( 2.91 \times 10^{0} \)  | III  |
| \( \text{O}_3 \rightarrow \text{O}^+ + \text{O}^+ \) | 1.0      | \( 5.57 \times 10^{1} \)  | I    |
| \( \text{O}_3 \rightarrow \text{O}_2 + \text{O} \) | 1.0      | \( 1.80 \times 10^{1} \)  | II   |
| \( \text{O}_3 \rightarrow \text{O}_3^* \) | 1.0      | \( 1.80 \times 10^{1} \)  | III  |

Notes: Following Shingledecker et al. (2018) we use Type I to indicate process (P2), Type II to indicate process (P3), and Type III to indicate process (P4). *Given in molecules/100 eV.

Figure 4. Percentage \( \text{H}_2\text{O}_2 \) vs. dose for model (a) in which radicals are assumed to react quickly. Following Moore & Hudson (2000), based on the slopes of linear fits to these data, we estimate equivalent measured \( G(\text{H}_2\text{O}_2) \)-values of 0.1 and 0.03 molecules/100 eV for the 16 K and 77 K simulations, respectively.

temperature-dependent chemistry of the system (Spinks & Woods 1990). However, following the method used in Moore & Hudson (2000), we can estimate what the experimental G-value might be from the slope of a linear fit to the abundance curves in Figure 4 over the pre-steady-state regime—corresponding to doses of ca. 0–10 eV, where dose is the product of the fluence and \( \phi_r \). From this, we calculate the yield of \( \text{H}_2\text{O}_2 \) at 16 K to be 0.1 molecules/100 eV—exactly what was mentioned by Moore & Hudson (2000) as the yield in pure \( \text{H}_2\text{O} \).

Shown in Figure 5 are the abundances of \( \text{H}_2 \), \( \text{O}_2 \), and \( \text{O}_3 \) versus fluence. In model (a), the abundance of \( \text{O}_2 \) at 16 K is kept low because of destruction via (6) to form \( \text{HO}_2 \) but increases at 77 K due, in part, to more efficient formation via

\[
\text{HO}_2 + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 + \text{OH}, \tag{R7}
\]

which has a small barrier of 490 K (Burkholder et al. 2014). Similarly, the increase in molecular oxygen abundance at 77 K in model (c) is further driven by

\[
\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2, \tag{R8}
\]

where the abundances of \( \text{OH} \) and \( \text{HO}_2 \) are enhanced relative to model (b) because of the effects of quantum tunneling through diffusion barriers by \( \text{H}, \text{H}_2 \), and \( \text{O} \)—as shown in Figure 3. The decreased abundance of these radicals at 77 K in model (b), combined with their destruction with atomic oxygen, leads to the drop in \( [\text{O}_2] \) in Figure 5(b).

Unfortunately, comparison of our \( \text{O}_2 \) results with experimental data, as with \( \text{H}_2\text{O}_2 \), is complicated by the fact that homonuclear diatomic molecules are IR-inactive. Thus, their abundances cannot be measured using standard techniques, such as Fourier Transform infrared spectroscopy. Nevertheless, it is well known that \( \text{H}_2 \) and \( \text{O}_2 \) form during water ice radiolysis based on analysis of both sputtering products as well as post-irradiation temperature-programmed desorption of the ice via mass spectrometry (Johnson & Quickenden 1997; Teolis et al. 2017). In principle, though, such measurements should be possible using Raman techniques (Rothard et al. 2017) and would be of great value, in part by enabling us to further refine both our radiochemical yields and chemical network. Interest in constraining \( \text{O}_2 \) abundances in irradiated water was recently renewed following its detection in the coma of comet 67P/C-G by Bieler et al. (2015). As can be seen in
Figure 5, the maximum abundance of O$_2$ with respect to water achieved here is $\sim 0.1\%$ in model (a) at 77 K, a value that increased only negligibly at still higher temperatures. Thus, our models predict that the radiolysis of pure H$_2$O ice is not the dominant mechanism behind the $\sim 3.8\%$ O$_2$ abundances relative to water measured by Rosetta (Bieler et al. 2015). In that study, moreover, no evidence for ozone was found, though an upper limit of $1 \times 10^{-4}\%$ relative to water was established. Interestingly, only in model (a) are the ozone abundances predicted to remain below this limit, even at 77 K.

**4. Conclusions and Outlook**

In this work, we have simulated the bombardment of pure O$_2$ and H$_2$O ices by energetic protons using a general rate-equation-based astrochemical code, modified to include radiation-chemical processes using the SH method. These models were carried out with the MONACO program (Vasyunin et al. 2017) and a network consisting of the radiolysis processes listed in Table 3 of Appendix A and the reactions noted in Appendix B. As illustrated in Figures 1 and 2, we were able to qualitatively reproduce both the abundance of O$_3$ in pure O$_2$ (Baragiola et al. 1999) and H$_2$O$_2$ in pure H$_2$O (Gomis et al. 2004a) utilizing the radiochemical processes given in Table 3. Thus validated, these processes, along with the reactions given in Table 4, can be added to existing chemical networks in order to better account for physicochemical effects caused by cosmic-ray bombardment of dust grain ice mantles.

Moreover, by simulating well-constrained experiments rather than interstellar environments we have been afforded a unique opportunity to compare the accuracy and physical realism of several approaches to modeling bulk chemistry over a variety of temperatures relevant to the ISM. As reported here, we have found that the standard approaches to bulk chemistry based on thermal diffusion or quantum tunneling through diffusion barriers less accurately reproduced the experimental data—particularly at low temperatures—than our model in which radicals and atomic oxygen were assumed to react quickly with neighboring species in the ice. This finding is in agreement with recent experiments by Ghesquière et al. (2018), who found no evidence for true bulk diffusion.

Regrettably, despite the large body of work in laboratory astrophysics on the irradiation of interstellar ice-analogs, it has not been possible until recently to incorporate many of the results of these experiments into astrochemical codes.
charged particle bombardment is known to drive the non-thermal desorption of even large molecules such as benzene (Shingledecker et al. 2018). However, our work presented here shows that not only can such models simulate radiation-chemical reactions, they might even be suitably used as a replacement for the simpler kinetic models sometimes employed (e.g., Baragiola et al. 1999; Gounis et al. 2004b). In summary, this study represents an attempt to shrink the gap between experiments and models, an increasingly urgent task in light of the upcoming launch of JWST. However, there is ample opportunity for even further refinements to our approach considering, for example, the effects of the implantation and subsequent reactions of the bombarding H+ ions. The inelastic component considered here at lower particle energies caused by the nuclear-elastic component of the stopping, the effects of the implantation and subsequent reactions of the bombarding H+ ions, the elastic component of stopping, and the effects of the implantation and subsequent reactions of the bombarding H+ ions, the elastic component of the stopping, and the effects of the implantation of radiation-chemical processes in ices and help to reduce uncertainties in future modeling research. In particular, in water ice, excitons and radical reactions and 104 K for all others. 

Note: In the absence of otherwise representative or theoretical data, we have assumed E = 0 K for radical-radical reactions, and 100 K for all others.

Table 4
Solid-Phase Reactions Used in Water Simulations

| Source | Ea (K) | b | h | Source |
|--------|---------|---|---|--------|
| Shingledecker et al. 2018 | 100 | 10 | 100 | See text |
| Gounis et al. 2004b | 100 | 10 | 100 | See text |
| Baragiola et al. 1999 | 100 | 10 | 100 | See text |
| Gounis et al. 2004b | 100 | 10 | 100 | See text |
| Baragiola et al. 1999 | 100 | 10 | 100 | See text |
| Gounis et al. 2004b | 100 | 10 | 100 | See text |
| Baragiola et al. 1999 | 100 | 10 | 100 | See text |
| Gounis et al. 2004b | 100 | 10 | 100 | See text |
| Shingledecker et al. 2018 | 100 | 10 | 100 | See text |
| Gounis et al. 2004b | 100 | 10 | 100 | See text |
| Baragiola et al. 1999 | 100 | 10 | 100 | See text |
| Gounis et al. 2004b | 100 | 10 | 100 | See text |
| Shingledecker et al. 2018 | 100 | 10 | 100 | See text |
| Gounis et al. 2004b | 100 | 10 | 100 | See text |
| Baragiola et al. 1999 | 100 | 10 | 100 | See text |
The chemical network used in this work consists of the reactions listed in Table 4, as well as the neutral–neutral reactions in Table 7 of Shingledecker et al. (2017).

**Appendix B**

**Chemical Network**

The chemical network used in this work consists of the reactions listed in Table 4, as well as the neutral–neutral reactions in Table 7 of Shingledecker et al. (2017).

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