WATER, O2, AND ICE IN MOLECULAR CLOUDS

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ABSTRACT

We model the temperature and chemical structure of molecular clouds as a function of depth into the cloud, assuming a cloud of constant density n illuminated by an external far-ultraviolet (FUV; 6 eV < hν < 13.6 eV) flux G0 (scaling factor in multiples of the local interstellar field). Extending previous photodissociation region (PDR) models, we include the freezing of species, simple grain surface chemistry, and desorption (including FUV photodesorption) of ices. We also treat the opaque cloud interior with time-dependent chemistry. Here, under certain conditions, gas-phase elementary oxygen freezes out as water ice and the elemental C/O abundance ratio can exceed unity, leading to complex carbon chemistry. Gas-phase H2O and O2 peak in abundance at intermediate depth into the cloud, roughly AV ∼ 3–8 from the surface, the depth proportional to ln(G0/n). Closer to the surface, molecules are photodissociated. Deeper into the cloud, molecules freeze to grain surfaces. At intermediate depths, PDRs are attenuated by dust extinction, but photodesorption prevents total freeze-out. For G0 < 500, abundances of H2O and O2 peak at values ∼10−7, producing columns ∼1015 cm−2, independent of G0 and n. The peak abundances depend primarily on the product of the photodesorption yield of water ice and the grain surface area per H nucleus. At higher values of G0, thermal desorption of O atoms from grains slightly enhances the gas-phase H2O peak abundance and column, whereas the gas-phase O2 peak abundance rises to ∼10−5 and the column to ∼2 × 1016 cm−2. We present simple analytical equations for the abundances as a function of depth, which clarify the dependence on parameters. The models are applied to observations of H2O, O2, and water ice in a number of sources, including B68, NGC 2024, and ρ Oph.

Key words: astrochemistry – ISM: abundances – ISM: lines and bands – ISM: molecules

Online-only material: color figures

1. INTRODUCTION

Oxygen is the third most abundant element in the universe, after hydrogen and helium, so a basic knowledge of oxygen chemistry in molecular clouds is essential in order to understand the chemical structure, thermal balance, and diagnostic line emission from star-forming molecular gas in galaxies. Early gas-phase chemical models (e.g., Langer & Gaedel 1989; Millar 1990; Bergin et al. 1998) predicted large abundances of H2O (∼10−6) and O2 (∼10−5–10−4) relative to hydrogen nuclei in molecular gas well shielded from far-ultraviolet (FUV, 6 eV < hν < 13.6 eV) photons. If gas-phase H2O and O2 were that abundant, they would be important coolants for dense gas (Goldsmith & Langer 1978; Hollenbach 1988; Neufeld et al. 1995). However, the Submillimeter Wave Astronomy Satellite (SWAS) made pointed observations in low-energy transitions of ortho-H2O (the 10−10J1 transition at 557 GHz) and O2 (the 3−3 transition at 487 GHz) toward numerous dense (but unshocked) molecular cores and determined that the line-of-sight-averaged and beam-averaged (SWAS beam ∼4′) abundance of H2O is of order ∼10−8 (Snell et al. 2000) and that of O2 is ∼10−6 (Goldsmith et al. 2000). More recent observations by the Odin mission set more stringent upper limits on O2, ∼10−7 (Pagani et al. 2003), with a reported detection at the ∼2.5 × 10−8 level in ρ Oph (Larsson et al. 2007). Although the water abundance derived from the observed water emission depends inversely on the gas density, and therefore is somewhat uncertain, understanding the two order of magnitude discrepancy between the gas-phase chemical models and the observations is essential to astrochemistry and to the basic understanding of the physics of molecular clouds.

Previous attempts to explain the low abundance of H2O and O2 observed by SWAS showed that time-dependent gas-phase chemistry by itself would not be sufficient (Bergin et al. 1998, 2000). Starting from atomic gas, a dense (n(H2) ∼ 105 cm−3) cloud only took ∼105 years to reach H2O abundances ∼10−6, close to the final steady-state values and much greater than observed.

The best previous explanation involved time-dependent chemistry linked with the freeze-out of oxygen species on grain surfaces and the formation of substantial water ice mantles on grains (Bergin et al. 2000). In these models, all of the oxygen in the molecular gas which is not tied up in CO adsorbs quickly (in ∼105 years for a gas density of ∼104 cm−3) to grain surfaces, forms water ice, and remains stuck on the grain as an ice mantle. As a result, the gas-phase H2O abundance drops from ∼10−6 to ∼10−8. The grains are assumed to be too warm for CO to freeze as a CO ice mantle, so that for a period from about 105 years to about ∼106 years, the gas-phase H2O abundance remains at the ∼10−8 level, fed by the slow dissociation of CO into O and the subsequent reaction of some of this O with H+. Then ultimately forms gas-phase H2O. The slow dissociation of CO is driven by cosmic-ray ionization of He; the resultant He+ reacts with CO to form O and C+. After ∼3 × 106 years, even the gas-phase CO abundance drops significantly as the dissociation process bleeds away the oxygen that ends up as water ice on grain surfaces. Therefore, after about 3 × 106 years, the gas-phase H2O also drops from ∼10−8 to < 10−9. This previous
scenario explained the observed H2O emission as arising from the central, opaque regions of the cloud, where the abundance has dropped to the observed values but has not had time to reach the extremely low steady-state values. The model relied, then, on a “tuning” of molecular cloud timescales so that they are long enough for the freeze-out of existing gas-phase oxygen that is not in CO onto grains, but not so long that the CO is broken down and the resultant O converted to water ice, which would cause the gas-phase H2O abundances to drop below the observed values. The model also relied on CO not freezing out on grains in the opaque cloud centers.

To add to the problems of modeling the SWAS data, the SWAS team observed a number of strong submillimeter continuum sources, such as SgrB, W49, and W51, and found the 557 GHz line of H2O in absorption, as the continuum passed through translucent clouds (AV ~ 1–5) along the line of sight (Neufeld et al. 2002, 2003; Plume et al. 2004). The absorption measurement provided an even better estimate of the H2O column, N(H2O) through these clouds because the absorption line strengths are only proportional to N(H2O), whereas the emission line strengths are proportional to n(H2)N(H2O)e−27K/T since the line is subthermal, effectively optically thin, and lies ΔE/k = 27 K above the ground state. Therefore, to obtain columns from emission line observations requires the separate knowledge of both the gas density and the gas temperature. The absorption measurements showed column-averaged abundances of H2O of ~10−7–10−6 with respect to H2 using observed CO columns and multiplying by 104 to obtain H2 columns. In the context of the time-dependent models with freeze-out, the difference between the abundances measured in absorption compared with those measured in emission was attributed to the presumed lower gas densities in the absorbing clouds compared to the emitting clouds. Because the freeze-out time depends on n−1, it was assumed that the lower density clouds had not had time to freeze as much oxygen from the gas phase, so that gas-phase H2O abundances were higher.

A variation of this model is that of Spaans & van Dishoeck (2001) and Bergin et al. (2003), where it was noticed that the water emission seemed to trace the photodissociation region (PDR; see Hollenbach & Tielens 1999), which lies on the surface of H2O that is not in CO onto grains, but not so long that the CO is broken down and the resultant O converted to water ice, which would cause the gas-phase H2O abundances to drop below the observed values. The model also relied on CO not freezing out on grains in the opaque cloud centers.

We propose in this paper a new model of the H2O and O2 chemistry in a cloud. In this model, we assume that the molecular cloud lifetime is sufficiently long to allow freeze-out and reduce the gas-phase H2O and O2 abundances to very low values in the central, opaque regions of the cloud. The key to understanding the H2O emission and the O2 upper limits observed by SWAS and Odin is to model the spatially dependent H2O and O2 abundances through each cloud. At the surface of the cloud, the gas-phase H2O and O2 abundances are very low because of the photodissociation by the ISRF or by the FUV flux from nearby OB stars. Near the cloud surface, the dust grains have little water ice because of photodesorption by the FUV field. Deeper into the cloud, the attenuation of the FUV field leads to a rapid rise of the gas-phase H2O and O2 abundances, which peak at a hydrogen nucleus column Nf ∼ 1021.5−22 cm−2 (or depths AVf ∼ several into the cloud) and plateau at this value for ΔAV ∼ several beyond AVf, insensitive to the gas density n and the incident FUV flux G0 (scaling factor in multiples of the average local interstellar radiation field). At these intermediate depths, photodesorption of some of the water ice by FUV photons keeps the gas-phase water abundance high (the “f” in Nf and AVf signifies the onset of water ice freeze-out, as will be discussed in Sections 2.5 and 3.3). The FUV is strong enough to keep some of the ice off the grains, but, due to efficient water ice formation followed by photodesorption, it is not strong enough to dissociate all gas-phase water. At greater depths, gas-phase reactions other than photodissociation begin to dominate gas-phase H2O destruction, and the steady-state gas-phase H2O and O2 abundances plummet as all the gas-phase elemental O is converted to water ice. Thus, the overall structure of a molecular cloud has three subregions: at the surface is a highly “photodissociated region,” at intermediate depths is the “photodesorbed region,” and deep in the cloud is the “freeze-out region.”

In this new model, the H2O and O2 emission mainly arises from the layer of high-abundance gas in the plateau that starts at Nf and extends somewhat beyond, so that the emission is a “surface” process rather than a “volume” process. For clouds with columns N > Nf, the H2O and O2 emissions become independent of cloud column, assuming the incident FUV field and gas density are fixed. The model gives column-averaged abundances through the dense cores of ∼10−6 for H2O and O2 for low values of G0 < 500, but the local abundances peak at values that are at least an order of magnitude larger than these values. For cloud columns N > Nf, the average H2O abundance scales as N−1.

The implications of this scenario for molecular clouds may be much broader than this particular model of H2O and O2 chemistry in clouds. Other molecules, such as CO, CS, CN, and HCN, require a spatial model of their distribution in a cloud, with photodissociation and photodesorption as the dominant processes near the cloud surface, and the freezing out of the molecules the dominant process deeper into the cloud. In addition, the adsorption process and creation of abundant ice mantles changes the relative gas-phase abundances of the elements. In the case considered in this paper, the C/O ratio in the gas may span from 0.5 at the cloud surface to unity or greater in the H2O freeze-out region. Such changes in the gas-phase C/O ratio have major implications on all gas-phase chemistry (e.g., Langer et al. 1984; Bergin et al. 1997).

The interesting and important caveat to this relatively simple steady-state model is the effect of time dependence in raising abundances of, for example, gas-phase H2O, O2, and CO above steady-state values in the opaque (AV > 5–10) interiors of clouds. One such effect is that at low densities, n ∼ 103 cm−3, species do not have time to freeze out within cloud lifetimes, and therefore have much higher gas-phase abundances. We have also uncovered a new time-dependent process that may elevate the H2O and O2 abundances for times t ≤ 105 years in the freeze-out region at very high AV even at high cloud densities n ∼ 104 cm−3. If the grains are sufficiently cold to freeze out CO (Tgr ∼ 20 K or G0 ∼ 500) at high AV, a CO/H2O ice mix rapidly (t ≤ 105−6 years) forms. The steady-state solution has very little CO ice with most of the O in H2O ice. However, the time to
convert CO ice to H$_2$O ice is very long, and the bottleneck is the cosmic-ray desorption of CO from the CO/H$_2$O ice mixture. This desorption provides gas-phase CO that then acts as a reservoir to produce gas-phase H$_2$O and O$_2$ until all the oxygen eventually freezes out as water ice (i.e., the same mechanism as described in Bergin et al. 2000 except that the gas-phase CO in this case comes from the CO ice). Depending on the assumptions regarding the CO desorption process, this cosmic-ray CO desorption timescale may range from $10^5$ to $\gg 10^7$ years. If the timescale is roughly 0.1–1 times the cloud age, a maximum gas-phase H$_2$O and O$_2$ abundance is produced at that time. Although not as large as the peak abundances produced at $A_V$, these abundances can be significant and can contribute to the total column of these species if the cloud has a high total column (but only if the CO desorption time is 0.1–1 times the cloud age).

This paper is organized as follows. In Section 2, we describe the new chemical/thermal model of an opaque molecular cloud illuminated by FUV radiation. The major changes implemented in our older PDR models (Kaufman et al. 1999) include the adsorption of gas species onto grain surfaces, chemical reactions on grain surfaces, and the desorption of molecules and atoms from grain surfaces. In Section 3, we show the results of the numerical code as functions of the cloud gas density $n$, the incident FUV flux $G_0$, and the grain properties. We present a simple analytical model that explains the numerical results and how the abundances scale with depth and with the other model parameters. We discuss time-dependent models for the opaque cloud center. In Section 4, we apply the numerical model to both diffuse clouds and dense clouds. Finally, we summarize our results and conclusions in Section 5. For the convenience of the reader, Table 3 in the Appendix lists the symbols used in the paper.

2. THE CHEMICAL AND THERMAL MODEL OF AN OPAQUE MOLECULAR CLOUD

2.1. Summary of Prior PDR Model and Modifications

The numerical code we have developed to model the chemical and thermal structure of an opaque cloud externally illuminated by FUV flux is based on our previous models of PDRs, which are described in Tielens & Hollenbach (1985), Hollenbach et al. (1991), and Kaufman et al. (1999, 2006). This one-dimensional (1D) code modeled a constant density slab of gas, illuminated from one side by an FUV flux of $1.6 \times 10^{-3} G_0 \text{ erg cm}^{-2} \text{ s}^{-1}$. The unitless parameter $G_0$ is defined above in such a way that $G_0 \sim 1$ corresponds to the average local interstellar radiation field in the FUV band (Habing 1968). The subscript “0” indicates that the flux is the incident FUV flux, as opposed to the attenuated FUV flux deeper into the slab. The code calculated the steady-state chemical abundances and the gas temperature from thermal balance as a function of depth into the cloud. It incorporated ~45 chemical species, ~300 chemical reactions, and a large number of heating mechanisms and cooling processes. The chemical reactions included FUV photoionization and photodissociation; cosmic-ray ionization; neutral–neutral, ion–neutral, and electronic recombination reactions, including reactions with charged dust grains; and the formation of H$_2$ on grain surfaces. No other grain surface chemistry was included in these prior models. The main route to gas-phase H$_2$O and O$_2$ through these gas-phase reactions is schematically shown in Figure 1. It starts with the ionization of H$_2$ by cosmic-rays or X-rays, which eventually leads to H$_3^+$ that recombines to form gas-phase water. It also recombines to form OH that reacts with O to form gas-phase O$_2$. The code contained a relatively limited carbon chemistry; we included CH and CH$_2$, as well as their associated ions, but did not include CH$_3$, CH$_4$, C$_2$H, or longer carbon chains, nor any carbon molecules that include S or N.

The code modeled regions that lie at hydrogen column densities $N \leq 2 \times 10^{22} \text{ cm}^{-2}$ (or $A_V \lesssim 10$) from the surface of a cloud. Therefore, it applied not only to the photodissociated surface region, where gas-phase hydrogen and oxygen are nearly entirely atomic and where gas-phase carbon is mostly C*, but also to regions deeper into the molecular cloud where hydrogen is in H$_2$ and carbon is in CO molecules. Even in these molecular regions, the attenuated FUV field can play a significant role in photodissociating H$_2$O and O$_2$, and in heating the gas.

The dust opacity is normalized to give the observed visual extinction per unit H nucleus column density that is observed in the diffuse interstellar medium (ISM; e.g., Savage & Mathis 1979; Mathis 1990). The extinction in the FUV, assumed to go as $e^{-b_\lambda A_V}$, is taken from PDR models described most recently in Kaufman et al. (1999, 2006), and mainly derived from the work of Roberge et al. (1991). Here $b_\lambda$ is the scale factor that expresses the increase in extinction as one moves from the visual to shorter wavelengths. However, the FUV extinction law in molecular clouds is not well known. We discuss in Section 3.2 how our results would vary if $b_\lambda$ varies.

In the following subsections (Sections 2.2–2.7), we describe the modifications to the basic PDR code that we have made to properly model the gas-phase H$_2$O and O$_2$ abundances from the surfaces of molecular clouds to the deep interiors, where the gas-phase elemental oxygen freezes out as water ice mantles on grain surfaces. The modifications include the freeze-out of gas-phase species onto grains, the formation of OH and H$_2$O as well as CH, CH$_2$, CH$_3$, and CH$_4$ on grain surfaces, and various desorption processes of species from grain surfaces. Figure 2 shows the grain surface formation process for water ice.

One key modification is the application of time-dependent chemistry to the deep, opaque interior. Here, certain chemical timescales are comparable to cloud lifetimes, and steady-state chemical networks, such as our PDR code, do not apply. The time-dependent code also increases the number of reactions and species we follow, and this particularly improves the treatment of the carbon chemistry in the cloud interior. Further discussion is found in Sections 2.3, 2.4, and 2.7.
Figure 2. Grain surface oxygen chemical network included in this modeling effort. Note that in addition, we include grain surface carbon chemistry (see text) and allow the sticking of all species onto grain surfaces and various desorption mechanisms. The grain surface oxygen reaction network begins with O sticking to grains, followed by accretion of H to form OH and then H₂O⁻. Here, “d” stands for the three desorption processes: thermal, photo, and cosmic ray. Near the cloud surface, FUV photons photodesorb ices, leading to some gas-phase H₂O and O₂. In addition, for high-FUV fields, which warm the grains, thermal desorption of the weakly bound O atoms can be important both near the surface and deep in the cloud. Finally, deep in the cloud, cosmic-ray desorption is important.

2.2. Dust Properties

The basic PDR code implicitly assumed an “MRN” (Mathis et al. 1977) grain size distribution \( n_g(a) \propto a^{-3.5} \), where \( a \) is the grain radius, extending from very small (\( \lesssim 10 \) Å) polycyclic aromatic hydrocarbons (PAHs) to large (\( \sim 0.25 \) μm) dust grains. With this distribution, the largest grains provide the bulk of the grain mass, and the intermediate-sized grains (\( \sim 100 \) Å) provide the bulk of the FUV extinction. The smallest particles and PAHs provide the bulk of the surface area, and dominate the grain photoelectric heating process and the formation of H₂ on grain surfaces. The code implicitly assumes an MRN distribution in the sense that the equations for attenuation of incident photons by dust, for grain photoelectric heating, for H₂ formation, and for gas–grain collisions and the charge transfer that may occur in such collisions all assume such a distribution.

For the process of the freeze-out of oxygen species onto grain surfaces, we also implicitly assume an MRN distribution, in the sense that we adopt a cross-sectional grain area \( \sigma_H \) appropriate for an MRN distribution. As will be shown in Section 3, \( \sigma_H \), which is one-fourth the surface area available for freeze-out, is an important parameter for determining the abundance of gas-phase H₂O in our models. Below in Section 2.5, we show that \( \sigma_H \) is roughly the total cross-sectional area of grains (per H) that are larger than about 20 Å. Smaller grains experience single-photon heating events, which clear them of ice mantles (Leger et al. 1985). In addition, cosmic-rays may clear small grains of ices (Herbst & Cuppen 2006). In an MRN distribution, the cross-sectional area of grains with radii larger than about 20 Å is \( \sigma_H \sim 2 \times 10^{-21} \) cm² per H.

We note, however, that the cross-sectional area is somewhat uncertain. It could be smaller if grains coagulate inside of dense molecular clouds. It could be larger due to ice buildup. We note that once all oxygen-based ices freeze-out onto such an MRN distribution, it forms a constant mantle thickness of \( \Delta a \sim 50 \) Å regardless of grain size. While this is insignificant to the large (\( \sim 0.1 \) μm) grains that contain most of the mass, it represents a very large change in radius and area of the smallest (\( \sim 20 \) Å) grains that provide most of the grain surface area. The increased surface area of grains at the end of this freezeout will proportionally increase subsequent gas–grain interaction rates. Thus, neutralization of ions by grains, formation of H₂ on grain surfaces, the freeze-out of species, and the cooling or heating of the gas by gas–grain collisions may all be enhanced by significant amounts in regions where water ice has totally frozen out on grains. However, because of the possibility of grain coagulation, which reduces grain surface area, and because of the uncertainty in the lower size cutoff of effective grains, we have chosen to fix \( \sigma_H \) and treat it as a (constrained) variable with values ranging from \( \sigma_H = 6 \times 10^{-22} \) to \( 6 \times 10^{-21} \) cm² per H.

2.3. Adsorption and Time-Dependent Chemistry

Adsorption is the process by which a gas-phase atom or molecule hits a grain and sticks to the surface due to van der Waals or stronger surface bonding forces. Typically, at the low gas temperatures we will consider, \( T_{\text{gas}} \lesssim 50 \) K, the sticking probability is of order unity for most species (Burke & Hollenbach 1983). We assume unit sticking coefficients here for all species heavier than helium. Thus, the timescale to adsorb (freeze) is the timescale for a species to strike a grain surface

\[
t_{f,i} \sim \left[ n_g(\sigma_{gr} v_i) \right]^{-1},
\]

where \( v_i \) is the thermal speed of species \( i \) and where the grain number density \( n_g \) times the grain cross section \( \sigma_{gr} \) is the average over the size distribution. As discussed above, in an MRN distribution with a lower cutoff size of \( a \sim 20 \) Å, \( n_g \sigma_{gr} \sim 2 \times 10^{-21} \) cm⁻¹, where \( n \) is the gas-phase hydrogen nucleus density in units of cm⁻³. Therefore, \( t_{f,i} \sim 8 \times 10^6 \text{(m}_O/\text{m}_i)^{1/2}(20^2 \text{cm}^2/\text{n})(30 \text{K}/T)^{1/2} \) years, where \( m_O \) is the mass of atomic O and \( m_i \) is the mass of the species. Since molecular cloud lifetimes are thought to be \( 2 \times 10^6 \) to \( 2 \times 10^7 \) years, and the molecules reside in regions with \( n \gtrsim 10^3 \) cm⁻³, this short timescale suggests that molecules should mostly freeze out in molecular clouds unless some process desorbs them from grains. Dust vacuums the condensibles quickly.

Consider the depletion of CO in regions where the grain temperatures are too high to directly freeze out CO. CO freezes out when grain temperatures are \( T_{\text{gr}} \lesssim 20 \) K (see Section 2.4 below). However, H₂O freezes out when grain temperatures are \( T_{\text{gr}} \lesssim 100 \) K at the densities in molecular clouds. Suppose that \( 20 \text{K} < T_{\text{gr}} < 100 \text{K} \), so that gas-phase elemental oxygen that is not in CO freezes out as water ice, but CO does not directly freeze. CO is continuously destroyed by He⁺ ions created by cosmic rays, producing C⁺ and O. The resultant O has two basic paths: it can reform CO, or it can freeze out on grain surfaces as water ice, never to return to the gas phase in the absence of desorption mechanisms. The latter process therefore slowly depletes the CO gas-phase abundance, by lowering the available gas-phase elemental O. We see this effect in the late time evolution of CO in Bergin et al. (2000). One effect, not included in Bergin et al., that slows this process is that for grain temperatures \( T_{\text{gr}} \gtrsim 20 \text{K} \), the adsorbed atomic O may be rapidly thermally desorbed before reacting with H, and therefore the production of H₂O ice by grain surface reactions may be substantially curtailed (this will be discussed further in Sections 2.5 and 3.2). Nevertheless, gas-phase H₂O will form and will freeze out, and therefore given enough time, the elemental O not incorporated in refractory (e.g., silicate) grain material is converted to H₂O ice. If elemental C does not evolve to a similarly tightly bound carbonaceous ice, there is the potential for the gas-phase C/O number ratio to exceed unity. This will have consequences for astrochemistry (e.g., Langer et al. 1984; Bergin et al. 1997; Nilsson et al. 2000), and we show some exemplary results in Section 3.5.

Consider as well the case where \( T_{\text{gr}} \lesssim 20 \text{K} \) deep in the cloud (i.e., at \( A_V > 5 \); this low \( T_{\text{gr}} \) corresponds to \( G_0 \lesssim 500 \)). In this case, the gas-phase CO freezes out with the H₂O, forming a CO/H₂O ice mix. In order for this CO ice to be converted...
to H2O ice, the CO needs to be desorbed by cosmic rays. It then reacts in the gas phase with He⁺ as described above, and eventually, the freed O goes on to form mostly water ice. The timescale for this CO cosmic-ray desorption can be quite long, and may dominate the slow evolution of the chemistry toward steady state.

Unfortunately, this timescale is not well known. First of all, cosmic-ray desorption rates are not well constrained. Second, the timescales depend on the structure of the CO/H2O ice mix, and this structure is not certain. If the molecules are immobile, the CO and H2O ice molecules are initially mixed and each monolayer contains this mix. However, there is some evidence that either pure CO ice pockets form, or the CO accretes on top of an already formed layer of water ice (Tielens et al. 1991; Lee et al. 2005; Pontoppidan et al. 2004, 2008). Even if the CO and H2O are initially mixed and immobile, cosmic rays desorb CO much more efficiently than H2O due to the much smaller binding energy of adsorbed CO compared with adsorbed H2O (Leger et al. 1985). This could lead to surface monolayers with very little CO compared to the protected layers underneath the surface. The cosmic-ray desorption rate is directly proportional to the fraction of surface sites occupied by CO. In the examples above, this fraction could range from zero to unity. Thus, the desorption timescale could range from large values (> 10⁷ years) to small values (∼ 10⁵ years). We compute these timescales in Section 2.4.

Because of the moderately long timescale for the depletion of either gas-phase or ice-phase CO via this freezing out of the elemental O in the form of water ice, we apply time-dependent chemical models (see Section 3.7) to the cloud interiors that are run for the presumed lifetimes (∼ 10⁷ years) of molecular clouds. Time-dependent models are also warranted for clouds of relatively low density, n ≲ 10⁵ cm⁻³, where t_f ≳ 2 × 10⁶ years (see Equation (1)).

### 2.4. Desorption

To desorb a species from a grain surface requires overcoming the binding energy that holds the species to the surface. Table 1 lists the binding energies of the key species we treat. Note that water has a very high binding energy and is therefore more resistant to desorption.

**Table 1**

| Species | Adsorption Energy (K) | Photodesorption Yield (UV Photon)⁻¹ | Cosmic-Ray Desorption Rate (mol⁻¹ s⁻¹) |
|---------|------------------------|-------------------------------------|--------------------------------------|
| O       | 800                    | 10⁻⁴                               | ...                                  |
| OH      | 1300                   | 10⁻³                               | ...                                  |
| H₂O     | 4800<sup>b</sup>       | 2 × 10⁻³ as H₂O                    | 4.4 × 10⁻¹²<sup>c</sup>              |
| O₂      | 1200                   | 10⁻³                               | 9.1 × 10⁻¹⁵<sup>d</sup>              |
| C       | 800                    | 10⁻³                               | ...                                  |
| CH      | 650                    | 10⁻³                               | ...                                  |
| CH₂     | 960                    | 10⁻³                               | ...                                  |
| CH₃     | 1200                   | 10⁻³                               | ...                                  |
| CH₄     | 1100<sup>b</sup>       | 10⁻³                               | 2.7 × 10⁻¹⁵<sup>d</sup>              |
| CO      | 960<sup>b</sup>        | 10⁻³                               | 6.0 × 10⁻¹³<sup>c</sup>              |
| S       | 1100                   | 10⁻³                               | ...                                  |
| Si      | 2700                   | 10⁻³                               | ...                                  |
| Fe      | 4200                   | 10⁻³                               | ...                                  |

**Notes.**

<sup>a</sup> All adsorption energies are from Hasegawa & Herbst (1993) unless otherwise noted.

<sup>b</sup> Aikawa et al. (1996).

<sup>c</sup> Herbst & Cuppen (2006) and Bringa & Johnson (2004).

<sup>d</sup> Hasegawa & Herbst (1993).

**Thermal desorption.** The rate Rₜₐₐₜ,ι per atom or molecule of thermal desorption from a surface can be written as

\[ Rₜₐₐₜ,ι \simeq vᵢe^{-Eᵢ/kTᵢ}, \]

where \( Eᵢ \) is the adsorption binding energy of species \( i \) and \( vᵢ = 1.6 \times 10^{11} \sqrt{(Eᵢ/k)/(mᵢ/m_H)} \) s⁻¹ is the vibrational frequency of the species in the surface potential well, \( k \) is Boltzmann’s constant, and \( mᵢ \) and \( m_H \) are the mass of species \( i \) and hydrogen, respectively. One can find the temperature at which a species freezes by equating the flux \( Fₜₐₐₜ,ι \) of desorbing molecules from the ice surface to the flux of adsorbing molecules from the gas

\[ Fₜₐₐₜ,ι \equiv Nₛ,ᵢRₜₐₐₜ,ιfₛ,ᵢ = 0.25nᵢvᵢ, \]

where \( Nₛ,ᵢ \) is the number of adsorption sites per cm² (\( Nₛ,ᵢ \sim 10^{15} \) sites cm⁻²), \( fₛ,ᵢ \) is the fraction of the surface adsorption sites that are occupied by species \( i \), \( nᵢ \) is the gas-phase number density of species \( i \), and \( vᵢ \) is its thermal speed. We have assumed sticking probability of unity. From these equations, one can calculate the freezing temperature \( Tₜᵢ \) of a species by solving for \( Tₜᵢ \)

\[ Tₜᵢ \simeq (Eᵢ/k)\left[\ln \left(\frac{4Nₛ,ᵢfₛ,ᵢvᵢ}{nᵢvᵢ}\right)\right]^{-1}, \]

\[ Tₜᵢ \simeq (Eᵢ/k)\left[57 + \ln \left(\frac{Nₛ,ᵢ}{10^{13} \text{ cm}^{-²}}\right)\left(\frac{vᵢ}{10^{13} \text{ s}^{-¹}}\right)\left(\frac{1 \text{ cm}^{-³}}{nᵢ}\right)\times \left(\frac{1 \text{ cm}^{-³} \text{ s}^{-¹}}{vᵢ}\right)\right]^{-1}. \]

This equation shows that at molecular cloud conditions the freezing temperature \( Tₜᵢ \) is about 0.02Eᵢ/k, or about 100 K for H₂O but only ∼20 K for CO (see Table 1). We include thermal desorption rates from our surfaces as given by these equations.
We compute the number of layers of an adsorbed species on the grain, and only thermally desorb from the surface layer.

*Photodesorption.* The flux \( F_{\text{pd},i} \) of adsorbed particles leaving a surface due to photodesorption is given by

\[
F_{\text{pd},i} = Y_i F_{\text{FUV}} f_{\lambda,i},
\]

where \( Y_i \) is the photodesorption yield for species \( i \), averaged over the FUV wavelength band, and \( F_{\text{FUV}} \) is the incident FUV photon flux on the grain surface. We write the FUV photon flux at a depth \( \lambda_V \) into the cloud as (see Tielens & Hollenbach 1985)

\[
F_{\text{FUV}} = G_0 F_0 \rho e^{-1.8A_V},
\]

where \( F_0 \approx 10^8 \) photons cm\(^{-2}\) s\(^{-1}\) is approximately the local interstellar flux of 6–13.6 eV photons and \( G_0 \) is the commonly used scaling factor (see Section 2.1).

Reliable photodesorption yields are often hard to find in the literature, but for the case of H\(_2\)O a laboratory study has been done for the yield created by Lyman \( \alpha \) photons (Westley et al. 1995a, 1995b). The mass loss at large photon doses is proportional to the photon flux, showing that desorption is not due to sublimation caused by absorbed heat. The yield is negligible when IR or optical photons are incident. As an incident photon is absorbed in the first two surface layers, the interpretation that radical formation in the surface layer is due to photodesorption leads one to re-examine the issue of whether grains near the surfaces of molecular clouds will indeed be saturated with radicals on their surfaces. While it is true that the photon dose is sufficient, this dose was delivered over a long timescale. Westley et al. (1995b) point out that it is possible in this case that radicals may recombine in the time between photon impacts within an area of molecular dimensions (\( \sim 10^{-15} \) cm\(^2\)), which might result in smaller yields than the saturated ones.

In light of the uncertainties in the wavelength dependence of the yield over the FUV range, the photodesorption products, and the level of saturation, we adopt \( Y_{\text{H}_2\text{O}} = 10^{-3} \) and \( Y_{\text{OH},w} = 2 \times 10^{-3} \) as our “standard” values, but we will show models in which these yields are varied by a factor of 10 from their standard values, maintaining their ratio of 0.5. We will also use the observations of \( A_V \) thresholds for water ice formation to constrain the absolute values of these yields (Section 4.2.1), and the observations of OH and H\(_2\)O in diffuse clouds to help determine their ratio (Section 4.1).

Recent laboratory measurements of CO photodesorption imply a yield similar to that for H\(_2\)O (Öberg et al. 2007). Therefore, we adopt \( Y_{\text{CO}} = 10^{-3} \) as our standard value for CO. Unless \( T_{\text{gr}} < 20\) K, adsorbed CO is anticipated to be rare because it thermally desorbs so rapidly. However, in cases with low \( G_0 \), CO may occupy \( \sim 1/3 \) of the surface sites at the H\(_2\)O freeze-out column.

For the other species there is less or no reliable photodesorption data in the literature. Since our grain surface is largely H\(_2\)O ice, and the photodesorption occurs via the production of radicals (and possibly, the reformation of H\(_2\)O from radicals), we assume that the yield for O is \( Y_O \sim 10^{-4} \) (a smaller yield since no reformation is possible). The yields for O, OH, and O\(_2\) are less important, because in our models they rarely occupy many of the surface sites. The first two are rare because they rapidly react with H to form H\(_2\)O. Table 1 lists the photodesorption yields that we adopted.

A complication arises if grains move *rapidly* from surface regions (higher temperature and possibly lower density) where H\(_2\)O ice can exist to deeper (lower temperature and higher density) regions where CO ice forms and then back again to the surface region. The fraction of the surface now covered by H\(_2\)O ice, \( f_{\text{H}_2\text{O}} \), is now nearly zero, since CO covers the surface. Therefore, H\(_2\)O and OH photodesorption rates are very low. We have ignored this effect, assuming a mix of CO and H\(_2\)O ice in each adsorbed monolayer.\(^7\) In this paper, the region where H\(_2\)O and OH photodesorption are important is the intermediate or “plateau” region where gas-phase H\(_2\)O and OH abundances peak. Here, the photodesorption and/or thermal desorption timescales of CO are much shorter than the dynamical timescales to bring CO-coated ice grains from the deep interior to the plateau region.

*Desorption by chemical reaction.* There have been some attempts to model the desorption of molecules due to chemical

\(^7\) Except, as discussed later in this section, when we test the sensitivity of our results to CO cosmic-ray desorption.
reactions on grain surfaces. D’Hendecourt et al. (1982) and Tielens & Allamandola (1987) discuss an exploding grain hypothesis in which the UV photons produce radicals in the grains, which are relatively immobile until the grain temperature is increased. At this point, they begin to diffuse and react, and the chemical heat causes a chain reaction exploding the grain and “desorbing” species in large bursts. Our photodesorption is a sort of steady-state version of this. O’Neill et al. (2002) examine the effects of hydrogenation on grain surfaces, and in some of their models they assume that the reaction of a newly adsorbed H atom with radicals on the surface, such as OH, will release enough energy to desorb the resultant hydrogenated molecule. In this case, it is the chemical energy carried in by the H atom, and not the photodissociation of the ice itself, which leads to desorption. In our standard case, we assume that H$_2$ desorbs on formation because of its low adsorption binding energy and its low mass, but that other forming molecules do not. However, we ran one case (see Section 3.5) in which we include this desorption process for all forming molecules in our grain surface chemistry.

Desorption by cosmic rays and X-rays. Deep in the cloud, cosmic-ray desorption of ices becomes important for maintaining trace amounts of O-based and C-based species in the gas phase. Cosmic-ray desorption rates per surface molecule (i.e., molecule in the top monolayer of ice) for various species are listed in Table 1. As discussed above, the desorption rates depend on the abundance of a particular adsorbed species in the surface monolayer. In our standard steady-state models, we assume that if there are no species (e.g., CO, CH$_4$, H$_2$O) that are adsorbed, that they are well mixed, and each monolayer of ice contains the same mix. However, as discussed above, for CO the fraction of the surface layer containing CO may range from zero to unity. The timescale for the cosmic-ray desorption of a species $i$ is given as

$$t_{cr,i} = \frac{x(i)}{4R_{cr,i} N_{i,f,co} \sigma_H},$$

where $x(i)$ is the abundance of the adsorbed ice species and $R_{cr,i}$ is the cosmic-ray desorption rate per surface atom or molecule and is given in Table 1. The cosmic-ray desorption time for H$_2$O$_{ice}$ is long ($\sim$10$^9$ years) and is not significant in our models. However, the timescale for CO desorption under certain circumstances may be comparable to the age of the cloud, and can therefore lead to a source of gas-phase CO, which can then serve as a source of gas-phase H$_2$O and O$_2$, as discussed above. Substituting from Table 1 for $R_{cr,CO}$, assuming an initially high abundance of CO ice, $x(CO_{ice}) = 10^{-4}$, and taking $f_{cr,CO} = 0.3$, we obtain $t_{cr,CO} \sim 2.5 \times 10^6$ years. However, both $R_{cr,CO}$ and $f_{cr,CO}$ are uncertain. In the case of the fractional surface coverage $f_{cr,CO}$, the cosmic-ray desorption process itself, acting on the top monolayer, could result in a very low value of $f_{cr,CO}$ by essentially purging the surface of CO and leaving a fairly pure monolayer of H$_2$O$_{ice}$ (see Section 2.3). On the other hand, there may be evidence for a nonpolar CO ice surface on top of a polar H$_2$O ice mantle resulting in $f_{cr,CO} = 1$ (see Section 2.3). Because of the uncertainty in the product $f_{cr,CO} R_{cr,CO}$, we will examine in Section 3.7 a range of values of this parameter extending from $10^{-15}$ to $10^{-11}$ s$^{-1}$. The corresponding timescale to remove all the ice is about $3 \times 10^3$ to $3 \times 10^7$ years, ranging from less than to much greater than cloud ages.

Cosmic rays also lead to the production of FUV photons (Gredel et al. 1989) at a level equivalent to $G_0 \sim 10^{-3}$ throughout the cloud. We include this flux in determining both the photodissociation of gas-phase molecules and the photodesorption of ices.

Following Leger et al. (1985) we assume that, in general, cosmic-ray desorption dominates over X-ray desorption and we therefore ignore this process. Of course, in regions close to X-ray sources and where the UV is shielded by dust, X-ray desorption will become more significant.

2.5. Timescales Related to Freeze-out

Several timescales are needed to fully understand the freezing process. Assuming that the grain size distribution extends to very small grains (or large molecules) whose size is of order a few Angströms, we first compute timescales relevant for single photons to clear grains of ice due to transient heating by the photon. The peak temperature that a silicate grain of radius $a$ achieves after absorbing a typical $\sim$10 eV FUV photon is given (Drapatz & Michel 1977; Leger et al. 1985)

$$T_{max} \sim 100 \left( \frac{20 \, \text{Å}}{a} \right)^{1.3} \text{K.}$$

The timescale for this grain to radiate away the energy of this photon is

$$t_r \sim 100 \left( \frac{100 \, \text{K}}{T_{max}} \right)^5 \left( \frac{20 \, \text{Å}}{a} \right)^3 \text{s.} \quad (10)$$

On the other hand, the timescale for a single H$_2$O molecule to thermally evaporate from an ice surface on the grain is given by

$$t_{evap,H_2O} \sim 4 \times 10^{-13} \left( \frac{4000 \, \text{K}}{T_{max}} \right)^4 \text{eV} \left( \frac{a}{10 \, \text{Å}} \right) \text{s.} \quad (11)$$

where $\Delta E/k = 4800$ K is the binding energy of the H$_2$O molecule (Fraser et al. 2001) and $4 \times 10^{-13}$ eV is the period of one vibration of the molecule in the ice lattice (see Equation (2) and the following text). For comparison with the above equations, $t_{evap,H_2O} \simeq 10^9$ s at $T_{max} = 50$ K, $3 \times 10^8$ s at $T_{max} = 100$ K, and 30 s at $T_{max} = 150$ K. Comparison with $t_r$ indicates that the ice mantle will evaporate before cooling when $T_{max} \sim 150$ K. Comparison with the equation for $T_{max}$ shows that $a \gtrsim 15-20$ Å is required for grains to be large enough such that single-photon events do not clear ice mantles. Thermal evaporation of H$_2$O will also cool the grain. Since the binding energy of an H$_2$O molecule is $\sim$0.5 eV, $\sim$20 H$_2$O molecules must evaporate to offset the heating due to the absorption of a single UV photon. However, we show below that 10 eV photons are absorbed by 20 Å grains more rapidly than O atoms hit the grains to form ice. Therefore, thermal evaporation cannot significantly cool the transiently heated grains compared with radiative cooling, and an entire ice mantle never builds up on the grain surface. The conclusion holds that $a \lesssim 20$ Å grains lose their ice in the presence of single-photon heating events. In summary, for the purposes of modeling oxygen freeze out and ice formation, we assume that the effective surface area for ice freezeout is given by the area of grains that are larger than $\sim$20 Å.

Several more timescales reveal the fate of an oxygen atom once it sticks to a grain. The timescale $t_{gr,O}$ for a given grain of radius $a$ to be hit by a gas-phase oxygen atom is given as

$$t_{gr,O} \sim 2.5 \times 10^4 \left( \frac{10^{-4}}{x(O)} \right) \left( \frac{10 \, \text{K}}{T_{gas}} \right)^{1/2} \times \left( \frac{0.1 \, \mu\text{m}}{a} \right)^2 \left( \frac{10^5 \, \text{cm}^{-3}}{n} \right) \text{s.} \quad (12)$$
where \( x(O) \) is the gas-phase abundance of atomic oxygen relative to hydrogen. Similarly, the timescale \( t_{\text{gr,H}} \) for the same grain to be hit by a hydrogen atom from the gas is given as

\[
t_{\text{gr,H}} \sim 6.0 \times 10^{-1} x(H)^{-1} \left( \frac{10^5 \text{ cm}^{-3}}{n} \right)^{1/2} \times \left( \frac{0.1 \mu\text{m}}{a} \right)^2 \left( \frac{10^5 \text{ cm}^{-3}}{n} \right) \text{s},
\]

where \( x(H) \) is the abundance of atomic hydrogen. Note that at the column or \( AV \) into the cloud where water begins to freeze out on grain surfaces, \( x(H) \) is likely less than unity because most \( H \) is in \( H_2 \). However, if \( x(H) \geq 0.25 x(O) \), then \( H \) atoms stick more frequently than \( O \) atoms. Provided photodesorption or thermal desorption does not intervene, and assuming that the \( H \) atoms are quite mobile on the surface and find the adsorbed \( O \) atom, \( O \) atoms will react with \( H \) to form \( OH \) and then \( H_2O \).

During these timescales need to be compared to the timescale for UV photons to photodesorb the \( O \) atom and the timescale for \( O \) atoms to thermally desorb from grains. The timescale for a grain of size \( a \gtrsim 100 \text{ Å} \) to absorb an FUV photon is given as

\[
t_{\gamma} \sim 30 G_0^{-1} e^{1.8 y} \left( \frac{0.1 \mu\text{m}}{a} \right)^2 \text{s}.
\]

The timescale to photodesorb an \( O \) atom from a surface covered with a covering fraction \( f_{s,O} \) of \( O \) atoms is then

\[
t_{\gamma - \text{des}} \sim 3 \times 10^8 G_0^{-1} e^{1.8 y} f_{s,O}^{-1} \left( \frac{0.1 \mu\text{m}}{a} \right)^2 \left( \frac{Y_O}{10^{-3}} \right)^{-1} \text{s},
\]

where \( Y_O \) is the photodesorption yield for atomic \( O \). The timescale for thermal desorption of an \( O \) atom on a grain is given as

\[
t_{\text{evap},O} \sim 9 \times 10^{-13} e^{30 K} \text{ s}.
\]

Therefore, the timescale for thermal evaporation of an \( O \) atom is \( 5 \times 10^{22} \text{s} \) for a \( 10 \text{ K} \) grain, \( 2 \times 10^{23} \text{s} \) for a \( 20 \text{ K} \) grain, and \( 0.3 \text{s} \) for a \( 30 \text{ K} \) grain. From Equations (12)–(16) one concludes that if grains are cooler than about 20–25 K and if \( x(H) > 0.25 x(O) \), an adsorbed \( O \) atom will react with \( H \) to form \( OH \) and then \( H_2O \) before it is thermally desorbed. Photodesorption of \( O \) never appears to be important.

In this paper, we are mainly interested in the abundance of gas-phase \( H_2O \) and \( O_2 \) at the point where oxygen species start to freeze out in the form of water ice. This “freeze-out depth” \( A_V \equiv A_{\gamma} \) is where the gas-phase oxygen abundance plummets and most oxygen is incorporated as water ice on grain surfaces. This occurs when the rate at which relatively undepleted gas-phase oxygen atoms hit and stick to a grain equals the photodesorption rate of water molecules from grain surfaces completely covered in ice, or \( t_{\gamma - \text{des}}(A_V) \sim t_{\text{gr},O}(A_V) \).

Using Equations(12) and (15) and taking \( Y \equiv Y_{\text{OH},w} + Y_{H_2O} \) as the total yield of photodesorbing water ice, we find

\[
A_V \approx 0.56 \ln \left[ \frac{0.8 G_0}{10^{-3}} \left( \frac{10^5 \text{ cm}^{-3}}{n} \right)^{1/2} \right] \left( \frac{10^5 \text{ cm}^{-3}}{n} \right)^{1/2} \text{s}.
\]

As discussed above, \( t_{\gamma} \ll t_{\text{gr},O} \), so that at this critical depth no ice forms on small (\( \lesssim 20 \text{ Å} \)) grains because single photons can thermally evaporate adsorbed \( O \), \( OH \), or \( H_2O \) before thermal radiative emission cools the grain and before another \( O \) atom sticks to the grain. Although ice may not form on a \( \lesssim 20 \text{ Å} \) grains, they may still contribute to the formation of gas-phase \( OH \) or \( H_2O \). Note that once an \( O \) atom sticks to a given grain, the timescale \( t_{\text{gr},H} \) for an \( H \) atom to stick (Equation (13)) may be shorter than the timescales \( t_{\gamma} \) for a photon to be absorbed. Thus, the \( O \) may be transformed into \( H_2O \) on the grain surface before a photon transiently heats the small grain and thermally evaporates the \( H_2O \) to the gas phase. Because of these complexities, the possibility of coagulation, and the uncertain nature of small grains, we have chosen to fix the cross-sectional grain area per \( H \) nucleus \( \sigma_H \) as constant with depth \( A_V \) in a given model, but to then run models with a range of assumed \( \sigma_H \).

2.6. Grain Surface Chemistry

Figure 2 shows the new grain surface oxygen chemistry that we adopt. We maintain the old method of treating \( H_2 \) formation on grain surfaces (Kaufman et al. 1999). The main new grain surface chemistry reactions are the surface reactions \( H + O \rightarrow OH \) and \( H + OH \rightarrow H_2O \). Miyauchi et al. (2008) discuss and review recent laboratory experiments that suggest rapid formation of water ice on grain surfaces. In addition, we include simple grain surface carbon chemistry. Similar to Figure 2, we allow the sticking of \( C \) to grains to form \( C_{\text{ice}} \), followed by reactions of surface \( H \) atoms to produce \( CH_{\text{ice}}, CH_2{\text{ice}}, CH_3{\text{ice}}, \) and \( CH_4{\text{ice}} \), as well as the desorption of all these species. We do not form \( CO \), \( CO_2 \), or methanol on grain surfaces in this paper.

In the model, we compare the timescale for \( O \) and \( OH \) to desorb with the timescale for a hydrogen atom to hit and stick to the grain surface. If the desorption timescale is shorter, then we desorb the radical and the grain surface chemistry does not proceed. However, if the desorption time is longer, then we assume that the reaction proceeds. We generally assume that the newly formed surface molecule does not desorb from the heat of formation, but must wait for another desorption process, or, for a further chemical reaction with \( H \), if possible. However, as in O’Neill et al. (2002), we also run a case where the heat

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8 In our runs, we find only a few cases where \( x(H) < x(O) \); this occurs at high \( A_V \) for cases with high \( G_0 \), where grains are so warm that \( O \) thermally desorbs before forming \( OH \) on the grain surface. In these cases, there is no buildup of adsorbed \( O \) atoms on the surface, and therefore no resultant formation of \( O_2 \) or \( CO_2 \) on grain surfaces, as might otherwise be expected (Tielens & Hagen 1982).
of formation desorbs the newly formed molecule. Implicit in this simple grain chemical code is the assumption that the H atom migrates and finds the O or OH before it desorbs or before another H atom adsorbs to possibly form H2. We note that, in general, it is rare to find even a single O or OH on the grain surface, because desorption or the reaction with H removes them before another O or OH sticks to the surface.

2.7. Ion–Dipole Reactions

A final change to our chemical code is the inclusion of enhanced rate coefficients for the reactions between atomic or molecular ions with molecules of large dipole moment, such as OH and H2O. We have used the UMIST rates (e.g., Woodall et al. 2007) and the rates quoted in Adams et al. (1985) and in Herbst & Leung (1986). These rates are larger than the rates without the dipole interactions by a factor \( \sim 10 \) at \( T = 300 \) K and, given their \( T^{-1/2} \) dependence, increase further at low temperatures.

3. MODEL RESULTS

In this section, we present computational results of our new model. In order to explore the sensitivity of the freeze-out processes to various input parameters, we first define a standard case. We then present a number of models in which the gas density, FUV field, grain properties, and photoelectric yield are varied. For each of these runs, we use the steady-state model of Kaufman et al. (1999) modified to include grain surface reactions, ion–dipole reactions, and desorption mechanisms as detailed in Section 2. Unlike our previous PDR models that were run to a depth \( A_V = 10 \), we often run our new models to \( A_V = 20 \) to ensure that we are well beyond the regions where photodesorption plays a role. At the end of this section, we discuss the effects of time dependence.

3.1. Standard Case

Most ortho-H2O detections in ambient (nonshocked) gas are located in Giant Molecular Clouds (GMCs), and, in particular, in the massive cores of these GMCs that are illuminated by nearby OB stars. Ortho-H2O has not yet been detected toward quiescent “dark clouds” such as Taurus. Therefore, for our standard case, we choose a gas density \( n = 10^4 \text{ cm}^{-3} \) and an FUV field strength \( G_0 = 10^2 \). We adopt the same gas-phase abundances as in the PDR models of Kaufman et al. (1999) and Kaufman et al. (2006). Details are given in Tables 1 and 2.

![Figure 3](image-url). Oxygen chemistry for the standard \((n = 10^4 \text{ cm}^{-3}, G_0 = 100)\) steady-state PDR model, including freeze-out, grain surface reactions, thermal desorption, photodesorption, and cosmic-ray desorption. Model parameters are those given in Table 1. The abundances of major O-bearing species are shown as a function of visual extinction from the cloud surface, \( A_V \).

In the standard case, the gas (grain) temperature varies from \( T = 120 \text{ K} \left( T_{gr} = 31 \text{ K} \right) \) at the surface, to \( T = 22 \text{ K} \left( T_{gr} = 15 \text{ K} \right) \) at the water peak plateau, to \( T = 16 \text{ K} \left( T_{gr} = 15 \text{ K} \right) \) for \( A_V = 10 \). The abundances of O-bearing species in the standard model are shown in Figure 3, while those of C-bearing species are shown in Figure 4. Here, the basic features of the results of freeze-out and desorption are clearly demonstrated.

The photodissociation layer. At the surface, the dominant species are precisely those found in gas-phase PDR models. Atomic oxygen is the most abundant O-bearing species, while the transition from C to CO occurs once significant shielding occurs at \( A_V \approx 1.5 \). Near the surface, all of the oxygen that is not in CO is atomic, and \( x(O) \geq x(CO) \). At the low dust temperature at the surface, thermal desorption of H2O is insignificant and the beginnings of an ice layer (less than a monolayer) are evident despite rapid photodesorption by the FUV. In steady state, photodesorption of this ice as well as gas-phase chemistry maintains a small abundance of gas-phase H2O.

The photodesorbed layer. By \( A_V \approx 2.8 \), enough water has been deposited on grain surfaces to form a monolayer, i.e., \( x(H_2O_{\text{gr}}) \approx 4n_{\text{gr}}\sigma_{\text{gr}}N_{H_2}\sigma_{H}/n \sim 8 \times 10^{-8} \sigma_{H}/(2 \times 10^{-21} \text{ cm}^2) \). At this point, the water ice abundance increases rapidly with depth. Here, the photodesorption rate decreases with depth due to attenuation of the FUV flux by grains, but the rate of freeze-out only decreases when the gas-phase O abundance decreases. For the gas-phase O abundance to decrease significantly requires many monolayers of ice. This is seen in Figure 3 as the increase in \( x(H_2O_{\text{gr}}) \) by two orders of magnitude at \( A_V \approx 3 \). Note the agreement of this freeze-out depth with \( A_V \) given in Equation (16).

As the gas-phase abundance of O decreases, the growth of water ice slows and the ice abundance saturates (i.e., all O nuclei locked in water ice) near \( A_V \approx 3.5 \). Fed by photodesorption, the gas-phase abundance of H2O maintains a broad plateau.
Figure 4. Carbon chemistry for the standard ($n = 10^4$ cm$^{-3}$, $G_0 = 100$) steady-state PDR model, including freeze-out, grain surface reactions, thermal desorption, photodesorption, and cosmic-ray desorption. Model parameters are those given in Table 1. The abundances of major C-bearing species are shown as a function of visual extinction from the cloud surface, $A_V$. For $A_V > 5$, the gas-phase CO abundance will not be as low as is shown here for the steady-state solution; time-dependent effects will keep the CO abundance elevated (see Section 3.7). In addition, the limited chemistry in the steady state PDR code drives the high abundance of CH$_4$ ice at high $A_V$; the time-dependent code, which has more extensive chemistry, finds a mixture of CO and CH$_4$ ice for the carbon-bearing ices in this case.

(A color version of this figure is available in the online journal.)

$N$(H$_2$O) $\sim 10^{-7}$ from $A_V \sim A_Vf \sim 3$ to $A_V \sim 6$, beyond which (i.e., deeper in the cloud) other gas-phase H$_2$O destruction mechanisms besides photodissociation become dominant. The abundance of gas-phase H$_2$O near the peak is determined by the balance of photodesorption from the surface layer of ice on the grains with photodissociation of H$_2$O by FUV photons. Both of these processes are proportional to the local attenuated FUV field; this leads to a plateau in the H$_2$O abundance independent of $G_0$ (see Section 3.3).

The abundances of other O-bearing molecules closely track the abundance of H$_2$O. OH is mainly a product of photodissociation of gas-phase water, while it is destroyed by photodissociation and by reaction with $S^+$, both of which depend on the attenuated FUV field. The O$_2$ is produced primarily through the reaction O + OH $\rightarrow$ O$_2$ + H and is destroyed by photodissociation. Thus, the gas-phase H$_2$O, OH, and O$_2$ abundances track one another from the beginning of freeze-out through the H$_2$O plateau. We discuss this in more detail in Section 3.3 below.

The freezeout layer. Beyond $A_V > 6$, photodesorption of water ice ceases to produce enough gas-phase H$_2$O or OH to maintain the H$_2$O and OH plateaus (and therefore the O$_2$ plateau). Other destruction mechanisms than photodissociation of H$_2$O take over, and gas-phase abundances of all O-bearing species drop as H$_2$O ice incorporates essentially all available elemental O.

The destruction of CO by He$^+$, followed by freeze-out of the liberated O atom, as described in Section 2.3, is responsible for the rapid drop in the steady-state gas-phase CO abundance at $A_V \sim 6$ (see Figure 4) as all of the oxygen becomes locked in water ice. In our rather limited steady-state carbon chemistry, C atoms end up incorporated into CH$_4$ ice once O is liberated from CO. In our time-dependent runs, which have more extensive chemistry, the standard case at $A_V = 10$ has $\sim 0.6$ of the elemental carbon in CH$_4$ ice and $\sim 0.4$ in CO ice after 2 $\times$ 10$^7$ years. The ratio of the CH$_4$ ice to the H$_2$O ice abundance is $\sim 0.15$–0.25 at this time. Öberg et al. (2008) discuss recent observational results on the ice content of grains in molecular clouds with emphasis on CH$_4$; they conclude that CH$_4$ ice does indeed form by hydrogenation on grain surfaces, as we have assumed in our models. However, they observe abundance ratios of CH$_4$ ice to H$_2$O ice that are typically 0.05, nearly three to five times smaller than in our standard model. This likely arises because our time-dependent code starts with carbon in atomic or singly ionized form, so that there is more opportunity for C or C$^+$ to transform to CH$_4$ ice than if the carbon started in the form of CO. Aikawa et al. (2005) provide theoretical models that result in the observed ratios of CH$_4$ ice/H$_2$O ice by initiating carbon in the form of CO. The purpose of this paper is to follow H$_2$O and O$_2$ chemistry, and not carbon chemistry. We have therefore also neglected grain surface reactions that could lead to CO$_2$ ice or methanol ice. Our CO$_2$ ice is formed by first forming gas-phase CO$_2$ by the reaction of gas-phase CO with OH, and then subsequently freezing the CO$_2$ onto the grain surfaces. In a subsequent paper we plan to study the possible fractionation signature (12CO$_2$ ice/$^{13}$CO$_2$ ice) of our gas-phase route to forming CO$_2$ ice in our subsequent paper, which examines carbon chemistry in more detail. In summary, our carbon chemistry here is simplified, and the abundances of carbon ices in the models are very crude.

3.2. Dependence on $G_0$, $n$, $Y_{H_2}$, $\sigma_H$, PAHs, and $b$.

Dependence on incident FUV flux, $G_0$. Figure 5 shows the effect of changing the FUV field strength, $G_0$, on the depth of the gas-phase water peak and the abundance at the peak, while keeping the density fixed. Here $G_0$ is varied from 1 to 10$^3$. The main effect of changing $G_0$ is to move the position of the water peak inward with increasing $G_0$. Varying $G_0$ from 1 to 10$^3$ changes the depth of freezeout from $A_V \sim 1$ to $A_V \sim 7$. Gas-phase H$_2$O peaks once ice has formed at least a monolayer on the grain surfaces, so the location of the water peak also moves inward (logarithmically) with increasing $G_0$. The peak gas-phase water abundance ($\sim 10^{-7}$) is insensitive to $G_0$ and insensitive to depth (i.e., $A_V$) in the water plateau. We also see that the depth where the gas-phase water starts to decline from its peak (plateau) value is also weakly (logarithmically) dependent on $G_0$, increasing with increasing $G_0$. Thus, the column of gas-phase water remains fairly constant and independent of $G_0$.

However, some differences arise in the case with $G_0 = 10^3$. Here, the assumption that every O sticking to a grain forms water ice breaks down. The high FUV field absorbed at the cloud surface leads to a high IR field that heats the grains to $T_{gr} \sim 25$ K even at $A_V \sim 8$, so that a significant fraction of O atoms is thermally desorbed from grains faster than they can form water ice, resulting in a higher gas-phase abundance of

$9$ The drop in the total CO gas + CO$_2$ ice abundance by a factor $\sim 2$ in the opaque interior compared to the intermediate shielded regions would be hard to measure without a precise (better than factor of 2) independent measure of the column along various lines of sight through the cloud.

$10$ We note that under optimum conditions CO$_2$ ice and methanol ice may carry nearly as much oxygen as water ice. However, generally they do not; therefore, their neglect should not appreciably affect our model of basic oxygen chemistry.
atomic O. At these large depths, the formation of gas-phase water is not mainly by photodesorption of water ice, but by cosmic-ray initiated ion–molecule reactions (see Figure 1). The high gas-phase elemental abundance of O leads to a high rate of formation of H$_2$O and O$_2$, whereas the high $A_V$ leads to low photodestruction rates of these two molecules. In addition, although the FUV field is severely attenuated, the residual FUV is sufficient to prevent the complete freeze-out of gas-phase H$_2$O. The combined effect is a deeper and higher peak in the gas-phase water abundance (which coincides with the peak in the O$_2$ abundance) as solid portions of these two molecules are frozen on grains, which suppresses H$_2$O$_{ice}$ formation and keeps more elemental O in the gas phase.

(A color version of this figure is available in the online journal.)

**Dependence on gas density, n**. In Figure 6, we vary the gas density from $10^3$ to $10^5$ cm$^{-3}$, keeping the rest of the parameters fixed at their standard values. Comparing this figure with Figure 5, we see that for $G_0 < 10^3$ the plateau water abundance is independent of gas density and $A_V$, while the plateau water abundance is independent of $n$ because both the formation rate per unit volume (photodesorption) and the destruction rate (photodissociation) are proportional to $n$. For a fixed value of $G_0$, lowering the gas density moves the water peak further in; the photodesorption rate goes only as the grain density $n_{gr} \propto n^2$, while the photodesorption rate goes only as the grain density $n_{gr} \propto n$ times the local FUV field. Therefore, the water peak moves into the cloud with decreasing density. However, the column or $A_V$ where the water starts to decline from its peak (plateau) value is insensitive to $n$. Thus, the plateau starts to become narrower and narrower (in $\Delta A_V$) as $n$ decreases. As a result, the column of gas-phase water increases with $n$ somewhat. We explain all these trends in more detail below in Section 3.3, where we present a simple analytical analysis.

**Dependence of gas temperature on $G_0$ and n**. Figure 7 presents the gas temperature as a function of $A_V$ for a range of our $G_0$, $n$ parameter space. This figure reveals the temperature at which most of the H$_2$O and O$_2$ is radiating, as we have marked the peak in the gas-phase water abundance (which coincides with the peak in the O$_2$ abundance) as solid portions of these curves. We see that over the parameter space $G_0 = 1-10^5$, the emission from H$_2$O and O$_2$ arises from regions of $T \sim 7-50$ K, with $T$ generally rising gradually with $G_0$. For $G_0 < 500$, there is a true “water plateau” and the solid line corresponds to the plateau region. $T \sim 7-50$ K in the plateau, and the gas temperature is often higher than the dust temperature because of grain photoelectric heating of the gas. For higher $G_0$, there is no true plateau but the gas-phase H$_2$O and O$_2$ peak at higher $A_V$, where the gas and dust temperatures are nearly the same. We will show in Section 3.4 that at high $A_V$, the dust temperature scales roughly as $G_0^{0.24}$. Here, we have made solid lines where the H$_2$O abundance is more than 0.33 of the peak abundance.

**Dependence on photodesorption yield, $Y_{H_2O}$**. Figure 8 presents the profiles of the gas-phase H$_2$O and O$_2$ abundances, and the H$_2$O ice abundance as the photodesorption yield $Y_{H_2O}$ of water ice is varied, maintaining $Y_{OH,w} = 2Y_{H_2O}$, but keeping all other parameters standard. In contrast to the lack of dependence of the plateau value of the gas-phase water abundance $x_{wp}(H_2O)$ on $n$ and $G_0$, $x_{wp}(H_2O)$ scales roughly linearly with $Y_{H_2O}$ for low $Y_{H_2O} < 10^{-3}$. This linear dependence can be easily understood:
Gas temperature $T$ as a function of $AV$ for a variety of $n$ and $G_0$ with all other parameters standard. Dashed lines refer to gas density $n = 10^4$ cm$^{-3}$, and in order of increasing $T$ at low $AV$ correspond to $G_0 = 1, 10, 100, 10^3$, and $10^4$. Dotted lines refer to gas density $n = 10^5$ cm$^{-3}$, and in order of increasing $T$ at low $AV$ correspond to $G_0 = 10^4$ and $10^5$ (Orion PDR conditions). The solid portion of each curve refers to the region of the “water plateau” for $G_0 < 500$, or to regions where the water abundance is at least 0.33 times its peak value for $G_0 > 500$.

(A color version of this figure is available in the online journal.)

Abundances of H$_2$O, H$_2$O$_{\text{ice}}$, and O$_2$ for the standard case ($n = 10^4$ cm$^{-3}$, $G_0 = 100$) as a function of $AV$ and of the photodesorption yield of water ice to form gas-phase H$_2$O, $Y_{\text{H}_2\text{O}}$. Results are shown for the standard yield of $10^{-3}$ and for yields of $10^{-2}$ and $10^{-4}$. H$_2$O$_{\text{ice}}$ also photodesorbs OH with a rate two times $Y_{\text{H}_2\text{O}}$ (see text). The labels refer to the log of the yield.

(A color version of this figure is available in the online journal.)

Dependence on effective grain area, $\sigma_H$. In Figure 9, we show the effect of varying $\sigma_H$ with all other parameters at their standard values. The abundance of gas-phase H$_2$O in the plateau $x_{\text{pl}}(\text{H}_2\text{O})$ increases nearly linearly with $\sigma_H$. The depth $AV \sim AV_f$ where the H$_2$O abundance first reaches its plateau value is insensitive to $\sigma_H$, as predicted by Equation (17). Similarly, the depth where H$_2$O finally begins to drop from its plateau value also is insensitive to $\sigma_H$. The abundance of O$_2$, like the abundance of H$_2$O, scales with $\sigma_H$.

Dependence on PAHs. We are most interested in the chemistry at $AV \sim 3–6$ where the H$_2$O and O$_2$ abundances peak. Because it is not clear if PAHs exist at such depths (Boulanger et al. 1990; Bernard et al. 1993; Ristorcelli et al. 2003), we have not included PAHs in our standard case but have assumed a grain surface area per H given by $\sigma_H$, which is appropriate to an MRN distribution extending down to 20 Å grains when computing the neutralization of the gas by collisions with small dust particles. If PAHs are present, the effect of neutralization is enhanced, which changes the gas-phase chemistry somewhat. We have found that the inclusion of PAHs into our standard case does not affect the results appreciably. There is a somewhat greater effect at lower density, such as $n \sim 100$ cm$^{-3}$, where the inclusion of PAHs does increase the total water column to high $AV$ by a factor of about 10, both by broadening the peak plateau and by increasing the peak abundance (for the case $G_0 = 1$).

Where thermal desorption of atomic O can compete with photodesorption, i.e., high grain temperatures from high FUV fields, this is not the case. In addition, at high values of $Y_{\text{H}_2\text{O}} > 10^{-3}$, the surface can become depleted in water ice compared with, for example, CO ice, which then lowers the desorption rate of H$_2$O into the gas. This leads to a smaller increase in gas-phase H$_2$O with increasing $Y_{\text{H}_2\text{O}}$ than would otherwise be the case.
Dependence on \( b_1 \). We have run our standard case but have assumed that the small grains responsible for FUV extinction are depleted, for example, by coagulation. In our test run, we have decreased all of our \( b_1 \) by a factor of 2, reduced \( \sigma_H \) by 2, and reduced grain photoelectric heating accordingly. The main effect is to increase the characteristic \( A_V \) where the \( H_2O \) and \( O_2 \) plateau by a factor of 2. However, the abundances of \( H_2O \) and \( O_2 \) in the plateau decrease because of the decrease in \( \sigma_H \). Therefore, the columns of gas-phase \( H_2O \) and \( O_2 \) only increase by a factor of about 1.5 from the standard case. The gas temperature does not appreciably change. In summary, the change in the intensities and average abundances of \( H_2O \) and \( O_2 \) is not large, and is expected to be less than a factor of 2.

Dependence of \( H_2O \) and \( O_2 \) columns on \( G_0 \) and \( n \). In Figure 10, we show the total columns of \( H_2O \) and \( O_2 \) for a cloud with high \( A_V \) > 10 as a function of the incident FUV flux \( G_0 \) and the cloud density \( n \). For low \( G_0 < 500 \), the \( H_2O \) and \( O_2 \) columns are roughly independent of \( G_0 \) and \( n \), and are of order \( 10^{15} \text{ cm}^{-2} \) for our standard values of photodesorption yield. These columns arise in the \( H_2O \) and \( O_2 \) plateaus, at intermediate cloud columns. In the steady-state models, there is so little gas-phase water in the interior of the cloud that the interior does not contribute significantly to the total column. Therefore, once the total column through the cloud \( N \) is large enough to include the plateau (\( N_H \gtrsim 10^{22} \text{ cm}^{-2} \)), the average abundance will scale as \( N_H^{-1} \). Thus, part of the reason for the low average abundances observed by SWAS and Odin is the dilution caused by the lack of \( H_2O \) and \( O_2 \); at the surface and deep in the interior of very opaque, high-column clouds. At higher \( G_0 > 500 \), we see the effect of the thermal evaporation of the \( O \) atoms from the grain surfaces. The effect is most dramatic for the gas-phase \( O_2 \) column, which rises to values \( N(O_2) \sim 2 \times 10^{16} \text{ cm}^{-2} \). This is close to what is needed for a detection by Herschel, and therefore it is in this type of environment that Herschel may potentially detect \( O_2 \). We note, however, that this result depends on the binding energy of \( O \) atoms to water ice surfaces. The value we have adopted (see Table 1) is standard in the literature but it refers to van der Waal binding to a chemically saturated surface. It is quite possible that the \( O \) binding energy is larger, and this would then increase the temperature (and \( G_0 \)) where this effect would be initiated.

3.3. Simple Analytical Analysis of the Results

The results in Sections 3.1 and 3.2 can be understood by a simple analytical chemical model that incorporates the main physics. Such a model, though approximate, has the advantage of allowing one to determine and understand the sensitivity to various model parameters, and serves to validate the numerical model. In this subsection, the chemical rates are all taken from the UMIST database, except for the ion–dipole rates and the photodesorption rates discussed in Section 2.7. In the following, the reader is referred to Table 3 in the Appendix for quick reference to symbols.

The abundance \( x(H_2O) \) of gas-phase \( H_2O \) can be roughly traced and understood by simple analytical formulae. Photodissociation dominates the destruction of gas-phase \( H_2O \) from the surface to the depth \( A_V \), where gas-phase destruction with \( H_2^+ \) generally takes over. From \( 0 < A_V < A_Vd \), the simple model assumes that \( H_2O \) is formed by photodesorption of \( H_2O \) ice. Therefore, by equating formation to destruction

\[
G_0F_0 e^{-1.8A_V} Y_{H_2O} f_{H_2O} R_{gr} \sigma_{fr} = G_0 R_{H_2O} e^{-1.7A_V} n(H_2O),
\]

or

\[
x(H_2O) = F_0 Y_{H_2O} f_{H_2O} R_{H_2O} e^{-0.1A_V},
\]

where \( R_{H_2O} = 5.9 \times 10^{-10} \text{ s}^{-1} \) is the unshielded PDR of \( H_2O \) in an FUV field of \( G_0 = 1 \). The difference in the \( b_1 \) factors of 1.7 and 1.8 is because the two processes are dominated by somewhat different FUV wavelengths. The fractional coverage

![Total H2O Column Density](image)

![Total O2 Column Density](image)

Figure 10. Total columns of \( H_2O \) (left panel) and \( O_2 \) (right panel) as a function of \( G_0 \) and \( n \), assuming clouds with \( A_V \) greater than the plateau values, or roughly \( A_V \geq 3 \sim 6 \). The increase of the column of \( H_2O \) and \( O_2 \) at \( G_0 \sim 500 \) is caused by the thermal desorption of \( O \) atoms from grain surfaces, which suppresses the formation of water ice and enhances the gas-phase abundance of elemental \( O \). Note that since the column is produced at intermediate \( A_V \), the column average abundance of \( H_2O \) and \( O_2 \) will fall as \( A_V \). Results are shown for the standard photoyield \( Y_{H_2O} = 10^{-3} \) for densities of \( 10^3 \), \( 10^4 \), and \( 10^5 \) cm\(^{-3} \), and for \( Y_{H_2O} = 10^{-4} \) for a density of \( 10^6 \) cm\(^{-3} \).

(A color version of this figure is available in the online journal.)
of the surface by water ice $f_{\text{v},\text{H}_2\text{O}}$ is given by equating the sticking of O atoms to grain surfaces to the photodesorption rate of H$_2$O (including both desorption of H$_2$O and of OH + H). Therefore, recalling that $Y = Y_{\text{H}_2\text{O}} + Y_{\text{OH},w}$,

$$n(O)v_0n_{\text{gr}}\sigma_{gr} = \frac{G_0F_0e^{-1.8A_Y}}{G_0F_0Y}f_{\text{v},\text{H}_2\text{O}}n_{\text{gr}}\sigma_{gr} \quad (21)$$

or

$$f_{\text{v},\text{H}_2\text{O}} = \frac{n(O)v_0 \ e^{-1.8A_Y}}{G_0F_0Y} \quad (22).$$

Once a monolayer forms, $f_{\text{v},\text{H}_2\text{O}} \sim 1$. We have found in our numerical runs that sometimes $f_{\text{v},\text{H}_2\text{O}}$ saturates at $\sim 0.5$ rather than 1.0, because of the presence of other ices such as CO ice or CH$_4$ ice. However, assuming a saturation value of unity, the critical depth $A_{\text{V}_f}$ at which a monolayer forms is then given as (this is equivalent to Equation (17) in Section 2.5)

$$A_{\text{V}_f} = 0.56 \ln \left( \frac{G_0F_0Y}{n(O)v_0} \right), \quad (23)$$

or a critical H nucleus column (Spitzer 1978) from the surface of

$$N_f = 2 \times 10^{21}A_{\text{V}_f} \text{ cm}^{-2}. \quad (24)$$

We therefore find, using Equations (20) and (22)

$$x(\text{H}_2\text{O}) = \frac{n(O)v_0Y_{\text{H}_2\text{O}}\sigma_H e^{1.7A_Y}}{YG_0R_{\text{H}_2\text{O}}} \quad \text{for} \quad A_V < A_{V_f}, \quad (25)$$

and

$$x_{\text{pl}}(\text{H}_2\text{O}) = \frac{F_0Y_{\text{H}_2\text{O}}\sigma_H e^{-0.1A_Y}}{R_{\text{H}_2\text{O}}} \quad \simeq 2 \times 10^{-7} \left( \frac{Y_{\text{H}_2\text{O}}}{10^{-3}} \right) \left( \frac{\sigma_H}{2 \times 10^{-21} \text{ cm}^2} \right) e^{-0.1A_Y} \quad \text{for} \quad A_{V_f} < A_V < A_{\text{V}_d}. \quad (26)$$

The abundance of gas-phase H$_2$O rises exponentially with depth (as $e^{1.7A_V}$) until a monolayer of water ice has formed on the grains. It then forms a plateau with value $x_{\text{pl}}(\text{H}_2\text{O})$ that is independent of $G_0$ and $n$ and weakly dependent on $A_V$. The plateau abundance goes linearly with $Y$ and $\sigma_H$. The lack of dependence on $G_0$ can be understood since both the formation and destruction of gas-phase H$_2$O depend linearly on $G_0$. Higher fluxes do decrease the surface abundance of gas-phase water, but the freeze-out depth is deeper, so there is more dust attenuation, and the gas-phase water abundance rises and peaks at the same constant value. More precisely, regardless of the incident FUV flux, the local attenuated FUV flux at the freeze-out point is always the same, because it must be the flux that photodesorbs an ice-covered grain at the rate that oxygen from the gas resupplies the surface with ice. Therefore, the gas-phase water abundance is the same as well, regardless of $G_0$, only depending on the assumed values of the grain parameters and the photodesorption yield. The lack of dependence on $n$ can be understood similarly since both the formation rate per unit volume and the destruction rate per unit volume depend linearly on $n$. On the other hand, $x(\text{H}_2\text{O}) \propto Y\sigma_H$, since the formation rate by photodesorption goes as this product whereas the destruction rate is independent of it.

In order to determine $A_{\text{V}_d}$ and to provide an approximation for $x(\text{H}_2\text{O})$ that applies for $A_V > A_{\text{V}_d}$, we need to include other destruction routes for gas-phase H$_2$O that begin to dominate at high $A_V$. We find that generally the route that takes over from photodissociation is reaction with H$_2^+$ to form H$_2$O$^+$, H$_2$O$^+$ recombines one-fourth of the time to reform water (not a net destruction) and three-fourths of the time to form OH (Jensen et al. 2000; Neufeld et al. 2002). The net rate coefficient for the destruction of gas-phase H$_2$O by H$_2^+$ is then

$$\gamma_{\text{H}_2^+} = 0.75(4.5 \times 10^{-9}T_{300}^{-1/2}) \text{ cm}^3 \text{ s}^{-1} \quad (27)$$

where $T_{300} = T/300$ K. Equating the formation of gas-phase H$_2$O by photodesorption to the destruction of H$_2$O by both photodissociation and H$_2^+$, we obtain a more general solution for $x(\text{H}_2\text{O})$ for $A_V > A_{\text{V}_f}$ that applies beyond $A_{\text{V}_d}$

$$x(\text{H}_2\text{O}) \simeq \frac{x_{\text{pl}}(\text{H}_2\text{O})}{1 + \left[ \frac{\gamma_{\text{H}_2^+}(A_V)}{G_0R_{\text{H}_2\text{O}}} \right] e^{1.7A_V}}, \quad A_V > A_{\text{V}_f}. \quad (28)$$

Note that the second term in the denominator, which represents destruction by H$_2^+$, begins to dominate when its value reaches and exceeds unity. At this point, $x(\text{H}_2\text{O})$ begins to drop from its plateau value.

H$_2^+$ is formed by cosmic rays ionizing H$_2$ followed by rapid recombination of H$_2^+$ with H$_2$. When gas-phase CO is depleted, it is destroyed by dissociative recombination with electrons. The electrons are provided by Si$^+$ and Si$^+$ at moderate $A_V$ and by H$_2^+$, He$^+$, and H$^+$ at high $A_V$, so the electron density is complicated. At high $A_V$, the code results suggest that the electron density is roughly $n(e) \simeq 2n(H_2^+)$. We then obtain

$$n(H_2^+)[\text{high } A_V] \simeq 10^{-3}T_{300}^{1/4}n^{1/2} \text{ cm}^{-3}. \quad (29)$$

with H nucleus density $n$ in cm$^{-3}$. In Equation (29), we have assumed a total (including secondary ionizations) cosmic-ray ionization rate of $5 \times 10^{-11}$ s$^{-1}$ for H$_2$ (Dalgarno 2000). At moderate $A_V$, Si$^+$ usually provides most of the electrons. Gas-phase Si$^+$ is produced by photoionization of gas-phase Si and destroyed by recombination with electrons. The Si$^+$ density, and therefore the electrons provided by Si$^+$, exponentially drops with $A_V$ as the FUV photons that photoionize Si drop with increasing dust attenuation. As long as most of the gas-phase silicon is Si$^+$, the electron density is high and this suppresses the abundance of H$_2^+$, prolonging the water plateau to higher $A_V$ (see Equation (28)). However, we find that once the gas-phase Si$^+$ density drops to $2n(H_2^+)[\text{high } A_V]$, so that the electrons provided by Si$^+$ are comparable to those provided by H$_2^+$, He$^+$, and H$^+$, $n(H_2^+)$ has risen to $\sim n(H_2^+)[\text{high } A_V]$ and the H$_2^+$ term in the denominator of Equation (28) dominates. Here, the gas-phase water abundance starts to fall. This occurs when

$$A_{\text{V}_d} = 0.59 \ln \left[ 4.5 \times 10^5G_0R_{\text{H}_2\text{O}}^{-1/2}T_{300}^{-0.2} \left( \frac{n_{\text{Si}^+}}{n_{\text{H}_2\text{O},gr}} \right)^{1/2} \right], \quad (30)$$

where $n_{\text{Si}^+} = 1.7 \times 10^{-6}n$ is the density of silicon both in the gas phase and as ice mantles on grains, and $n_{\text{H}_2\text{O},gr} \sim 3 \times 10^{-4}n$ is the density of water molecules incorporated in ice mantles.

We have checked our analytical expressions for $A_{\text{V}_f}$ (Equation (23)), $A_{\text{V}_d}$ (Equation (30)), and $x_{\text{pl}}(\text{H}_2\text{O})$ (Equation (26)) and find good agreement ($A_{\text{V}_f}$ and $A_{\text{V}_d}$ better than $\pm 25\%$ and $x_{\text{pl}}(\text{H}_2\text{O})$ good to a factor of 2 over our $(G_0, n)$ parameter space for $G_0 \lesssim 500$). For $G_0 > 500$, the grains are so warm that O atoms adsorbed to grains thermally evaporate before reacting with H atoms to form OH on the grain surface. As
discussed in Section 3.2, this results in a change in the behavior of gas-phase H2O.

The abundance of O, OH, and O2 in the H2O plateau region \( A_{Vf} < A_V < A_{Vd} \) can also be analytically estimated from the above expression for \( x_{pl}(H_2O) \). We first find \( x_{pl}(OH) \) by equating formation by photodissociation of H2O and photodesorption of OH from water ice with destruction by photodissociation of OH and reaction with \( S^+ \) and \( He^+ \). The photodesorption rate of OH is two times the rate of H2O photodesorption, and therefore two times the rate of H2O photodissociation. On the other hand, the destruction of OH by \( S^+ \) and \( He^+ \) is roughly two times that of OH photodissociation. Therefore,

\[
x_{pl}(OH) \sim \left( \frac{R_{H_2O}}{R_{OH}} \right) x_{pl}(H_2O) \sim 1.7 x_{pl}(H_2O),
\]

\( A_{Vf} < A_V < A_{Vd} \) \( (31) \)

where \( R_{OH} = 3.5 \times 10^{-10} \text{ s}^{-1} \) is the unshielded PDR of OH when \( G_0 = 1 \). Thus, OH tracks H2O with somewhat greater abundance in the plateau, as observed in Figure 3.

The gas-phase O abundance is determined by balancing the formation of O by photodissociation of OH with the removal of O by adsorption onto grains

\[
x_{pl}(O) \simeq \left[ \frac{G_0 R_{OH} e^{-1.7 A_V}}{\sigma_{RH} v_O} \right] x_{pl}(OH) \simeq 4 \times 10^{-5} \left( \frac{G_0/n}{10^{-2}} \right) \left( \frac{e^{-1.7 A_V}}{10^{-1}} \right) \left( \frac{x_{pl}(H_2O)}{10^{-7}} \right). \tag{32}
\]

Therefore, \( x_{pl}(O) \) exponentially declines with \( e^{-1.7 A_V} \), due to the declining photodissociation of OH, but at a constant (with \( A_V \)) collision rate of O with grains, as seen in Figure 3. It also increases with \( G_0/n \) for fixed \( A_V \). This formula breaks down when the right-hand side exceeds \( 10^{-4} \), where \( x_{pl}(O) \) saturates since all elemental gas-phase O is now in atomic form.

The O2 abundance follows from the abundances of O and OH since O2 is formed by the neutral reaction of OH with O (rate coefficient \( \gamma_{OH} = 4.3 \times 10^{-11} (300 \text{ K}/T)^{1/2} e^{-30 K/T} \text{ cm}^3 \text{ s}^{-1} \)). The O2, like H2O and OH, is destroyed by photodissociation in the plateau region. Therefore,

\[
x_{pl}(O2) \simeq \left[ \frac{1.7^2 \gamma_{OH}}{\sigma_{RH} v_O} \right] \frac{R_{OH}}{R_{O2}} e^{0.1 A_V} \left[ x_{pl}(H_2O) \right]^2 \simeq 1 \times 10^{-7} e^{0.1 A_V} \left( \frac{2 \times 10^{-21} \text{ cm}^2}{\sigma_{HT}} \right) \times \left( \frac{30}{T} \right) e^{-30/T} \left( \frac{x_{pl}(H_2O)}{10^{-7}} \right)^2, \tag{33}
\]

where \( R_{O2} = 6.9 \times 10^{-10} \text{ s}^{-1} \) is the unsheilded rate of photodissociation of O2 in a \( G_0 = 1 \) field. The \( [x_{pl}(H_2O)]^2 \) dependence, which translates to a \( Y_{H_2O}^2 \) dependence in the plateau for low \( Y_{H_2O} < 10^{-3} \), is clearly seen in Figure 8. Note also that Equation (33) explains the lack of dependence of \( x_{pl}(O2) \) on \( n \) and \( G_0 \), and also predicts that \( x_{pl}(O2) \propto \sigma_{HT} \) as observed in the numerical models.

In summary of the above, the approximate analytical equations can be used in the cases with \( G_0 \approx 500 \) to understand and quantitatively estimate: (1) \( x_{pl}(H_2O, \text{OH, O, and O}_2) \) and their dependence (or independence) on \( n, G_0, Y, \) and \( \sigma_{HT} \); (2) the depth \( A_{Vf} \) of the onset of the plateau, the depth \( A_{Vd} \) of the termination of the plateau, the width \( \Delta A_V = A_{Vd} - A_{Vf} \) of the plateau, and their dependence on the above parameters. At high \( Y_{H_2O} > 10^{-3} \), the abundances of O, OH, O2, and H2O are overestimated by factors of order 2 in the above formulae because we have ignored the presence of other ices, which reduce the fractional surface coverage of water ice, and therefore the production of gas-phase H2O and its photodissociation products.

Finally, the above analytical expressions can be used to predict the optimum conditions for observing H2O and O2. In general, for our model runs, the intensity of the H2O ground state ortho line at 557 GHz and para line at 1113 GHz can be estimated by assuming that the emission is “effectively thin.” In other words, although the optical depth in the ground state may be larger than unity, the gas density is so far below the critical density \( (\sim 10^8 \text{ cm}^{-3}) \) that self-absorbed photons are re-emitted and eventually escape the cloud (see discussion in Section 5). In this limit, every collisional excitation results in an escaping photon, and

\[
I_{557} \simeq \frac{h v \left[ x_{o} n \gamma_{ex,o} + x_{p} n \gamma_{ex,p} \right] N(o - H_2O)}{4 \pi}, \tag{34}
\]

where \( \gamma_{ex,o} \approx 2.5 \times 10^{-10} e^{-26.7/T} \) and \( \gamma_{ex,p} \approx 3.5 \times 10^{-11} e^{-26.7/T} \text{ cm}^3 \text{ s}^{-1} \) (valid for \( T \lesssim 30 \text{ K} \)) are the rate coefficients for the collisional excitation of the 557 GHz transition by impact with ortho- and para-H2, respectively (Faure et al. 2007; Dubernet et al. 2006). Here, \( x_o(x_p) \) is the abundance of ortho(para)-H2 with respect to H nuclei. \( h v \) is the energy of the 557 GHz photon, and \( N(o - H_2O) \) is the column of ortho water. Similarly, the para H2O 1113 GHz line intensity is

\[
I_{1113} \simeq \frac{h v \left[ x_{o} n \gamma_{ex,o} + x_{p} n \gamma_{ex,p} \right] N(p - H_2O)}{4 \pi}, \tag{35}
\]

where \( \gamma_{ex,o} \approx 3 \times 10^{-10} e^{-53.4/T} \) and \( \gamma_{ex,p} \approx 9.0 \times 10^{-11} e^{-53.4/T} \text{ cm}^3 \text{ s}^{-1} \) (valid for \( T \lesssim 30 \text{ K} \)) are the rate coefficients for the collisional excitation of the 1113 GHz transition by impact with ortho- and para-H2. From the above equations, assuming most of the H2O column arises in the plateau between \( A_{Vf} \) and \( A_{Vd} \), the ortho(para)-H2O column is given as

\[
N(o(p) - H_2O) \simeq 2 \times 10^{21} (A_{Vd} - A_{Vf}) \times x_{pl}(H_2O) f_o(f_p) \text{ cm}^{-2}, \tag{36}
\]

where \( f_o(f_p) \) is the fraction of H2O in the ortho(para) state. Substituting our analytic equations for these parameters, we obtain

\[
I_{557} \simeq 3 \times 10^{-7} f_o [x_o + 0.14 x_p] \left( \frac{n}{10^4 \text{ cm}^{-3}} \right) \times \left( \frac{Y_{H_2O}}{10^{-3}} \right) \left( \frac{\sigma_H}{2 \times 10^{-21} \text{ cm}^2} \right) \times \Delta A_V e^{-0.1 A_V} e^{-26.7/T} \text{ erg cm}^{-2} \text{ s}^{-1} \text{ sr}^{-1}, \tag{37}
\]

12 We include the 1113 GHz line because it is accessible with the upcoming Herschel Observatory.

13 Note that the maximum values of \( x_o \) and \( x_p \) are 0.5.
Figure 11. Average (see text) gas temperature in the water plateau region or the peak water abundance region for a range of densities and FUV field strengths incident on the cloud surface. Note that the temperature only increases by a factor of ∼3 while the incident FUV flux G0 increases by 10^3. The plateau retreats deeper into the cloud as G0 increases, which suppresses a more dramatic increase in T.

Thus, again assuming optically thin emission, the intensity

\[ I_{487} \propto N(O) e^{-25kT}/Z(T), \]

where \( N(O) \) is the partition function. An approximation to \( Z(T) \) for 0K < T < 25K is given as \( Z(T) \approx 3 + 2.1T + 0.1T^2 \). Using the equations from this subsection, we then estimate

\[
I_{487} \simeq 6 \times 10^{-6} \left( \frac{\Delta A_V}{Z(T)} \right) \left( \frac{30 \text{ K}}{T} \right) \left( \frac{Y_{\text{H}_2\text{O}}}{10^{-3}} \right)^2 \times \left( \frac{\sigma_H}{2 \times 10^{-21} \text{cm}^2} \right) e^{-55/T} e^{0.05(A_V+AVd)} \text{ erg cm}^{-2} \text{s}^{-1} \text{ sr}^{-1}. \]

(39)

Note that again, this equation breaks down for \( G_0 \gtrsim 500 \), and the equation will underestimate the intensity for higher \( G_0 \) since the O2 column rises. In general, however, the equation predicts little n dependence (there is a small n dependence in the \( A_V \) terms). At low \( G_0 \lesssim 500 \), the equation predicts only moderate \( G_0 \) dependence. Although various terms depend on T, the temperature of the O2 plateau region is not sensitive to \( G_0 \) since the plateau retreats further into the shielded region for higher \( G_0 \). In addition, the T dependence in the \( \exp(-55/T) \) term is partially cancelled by the \( T Z(T) \) term in the denominator.

3.4. The H2O 557 and 1113 GHz and O2 487 GHz Line Intensities

Using the numerical models, Figures 12 and 13 present H2O \( I_{557} \) and \( I_{1113} \) and O2 \( I_{487} \) contours as functions of \( n \) and \( G_0 \) for fixed standard values of the other parameters. We have assumed that the H2O ortho-to-para ratios are in LTE with the grain temperature (which in the plateau is nearly the same as the gas temperature except for very low ratios of \( G_0/n \), which bring the plateau very close to the surface of the cloud where \( T > T_{gr} \)). The grain temperature is appropriate since a given H2O molecule forms on a grain and spends too little time in the gas to equilibrate to the gas temperature before it is photodissociated. The grain temperature in the plateau is approximately (Hollenbach et al. 1991)

\[ T_{gr,pl} \simeq (3 \times 10^4 + 2 \times 10^3 G_0^{2/3})^{0.2}. \]

(40)

A fit to the LTE ortho-to-para ratio of H2O valid to 10% in the region 5K < T < 20K and good to 20% for T > 20K (e.g., Mumma et al. 1987) is given as

\[ \frac{f_o}{f_p} = 0.8 e^{-\frac{22K}{T}} + 2.2 e^{-\left(\frac{13K}{T}\right)^2}. \]

(41)

The H2 ortho-to-para ratio is calculated in steady state using the rates and processes described by Burton et al. (1992). They are neither 3 nor LTE. They are insensitive to n in the plateau, but sensitive to \( G_0 \), which affects T. The H2 ortho-to-para ratio \( x_o/x_p \simeq 0.5 \) at \( G_0 = 3 \times 10^4 \), 0.3 at \( G_0 = 1.5 \times 10^4 \), and 0.1 for \( G_0 = 4 \times 10^3 \). For lower values of \( G_0 \), \( x_o/x_p < 0.1 \) so that para H2 collisions dominate the excitation of water.

The 557 and 1113 GHz intensities behave as described by the analytical formulae (Equations (37) and (38)) presented in Section 3.3 for \( G_0 \lesssim 500 \). The H2O intensities rise roughly linearly with \( n \). For a fixed density, \( I_{557} \) and \( I_{1113} \) tend to rise with \( G_0 \) (which raises \( T_{gr} \), as shown in Equation (40), and which tends to raise T as can be seen in Figure 11) partly due to the excitation factors \( e^{-26.7/T} \) and \( e^{-53.4/T} \), but also because increasing T...
Figure 12. H$_2$O intensities for a range of densities and FUV field strengths incident on the cloud surface. Contours are labeled with the logarithm of intensity, measured in units of erg s$^{-1}$ cm$^{-2}$ sr$^{-1}$. Left panel: intensity of the ortho-H$_2$O ground state transition $1_{10}$ - $0_{10}$ at 557 GHz. To convert to units of K km s$^{-1}$, multiply contour levels by 5.6 x 10$^6$; Right panel: intensities of the para-H$_2$O ground state transition $1_{11}$ - $0_{00}$ at 1113 GHz. To convert to units of K km s$^{-1}$, multiply contour levels by 7.0 x 10$^5$.

Figure 13. The O$_2$ 487 GHz intensity for a variety of densities and FUV field strengths incident on the cloud surface. Contours are labeled with the logarithm of intensity, measured in units of erg s$^{-1}$ cm$^{-2}$ sr$^{-1}$. To convert to units of K km s$^{-1}$, multiply contour levels by 8.4 x 10$^6$. Note the relative constancy of the O$_2$ intensity for $G_0 < 100$, since the column and temperature of the O$_2$ plateau region stay quite constant.
a factor of roughly 100. We do not pursue this type of model further here, but note that it could warrant further study, although it appears to predict excessive H$_2$O and O$_2$ intensities. In the original O’Neill et al. work, photodesorption and cosmic-ray desorption were not included.

### 3.6. Model with No Grain Chemistry

In order to test the importance of the formation of OH, H$_2$O, and carbon molecules on grain surfaces in our model, we have run the standard case ($G_0 = 100$, $n = 10^3$) and two other cases ($G_0 = 100$, $n = 10^5$ cm$^{-3}$ and $G_0 = 10$, $n = 10^4$ cm$^{-3}$) with only H$_2$ formed on grain surfaces and no other grain chemistry. Like the model described above in Section 3.5, one main effect is to push the peak in the H$_2$O and O$_2$ abundances lower because the frozen CO is not liberated to the gas to provide elemental gas-phase O to form them. If the timescale is very short, the CO ice is desorbed quickly and the gas has time to deplete the elemental gas-phase O as water ice on the grain surfaces. The results are shown in Figures 14 and 15, where we present the abundances of O$_2$, H$_2$O, and CO plotted as a function of the age of the cloud, the density of the cloud, and the cosmic-ray desorption rate of CO. If the cosmic-ray desorption timescale for CO ice, $t_{cr,CO}$ is long, the H$_2$O and O$_2$ abundances are low because the frozen CO is not liberated to the gas to provide elemental gas-phase O to form them. If the timescale is very short, the CO ice is desorbed quickly and the gas has time to deplete the elemental gas-phase O as water ice on the grain surfaces.

(A color version of this figure is available in the online journal.)

#### Figure 14

Abundances of H$_2$O (solid), CO (dot-dashed), and O$_2$ (dotted) at $A_V = 10$ at a cloud age of $2 \times 10^6$ years, for a range of CO cosmic-ray desorption rates. Our standard CO cosmic-ray rate is given by $k_{CO,cr}$ and is given in Table 1. Results are shown for rates from $10^{-2}$ to $10^2$ times the standard rate, for $G_0 = 100$ and densities $n_1 = 10^3$, $10^4$, and $10^5$ cm$^{-3}$. The higher densities have lower abundances due to freeze-out of gas species. Note that the H$_2$O and O$_2$ abundances are only significant (i.e., comparable to the plateau values), for low densities. The timescale $t_{cr,CO}$ for cosmic-ray desorption of CO ice (see Equation (8)) is given at the top.

#### Figure 15

Same as Figure 14 but for an age of of $2 \times 10^7$ years. Note that the H$_2$O and O$_2$ abundances are never significant compared to their plateau values. The numerical results and analytical solutions presented so far are for steady-state solutions to the chemistry. However, as noted in Sections 2.3 and 2.4, in the opaque interior of molecular clouds at $A_V > A_VC$, the chemical timescales may exceed or be comparable to the cloud age, so that time-dependent solutions to the chemistry are needed. The long chemical timescales include the freeze-out of gas species onto grains for $n < 10^3$ cm$^{-3}$ (see Equation (1)), the cosmic-ray desorption of CO ice (see Section 2.4), and the conversion of gas-phase CO to water ice, which is initiated by He$^+$ (see Section 2.3). In the opaque “freeze-out” regions, the attenuated FUV flux plays little role in the chemistry so that the time-dependent abundances do not vary with $A_V$. Therefore, we present results at a representative $A_V = 10$ for the abundances of gas and ice species as a function of the age of the cloud, the density of the cloud, and the cosmic-ray desorption rate of CO.

#### 3.7. Time Dependence

The time-dependent code is that of Bergin et al. (2000), updated to have the same grain chemistry and desorption processes as described above for the steady-state code. It includes more species than the PDR surface code, and therefore tracks the carbon chemistry more accurately in the inner regions. It takes as initial conditions the chemistry of translucent clouds: all of the hydrogen is initially molecular H$_2$ with the other species atomic (for ionization potentials > 13.6 eV) or singly ionized otherwise.

The results are shown in Figures 14 and 15, where we present the abundances of O$_2$, H$_2$O, and CO plotted as a function
of the cosmic-ray desorption rate of CO ice, for two times representative of cloud ages (2 × 10⁶ years in Figure 14 and 2 × 10⁷ years in Figure 15), for the standard G⁰ = 10⁰, and for three densities (10⁴, 10⁵, and 10⁶ cm⁻³). Of particular note is Figure 15, where one sees the gas-phase molecules increase in abundance as the cosmic-ray desorption rate increases, reach a peak when the timescale for cosmic-ray desorption of CO is about 0.1–1.0 times the cloud evolution time of 2 × 10⁷ years, and then decrease as the cosmic-ray rate increases further and the desorption time becomes less than ∼2 × 10⁶ years. If the rate is too low, then the CO ice remains on the grain and the gas-phases abundances are low. If the rate is too high, then the CO ice rapidly desorbs, but then the CO in the gas breaks down by reaction with He⁺ and the gas-phase elemental oxygen freezes out as water ice, thereby lowering the gas-phase abundances of CO, H₂O, and O₂. The main point is that in all cases for t = 2 × 10⁷ years and for most cases with t = 2 × 10⁶ years, the abundances of H₂O and O₂ at high A_V, even when time-dependent chemistry is taken into account (steady-state chemistry is more extreme in this respect as seen in Figure 3), are substantially lower than the peak abundances of these molecules at intermediate A_V. Thus, most of the columns of these molecules in molecular clouds are neither provided by the interior regions, where they are frozen out, nor by the surface, where they are photodissociated. Rather, most of the column arises from the intermediate zone.

3.8. Chemistry: The Gas-Phase C/O Ratio

Figures 16 and 17 show the gas-phase elemental abundance of C and the gas-phase abundance ratio of elemental C/O, as a function of A_V, for two different cloud ages, t = 2 × 10⁶ years and t = 2 × 10⁷ years, respectively. In each figure, we plot the standard case, the standard case but with the density changed to n = 10⁴ and 10⁵ cm⁻³, and the standard case but with the incident FUV field changed to G⁰ = 1 and 10⁵. For these results, we have used our time-dependent models, since the interesting effect of C/O exceeding unity occurs at high A_V, where the time-dependent models are more relevant and are more accurate in treating the carbon chemistry. At early times, t ∼ 2 × 10⁶ years, the C/O ratio generally stays below unity at high A_V. The exception is the high density (n = 10⁵ cm⁻³) case, but here the gas-phase elemental abundance of carbon is extremely low, which implies low abundances of any organic molecules produced in this carbon-rich environment. At late times, t ∼ 2 × 10⁷ years, we see that all cases except the high G⁰ = 1⁰⁵ case result in gas-phase C/O > 1 for A_V ≥ 8, due to the preferential freeze-out of water ice which robs the gas of elemental O. For those cases with C/O > 1, the gas-phase elemental C abundance increases with increasing G⁰ and decreasing n, due to increased thermal desorption rates of carbon molecules and decreased freeze-out rates, respectively.¹⁵ Figure 17 shows that for densities n ∼ 10⁵–10⁶ cm⁻³ and G⁰ = 1–10⁰, strong chemical effects might be observed deep in clouds, with high abundances of gas-phase hydrocarbons and other carbon molecules rather than CO. Unfortunately, these results can only be viewed as suggestive, because the gas-phase C depends on the desorption rate of CO, CH₄, and other

¹⁵ At t = 2 × 10⁷ years, the time-dependent code shows that CO and CH₄ ice dominates the carbon ices for G⁰ ≤ 500, and CO₂ and C₂H ice dominates at higher G⁰, due to thermal desorption of the more weakly bound CO and CH₄.
carbon species frozen to grain surfaces, and these are uncertain. Nevertheless, it appears that regions with C/O > 1 and high gas-phase elemental C abundance can appear deep in the cloud. This is consistent with the chemistry of GMC cores such as Orion A (e.g., Bergin et al. 1997) and regions in the Taurus Molecular Cloud (e.g., Pratap et al. 1997). In addition, in these deep layers significant amounts of CH$_2$ may form, and its release to the gas stimulates the carbon chemistry. In summary, the freeze-out of the oxygen into water ice can have profound effects on the carbon chemistry deep in the cloud and the ability of the cloud to produce carbon chain molecules or hydrocarbons.

3.9. Limb Brightening and Surface to Volume Effects

Because our model suggests a peak in the H$_2$O and O$_2$ abundance at intermediate depths into a molecular cloud, one might expect clouds to be limb-brightened if viewed with beams smaller than the cloud. We make here two caveats to this prediction. First, GMCs are clumpy, and the clumpiness means that $A_{Vf}$ will occur at different physical depths (i.e., radii) in the clouds, depending on the particular radial ray through the cloud and where it intersects clumps. This will have the effect of smearing the limb-brightening. In addition, although the 557 and 1113 GHz H$_2$O transitions are “effectively thin,” they do suffer numerous scattering events since the optical depth in the lines is greater than unity. This scattering will reduce the limb-brightening effect for the H$_2$O transitions. The O$_2$ does not suffer scattering, so it may be more promising. However, the sensitivity of Herschel may require large O$_2$ columns > $10^{16}$ cm$^{-2}$, and these may only be achieved for high $G_0$. In such cases, the peak O$_2$ abundance occurs deep in the cloud, $A_{Vf} \sim 8$, and makes limb brightening only possible to detect in very high column but extended nearby clouds illuminated by high fields. Nevertheless, Herschel observations of O$_2$ in clouds may find regions of limb-brightening.

One still would like to map the clouds, however, even if limb brightening is hard to detect. The regions of high $G_0$ may be fairly limited in spatial extent, and our models predict higher H$_2$O and especially O$_2$ columns in these regions, which Herschel may spatially resolve. In addition, the H$_2$O and O$_2$ plateaus extend for $\Delta A_{Vf} \sim 3$. For gas densities of $n \sim 10^4$ cm$^{-3}$, this corresponds to $\sim 0.2$ pc, which at 500 pc corresponds to an angular size $\sim 1.5'$. Therefore, for a PDR slab viewed edge-on, Herschel may resolve the plateau region.

Even for clouds that are too small in angular extent to map, our model can be tested by correlation studies of the H$_2$O and O$_2$ intensities with the intensities of rotational transitions of other molecules known to trace either the surface or the volume of the cloud. For example, $^{13}$CO and C$^{18}$O are thought to generally trace the volume of the cloud, whereas PDR species, such as CN, trace the “surface” of the cloud (Fuente et al. 1995; Rodriguez-Franco et al. 1998). We are investigating such observational correlations in Melnick et al. (2000).

4. APPLICATIONS TO SPECIFIC SOURCES

4.1. Diffuse Clouds

The diffuse clouds that we model, based on those observed by SWAS toward W51 and W49 where H$_2$O 557 GHz is seen in absorption, are characterized by $G_0 \sim 1$–10, $n \sim 100$ cm$^{-3}$, and $A_{Vf} \sim 1$–5 (these are sometimes called “translucent clouds”; Snow & McCall 2006). Diffuse clouds are illuminated on all sides by the diffuse interstellar FUV field, whereas our models are those of 1D slabs illuminated from one side. To roughly construct a model of a diffuse cloud of total thickness $A_{Vf}$, we take the results from $A_{Vf} = 0$–0.5$A_{Vt}$ and assume a mirror image for the rest of the cloud from 0.5$A_{Vt}$ to $A_{Vf}$.

We compare a single model fit of a diffuse cloud with the 54 and 68 km s$^{-1}$ velocity components observed by SWAS toward the background submillimeter source W49 (Plume et al. 2004), as well as in the single absorption component toward W51 (Neufeld et al. 2002). For all of these three components, both OH and H$_2$O column densities have been measured, with N(H$_2$O) $\sim 10^{13}$–3 $\times 10^{13}$ cm$^{-2}$ and N(OH)/N(H$_2$O) $\sim 3$–4. Our diffuse cloud model with $n = 10^2$ cm$^{-3}$ and $G_0 = 1$ gives N(H$_2$O) $= 3 \times 10^{13}$ cm$^{-2}$ and N(OH)/N(H$_2$O) $= 3.5$ for a total cloud extinction of $A_{Vf} = 4.4$ magnitudes. We find that assuming a photodesorption yield $Y_{OH,w} \simeq 2 \times Y_{H_2O}$ provides the best fit to the observed N(OH)/N(H$_2$O) ratios. The same model also provides predicted $^{12}$CO and atomic C columns and line intensities of the $^{12}$CO J = 1–0, J = 3–2, and [CI] 609 $\mu$m lines, all of which were observed in the W49 components. The models overpredict the columns and the intensities of the CO J = 1–0 and [CI] lines by a factor $\sim 2$ that may be explained by dilution of the emission lines in the beam. The $J = 3$–2 line, however, is predicted to be a factor $\sim 2$ smaller than is observed; a better fit for this line is found at higher densities, but makes the fit of all the other observed lines poorer. We note that Bensch et al. (2003) had similar problems in fitting a PDR model to the diffuse cloud CO and [CI] results.

Comparing our H$_2$O column to the model $A_{Vf}$, we find a column-averaged H$_2$O abundance of $3 \times 10^{-7}$ with respect to H nuclei. The observational papers cited above quote H$_2$O/H$_2$ abundance ratios $>10^{-7}$. These high abundances, however, were derived from the observed CO columns by multiplying the CO columns by $10^4$ to obtain H$_2$ columns. In our models, we find H$_2$ columns of $4 \times 10^{21}$ cm$^{-2}$ and H$_2$O/H$_2$ abundance ratios $\sim 10^{-8}$. The H$_2$/CO column-averaged abundance ratio in the model is 1.3 $\times 10^5$. In these translucent clouds, CO is photodissociated much more than H$_2$, which self-shields much more effectively. Considerable H$_2$ exists in regions where the gas phase carbon is mostly C$^+$. These translucent clouds are examples of “dark H$_2$” which is not traced by CO.

4.2. Dense, Opaque Clouds

4.2.1. $A_{V}$ Thresholds for Ice Formation

Whittet et al. (2001) have presented plots of the water ice columns versus cloud extinction in which a clear threshold $A_{V}$ for water ice is inferred. In our model we associate that threshold $A_{V}$ with $A_{Vf}$, since the ice very rapidly builds up with increasing $A_{V}$ once the grain has a monolayer of ice. Whittet et al. (2001) and Williams et al. (1992) find that $A_{Vf}$ $\sim 1.6$ for Taurus (their total $A_{V}$ threshold is 3.2, but that included both sides of the cloud since a background IR source was used in this absorption measurement). Assuming the radiation field incident on the Taurus cloud is $G_0 \sim 1$ and that the surface gas density is $10^3$ cm$^{-3}$, we predict from our analytical model with $Y = 3 \times 10^{-3}$ (i.e., $Y_{H_2O} = 10^{-3}$, recall that $Y$ is the total yield of both H$_2$O and of OH + H being ejected from water ice) that $A_{Vf} = 2$, slightly higher than the threshold inferred above. Note that the threshold $A_{Vf}$ in our model mainly depends on ln$(G_0 Y/n)$ and so

\footnote{In some cases, CO is frozen on grains in very high $A_{V}$ regions at cloud centers; see, for example, Bergin & Tafalla (2007) for a review of the observations.}
to the extent that we know $G_0/n$, we can constrain $Y$. We therefore see that $Y \sim 3 \times 10^{-3}$ is a reasonable, but possibly slightly high, choice for interstellar ice grains.\footnote{See also Nguyen et al. (2002) for another model of the ice distribution in Taurus.} Measurements of an ice threshold using internal embedded IR sources are much less reliable tests of our models, since considerable extinction along the line of sight can occur very close to the IR source, where the dust may be heated to ice sublimation temperatures.

4.2.2. B68

B68 is one of the best-studied, nearby, isolated molecular clouds (Alves et al. 2001; Zucconi et al. 2001). It lies at $\sim$160 pc, with a mean density of $\bar{n} \sim 10^5$ cm$^{-3}$, an $A_V$ through the cloud center of $\sim$30, and a central temperature of 7 K. Extinction and dust continuum maps have recently provided a detailed view of the density and temperature structure of the cloud (Alves et al. 2001; Zucconi et al. 2001). Previous models of the CO lines and the exterior temperature of the cloud suggest $G_0 \sim 0.25$–1 (Bergin et al. 2002). The angular size of the cloud is $\sim$1/3, smaller than the SWAS beamsize.

SWAS has performed long integrations on B68 searching for the 557 GHz $H_2O$ line and the 487 GHz O$_2$ line, setting stringent $3\sigma$ upper limits on the line strengths (assuming thermal linewidths) from these undetected transitions of $I_{557} \lesssim 4 \times 10^{-9}$ erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$ and $I_{487} \lesssim 6 \times 10^{-9}$ erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$. Utilizing the known distribution of density $n$ with $A_V$, and assuming $G_0 = 0.5$ and our standard values of $Y$ and $\sigma_H$, we have modeled the $H_2O$ and O$_2$ abundance profiles and the expected observed line strengths in B68. To compare with the observed intensities, we calculate the intensity expected in the model and then dilute the intensity by the cloud area divided by the SWAS beam area. Averaged over the SWAS beam, the predicted line intensities of $I_{557} \sim 4 \times 10^{-11}$ erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$ and $I_{487} \sim 1 \times 10^{-12}$ erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$ lie well below the upper limits set by SWAS. We predict a non–beam-diluted line intensity $I_{1113} \sim 10^{-8}$ erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$, which is not detectable by Herschel. Because the 557 and 487 GHz line intensities are sensitive to $G_0$ (via the gas and dust temperatures), regions like B68 with low FUV fields are not promising targets for $H_2O$ and O$_2$ detections.

Another interesting effect in our modeling of B68 arises because our models incorporate the observed increase of density with depth $A_V$. From Figure 6, one sees that this reduces the width $\Delta A_V$ of the $H_2O$ plateau since the lower density surface gas means that $A_V$ is larger, whereas the higher density gas in the interior makes $A_V$ smaller. However, this effect is not large since our B68 model has $n = 1.3 \times 10^5$ cm$^{-3}$ at $A_V = 1$, $n = 1.7 \times 10^5$ cm$^{-3}$ at $A_V = 2$, and $n = 2.4 \times 10^5$ cm$^{-3}$ at $A_V = 3$ (roughly the extent of the $H_2O$ plateau). We find that our predicted column of $H_2O$ in our density-varying model differs by only 10% from a constant density, $n = 1.7 \times 10^5$ cm$^{-3}$, model.

4.2.3. NGC 2024

NGC 2024 is a dense, $n \sim 10^5$ cm$^{-3}$, star forming molecular cloud in Orion illuminated by a relatively intense, $G_0 \sim 10^4$, FUV field (Gianini et al. 2000). Contrasted with B68, it provides a test of our models for elevated radiation fields (i.e., $G_0 > 500$). SWAS has observed both the $H_2O$ 557 GHz line and the $O_2$ 487 GHz line in this source. We have re-analyzed the SWAS data from the archives and obtained a beam-averaged intensity of $3 \times 10^{-7}$ erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$ for the 557 GHz line and a $3\sigma$ upper limit on the 487 GHz line of $4 \times 10^{-8}$ erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$ (see also Snell et al. 2000 for the 557 GHz line and Goldsmith et al. 2000 for the 487 GHz upper limit).

Our models (see Figures 12 and 13) reproduce the $H_2O$ 557 GHz line with beam-averaged gas densities $n \sim 10^{4.8}$ cm$^{-3}$ and $G_0 \sim 10^4$, assuming that the ortho/para $H_2O$ ratio is in LTE with the grain temperature and the ortho/para ratio of $H_2$ is the steady-state value from the formulation by Burton et al. (1992). Here, in our peak water plateau, the gas temperature is $\sim 27$ K, and the ortho/para ratio of $H_2O$ is 2.7. In the model, the $O_2$ 487 GHz line intensity is predicted to be $4 \times 10^{-9}$ erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$, well below SWAS detectability. The peak (plateau) abundances for $H_2O$ and $O_2$ in the model are (see Figures 5 and 6) $10^{-3}$ and $3 \times 10^{-6}$, respectively. The column-averaged abundances, assuming $N \sim 4 \times 10^{19}$ cm$^{-2}$ or $A_V \sim 20$ through the cloud (Gianini et al. 2000), based on CO column densities greater than few $10^{18}$ cm$^{-2}$ over a $\sim 4'$ region is $\tau(H_2O) \equiv (N(H_2O)/N) \equiv 1.1 \times 10^{-6}$, and $\tau(O_2) \equiv 1.7 \times 10^{-7}$. We conclude that the models also provide good fits to NGC 2024, using reasonable values of $n$ and $G_0$, and predict peak abundances that are approximately ten times greater than the column-averaged abundances. We predict $I_{1113} \sim 3 \times 10^{-7}$ erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$, which is detectable by the HIFI instrument on the Herschel Observatory.

4.2.4. O$_2$ Observed by Odin in $\rho$ Oph

Larsson et al. (2007) have reported the detection of the ground state transition of $O_2$ at 119 GHz with the space submillimeter telescope Odin. Note that this is a different transition than the $O_2$ transition observed by SWAS, and at a much longer wavelength. Therefore, although the Odin telescope has twice the diameter of SWAS, the Odin beam size at 119 GHz ($\sim 10'$) is more than twice that of the SWAS beam at 487 GHz. At the distance of $\rho$ Oph, the Odin beam corresponds to 0.4 pc. The beam was centered on a 450 $\mu$m peak, and the submillimeter dust emission and the CO isotopic rotational emission suggest an $H_2$ column of $2 \times 10^{22}$ cm$^{-2}$ ($A_V \sim 20$). A temperature of 30 K has been obtained for both the gas (e.g., Loren et al. 1990) and the dust (I. Ristorcelli et al. 2009, in preparation) in this region. Using these parameters, and assuming the $O_2$ to be optically thin and in LTE, Larsson et al. find a column $N(O_2) \sim 1 \times 10^{15}$ cm$^{-2}$ for an abundance relative to $H_2$ of $\sim 5 \times 10^{-8}$ but an abundance in our units (relative to H nuclei) of $x(O_2) = 2.5 \times 10^{-8}$. The authors acknowledge a possible uncertainty of at least a factor of 2 in their estimate of the $O_2$ abundance.

The $\rho$ Oph region observed is illuminated on the back side by a B2 V star, with the cool dense cloud core sitting in front of the photodissociation region. The relatively high dust temperature, and the likely distance of the B star from the cloud, suggest $G_0 \sim 100$–1000 shining on the cloud surface (Cesarsky et al. 1976; Kamegai et al. 2003). The 0.4 pc size, coupled with the observed total $H_2$ column, suggests $n \sim 10^{10}$ cm$^{-3}$ in this dense region. Setting $G_0 = 300$ and $n = 10^5$ cm$^{-3}$, and using standard parameters, we obtain a column $N(O_2) = 1.4 \times 10^{15}$ cm$^{-2}$. In our model, the gas and dust temperatures at the $O_2$ abundance peak are $\sim 20$ K. We predict (see Figures 12 and 13) an $H_2O$ 557 GHz intensity of $I_{557} = 10^{-7}$ erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$, and an $O_2$
487 GHz intensity of $I_{487} = 2 \times 10^{-9} \text{erg cm}^{-2} \text{s}^{-1} \text{sr}^{-1}$ from this region. We have analyzed SWAS archival data on this source and have found a measured $H_2O$ 557 GHz intensity of $1.3 \times 10^{-7} \text{erg cm}^{-2} \text{s}^{-1} \text{sr}^{-1}$ and a $3\sigma$ upper limit of $2 \times 10^{-8} \text{erg cm}^{-2} \text{s}^{-1} \text{sr}^{-1}$ for the $O_2$ 487 GHz line. We predict $N(O_2) \sim 3 \times 10^{-7} \text{cm}^{-2} \text{s}^{-1} \text{sr}^{-1}$, which may be marginally detectable by the HIFI instrument on Herschel. In summary, our model successfully fits the $H_2O$ and $O_2$ observations of Sgr A, using reasonable parameters for this region.

### 4.2.5. Upper Limits on $O_2$ Observed by Odin

Pagani et al. (2003) report $3\sigma$ upper limits on $N(O_2)$ in a number of sources. As examples of sources with low incident $G_0$, the upper limits for TMC1 and L183 (L134N) are $7 \times 10^{14}$ and $1.1 \times 10^{15} \text{cm}^{-2}$, respectively. Although the Odin beam is large, these sources are extended enough so that beam dilution is not a significant factor. In addition, although much of the Taurus cloud has relatively low total $A_V$, these regions appear to have sufficiently high $A_V > 10$ to encompass the $O_2$ plateaus. Using an estimated $G_0 \sim 1$ and $n \sim 10^4 \text{cm}^{-3}$, our models predict a column of $N(O_2) \sim 4 \times 10^{14} \text{cm}^{-2}$ (see Figure 10) on both sides of the cloud, for a total column of $8 \times 10^{14} \text{cm}^{-2}$. This prediction lies very close to the observed upper limits. If future observations or analysis drive this upper limit down below our predicted value, then either beam dilution or a lower value of $Y_{H_2O}$ need to be invoked to reconcile observations with the models. Note that the upper limits on $N(O_2)$ set upper limits on $Y_{H_2O} \lesssim 10^{-3}$.

More challenging to our model are the upper limits quoted for sources with relatively high $G_0$. For example, Pagani et al. (2003) report $3\sigma$ upper limits of $N(O_2) < 1.9 \times 10^{15} \text{cm}^{-2}$ for Orion A. This column is averaged over the $9^\circ$ beam of Odin, which corresponds to a linear extent (diameter) of about 1.4 pc at the distance of Orion. If there were no extinction from the source of the FUV (primarily $\Theta^1 C$ in the Trapezium), the FUV flux at a distance of 0.7 pc from the star corresponds to $G_0 \sim 4 \times 10^3$. Taking this as the average $G_0$ incident on the molecular cloud in the beam, our model predicts $N(O_2) < 10^{16} \text{cm}^{-2}$ (see Figure 10), significantly higher than the observed upper limit. We offer two possible explanations for this discrepancy. First, $\Theta^1 C$ may be inside a cavity in the cloud carved out by the champagne flow created by the Trapezium. In this case, extinction by the intervening cloud would diminish $G_0$ in the outer regions of the beam, and thereby diminish the beam average column of $O_2$. A second possibility arises from the fact that the enhancement of the $O_2$ column at high $G_0$, as discussed in Section 3.2, is caused by the thermal evaporation of $O$ atoms from grain surfaces before they can react to form water ice on the surface. We have adopted a binding energy for atomic $O$ to the grain surface of $E_O/k \approx 800 \text{K}$ (see Table 1). However, this binding energy is uncertain and in our view may be low, given that $O$ is a radical. A modest increase in this binding energy would result in a much higher critical $G_0$ where the enhancement of $N(O_2)$ occurs, since the grain temperature is a weak function of $G_0$ ($T_g \propto G_0^{0.2}$) and thus the critical $G_0$ goes as $E_O/k$. In other words, increasing $E_O/k$ to 1200 K would increase the critical $G_0$ from about 500 to about 4000, and provide a solution consistent with the observations.

Sandqvist et al. (2008) use Odin observations to place an upper limit of $N(O_2) < 6 \times 10^{16} \text{cm}^{-2}$ toward Sgr A. As noted in this paper, this is consistent with our model clouds for any incident $G_0$ and any density $n$ for standard local gas-phase elemental abundances of $O$ and $C$.

### 5. SUMMARY, DISCUSSION AND CONCLUSIONS

We have constructed both a detailed numerical code and simple analytical equations to follow the abundances of the main oxygen-bearing species as a function of depth in molecular clouds. We take clouds of constant density $n$, illuminated by an external FUV (6 eV < h$v < 13.6$ eV) field characterized by the unitless parameter $G_0$ normalized to the local (Milky Way) interstellar FUV field. We explore the range $10^3 \text{cm}^{-3} < n < 10^6 \text{cm}^{-3}$ and $1 < G_0 < 10^5$. Our models incorporate thermal balance, gas-phase chemistry, a simple grain surface chemistry that includes the formation of $H_2$, $H_2O$, and $CH_4$ on grain surfaces, the sticking of gas-phase species to grain surfaces, and various desorption processes such as photodesorption, thermal desorption, and cosmic-ray desorption.

The abundances of chemical species vary considerably as a function of depth into a molecular cloud. At the surface, molecules are photodissociated and the gas is primarily atomic (e.g., $O$) or, for species with ionization potentials less than 13.6 eV, singly ionized (e.g., $C^+$). Here, although dust grains may be cold enough to prevent rapid thermal desorption, ices do not form because photodesorption keeps the refractory dust clear of ice mantles (the same is true of dust in the diffuse ISM). Very deep in the cloud, again assuming grains cold enough to prevent thermal desorption, photodesorption is negligible and ices form, causing gas-phase abundances of condensibles to plummet. Here, time-dependent effects (generally associated with cosmic rays) dominate the gas-phase chemistry due to the time required to deplete condensibles onto grains, to desorb CO ice by cosmic rays, and to destroy gas-phase CO (by He$^+$ produced by cosmic rays). These processes are slow, and have timescales comparable to, or longer than, typical molecular cloud lifetimes. At intermediate depths, photodesorption of ices supply gas-phase elements, and the partial shielding of the photodissociating external FUV flux allows gas-phase molecular abundances to peak.

We have focused in this paper on oxygen chemistry, and followed in particular the gas-phase species $O$, $OH$, $O_2$, and $H_2O$, as well as water ice. Our answer to the longstanding astrochemical question, “Where is elemental O in molecular clouds?,” is that oxygen that is not in CO is primarily atomic O to a depth $A_V \sim 200$ (see Equation (23)), and is water ice at larger depths. The freeze-out depth $A_V$ where significant water ice forms is proportional to $\ln(G_0/n)$, and is typically 3–6. Refractory silicate grains contain a modest abundance of $O$ ($\sim 10^{-4}$), but the bulk is likely gas-phase O and CO along with CO ice and $H_2O$ ice. For example, in our standard model, integrating to $A_V = 10$, the O not in refractory grains is divided $56\%$ $H_2O$-ice, $25\%$ gas-phase O, $10\%$ CO-ice, and $8\%$ gas-phase CO.

Our models also give an indication of the origin of water in molecular clouds. In the steady-state standard model, at $A_V$ the formation rate of gas-phase $H_2O$ is $2\%$ via gas-phase reactions and $98\%$ by photodesorption of $H_2O$ that has been formed on grains. At $A_{V_{diss}}$, the percentages are $30\%$ and $70\%$, respectively; midway in the plateau, they are $8\%$ and $92\%$, respectively.18 These percentages depend on $G_0$ and $n$, but as long as $G_0 \lesssim 500$, these numbers are representative. At higher $G_0 > 500$, where $O$ atoms thermally desorb from

18 A warning to future modelers: these percentages are not trivial to compute since there is a great deal of cycling of $H_2O$ and $OH$ to $H_2O^+$ (via reaction with $H^+$) and then back to $H_2O$ and $OH$ (via dissociative electronic recombination). This cycling gives, of course, no net production of these molecules.
grains before forming OH and eventually water ice, most of the water production is via gas-phase reactions. The production of water ice is about three times greater than the production of gas-phase water by photodesorption of water ice, because two-thirds of the water ice is photodesorbed as OH. Thus, one needs to modify these numbers if one wants to estimate the formation of water in any form in a cloud: for example, in the standard case midway in the plateau, the percentages are 3% by gas-phase reactions and 97% by grain surface reactions.

We plan a follow-up paper to examine carbon chemistry. We note that Figure 14 shows that for all densities considered and by $t > 2 \times 10^6$ years, gas-phase CO is largely absent in cloud interiors. This is in rough agreement with observations that show CO depletions in dense cloud interiors. Thus, CO is not always a volume tracer. However, the sequel paper will include more grain surface carbon chemistry such as the formation of CO$_2$ and methanol on grain surfaces. In addition, we will examine the effects of initial conditions on time-dependent chemistry, and compare observations with a wide variety of models with varying cosmic-ray desorption rates and gas density profiles through the cloud.

For $G_0 \lesssim 500$, the abundances of gas-phase OH, O$_2$, and H$_2$O peak and plateau at values $\sim 10^{-7}$ between $A_{\nu}$ and $A_{V\nu}$ (see Equations (26), (31), and (33)). These abundances are independent of $n$ and $G_0$ because both their formation rate (ultimately from photodesorption of H$_2$O ice) and their destruction rate (from photodissociation) depend on the product $nG_0$. However, since their formation is linked with H$_2$O ice photodesorption, these plateau abundances do increase with increasing ice photodesorption yield, $Y_{\text{H}_2\text{O}}$ and $Y_{\text{OH,ur}}$, and also with the grain cross-sectional area per H nucleus $\sigma_H$ (see same equations).

For higher values of $G_0 \gtrsim 500$, the chemistry undergoes a change, as O atoms no longer form H$_2$O ice on grain surfaces. Here, the grains are warm enough ($\gtrsim 20$K), so O atoms thermally desorb before reacting with H atoms. This pushes the freeze-out to greater depths and enhances the abundances of gas-phase O, OH, O$_2$, and H$_2$O by keeping more of the elemental oxygen in the gas phase. Because O$_2$ formation goes as the product of O and OH abundances, O$_2$ is the most sensitive to this change and its local abundance reaches $10^{-5}$, while its column climbs to $\sim 2 \times 10^{16}$ cm$^{-2}$. We note that the observations of Pagani et al. (2003) may suggest a higher binding energy for O on grains than adopted, and in this case the critical $G_0$ where this occurs may be significantly higher than 500.

Deep in the cloud interior at $A_V \gg A_{\nu}$, the gas-phase abundances drop as ices become dominant, the exact values of the abundances depending on cloud lifetimes and the cosmic-ray desorption rates assumed (see Figures 14 and 15). Here, time-dependent chemistry dominates.

Poelman et al. (2007) have suggested that the SWAS results do not rule out substantial gas-phase H$_2$O abundances and columns in the centers of clouds, because of optical depth effects, which “hide” the H$_2$O in the centers. However, as this saturation effect occurs, the line center antenna temperature approaches the gas temperature of the emitting region. In our model, this gas temperature is typically 10–20 K. Even in the cold interior of clouds, one would expect temperatures of 5–10 K. The SWAS-observed antenna temperatures in regions of detected H$_2$O are of order $T_A < 1$ K. This result alone suggests the H$_2$O is in the “effectively optically thin” regime. Our model does include an escape probability formalism for the H$_2$O lines. We find, in agreement with Poelman et al, that significant collisional deexcitation and saturation of the line occurs when $\tau n/n_{cr} > 1$, where $\tau$ is the line center optical depth and $n_{cr}$ is the critical density ($\sim 10^8$ cm$^{-3}$ for the 557 GHz line). Thus, the requirement for 557 GHz line saturation is roughly

$$\left[ \frac{N(\text{H}_2\text{O})}{6 \times 10^{12} \text{ cm}^{-2}} \right] \frac{n}{n_{cr}} \gtrsim 1. \quad (42)$$

Since our models have $N(\text{H}_2\text{O}) \sim 10^{15}$ cm$^{-2}$ and $n \lesssim 10^6$ cm$^{-3}$, we are almost always within the effectively optically thin regime, except perhaps for the highest densities $n \sim 10^6$ cm$^{-3}$. Furthermore, if the H$_2$O columns and densities were high enough that line saturation occurred, the line fluxes would exceed those observed by SWAS. We argue that SWAS observations indicate effectively thin 557 GHz emission, and that there is no evidence for hidden H$_2$O in the centers of clouds.

Bergin et al. (2000) listed ingredients for a successful astrochemical model of a molecular cloud. Slightly updated, they included: (1) low column-averaged abundances ($\lesssim 10^{-7}$) of gas-phase O$_2$, (2) low column-averaged abundances ($\lesssim 3 \times 10^{-8}$) of gas-phase H$_2$O, (3) an explanation of the apparently higher abundances of H$_2$O when it is observed in absorption in translucent clouds, (4) column-averaged water ice abundances of $\sim 10^{-4}$, and (5) existence of complex carbon-bearing species in the gas phase in some regions. As noted above, the model presented in this paper fulfills all of these criteria.

In addition, we have successfully applied, in a simple way, these models to observations of the $A_V$ threshold for the onset of water ice, the strict upper limits for the gas-phase H$_2$O abundance in B68 made by SWAS, the possible detection of O$_3$ in $\rho$ Oph made by Odin, the detection of H$_2$O and upper limits for O$_3$ made by SWAS for NGC 2024, and upper limits of the O$_2$ abundance set by Odin.

These successes imply that the proper modeling of the interstellar chemistry of molecular clouds must include as ingredients: photodissociation, freeze-out on grains, grain surface chemistry, desorption processes, and, in the very opaque central regions, time-dependent chemistry. At the surface, photodissociation and photodesorption dominate. Deep in the cloud, dust vacuums the condensibles and slow cosmic-ray processes are important, requiring time-dependent chemistry. At intermediate depths, gas-phase molecular species, such as O$_2$ and H$_2$O, peak in abundance, and provide the source of their submillimeter emission.

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### APPENDIX

#### Symbols Used in the Text

| Symbol | Definition |
|--------|------------|
| a      | grain radius |
| $A_V$  | visual extinction from surface of the cloud |
| $A_{Vf}$ | visual extinction where there is onset of water ice freeze-out, monolayer of ice forms |
| $\Delta A_V$ | width of the plateau of gas-phase H$_2$O or O$_2$, or $(A_{Vf} - A_{V})$ |
| $E_i$  | binding energy of species $i$ to grain surface |
| $f_{so} (f_p)$ | fraction of H$_2$O in the ortho(para) state |
| $f_{si}$ | fraction of surface sites occupied by species $i$ |
| $F_{FU}$ | flux of FUV photons at the cloud surface |
| $F_0$  | $10^8$ photons cm$^{-2}$ s$^{-1}$, the flux of FUV photons corresponding to $G_0 = 1$ |
| $F_{pd,i}$ | flux of molecules of species $i$ photodesorbing from surface |
| $F_{td,i}$ | flux of molecules of species $i$ thermally desorbing from surface |
| $G_0$  | unitless parameter measuring incident FUV flux normalized to $1.6 \times 10^{-2}$ erg cm$^{-2}$ s$^{-1}$ or to $10^8$ photons cm$^{-2}$ s$^{-1}$, roughly the local interstellar value |
| $\gamma_{He}$ | net rate coefficient for destruction of H$_2$O by He$^+$ |
| $\gamma_H^+$ | net rate coefficient for destruction of H$_2$O by H$_2^+$ |
| $I_{O_2}$ | rate coefficient for gas-phase reaction of OH with O to form O$_2$ |
| $I_{287}$ | intensity of the O$_2$ 287 GHz transition, in erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$ |
| $I_{557}$ | intensity of the H$_2$O 557 GHz transition, in erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$ |
| $J_{1113}$ | intensity of the H$_2$O 1113 GHz transition, in erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$ |
| n     | gas-phase hydrogen nucleus number density [∼ n(H) + 2n(H$_2$ + n(H$^+$))] |
| $n_{gr}$ | number density of grains |
| $v_i$ | vibrational frequency of species $i$ bound to a grain surface |
| N     | gas-phase column density of hydrogen nuclei |
| $N_i$ | gas-phase column density of species $i$ |
| $N_{f,i}$ | column density of hydrogen nuclei for onset of water ice freeze-out |
| $N_{s,i}$ | number of adsorption sites per cm$^2$ on a grain surface ($\approx 10^{15}$ cm$^{-2}$) |
| $R_{td,i}$ | thermal desorption rate of per atom or molecule of species $i$ from a surface |
| $R_{cr,i}$ | cosmic-ray desorption rate per surface atom or molecule, $i$ |
| $R_{H_2O}$ | $5.9 \times 10^{-10}$ s$^{-1}$, the unshielded PDR per molecule of H$_2$O for $G_0 = 1$ |
| $R_O$   | $6.9 \times 10^{-10}$ s$^{-1}$, the unshielded PDR per molecule of O$_2$ for $G_0 = 1$ |
| $R_{OH}$ | $3.5 \times 10^{-10}$ s$^{-1}$, the unshielded PDR per molecule of OH for $G_0 = 1$ |
| $\sigma_H$ | grain cross-sectional area per H nucleus |
| $\sigma_{gr}$ | cross-sectional area of a single grain |
| $t_{tr,i}$ | timescale for cosmic-ray desorption of adsorbed ice species $i$ with abundance $x(i)$ from a surface |
| $t_{ads,H_2O}$ | time for an adsorbed H$_2$O molecule to thermally evaporate from a grain surface |
| $t_{pd,i}$ | time for an adsorbed O atom to thermally evaporate from a grain surface |
| $t_{f,i}$ | timescale for species $i$ to hit (and stick to) a grain |
| $t_{G0}$ | timescale for a grain of size $a > 100$ Å to absorb an FUV photon at the cloud surface |
| $t_{evap,H_2O}$ | timescale for a grain of size $a > 100$ Å to absorb an FUV photon at $A_{V f}$ |
| $t_{evap,O}$ | timescale to photodesorb an O atom from a grain with covering factor $f_{1O}$ |
| $t_{f,i}$ | time to a given grain to be struck by a gas-phase atom or molecule of species $i$ |
| $t_{pd}$ | timescale for a grain to radiate much of its thermal energy |
| $T_{ave}$ | the average of the gas $T$ at $A_{V f}$ and at the $A_{V}$ where the H$_2$O abundance peaks |
| $T_{max}$ | peak temperature of a grain after absorbing one FUV photon |
| $T_{300}$ | $T/300$ K, where $T$ is the gas temperature |
| $x(i)$ | abundance of species $i$ relative to H nuclei |
| $x_o$  | abundance of ortho-H$_2$ |
| $x_p$  | abundance of para-H$_2$ |
| $x_{pl,i}$ | abundance of species $i$ in the plateau region between $A_{Vf}$ and $A_{V}$ |
| $Y_i$  | photodesorption yield of species $i$ from a grain surface |
| $Y_{H_2O}$ | yield of H$_2$O, the total yield of H$_2$O and OH being desorbed from water ice surface |
| $Y_{OH}$ | photodesorption yield of species $i$ from a surface |
| $Z(T)$ | partition function for O$_2$ |

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