THE EFFECT OF H₂O ON ICE PHOTOCHEMISTRY

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Received 2010 April 2; accepted 2010 May 31; published 2010 July 7

ABSTRACT

UV irradiation of simple ices is proposed to efficiently produce complex organic species during star formation and planet formation. Through a series of laboratory experiments, we investigate the effects of the H₂O concentration, the dominant ice constituent in space, on the photochemistry of more volatile species, especially CH₄, in ice mixtures. In the experiments, thin (~40 ML) ice mixtures, kept at 20–60 K, are irradiated under ultrahigh vacuum conditions with a broadband UV hydrogen discharge lamp. Photodestruction cross sections of volatile species (CH₄ and NH₃) and production efficiencies of new species (C₂H₆, C₂H₄, CO, H₂CO, CH₃OH, CH₃CHO, and CH₃CH₂OH) in water-containing ice mixtures are determined using reflection-absorption infrared spectroscopy during irradiation and during a subsequent slow warm-up. The four major effects of increasing the H₂O concentration are: (1) an increase of the destruction efficiency of the volatile mixture constituent by up to an order of magnitude due to a reduction of back reactions following photodissociation, (2) a shift to products rich in oxygen, e.g., CH₃OH and H₂CO, (3) trapping of up to a factor of 5 more of the formed radicals in the ice, and (4) a disproportional increase in the diffusion barrier for the OH radical compared with the CH₃ and HCO radicals. The radical diffusion temperature dependencies are consistent with calculated H₂O-radical bond strengths. All the listed effects are potentially important for the production of complex organics in H₂O-rich icy grain mantles around protostars and should thus be taken into account when modeling ice chemistry.

Key words: astrochemistry – circumstellar matter – ISM: molecules – methods: laboratory – molecular data – molecular processes

Online-only material: color figures

1. INTRODUCTION

Observations of complex molecules toward star-forming regions and in comets demonstrate the existence of efficient pre-biotic formation mechanisms (e.g., Belloche et al. 2009; Crovisier et al. 2004). Photochemistry in icy grain mantles was suggested as a path to chemical complexity more than three decades ago (Greenberg & Hong 1974). Despite this history and a recent surge in interest, most mechanisms that produce complex molecules during UV and ion irradiation of simple ices remain poorly understood. The photochemistry has been quantified for some pure ices (Gerakines et al. 1996; Öberg et al. 2009a). In astrophysical settings, the chemistry is complicated by the observation that most ices are mixed. Predicting the outcome of ice irradiation in space thus requires a quantitative understanding of how different mixture constituents affect the ice photochemistry. Because of its prominence and its known effects on the ice binding environment, this study focuses on the effect of H₂O ice during UV irradiation of binary ice mixtures. These mixtures are not proposed to perfectly mimic the multi-component ice mixtures found in space but are used to probe the fundamental principles of ice photochemistry, principles that can then be applied to more complicated ice systems through a combination of modeling and further experiments.

Ices are common during star formation, with H₂O ice reaching abundances of 10⁻⁴ with respect to H₂ (e.g., Boogert et al. 2008). Simple ices—H₂O, CO, CO₂, NH₃, CH₄, and CH₃OH—form in molecular cloud (cores) through direct freeze-out and through hydrogenation and oxygenation of atoms—O, C and N—and of unsaturated molecules such as CO on grain surfaces (Tielens & Hagen 1982; Watanabe & Kouchi 2002; Ioppolo et al. 2008). From observed ice spectral features and ice maps (Bergin et al. 2002; Pontoppidan et al. 2003; Pontoppidan 2006), the formation of ices is sequential, starting with H₂O and CO₂ (and probably CH₄ and NH₃ as well). Deeper into the cloud core or later during the core contraction CO freezes out catastrophically, resulting in a second ice phase dominated by CO and later CH₃OH. The photochemistry of CH₃OH:CO ice mixtures, investigated in Öberg et al. (2009a), and of CH₄, NH₃, and CO₂ in H₂O ice mixtures are then prime targets for laboratory experiments.

Irradiation of CH₃OH and CH₃OH:CO ices result in the formation of most complex C,H,O-bearing species, such as HCOOCH₃, CH₃CHO, and CH₃H₂O, found in protostellar hot cores (Öberg et al. 2009a). The same molecules may also form from irradiation of CH₃:H₂O ice mixtures, however, and the relative contribution from the two ice phases to the observed complex molecule abundances is unknown. Understanding the chemistry in the H₂O-rich ice is furthermore required to predict the formation rates of the pre-biotically important N-bearing...
complex molecules, since the main source of N in the ice, NH₃/NH₂⁺, probably forms mixed with H₂O (Bottinelli et al. 2010).

The response of ice mixtures to irradiation also governs the amount of, e.g., CH₄ that remains for thermal desorption close to the protostar. Thermal desorption of CH₄ ice is thought to result in a complex warm-carbon-chain-chemistry around some protostars (Sakai et al. 2008). One of the aims here is to investigate how the CH₄ ice photodestruction rate depends on H₂O-ice concentration and ice temperature.

Irradiation of H₂O-rich ices was first investigated in the 1960s and 1970s (e.g., Hagen et al. 1979). Since then there has been a handful of studies that have included the effects of H₂O on the overall photochemistry and two dedicated studies on the effect of different H₂O concentrations on the CH₃ chemistry during proton bombardment at 10 K (Moore & Hudson 1998) and on the CH₃OH UV photochemistry at 3 K (Krim et al. 2009). Moore & Hudson (1998) found an increasing production of CH₃OH, CH₃CHO, and CH₃CH₂OH and a decreasing production of C₂H₆ with H₂O concentration in H₂O:CH₄ mixtures. Krim et al. (2009) found an almost constant CH₃OH conversion into CO, CO₂, and H₂CO for a pure and an H₂O:CH₃OH 1:1 ice, but a factor of 3–7 conversion increase in an H₂O:CH₃OH 10:1 mixture. In both studies, all changes were explained by the production of increasing amounts of OH radicals with H₂O concentration and subsequent radical–radical reactions or H-abstraction by OH.

H₂O may however affect the photochemistry in more ways than increasing the number count of OH radicals in the ice. The binding energies in H₂O-rich ices are typically different compared with pure ices (Collings et al. 2003), which may affect radical diffusion. Radicals may also become physically trapped in H₂O ice at low temperatures as is often observed for volatile molecules (Collings et al. 2004). These radical-H₂O interactions have probably different strengths for different radicals, which may drive the chemistry in otherwise unexpected directions.

We investigate the relative importances of these potential effects of H₂O on the photochemistry of CH₄, NH₃, and CO₂ ices. The focus is on quantitative comparisons between pure and binary H₂O:CH₄ ices at different concentrations and temperatures, both during irradiation and during the subsequent warm-up.

2. EXPERIMENTS

The experiments are carried out on the set-up CRYOPAD (Öberg et al. 2005) under ultra-high vacuum conditions (∼10⁻⁹–10⁻¹⁰ mbar). Ices are deposited diffusively at 18 K by introducing a gas (mixture) in the vacuum chamber along the surface normal of a gold substrate, which is temperature controlled down to 18 K with a 2 K uncertainty. 10–20 mbar gas mixtures are prepared in a separate glass manifold with a base pressure of 10⁻⁷ mbar. The CH₄, NH₃, and CO₂ (CO₂ was used to minimize overlap with gas-phase CO₂ features from outside of the vacuum chamber) gases have a minimum purity of 99.9% (Indugas). Samples containing H₂O are prepared from the vapor pressure of deionized H₂O, further purified through freeze thawing.

The original ice mixture as well as changes in the ice composition induced by UV irradiation are quantified through infrared spectroscopy in reflection-absorption mode (RAIRS). The relative RAIRS band strengths are consistent with relative transmission band strengths in the investigated ice thickness regime and thus certain within 20%–30% (Öberg et al. 2009c).

| Ice          | H₂O:x | Temp. (K) | Thick. (ML) | Cross Section (10⁻¹⁸ cm²) |
|--------------|-------|-----------|-------------|--------------------------|
| CH₄          | 0:1   | 30        | 47          | 0.5(0.3)                 |
| H₂O:CH₄     | 1:3   | 20        | 42          | 2.8(1.4)                 |
| H₂O:CH₃     | 2:1   | 20        | 37          | 2.9(1.5)                 |
| H₂O:CH₂     | 4:1   | 20        | 37(29.8)    | 4.9(2.5)                 |
| H₂O:CH₃     | 4:1   | 40        | 38(30.8)    | 4.6(2.3)                 |
| H₂O:CH₄     | 5:1   | 60        | 38(32.6)    | 3.9(2.0)                 |
| NH₃         | 0:1   | 30        | 51          | 1.4(0.7)                 |
| H₂O:NH₃     | 1:1   | 20        | 54          | 1.5(0.8)                 |
| H₂O:NH₃     | 4:1   | 20        | 43          | 5.0(2.5)                 |
| CO₂         | 0:1   | 30        | 15          | ...                      |
| H₂O:CO₂     | 6:1   | 20        | 35          | ...                      |

Absolute band strengths have a 50% uncertainty, but this does not affect the quantification of the chemistry, where yields are calculated in fractions of the original ice.

The ices are irradiated by a hydrogen-discharge UV lamp, peaking at Lyα but extending between 6 and 11.5 eV (Muñoz Caro & Schutte 2003). All ices are irradiated with a UV flux of ∼1.1(±0.5) × 10¹³ s⁻¹ cm⁻² for 6 hr, resulting in a total fluence of ∼2.3 × 10¹⁷ cm⁻². This is comparable to the fluence an ice in a cloud core is exposed to during 10⁶ years because of cosmic-ray-induced UV photons at a flux of 10¹⁶ cm⁻² s⁻¹ (Shen et al. 2004). The lamp calibration is described in Öberg et al. (2009c).

Table 1 lists the photochemistry experiments in terms of their mixture composition, ice temperature during UV irradiation, and total thickness. Following irradiation at 20–100 K, all experiments are heated by 1 K minute⁻¹ to 150–250 K, while acquiring RAIRS every 10 minutes. The ice thicknesses range between ∼15 and 54 monolayers (ML), but most experiments are carried out with ∼40 ML ices. These ice thicknesses are similar to what is expected in the dense and cold stages of star formation and they are also in the linear regime for RAIRS. The ices are also thick enough that photodesorption will not significantly affect the bulk of the ice, based on previously measured UV photodesorption yields (Öberg et al. 2009c, 2009b).

3. RESULTS

The following five subsections focus on (1) the photodestruction cross sections of CH₄, NH₃, and CO₂, (2) the identification of the photoproducts, (3) the H₂O:CH₄ photochemistry as a function of H₂O concentration during irradiation and (4) during warm-up, and (5) the effects of temperature on the H₂O:CH₄ UV photochemistry in dilute mixtures.

3.1. Photodestruction Cross Sections in Pure and Mixed Ices

The photodestruction rate of a species determines the production rate of radicals in the ice. Its maximum value is the photodissociation rate, as measured in the gas phase. Previous ice experiments have however shown that the measured ice photodestruction rates are substantially lower than the gas-phase photodissociation rates (Cottin et al. 2003), probably because of fast back reactions between the dissociation fragments. Figure 1 shows the ¹³CO₂, CH₄, and NH₃ spectral features before and after a UV fluence of ∼2.3 × 10¹⁷ cm⁻² in pure ices and H₂O:X ≈ 5:1 ice mixtures at 20–30 K. During irradiation, more CH₄ and NH₃ are destroyed in the mixtures than in the pure ices.
This effect is shown quantitatively in Figure 2, where the loss of CH₄ and NH₃ in the different ices is plotted as a function of UV fluence (overlap with gas-phase CO₂ lines prevents a similar analysis for CO₂ ice). The photodestruction cross sections are calculated from the first 4 × 10¹⁶ photons cm⁻², where the curves are still approximately linear, and the results are listed in Table 1—the listed uncertainties are absolute and the fit uncertainties are 10%–20%. The photodestruction cross sections for pure CH₄ and NH₃ are 0.5 and 1 × 10⁻¹⁸ cm², respectively. Both are an order of magnitude lower than the measured gas-phase photodissociation cross sections (van Dishoeck 1988). They are still higher than previously reported values for 1000 ML ices (Cottin et al. 2003), suggesting that those experiments may have suffered from optical depth effects.

The photodestruction cross sections are up to an order of magnitude higher in the H₂O ice mixtures, close to the gas-phase photodissociation values. In the case of CH₄, even the small amount of H₂O in the H₂O:CH₄ 1:3 ice mixture results in a factor of 5 higher destruction cross section, while an H₂O-dominated ice (5:1) is required to increase the NH₃ cross section significantly.

The increasing UV photodestruction with H₂O concentration suggests that H₂O molecules surrounding the photodissociated volatiles may trap some of the radicals and thus inhibit reformation of CH₄ and NH₃. The reason behind the differences between different species is difficult to assess without further modeling, but the effect seems larger, the lighter volatile dissociation products of the different species is difficult to assess without further modeling, and CH₃CH₂OH in a subset of the experiments.

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### 3.3. H₂O Concentration Effects at 20 K

Figure 5 shows that irradiation of pure CH₄ ice results in the production of C₂H₆, C₂H₄, and larger hydrocarbons, as

![Figure 1. A ¹³CO₂, a CH₄, and an NH₃ ice spectral feature before (solid) and after (dashed) a UV fluence of 2.3 × 10¹⁷ cm⁻² at 20–30 K for pure ices (bottom panel) and for H₂O:X ~ 5:1 ice mixtures (top panel).](image-url)
expected—no C$_2$H$_2$ was observed and in general the products are hydrogen rich. Adding H$_2$O to the CH$_4$ ice results in the appearance of CO, H$_2$CO, CH$_3$OH, CH$_3$CHO and CH$_3$CH$_2$OH spectral features. The same bands are visible in all H$_2$O ice mixtures, but the relative contributions of different bands change with concentration.

The effect of H$_2$O concentration on the final product abundances, with respect to CH$_4$, is quantified in Figure 6. The identified products can be sorted into three groups: (1) hydrocarbons which have increasing abundances with CH$_4$ concentration, (2) small organics like CH$_3$OH that form from a CH$_4$ and an H$_2$O fragment, and (3) larger organics like CH$_3$CH$_2$OH that form from two CH$_4$ fragments and one H$_2$O fragment. The molecules in each group are then expected to form as

\[
\frac{N_{C_2H_6}}{N_{CH_4}} \propto [CH_4],
\]

\[
\frac{N_{CH_3OH}}{N_{CH_4}} \propto (100 - [CH_4]), \text{ and}
\]

\[
\frac{N_{CH_3CH_2OH}}{N_{CH_4}} \propto (100 - [CH_4])[CH_4].
\]

Figure 4. Spectrum of an irradiated H$_2$O:CH$_4$ 2:1 mixture at 20 K is plotted on top together with pure (black) and H$_2$O mixtures (red) of expected products. The H$_2$O mixture spectra are taken from the NASA Goddard Cosmic ice laboratory spectral database by Moore et al. (http://www-691.gsfc.nasa.gov/cosmic.ice.lab).

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

Qualitatively, the abundance patterns of these three molecules agree with the curve predictions. The difference in, e.g., the peak position of the curve in Figure 6(c) indicates that the effects of diffusion and different photodestruction cross sections for different mixtures cannot be neglected when making quantified predictions, however. In addition, the production dependencies of H$_2$CO, CO, and CH$_3$CHO are expected to be complicated by multiple formation pathways, all involving multiple dissociation events as shown in Figure 3.

Four of the detected photoproducts, C$_2$H$_6$, CH$_3$OH, H$_2$CO, and CO, form abundantly enough to quantify their production as a function of fluence during UV irradiation (Figure 7). C$_2$H$_6$ and CH$_3$OH form immediately upon irradiation in all experiments. The H$_2$CO production is delayed in the H$_2$O-dominated mixture and CO production does not begin before $5 \times 10^{16}$ photons cm$^{-2}$ in any mixture as expected for a reaction pathway through multiple photodissociation events.

The initial photoproduction rates of C$_2$H$_6$, CH$_3$OH, and H$_2$CO are calculated from the abundance growth during the first $4 \times 10^{16}$ photons cm$^{-2}$ when the growth is still roughly linear. Table 3 lists the resulting formation "cross sections." These numbers do not represent physical photoproduction cross sections,

| Species | Band (cm$^{-1}$) | Band Strength$^a$ (cm$^{-1}$) | Reference |
|---------|-----------------|-------------------------------|-----------|
| CH$_4$  | 1300            | $6.1 \times 10^{-18}$        | Moore & Hudson (1998) |
| NH$_3$  | 1070            | $1.7 \times 10^{-17}$        | D’Hendecourt & Allamandola (1986) |
| CO$_2$  | 2343            | $7.6 \times 10^{-17}$        | Gerakines et al. (1995) |
| H$_2$O  | 1670            | $1.2 \times 10^{-17}$        | Gerakines et al. (1995) |
| C$_2$H$_6$ | 2976          | $1.1 \times 10^{-17}$        | Moore & Hudson (1998)$^b$ |
| cH$_4$  | 821             | $1.9 \times 10^{-18}$        | Pearl et al. (1991) |
| C$_2$H$_4$ | 1436          | $2.9 \times 10^{-18}$        | Moore & Hudson (1998)$^b$ |
| H$_2$CO | 1500            | $3.9 \times 10^{-18}$        | Schutte et al. (1993) |
| CH$_3$OH | 1026           | $2.8 \times 10^{-17}$        | D’Hendecourt & Allamandola (1986) |
| CH$_3$CH$_2$OH | 1044      | $7.3 \times 10^{-18}$        | Moore & Hudson (1998)$^b$ |
| CH$_3$CHO | 1350          | $6.1 \times 10^{-18}$        | Moore & Hudson (1998)$^b$ |
| CO     | 2139            | $1.1 \times 10^{-17}$        | Gerakines et al. (1995) |

Notes.

$^a$ The band strengths are known within $\sim 20\%$--$30\%$ when comparing results from different references, ice mixtures, and ice temperatures.

$^b$ In an H$_2$O ice matrix.
Figure 5. Difference spectra of CH$_4$ ice and H$_2$O:CH$_4$ ice mixtures after a UV fluence of $2.3 \times 10^{17}$ photons cm$^{-2}$. The marked peaks are: (a) C$_2$H$_6$, (b) CO, (c) XCHO, (d) H$_2$O, (e) H$_2$CO, (f) CH$_3$OH, (g) C$_2$H$_6$, (h) C$_2$H$_4$, (i) CH$_3$CHO, (j) CH$_4$, (k) CH$_3$OH, (l) CH$_3$CH$_2$OH, (m) CH$_3$OH, and (n) C$_2$H$_4$.

Figure 6. Normalized, final abundances of the identified photoproducts as a function of CH$_4$ concentration in the ice. The error bars only include the relative uncertainties and the absolute uncertainties are about a factor of 2. The dotted lines are the qualitative predictions using Equations (1)–(3).

Figure 7. Quantified production of C$_2$H$_6$, CH$_3$OH, H$_2$CO, and CO in the different mixtures (crosses: pure CH$_4$; blue stars: H$_2$O:CH$_4$ 1:3; green diamonds: 2:1; red triangles: 4:1) as a function of UV fluence.

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

Table 3

| Product      | Pure CH$_4$ | 1:3  | 2:1  | 4:1  |
|--------------|-------------|------|------|------|
| C$_2$H$_6$   | 0.30[0.10]  | 0.52[0.18] | 0.29[0.10] | $<0.20$ |
| CH$_3$OH     | 0.04[0.01]  | ...  | 0.11[0.04] | 0.23[0.08] | 0.56[0.19] |
| H$_2$CO      | ...         | $<0.02$ | 0.15[0.05] | 0.10[0.04] |
| Total$^a$    | 0.34        | 0.63  | 0.67  | $<0.86$ |
| Total (%)$^b$| $\sim100$   | 41    | 33    | $<22$  |

Notes. Fit uncertainties are in brackets.

$^a$ The total formation cross section of new molecules.

$^b$ $\%$ of the photodestruction cross section that is accounted for by the total formation cross section taking into account that some molecules require multiple CH$_4$ fragments to form.

Since diffusion is required for their formation; it is, however, a convenient way of parameterizing their formation. The total formation cross section of complex molecules, in number of product molecules with respect to CH$_4$, increases somewhat with H$_2$O concentration. When taking into account that some products require multiple CH$_4$ fragments, an approximately constant fraction of the original CH$_4$ is incorporated into more complex molecules at all concentrations. Furthermore, the CH$_4$ photodestruction cross section increases with an order of magnitude, between pure CH$_4$ and the 4:1 mixture, and the formation efficiencies normalized to the photodestruction cross sections thus decrease significantly with H$_2$O concentration. The presence of H$_2$O then slows down the chemistry of the radicals in the ice, even though this effect is “compensated for” under laboratory timescales by the even more efficient slow down of back reactions into CH$_4$. 

(A color version of this figure is available in the online journal.)
3.4. Warm-up of Irradiated Ices

During warm-up of the UV-irradiated ices, formation of new species together with sequential desorption change the ice mixture with temperature (Figure 8). In the H$_2$O-poor 1:3 mixture CH$_3$OH is the only molecule that forms perceptively during warm-up, in the 2:1 mixture CH$_3$CHO is alone to form until reformation of the H$_2$O-ice network around 130 K. The different formation patterns in the H$_2$O-poor and H$_2$O-rich ices suggest different diffusion environments. Specifically, OH diffusion seems hindered in the H$_2$O-rich ice, while HCO can still diffuse and react with CH$_3$ to form CH$_3$CHO. All species are partially trapped in the H$_2$O ice, so that even C$_2$H$_6$ desorption is only complete around the H$_2$O desorption temperature of $\sim$150 K.

3.5. Ice Temperature Effects During Irradiation at 20–60 K

Increasing the ice temperature should speed up the thermal diffusion of radicals in the ice and thus the ice chemistry. Figure 9 shows that the most notable changes in the irradiated ice spectra at 20, 40, and 60 K are instead due to outgassing or a decreased production of volatile species, such as H$_2$CO and CO, at the higher temperatures. The decreased production of these secondary and tertiary dissociation products can be understood if the intermediate radicals, e.g., HCO diffuse fast enough at higher temperatures to react with another radical before absorbing a second photon and dissociating to CO. This scenario is supported by an earlier onset in the CH$_3$CHO production at 60 K compared to 20 K (Figure 10) and also consistent with the warm-up results that reveal HCO diffusion above 30 K.

In contrast, there is no evidence for an increased formation efficiency of CH$_3$OH and CH$_3$CH$_2$OH or for the formation of more complex molecules such as (CH$_2$OH)$_2$. Rather, the CH$_3$OH production cross section decreases from 5.6 to $3.3 \times 10^{-18}$ cm$^2$/NCH$_4$($0$) between 20 and 60 K. The lack of a positive temperature effect on the CH$_3$OH production, illustrated in Figure 10, suggests that CH$_3$OH and CH$_3$CH$_2$OH formation depends mainly on CH$_3$ diffusion that is efficient already at 20 K; OH and CH$_2$OH diffusion must be too slow, even at 60 K, in an H$_2$O-dominated ice to affect their formation. In addition, the decreasing cross section with temperature is probably due to thermal desorption of some of the produced CH$_3$ at 60 K before it has time to react.

4. CALCULATIONS OF BINDING ENERGIES

To aid the interpretation of the experiments, we calculated the binding energies of radical-H$_2$O complexes using the CCSD(T) (coupled cluster with single, double, and perturbative triple excitations) method with the aug-cc-pVTZ basis set (Kendall et al. 1992). In order to correct for the Basis Set Superposition Error, the Boys–Bernardi counterpoise method (Boys &
have been used to derive the relative diffusion barriers directly. High-level calculations (Soloveichik et al. 2010) averaged. 

Figure 10. Quantified production of C2H6, CH3OH, CH3CHO, H2CO, and CH2CH2OH in H2O:CH4 4:6:1 mixtures at 20 K (stars) and 60 K (red diamonds) as a function of UV fluence. The lines show the 2–3 data point averages.

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

Bernardi 1970) was used. The internal geometries of the interacting species were kept constant while a large number of different relative orientations and intermolecular distances were scanned. The thus located lowest energy minima were used to calculate the binding energies. The reported energies are electronic energies relative to the infinitely separated interaction partners. No account of zero-point energy was made. All calculations were performed using the Gaussian 03 program package (Frisch et al. 2004).

The calculations were carried out for the predicted three most common radicals in the ice, OH, HCO, and CH3. The resulting binding energies are: 0.23 eV (2700 K) for H2O–OH, 0.11 eV (1300 K) for H2O–HCO, and 0.07 eV (800 K) for H2O–CH3. The H2O–OH result is in good agreement with other recent high-level calculations (Soloveichik et al. 2010).

5. DISCUSSION

5.1. The Influence of H2O

Under laboratory conditions, the most important effect of increasing the H2O concentration is to drive the chemistry away from C2H7 chains and toward products with a higher and higher concentration of OH. The same effect was noted by Moore & Hudson (1998) during proton bombardment of H2O:CH4 ice mixtures. This can be understood from simple rate equations where the production rates of various molecules are proportional to the production rates of CH3/CH2 and OH in the ice, i.e., the photodestruction cross sections of CH4 and H2O. The absolute values of these reaction rates also depend on the diffusion rates of radicals. If the destruction and diffusion rates had been constant, the relations shown in Figure 6 could have been used to derive the relative diffusion barriers directly.

H2O does, however, change the CH4 photodestruction cross section. Since this increased destruction efficiency is not accompanied by an equally large increase in production efficiencies of new molecules, H2O must slow down the overall diffusion of radicals in the ice to the point of trapping them. H is not expected to be trapped at 20 K, however, and the existence of larger radicals in the ice indicates that many of the H atoms formed during dissociation either escape from the ice or react to form H2. A significant amount of the produced heavier radicals, especially CH3, must also remain mobile in or on top of the ice to account for the production of any complex molecules during irradiation at 20 K in the H2O-rich ices. Without detailed modeling, it is not possible to estimate the relative importances of surface and bulk diffusion for the chemistry. It is however unlikely that all radicals are trapped in the bulk of the ice at 20 K, since even in the most dilute mixtures ~20% of the dissociated CH4 molecules recombine to form more complex molecules. This corresponds to at least 8 ML of chemically active ice in a 40 ML-thick ice, and the ice would thus have to be very porous to explain all chemistry with diffusion on external and internal (in large pores) ice surfaces. It would also be strange if diffusion in H2O ices is fundamentally different compared with diffusion in CH3OH ices, where bulk diffusion is definitely required to explain the ice photochemistry results (Oberg et al. 2009a), considering the similar behavior of the two ices during segregation studies (Ehrenfreund et al. 1999; Bernstein et al. 2005).

Trapping of some of the radicals in the ice bulk is, however, needed to explain that up to 80% of the dissociated CH4 is not converted into more complex molecules in the H2O:CH4 5:1 ices. This is consistent with the commonly observed trapping of molecules such as CO and CO2 in H2O-rich ices (Collings et al. 2004). It may also explain some earlier results; trapping of CH3OH photofragments in the H2O:CH3OH 10:1 ice mixture in Krim et al. (2009) would prevent the radicals from reacting with each other and thus favor dissociation into smaller and smaller fragments (CH2OH, H2CO, HCO, CO), explaining their result of high H2CO and CO yields in H2O-rich ices without invoking efficient H abstraction by OH radicals.

When the ice is heated, some of the bound radicals overcome their entrapment and react to form new species. In all H2O:CH4 ice mixtures, the most abundant radicals are expected to be CH3 (see below) and OH, the two major photoproducts of CH4 and H2O. CH3OH is thus always expected to form more abundantly during warm-up of the irradiated ices than, e.g., CH3CHO, consistent with the results in Figure 7 for the H2O:CH4 1:3 experiment. In the 2:1 mixture, almost no CH3OH forms initially during warm-up, however. Instead a significant amount of CH3CHO forms, followed later by CH3OH formation during the H2O ice reformation temperature of ~120–130 K. An increasing H2O concentration thus increases the OH diffusion barrier relative to the HCO diffusion barrier. This is physically reasonable since OH and H2O are expected to bond stronger than HCO and H2O. The importance of the relative diffusion barriers of OH and HCO to drive the chemistry demonstrates that radical–radical reactions in ice are only efficient when both radicals (i.e., CH3OH and CH3HCHO) taking part in the reaction are mobile.

5.2. Toward Quantifying the H2O:CH4 Photochemistry

CH4 is known to dissociate into a number of different fragments during UV photolysis in the gas phase. The dissociation cross section is wavelength dependent; e.g., almost no CH2 is observed to form from dissociation with Lyα photons (Mordaunt et al. 1993) even though it is expected to be an important channel at lower photon energies (Slanger & Black 1982). By comparing the initial C2H6 and C2H4 formation efficiencies in pure UV-irradiated CH4 ice, it is possible to constrain the CH4 photodissociation branching ratio in ices irradiated with a hydrogen lamp output consisting of both Lyα photons and broadband emission.

In the pure CH4 ice, the initial growth of both C2H6 and C2H4 is assumed to be caused by CH3+CH3 and CH2+CH2.
radical reactions, ignoring second generation photodissociation products. Further assuming that the diffusion barriers of CH$_3$ and CH$_2$ are comparable, the CH$_4$ branching ratio can be constrained from the initial C$_2$H$_6$ and C$_2$H$_4$ production rate, which is $\sim 9:1$. Gerakines et al. (1996) find a comparable C$_2$H$_6$/C$_2$H$_4$ product ratio (8:1). Since each reaction requires two radicals, the dissociation branching ratio is inferred to be CH$_3$:CH$_2$ $\sim$ 3:1. This is consistent with a chemistry driven largely by Ly$\alpha$ photons.

The diffusion barriers are more difficult to constrain directly from the experiment. The calculated bond strengths of 800, 1300, and 2700 K for the H$_2$O–CH$_3$, –HCO, and –OH complexes are not identical to ice diffusion barriers, but the relative values should agree with the experimental results. Indeed, the data show that OH has a higher diffusion barrier than HCO in H$_2$O-dominated ices (efficient thermal diffusion at 30 and 120 K, respectively) and that CH$_3$ must be already diffusing at 20 K to explain any complex molecule production at this temperature. The calculated bond strengths are thus a good starting point for models, where the quantified formation rates of molecules can be used to extract diffusion barriers, similarly to what is currently being done for the CH$_3$OH photochemistry (R. T. Garrod & K. I. Öberg 2010, in preparation). Already, both calculations and experiments suggest that the temperature window between diffusion and desorption in H$_2$O-dominated ices is quite small for the investigated radicals, which may explain the low production yield of complex organics during warm-up (a few % of all dissociated CH$_4$) observed here compared to the efficient production of complex molecules observed during warm-up of irradiated CH$_3$OH-ices (Öberg et al. 2009a).

The calculations also show that predicting radical diffusion barriers from the bond strengths of the parent molecule to H$_2$O can be quite reasonable (Garrod et al. 2008); the H$_2$O–H$_2$O, H$_2$O–H$_2$CO, and H$_2$O–CH$_4$ bond strengths are 0.2, 0.07–0.13, and 0.03 eV, respectively (e.g., Szczesiak et al. 1993; Bene 1973), which is very similar to the bond strengths calculated for the H$_2$O-radical complex interactions. There thus seems to be a direct dependence between the H$_2$O-molecule and H$_2$O-radical interactions.

### 5.3. Astrophysical Implications

As shown previously for pure and mixed CH$_3$OH ices, UV irradiation of H$_2$O:CH$_4$ ices readily results in the production of complex molecules and this production can be quantified. After a UV fluence corresponding to $\sim 10^6$ years in a cloud core, up to 50% of the original CH$_4$ and 25% of the NH$_3$ ice have dissociated into radicals that can react into more complex species. At low temperatures most of these radicals are trapped in the ice, i.e., only $\sim 10\%$ of the original CH$_4$ ice can be converted into complex molecules during UV irradiation at low temperatures. As the protostar turns on and heats the ice, many of the trapped radicals will become mobile, resulting in a second equally important formation step of complex molecules—this step will probably be more important in space than in the lab because of the lower heating rate in astrophysical environments. Taking a typical CH$_4$ ice abundance of $\sim 4\%$ with respect to H$_2$O ice and an H$_2$O ice abundance of $\sim 10^{-4}$ with respect to H$_2$ toward protostars (Öberg et al. 2008), this corresponds to a potential production of complex molecules of $0.04 \times 10^{-4} \times 0.1 = 4 \times 10^{-7}$ with respect to H$_2$. This is high enough to contribute significantly to typical hot core abundances of complex molecules $\sim 10^{-9}$–$10^{-6}$ (Bisschop et al. 2007).

Several of the CH$_3$OH and H$_2$O:CH$_4$ photochemistry products are the same, e.g., CH$_3$CH$_2$OH and CH$_3$CHO, and the relative importance of the two production pathways during star formation will depend on the relative abundances of CH$_3$OH and CH$_4$ ice on the grains as well as what other ice constituents are mixed with H$_2$O. Both the H$_2$O- and the CO/CH$_3$OH-rich ice phases must clearly be modeled to accurately predict the total formation rates of C- and O-containing complex molecules in space.

In addition, it is crucial to understand the effects of H$_2$O quantitatively to constrain when and where N-containing complex molecules form—their main formation pathway is probably from NH$_3$ in an H$_2$O-rich ice. While the production of radicals seems to be the most important effect of H$_2$O on the ice photochemistry under laboratory conditions, this is not necessarily the case for the timescales and ice compositions present at star and planet formation. Rather, detailed modeling is required that extracts the microscopic properties of the H$_2$O-rich ice chemistry from the laboratory experiments, such as the composition-dependent diffusion barriers, and applies these results to astrochemical models. Only when a simple system, such as H$_2$O:CH$_4$, is understood at this detailed level, can we expect to accurately model the more elusive nitrogen chemistry in H$_2$O-rich environments and thus provide predictions of, e.g., the prebiotic amino acid production.

Estimating ice lifetimes is easier than predicting the chemical evolution, though the composition dependence of CH$_4$ photodestruction introduces some uncertainty. Table 4 lists the photodestruction timescales for 20–30 K CH$_4$ ice in pure, 2:1 and 4:1 H$_2$O:CH$_4$ ices subject to a weak UV field induced by cosmic rays, the interstellar radiation field, and the 1000 times higher UV flux inferred toward the L1527 outflow (Spaans et al. 1995). Outside of protected cloud cores, the CH$_4$ ice lifetime is thus short compared to most other timescales, especially in H$_2$O-rich ice mixtures relevant for protostars. For large quantities of CH$_4$ ice to survive to thermally desorb around protostars and drive warm-carbon-chain-chemistry as suggested by Sakai et al. (2008), it requires that the ices are well protected up until that point. This may be a reason for the low number of observations of such a chemistry during the protostellar stage.

## 6. CONCLUSIONS

1. The photodestruction cross section of NH$_3$ and CH$_4$ in H$_2$O ice mixtures increases with H$_2$O concentration by up to a factor of 10 with implications for the CH$_4$ ice lifetime in protostellar envelopes. Simultaneously, the production efficiency of stable molecules in the H$_2$O:CH$_4$ ice increases by a factor of 2. This is explained by trapping of radicals in the H$_2$O-ice matrix, which prevents back reactions between, e.g., CH$_3$ and H.

2. The H$_2$O:CH$_4$ photochemistry produces C$_2$H$_6$, CH$_3$OH, and CH$_3$CH$_2$OH as a function of CH$_4$ concentration, in a way that can be directly related to the number of OH.
and CH$_2$/CH$_3$ groups in each product. The production of CH$_3$CHO, H$_2$CO, and CO has a fluence delay consistent with formation through more steps compared to, e.g., CH$_3$OH.

3. On laboratory timescales, increasing the ice temperature from 20 to 60 K has a limited effect on the chemistry, probably because HCO is the only important reactant that becomes mobile in this temperature interval in H$_2$O-dominated ice mixtures.

4. The CH$_4$ photodissociation branching ratio of CH$_3$ and CH$_2$ is $\gtrsim$3:1, as derived from the relative production efficiencies of C$_2$H$_6$ and C$_2$H$_4$.

5. OH diffusion is fast in the H$_2$O:CH$_4$ 1:3 mixture but not present in the H$_2$O-dominated ice mixtures below 100 K. HCO diffusion is possible above 30 K in the H$_2$O-rich ice mixtures and CH$_3$ diffusion seems efficient at 20 K in all mixtures, consistent with calculated H$_2$O-radical complex bond strengths. OH diffusion is thus more severely slowed down with H$_2$O concentration than the other radicals, which counteracts the higher OH production rate in H$_2$O-richer ices.

6. Because H$_2$O is both a source of OH radicals and preferentially trap OH compared to more volatile radicals, predicting the photoproduction branching ratio of different complex molecules in space requires microscopic modeling of the H$_2$O:CH$_4$ experiments rather than direct comparison with experiments.

This work has benefitted from discussions with Herma Cuppen and Robin Garrod. Support for K.I.O. is provided by NASA through Hubble Fellowship grant awarded by the Space Telescope Science Institute, which is operated by the Association of Universities for Research in Astronomy, Inc., for NASA. Astrochemistry in Leiden is supported by a SPINOZA grant of the Netherlands Organization for Scientific Research (NWO) and NOVA. The work by S.A. was partly funded by an NWO-CW Top grant. Some of the electronic structure calculations were performed at C3SE (Chalmers Centre for Computational Science and Engineering) computing resources.

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