PHOTOCHEMICAL HEATING OF DENSE MOLECULAR GAS

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Received 2015 February 11; accepted 2015 July 16; published 2015 September 8

ABSTRACT

Photochemical heating is analyzed with an emphasis on the heating generated by chemical reactions initiated by the products of photodissociation and photoionization. The immediate products are slowed down by collisions with the ambient gas and then heat the gas. In addition to this direct process, heating is also produced by the subsequent chemical reactions initiated by these products. Some of this chemical heating comes from the kinetic energy of the reaction products and the rest from collisional de-excitation of the product atoms and molecules. In considering dense gas dominated by molecular hydrogen, we find that the chemical heating is sometimes as large, if not much larger than, the direct heating. In very dense gas, the total photochemical heating approaches 10 eV per photodissociation or photoionization, competitive with other ways of heating molecular gas.

Key words: molecular processes – protoplanetary disks – radiation mechanisms: thermal

1. INTRODUCTION

Photochemical heating is important in dense photon transition regions (PDRs), especially where the gas changes from atomic to molecular. There are two main types of photochemical heating: “direct,” coming from the kinetic energy of the immediate products of photoionization or photodissociation, and “chemical,” arising from exothermic reactions of the products with abundant neutral species. The latter type of heating has received much less attention than the former, partly because it is sensitive to the detailed physical conditions of the gas, i.e., to density, temperature, and chemistry. In this paper, we develop photochemical heating for the dense and warm inner regions of protoplanetary disks and treat direct and chemical heating on an equal footing. We also discuss how the results may apply generally to diffuse and dense interstellar gas.

Early consideration of photochemical heating arose in connection with the photoionization of cool, diffuse interstellar gas (Spitzer 1978). Thus, the photoionization of the carbon atom imparts a small amount of kinetic energy to the products, a C+ ion and an electron. Recombination then leads to escaping radiation and the net heating per ionization is small, ≲1 eV per photoionization. Spitzer mentioned the possibility of chemical heating from the reaction of C+ with molecular hydrogen (Dalgarno & Oppenheimer 1974). This is not important for cool, diffuse gas because C+ interacts weakly with H2 by radiative association, and also because it depends on the abundance of H2, which may be small in this case.

Henry & McElroy (1969) treated chemical heating in connection with the photoionization of H2 by photons with \( h \nu > 15.44 \text{ eV} \) from solar EUV irradiation of Jupiter’s upper atmosphere. They examined the thermal consequences of the reactions of H2, e.g.,

\[
\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{e}, \quad \text{H}_3^+ + \text{e} \rightarrow \text{H}_2 + \text{H},
\]

and obtained chemical heating of order 10 eV per ionization of H2. These same processes were used by Glassgold & Langer (1973) and Cravens & Dalgarno (1978) for cosmic-ray heating of interstellar molecular gas. A comprehensive treatment of heating by cosmic rays and X-rays, based on the analysis of electron interactions in a mixture of H, H2, and He gas by Dalgarno et al. (1999), has been given by Glassgold et al. (2012; henceforth GGP12).

Chemical heating was actively developed for heating inner cometary comae from the photodissociation of H2O by solar FUV and EUV radiation\(^5\) (Marconi & Mendis 1982; Ip 1983; Crovisier 1984, 1989; Rodgers & Charnley 2002). Some of these papers focused on direct heating, but Marconi & Mendis also included chemical heating. Some level of photochemical heating was included by Gorti & Hollenbach in their modeling of protoplanetary disks (Gorti & Hollenbach 2004, 2009, 2011), but with few details. Woitke et al. (2009) and Woods & Willacy (2009) included C+ and H2 photochemical heating in related studies.

In this paper, we treat both direct and chemical heating of dense molecular gas dominated by molecular hydrogen and exposed to FUV radiation. Although the inner regions of protoplanetary disk atmospheres provide the prime motivation, we also discuss molecular clouds and PDRs. We will find that chemical heating can be at least the same order as direct heating, and in some cases much larger. The latter situation tends to occur for targets like H2 and CO, whose dissociation requires FUV photons with energies greater than 11 eV. Some of the chemical heating is extracted from the chemical energy of the neutrals with which the dissociation products interact, or which they generate.

When photodissociation or photoionization occurs, the incident photon energy is converted into the kinetic energy of the products, which leads to direct heating. The remainder goes into a product radical or ion with greater chemical energy that can engage in reactions that generate more heating. The photoionization of carbon provides a simple example, \( h \nu + \text{C} \rightarrow \text{C}^+ + \text{e} \). Most of the kinetic energy goes to the electron, and the other product is the reactive C+ ion. In the dense molecular regions of interest here, it will react with H2 or other species rather than recombine radiatively, and these reactions can lead to further heating. Some of the species in the initial photo process or in subsequent reactions may be

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\(^5\) In this paper, we use the Lyman limit \( \lambda = 911.7 \text{ Å} \) to distinguish EUV from FUV radiation.
produced in excited levels, and some of this excitation may also be extracted as heat by collisional de-excitation by abundant species like H, H₂, and He if the density is high enough. In some cases, more energy can be obtained as heat than possessed by the initiating photon. This somewhat surprising outcome is a consequence of the fact that photodissociation regions are not in complete thermodynamic chemical equilibrium. They contain atoms and radicals with significant chemical energies that can be tapped by exothermic chemical reactions initiated by either the primary or the secondary products of the initial photodissociation or photoionization. This process obeys the laws of total energy and mass conservation, which are automatically obeyed in our treatment of chemical reactions and their energetics. The chemical energy of the reactants is potential energy in the usual sense, i.e., electrostatic energy of ions and electrons in the atoms and molecules of the gas. Additional heating results when some of the chemical energy is converted into kinetic energy while conserving the total energy. A particularly interesting example is the heating that results when the formation on dust grains leads to excited H₂ molecules, whose excitation can be converted to heat by collisional de-excitation at high densities. This possibility arises because molecular dissociation usually leads either directly or indirectly to H atoms, as will be discussed at length in Section 3.

Here our main goal is to call attention to the potentially significant role of photochemical heating in photodissociation regions. To illustrate this process, we discuss a number of simplified examples and give qualitative numerical estimates which would need to be refined for specific applications. In the next section, we give a short general development and then take up specific cases in Section 3. The significance of our results is discussed in Section 4 and in the brief conclusion in Section 5.

2. METHOD

We consider the photochemical heating of slightly ionized molecular gas by FUV radiation with wavelengths \( \lambda > 911.7 \) Å. The heating rate per unit volume is expressed as

\[
\Gamma_{\text{phchem}} = \Gamma_{\text{dir}} + \Gamma_{\text{chem}},
\]

where the “direct” heating \( \Gamma_{\text{dir}} \) comes from the kinetic energy of the dissociation (or ionization) products and the chemical heating \( \Gamma_{\text{chem}} \) comes from their chemical reactions. Each of the terms in Equation (2) is a sum over neutral species X of the form

\[
\Gamma(X) = G(X) n(X) Q(X),
\]

where \( G(X) \) is the photodissociation or photoionization rate of X with volumetric density \( n(X) \), and \( Q(X) \) is the heating energy, either direct or chemical, per photodissociation (or photoionization). Atomic species such as neutral carbon can contribute as well as molecules, and then \( G(X) \) is the photoionization rate. Equation (2) would appear as one term in the heat equation of a full thermal-chemical model that would also include a system of chemical equations as well as equations for the dynamics and radiative transfer. We focus here on the microscopic physics and chemistry of the photochemical heating of selected molecules and make qualitative estimates for these species. These results potentially apply to both time-varying and steady astrophysical situations. We do not incorporate the findings in a general thermal-chemical model in this paper, but provide several exemplary applications to protoplanetary disks.

The absorption of a FUV photon may result in fluorescence rather than dissociation. This can lead to heating when the final molecule’s low-lying ro-vibrational levels are collisionally excited. The primary example is molecular hydrogen (e.g., Tielens 2005, Section 3.4; Woitke et al. 2009). In this case, \( \Gamma_{\text{dir}} = 0 \), \( G(X) \) is the photo-excitation rate and \( Q(X) \) is the photo-excitation heating per excitation derived from collisional de-excitation. The most important case of \( H_2 \) is discussed in Section 3.2.

The chemical reactions initiated by photodissociation also produce species in excited states that can lead to heating following collisional dissociation. This excitation energy is not always negligible, and it introduces a significant dependence on density due to variations in the critical density from transition to transition. The critical density for a transition \( u \rightarrow l \) is \( n_{ul,t}^2 = A_{ul,t}/k_{ul,t} \), where \( A_{ul,t} \) is the effective A-value of the transition and \( k_{ul,t} \) is the rate coefficient for collisional de-excitation. Depending on the nature of the transition, both \( A_{ul,t} \) and \( k_{ul,t} \) can vary widely. Again \( H_2 \) provides an important example where the critical densities of the pure rotational transitions are \( \sim 10^3 \)–\( 10^4 \) cm\(^{-3} \) for modest excitation temperatures, whereas those for ro-vibrational transitions are many orders of magnitude larger, \( \sim 10^{10} \) cm\(^{-3} \) (Le Bourlot et al. 1999). Taking into account the possible large differences in excitation energy, the resulting chemical heating is very sensitive to density. Indeed, the small scale of the pure rotational energy of \( H_2 \) compared to the level of chemical heating (tenths versus several eV) means that the former can usually be ignored.

In the next section, we estimate the heating energy \( Q(X) \) for some abundant neutrals X in interstellar and circumstellar matter. We assume that the FUV photo-rate \( G(X) \) and the run of density \( n(X) \) are known for each application. Not only is the photo-rate sensitive to the details of the radiation source, it is altered by attenuation and scattering, which are sensitive to composition. Beyond the first two factors in Equation (3), the heating energy also depends on the temperature and chemical composition of the gas. In a self-consistent model of the gas, the photochemical heating rates in Equation (3) would be included in the heat equation, and thus affect the density and temperature. We do not attempt to make such complete models here but only estimate the rough magnitudes of the heating rates for two extreme density regimes. We discuss but do not treat in detail gas heating due to the photoelectric effect on dust particles (Tielens 2005, Section 3.3) or heating by cosmic-ray- or X-ray-generated electrons (GGP12), which are both treated in the cited references. In general, dense gas is dissociated and ionized by FUV, X-rays, and cosmic rays. Model calculations of gas thermal properties should include heating from all of these sources, as developed here and in GGP12. Other than the formation of molecular hydrogen, the entire analysis in this paper is based on gas phase chemistry.

The approach followed in this paper is based on previous experience in modeling PDRs and protoplanetary disks which helps identify the most abundant species in the molecular regions of interest. The detailed estimates for specific cases that follow should serve as paradigms for the calculation of...
photochemical heating for situations not treated here. An alternate approach was introduced by Clavel et al. (1978) and recently used by Du & Bergin (2014) for protoplanetary disks. A similar methodology has been employed in PDR codes (Le Petit et al. 2006; Rollig et al. 2007). Clavel et al. simply added up all of the energy yields for the exothermic reactions in their thermal-chemical model of dark clouds. They pointed out that this method is prone to over-estimating the chemical energy because it assumes that all of the energy yield goes into the kinetic energy of the products of chemical reactions and thus into heating. Indeed, much of the following discussion deals with the extent to which the available energy goes into heating, as opposed to excitation and fluorescence. The special focus of the present paper is on the heating associated with the absorption of external FUV radiation.

3. PHOTOCHEMICAL HEATING OF ABUNDANT SPECIES

Photodissociation and chemical heating depend on the electronic structure of the individual species. In this section we show how photochemical heating is obtained for some of the more important species that arise in applications to interstellar and circumstellar matter. In accord with Equation (3), photochemical heating is important only where the relevant FUV flux and the density of the absorber are significant. The examples discussed here were chosen because they are operative in the inner regions of protoplanetary disk atmospheres. We start with atomic carbon, which at first sight might seem to be the simplest case. However, unlike the other molecular species treated in this section, it is more complicated because of the enhanced reactivity of C\(^+\) as compared to the neutral fragments mainly generated by molecular photodissociation. The case of atomic carbon illustrates another issue, which is that it may not be very abundant where the reactants exist that can lead to photochemical heating. In photodissociation reactions, C is transformed into CO, often passing first through C\(^+\). The formation of CO depends on the formation of H\(_2\) and H\(_2\)O, CO, and C are all destroyed by photons in the same FUV band, with H\(_2\) eventually generating most of the attenuated energy. In transition regions from atomic to molecular, photoinitiation of C may occur in the presence of H\(_2\), and this indeed occurs in the inner atmospheres of protoplanetary disks. However, even this case is complicated because heavier molecules may also form if the disk is sufficiently warm, and then C\(^+\) is destroyed by other molecules such as H\(_2\)O and H\(_2\).

3.1. Atomic Carbon

With an ionization potential of IP = 11.26 eV, the ionization threshold of atomic carbon is 1101 Å. The photoionization cross-section varies by no more than 10% in the interval between 911.7 and 1101 Å (Canto et al. 1981) with an average value of \(1.58 \times 10^{-17} \text{ cm}^2\). The energy generated by the reaction,

\[ h\nu + C \rightarrow C^+ + e \]

is

\[ \Delta E = h\nu + E_{\text{excn}}(C) - E_{\text{excn}}(C^+) - \text{IP}(C), \]

where \(E_{\text{excn}}(C)\) and \(E_{\text{excn}}(C^+)\) are the excitation energies of the initial atom and the final ion. For the moderate-temperature molecular environments under consideration, they are just the excitations of the ground fine-structure levels of C and C\(^+\) and no more than 0.00743 and 0.0165 eV, respectively. Such small quantities can be ignored in considering heating energies of order 1 eV or more. Thus a good estimate of the direct heating energy is

\[ Q_{\text{dir}}(C) = h\nu - \text{IP}(C), \]

where \(\nu\) is the spectrum- and cross-section-weighted average frequency. Assuming for purposes of estimation that the incident FUV radiation is roughly constant in the 911.7–1101 Å band, and recalling that the cross-section is almost constant, then the mean photon energy is 12.4 eV and the direct photochemical heating for atomic C is

\[ Q_{\text{dir}}(C) = 1.14 \text{ eV}. \]

This estimate applies to both diffuse and dense gas. It is often cited as the heating from the photoionization of C in neutral gas (e.g., Tielens 2005, Sections 2 and 3), but it is only a small part of the story, as shown below.

The chemical heating of C\(^+\) depends on the abundance of the species with which it interacts. In molecular regions, H\(_2\) is the obvious candidate, but the relevant rate coefficients are small at low temperatures\(^8\), i.e.,

\[ k(C^+ + H_2 \rightarrow CH + H) = 7.5 \times 10^{-10} \times e^{-4620/T} \text{ cm}^3 \text{s}^{-1}, \]

and

\[ k(C^+ + H_2 \rightarrow CH_2 + h\nu) \sim 4.0 \times 10^{-16} \text{ cm}^3 \text{s}^{-1}, \]

where \(k\) stands for rate coefficient (units of cm\(^3\) s\(^{-1}\)). Reaction (R1) is slightly endothermic, whereas Reaction (R2) is exothermic, but its rate coefficient is small because it is a radiative process. The value for (R1) is an approximate fit to the experimental values determined by Herráez-Aguilar et al. (2014). Oxygen molecules such as water are readily formed by radical reactions in warm regions with \(T > 300 \text{ K}\), and we will also estimate the chemical heating from the reaction:

\[ k(C^+ + H_2O \rightarrow HCO^+ + H) = 2.1 \times 10^{-9} \text{ cm}^3 \text{s}^{-1}. \]

At temperatures near 1000 K, characteristic of the molecular transition region in protoplanetary disks at small radii, Reactions (R1) and (R3) are both important, and we calculate their chemical heating for warm (>300 K) and strongly molecular regions (\(x(H_2) \gg x(H)\)). If H\(_2\)O is not present or has a low abundance, as in cool interstellar clouds, then the reaction of C\(^+\) with H\(_2\)O can be ignored.

3.1.1. Chemical Heating of C\(^+\) Reacting with H\(_2\)

Following the initiating Reaction (R1), successive fast exothermic reactions with H\(_2\) lead to CH\(_3\)\(^+\). The next H\(_2\) hydrogenation reaction is endothermic by \(\sim 2.6\) eV, and CH\(_3\)\(^+\) is

\(^8\) A list of two-body reactions is given in Table 8 at the end of the paper along with their maximum energy yields obtained from Table 9, which gives the chemical energies of the relevant species.
destroyed by fast dissociative recombination with electrons,

\[ k(e + CH_3^+ \rightarrow \text{products}) = 2.0 \times 10^{-5} T^{-0.61} \text{cm}^3\text{s}^{-1}. \]  

(R4)

The products and branching ratios (Thomas et al. 2012) are given in Table 1.

The CH radicals produced in branches 2 and 3 are converted into CH$_2$ by the neutral reaction with H$_2$ with a rate coefficient:

\[ k(CH + H_2 \rightarrow CH_2 + H) = 2.9 \times 10^{-10} \times e^{-1670/T} \text{cm}^3\text{s}^{-1}. \]  

(R5)

The rate coefficient for the reaction of CH$_2$ with H$_2$ is very small, and instead CH$_2$ interacts with atomic oxygen to produce CO:

\[ k(O + CH_2 \rightarrow CO + 2H) = 2.0 \times 10^{-10} \times e^{-270/T} \text{cm}^3\text{s}^{-1}, \]  

(R6a)

\[ k(O + CH_2 \rightarrow CO + H_2) = 1.4 \times 10^{-10} \times e^{-270/T} \text{cm}^3\text{s}^{-1}. \]  

(R6b)

The overall effect of all of these reactions that follow from the photoionization of atomic C can be assessed by adding all of the contributing reactions, i.e., Equation (4), Reaction (R1), the three fast ion-hydrogenation reactions (CH$_3^+ + H_2 \rightarrow CH_2H_2^+ + H$, $n = 0$–2), the CH$_3^+$ dissociative recombination Reaction (R4) with branching ratios in Table 1, and Reactions (R6a) and (R6b) for the production of CO. Table 2 lists the net energy production from all of these reactions for each dissociative recombination branch. Each entry conserves energy and species number. There are now seven rows instead of four because the formation of CO (Reactions (R6a) and (R6a)) has two outcomes with weights of 60% and 40%. The fourth column gives the total available energy, $\Delta E$, including direct heating of 1.14 eV. The remainder goes into heating and excitation. Some of the branch energies exceed the mean incident photon energy of 12.4 eV, as expected on the basis of the discussion in Section 1.

The last column in Table 2 is the number of H atoms produced in each branch from the chemical reactions generated by the C$^+$ ion in the photoionization of atomic C. There are implications for gas heating from the energy generated in the formation of H$_2$ on grains,

\[ H + H + Gr \rightarrow H_2 + Gr^*. \]  

(R7)

The symbol Gr$^*$ indicates that the grain is left excited in the H$_2$ formation process. The rest of the 4.5 eV binding energy goes into the kinetic and internal excitation energy of the newly formed molecule. Some of this energy can heat the gas and is often referred to as H$_2$ formation heating, but the partitioning into H$_2$ kinetic and excitation energy and grain excitation is poorly understood. A frequent assumption is that there is equipartition among the three possibilities. However, on the basis of laboratory experiments by Lemaire et al. (2010), we have modeled protoplanetary disks assuming that $\sim$30% of the binding energy ($\sim$1.3 eV) goes into the ro-vibrational excitation and very little into kinetic energy (Ádámkovics et al. 2014; henceforth AGN14). Recovery of the excitation energy as heat requires high densities to collisionally de-excite the molecules, $\leq 10^9\text{cm}^{-3}$ for pure rotational transitions and much higher densities for vibrational excitation, $10^6$–$10^{11}\text{cm}^{-3}$ (Le Bourlot et al. 1999). By way of comparison, the Meudon PDR code uses twice this H$_2$ excitation energy and a small amount of kinetic energy $\sim$0.6 eV (Le Bourlot et al. 2012). If $\Delta E(H_2)_{\text{form}}$ is the heating from the formation of an H$_2$ molecule, then each dissociation channel in Table 2 leads to additional heating of $N(H)\Delta E(H_2)_{\text{form}}$, where $N(H)$ is the number of H atoms generated given in the last column of Table 1. Each photochemically produced H atom combines with the required second atom on a grain surface. With an average value of $N(H) = 5$, H$_2$ formation heating is comparable to the chemical energy in the fourth column of Table 2, which does not include H$_2$ formation heating. H$_2$ formation heating is usually included in thermal-chemical calculations of interstellar and circumstellar matter as a general heating process; it is not explicitly tabulated here to avoid duplication with the usual treatment. It is of course important to remember that $\Delta E(H_2)_{\text{form}}$ depends on the density of the gas and on the properties of the grain surface, particularly on the assumption that the grains have atomic hydrogen accessible for molecule formation. The kinetic part is generally available in any H$_2$ region, whereas the H$_2$ excitation energy requires high densities to be converted into heating. One case where this distinction vanishes is the very high density regions of protoplanetary disks. However, the exact value of H$_2$ formation heating remains uncertain, as discussed, for example, by Bechellerie et al. (2009) and Le Bourlot et al. (2012).

Table 2 lists 8.0 eV as the mean energy available following the photoionization of a C atom and leading mainly to the formation of CO. Not all of this is available for heating, however, except possibly at very high densities. Because Reaction (R1) is slightly endothermic and the subsequent hydrogenation reactions are slightly exothermic, the energy produced just to reach CH$_3^+$ via $h\nu + C + 3H_2 \rightarrow CH_3^+ + 3H$ is only 1.7 eV. Of this, 1.1 eV goes into the kinetic energy of the photoelectron, and 0.6 eV is shared between the kinetic energy of the H atoms from the hydrogenation and excitation of the hydrocarbon ions CH$_3^+$ ($n = 1$–3). Assuming equal sharing between kinetic and excitation energy, the heating generated by forming CH$_3^+$ is $\approx$1.4 eV.

The dissociative recombination of the CH$_3^+$ ion provides energetic H atoms and H$_2$ molecules that can heat the gas directly. Other than the branching ratios, however, there is very little experimental information on the energetics of the dissociative recombination of CH$_3^+$ except for the fourth branch (with an available energy of 3.4 eV) where half the time the C atom is produced in the $^1\text{D}_2$ level at 1.26 eV (Thomas et al. 2012). For a handful of cases where storage ring experiments provide information on the energetics of the dissociation of heavy molecular ions, the results vary widely (e.g., Thomas et al. 2005; R. D. Thomas 2015, private communication).
We estimate that, on average, there is equal sharing between kinetic and excitation energy in both the production and recombination of CH$_3^+$. Thus, of the $\approx$1.7 eV available in the production of CH$_3^+$ from C$^+$, direct heating accounts for 1.1 eV and 0.6 eV for heating and excitation, for an estimated heating of $\approx$1.4 eV. Of the 6.3 eV available from the dissociative recombination of CH$_3^+$, $\approx$3.1 eV might be available for heating. Adding in the 1.14 eV in direct heating, there is an estimated 4.6 eV in heating and an additional 3.4 eV in excitation.

To summarize, the heating made available from the photoionization of atomic C and the subsequent interaction of the C$^+$ ion with H$_2$ is in two limiting cases: (i) $\approx$4.6 eV for moderately dense H$_2$ regions, i.e., those not dense enough for newly formed species to be collisionally de-excited; and (ii) $\approx$8 eV for very high density regions where collisional de-excitation is effective. In both cases, the direct heating of 1.14 eV has been included in these estimates.

3.1.2. Heating of C$^+$ Reacting with H$_2$O

The primary reaction of C$^+$ with H$_2$O leads to HCO$^+$ and ground state H:

$$k(C^+ + H_2O \rightarrow HCO^+ + H) = 2.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}. \quad (R3)$$

This is followed by the dissociative recombination of HCO$^+$, which 87% of the time leads to CO + H and has the measured rate coefficient (Hamberg et al. 2014).

$$k(e + HCO^+ \rightarrow CO + H) = 1.8 \times 10^{-5} T^{-0.79} \text{ cm}^3 \text{ s}^{-1}. \quad (R8)$$

The combined effect of Reactions (R3) and (R8) is

$$e + C^+ + H_2O \rightarrow CO + 2H, \quad (8)$$

which has a maximum energy yield of 12.7 eV, 5.25 eV from Reaction (R3) and 7.46 eV from Reaction (R8). The heating from the formation of two H$_2$ molecules is not included here for the reason discussed in the previous subsection. Some fraction of the energy from Equation (8) may lead to excitation that can be recovered at very high densities. We estimate that 50% of the 5.25 eV available from Reaction (R3), or 2.6 eV, leads to heating at moderate densities with the full amount becoming available at very high densities.

The CO produced in the recombination of HCO$^+$ may be in the ground level ($X^1Σ^+$, $\sim$ 50%) or the next two electronic levels ($a^3Π$, 6.0 eV; $\sim$ 25%) and ($a'$ $^3Π^+$, 6.3 eV; $\sim$ 25%) according to Hamberg et al. (2014). The excited levels are slow to decay to the ground level, e.g., $A(a \rightarrow X) = 133 \text{ s}^{-1}$, and collisional de-excitation requires H$_2$ densities greater than $10^{12}$ cm$^{-3}$. Thus, only a small amount of energy is available for heating when the recombination of HCO$^+$ is to excited electronic levels of CO, $\approx$1.0 eV. On averaging over both outcomes for the dissociative recombination of HCO$^+$, $\sim$4.2 eV is available for kinetic energy and excitation instead of 7.5 eV. If equal amounts go into kinetic energy and excitation, then the recombination of HCO$^+$ leads to heating of $\sim$2.1 eV at moderate densities and twice that at very high densities.

To summarize, these estimates of C$^+$ reacting with H$_2$O lead to the following contributions to photochemical heating for (i) moderately dense regions: 1.1 eV direct, 2.6 eV from Equation (R3), and 2.1 eV from Equation (R8) for a total of 5.8 eV; and (ii) very dense regions: 1.1 eV direct, 5.2 eV from Equation (R3), and 4.2 eV from Equation (R8) for a total of 10.6 eV.

3.1.3. Summary of C$^+$ Chemical Heating

The chemical heating per photoionization $Q_{chem}(C)$ depends on the probabilities and energy yields for C$^+$ reacting with H$_2$ or with H$_2$O, i.e., $f(C^+ + H_2)$ and $f(C^+ + H_2O)$, and the corresponding energy yields, $\Delta E(C^+ + H_2)$ and $\Delta E(C^+ + H_2O)$,

$$Q_{chem}(C^+) = f(C^+ + H_2) \Delta E(C^+ + H_2) + f(C^+ + H_2O) \Delta E(C^+ + H_2O). \quad (9)$$

The fractions depend on the corresponding rate coefficients and abundances:

$$f(C^+ + H_2) = \frac{k(R1) x(H_2)}{k(R1) x(H_2) + k(R3) x(H_2O)}.$$  \hspace{1cm} (10)

$$f(C^+ + H_2O) = \frac{k(R3) x(H_2O)}{k(R1) x(H_2) + k(R3) x(H_2O)}.$$  \hspace{1cm} (10)

Because Reaction (R1) has a substantial energy barrier, $f(C^+ + H_2)$ is much less than $f(C^+ + H_2O)$ until temperatures as high as 600 K are reached. Table 3 gives the estimates for $\Delta E(C^+ + H_2)$ and $\Delta E(C^+ + H_2O)$ made in the preceding paragraphs in the two limits discussed there. Equation (10)
shows how the photochemical heating of atomic C via the reaction of C\(^+\) and H\(_2\)O depends on the abundance of H\(_2\)O and the corresponding rate coefficient. They depend explicitly on the chemistry through the abundances of H\(_2\) and H\(_2\)O and on the temperature through the rate coefficients. These numbers are significantly larger than the conventional direct heating in Equation (7), 1.14 eV, which is included in all of the entries in Table 3. If reactions with other molecules are relevant, then they would be treated in a similar manner.

### 3.2 Molecular Hydrogen

The photodissociation of H\(_2\) follows the absorption of FUV photons into excited electronic levels that decay by fluorescence to the X\(^2\Sigma\)\(^+_u\) ground level (\(~85\%) and to the 2 H(\(^3\)S\(_{1/2}\)) continuum (\(~15\%). Most of the dissociation occurs from the B\(^3\Sigma\)\(^+_u\) level starting at 11.37 eV above the ground X\(^2\Sigma\)\(^+_u\) level. Applying energy conservation to both the initial excitation reaction and the subsequent dissociation, we find that

\[
\nu_{in} + E_{excn}(X) = \nu_{diss} + D(H_2) + \Delta E_{kin},
\]

where \(\nu_{in}\) is the energy of the exciting photon, \(E_{excn}(X)\) is the initial (ro-vibrational) excitation of the target H\(_2\) molecule, \(\nu_{diss}\) is the energy of the photon emitted in the dissociation of H\(_2\), \(D(H_2) = 4.48\) eV is the dissociation energy, and \(\Delta E_{kin}\) is the kinetic energy of the dissociated H atoms.

Averaging over the incident photon energy distribution, we can use Equation (11) to estimate \(\Delta E_{kin}\), the mean direct heating per photodissociation. Assuming that the incident FUV photon spectrum is approximately uniform over the 911.7–1100 Å band, the mean value of the dissociating photon energy is \(\nu_{in} = 12.5\) eV, and the above equation becomes

\[
\nu_{diss} + \Delta E_{kin} - E_{excn}(X) = h\nu_{in} - D(H_2) = 8.0\text{ eV}. \tag{12}
\]

If the initial molecule is thermally excited with \(T_{excn} \sim 500–1000\text{ K}\), then \(E_{excn}(X) \sim 0.05–0.10\text{ eV}\) is a small and ignorable correction. The outgoing photon energy \(h\nu_{diss}\) may be lower or higher than \(E(B) - D(H_2) = 6.89\text{ eV}\): higher because the absorption may lead to an excited B state and lower because dissociation can lead to a range of continuum states above the dissociation limit. If we ignore these possibilities and approximate \(h\nu_{diss}\) by \(E(B) - D(H_2) \approx 6.9\text{ eV}\), then Equation (12) yields \(\Delta E_{kin} \sim 1.2\text{ eV}\) with considerable uncertainty, possibly of the same order of magnitude. This estimate of the direct heating on dissociation of the H\(_2\) molecule assumes that the excitation energies before and after the photon is absorbed are negligible.

The heating associated with the photodissociation of H\(_2\) is only a small part of the total heating because most of the FUV radiation absorbed by H\(_2\) goes into fluorescent radiation from the B to the X ground level (\(~85\%\)), as opposed to dissociation (\(~15\%\)). Energy conservation applied to the dominant fluorescent mode reads,

\[
h\nu_{in} + E_{excn}(X) = h\nu_{flu} + E_{exfin}(X), \tag{13}
\]

where \(E_{excn}(X)\) and \(E_{exfin}(X)\) are, respectively, the initial and final average excitation energies and \(h\nu_{flu}\) is the average energy of the fluorescent photons from the B level, \(h\nu_{flu} \approx E(B) - D(H_2) = 6.9\text{ eV}\). The heating is generated by collisional de-excitation of the ro-vibrational levels of the final X ground level, and is likely to be considerably smaller than 6.9 eV.

Similar considerations of H\(_2\) photo heating were given in some detail in Section 3.4 of the Tielens (2005) textbook with the same overall conclusion, i.e., heating from collisional de-excitation of ro-vibrational levels of the ground state associated with B to X fluorescent decay is the dominant mechanism. We use his estimate for the excitation of the H\(_2\) molecule following the decay of the transition from the B to the X level, \(E_{exfin}(X) = 2\text{ eV}\), and assume that this can be recovered by collisional de-excitation at very high densities. Expressing this in terms of photodissociation rates by multiplying by 0.85/0.15, this becomes 11.5 eV per photodissociation. Combining this estimate with the 1.2 eV for direct photodissociation heating, the average total heating in dense regions is 12.5 per photodissociation.

### 3.3 Carbon Monoxide

Like H\(_2\), the photodissociation of CO, 

\[
\nu + CO \rightarrow C + O, \tag{14}
\]

proceeds by absorption of lines with wavelengths from 912–1076 Å or 11.5–13.6 eV (van Dishoeck & Black 1988; Visser et al. 2009). The high dissociation energy of CO (11.09 eV) means that only modest amounts of the incident FUV energy are available for either direct heating or product excitation. The excited levels of CO are pre-dissociating and decay mainly into the ground levels of C and O. Those incident photons close to the Lyman limit could provide enough energy to excite the first forbidden levels of either C I or O I at 1.26 and 1.97 eV, respectively, which would be collisionally de-excited at high density. However, we will ignore this possibility and assume that the small amount of energy available from Equation (14) goes into direct heating.

The mean energy of the dissociating photons is 12.5 eV, and so the energy yield of Equation (14) is \(~1.4\text{ eV}\), which we assume all goes into heating. This is a slight overestimate because we are ignoring the excitation of the C I and O I ground fine-structure levels, whose upper levels are at 0.0053 and 0.028 eV, respectively.

The dominant sources of the photochemical heating of CO are the chemical reactions initiated by the C and O dissociation products. For the O fragment, the dominant reactions in dense, warm molecular regions are

\[
O + H_2 \rightarrow OH + H, \tag{R9}
\]

and,

\[
OH + H_2 \rightarrow H_2O + H. \tag{R10}
\]

These two reactions are equivalent to

\[
O + 2H_2 \rightarrow H_2O + 2H, \tag{15}
\]

| Density          | \(\Delta E(C^+ + H_2)\) | \(\Delta E(C^+ + H_2O)\) |
|------------------|--------------------------|--------------------------|
| Moderately dense | 4.6                      | 5.8                      |
| Very dense       | 8.0                      | 10.6                     |

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with a net energy yield of 0.57 eV. Some part of this may go into the excitation of H$_2$O and OH and be converted into heat at high densities by collisional de-excitation. The maximum net chemical heating from the reactions of the O fragment is $\approx 0.6$ eV. The chemical heating from the C atom involves the reaction

$$\text{C} + \text{OH} \rightarrow \text{CO} + \text{H}, \quad (R11)$$

which has an energy release of 6.7 eV.

To summarize, this analysis of the photochemical heating of CO gives a small amount of direct heating, $Q_{\text{dir}}(\text{CO}) = 1.4$ eV, and a large amount of chemical heating, $Q_{\text{chem}}(\text{CO}) = 7.3$ eV, in very dense regions where collisional de-excitation of excited molecules is enabled. In moderately dense regions, $Q_{\text{chem}}(\text{CO}) \approx 3.6$ eV, assuming that half of the available chemical energy is in kinetic energy. In addition, three H atoms are created and contribute to H$_2$ formation heating.

### 3.4. Water

The photodissociation cross-section of water has been well measured (e.g., Lee & Suto 1986; Fillion et al. 2001; Parkinson & Yoshino 2003; Mota et al. 2005) and summarized by Mota et al. (2005). It is customary to divide the wavelength-dependent cross-section into two bands:

- **Band 1** from threshold (2475 Å) to $\approx 1450$ Å
- **Band 2** from $\approx 1450$ Å to the Lyman limit.

The cross-section in Band 1 is basically smoothly varying, with a broad maximum centered near 1650 Å. The measurements show that photodissociation in Band 1 directly yields the electronic ground states of OH and H,

$$h\nu + \text{H}_2\text{O}(\bar{X}) \rightarrow \text{OH}(X) + \text{H}(^2\text{S}_1/2) \quad (\text{Band 1}). \quad (16)$$

According to the experiment of Andersson et al. (2008), 88% of the available energy goes into fragment kinetic energy, 10% into vibrational excitation, and 2% into the rotational energy of the ground level of OH. The last two could be available for a small amount of heating after collisional de-excitation.

Shortward of 1450 Å, the Band 2 cross-section has small oscillations around a well-defined continuum, although the oscillations became very large below 1250 Å. According to experiments by Harich et al. (2000) with Ly$\alpha$ photons, there are three main channels for Band 2 photodissociation,

$$h\nu + \text{H}_2\text{O}(\bar{X}) \rightarrow \text{OH}(X^\ast) + \text{H}(^2\text{S}_1/2) \quad (\text{Branch 2a, 66%}), \quad (17)$$

$$h\nu + \text{H}_2\text{O}(\bar{X}) \rightarrow \text{OH}(A) + \text{H}(^2\text{S}_1/2) \quad (\text{Branch 2b, 13%}), \quad (18)$$

$$h\nu + \text{H}_2\text{O}(\bar{X}) \rightarrow \text{O}(^3\text{P}) + 2\text{H}(^2\text{S}_1/2) \quad (\text{Branch 2c, 21%}), \quad (19)$$

where OH$(X^\ast)$ here indicates that OH is left in highly excited levels even for $\nu'' = 0$ and 1. We ignore any possible contribution of this energy to heating.

We first estimate the direct heating from product kinetic energy for the four ways that H$_2$O photodissociates. For the relatively soft photons of Band 1, the effective photons have a mean energy of 7.5 eV, and with $D(\text{H}_2\text{O}) = 5.10$, 2.42 eV is available for heating. Using the results in Andersson et al. (2008), 88% goes into kinetic energy and the direct heating from Band 1 is

$$Q_{\text{dir}}(\text{Band 1}) = 0.88 \left[ h\nu - D(\text{H}_2\text{O}) \right] \approx 2.14 \text{ eV}. \quad (20)$$

For Branch 2a, the OH X ground level is left in highly excited rotational and vibrational states. We assume conservatively that this involves the energy equivalent of the excitation of the OH A level, 4.0 eV. Because we also assume that the critical density of the OH X transitions is very high, little of the high-OH X excitation energy is available for heating. The mean photon energy of the broad Band 2 cross-section from 1100 to 1450 Å is 9.67 eV, and a rough estimate of the available energy is

$$\Delta E_{\text{chem}}(\text{Band 2a}) \approx h\nu - D(\text{H}_2\text{O}) - E(A - X) \approx 0.57 \text{ eV}. \quad (21)$$

About one-half of this is available for direct heating. The estimate for Branch 2b is basically the same because this branch leads to OH in its first electronic level A, and so Equation (21) is a good estimate for this case. The excitation in this case is lost by fluorescence near 3000 Å because the OH A level requires very high densities for de-excitation. Finally, Branch 2c leads to the ground level of the O I atom and requires 9.51 eV to completely dissociate H$_2$O. Recalling that the mean photon energy is 9.67 eV, only $\approx 0.16$ eV is available for heating and excitation. Averaging over the branching ratios in Equations (17)–(19) and assuming one-half of this is available for direct heating, the average direct heating from Band 2 is $\approx 0.24$ eV.

All of the H$_2$O photodissociation pathways can generate chemical heating initiated by the O and OH Reactions (R9) and (R10) in warm regions and discussed in Section 3.3 on CO. Reactions (R9) and (R10) involve chemical energy changes of 0.63 eV and 0.56 eV, respectively, and roughly one-half might go directly into heating in moderately dense regions, while the full amounts might be available in very dense regions. All of these considerations are summarized by the estimates in Table 4. The chemical heating in columns 3 and 4 is based on the assumption that one-half of the chemical energy associated with the formation of OH and O and their subsequent reactions goes into heating. It is noteworthy that the photochemical heating from Bands 1 and 2 is rather different. Inspection of Equation (16) with Equations (17)–(19) shows that the outcomes from Branch 2 involve higher-energy products from which it is more difficult to extract heating as discussed above. The average value for Branch 2 is calculated

| Branch   | Direct | Chemical | Chemical | Total | $N$ (H) |
|----------|--------|----------|----------|-------|--------|
|          |        | Moderately Dense | Very Dense |       |        |
| Band 1   | 2.14   | 0.60     | 0.91     | 3.05  | 2      |
| Band 2   | 0.24   | 0.55     | 0.86     | 1.10  | 2.2    |

Note. $^a$ Units are eV per photodissociation.

### Table 4

Photochemical Heating of H$_2$O$^a$

- Branch 1: High energy release of 6.7 eV.
- Branch 2a: OH X ground level is left in high excitation.
- Branch 2b: OH A level is lost by fluorescence.
- Branch 2c: OH A level requires very high densities.

### References

- Andersson et al. (2008)
- Parkinson & Yoshino (2003)
- Mota et al. (2005)
- Fillion et al. (2001)
- Lee & Suto (1986)
- Harich et al. (2000)
by a simple average over 2a, 2b, and 2c using the branching ratios in Equations (17)–(19).

To obtain these results, we assumed that the incident FUV field was constant over Bands 1 and 2. If that is not the case, then a more accurate accounting can be obtained by carrying out a similar analysis on a smaller wavelength scale. Special attention may be required in treating the Lyα line, e.g., in the case of protoplanetary disks where it is very strong (e.g., Schindhelm et al. 2012). For densities intermediate between the limiting moderate and very dense cases used here for purposes of rough estimation, the level populations of the relevant species need to be calculated, including collisions as well as radiative decay. The last column of Table 4 indicates that a significant amount of the heating may arise from the conversion of atomic to molecular hydrogen that would be ordinarily included in H₂ formation heating.

### 3.5. OH

According to theoretical calculations by van Dishoeck & Dalgarno (1984), there are four main channels for the photodissociation of OH from 900 to 1900 Å, summarized in Table 5. The second column lists the excited OH level and the third column the energy level of the product O atom. Shortward of 1400 Å, Channels 2–4 lead to excited levels of the oxygen atom, ¹D₂ at 1.97 eV and ¹S₀ at 4.19 eV (both measured from ground). The ¹S₀ level quickly decays to the ¹D₂ level which can be collisionally de-excited. The fragment kinetic energy in the fifth column of the table is the average photon energy diminished by the sum of the OH dissociation energy 4.41 eV and the Oi excitation energies for branches 2–4. The calculations were performed by dividing each branch into 100 Å intervals, assuming that the FUV flux is constant for each branch. Because of shielding by H₂, C, CO, and N₂ from 900 to 1100 Å, the contributions from channels 3 and 4 may be significantly reduced. Of course most of the entire wavelength band from 900 to 1900 Å is shielded by dust and molecules such as water.

The O atoms may be collisionally de-excited and contribute to heating at large densities. The ¹D₂ states have relatively small A-values and are likely to be collisionally de-excited in dense regions with n_H > 10¹⁰ cm⁻³, thus leading to ~2.0 eV in heating. The ¹S₀ level has a much higher critical density, n_H > 10¹² cm⁻³, and so the emission of a 5577 Å photon is more likely than collisional de-excitation in many applications. In any case, channels 2–4 will all lead to heating of ~2.0 eV by collisional de-excitation of the ¹D₂ level, ignoring the small heating from collisional de-excitation of the fine-structure levels of the ground level.

There will also be some chemical heating from the reactions of the product radicals O and H. The chemical heating for O has already been estimated in the discussion of the photochemical heating of CO following Equation (15) and is 0.6 eV for all branches. The chemical heating for Branches 2–4 will be further enhanced by 2.0 eV by the collisional de-excitation of the ¹D₂ level. These estimates are summarized in Table 6.

### Table 5

| Branch | OH Level | Product | Wavelength (Å) | KE (eV) |
|--------|----------|---------|---------------|---------|
| 1      | ¹Σ⁺      | O(¹P₂)  | 1300–2000     | 3.5     |
| 2      | ¹Δ       | O(¹D₂)  | 1000–1500     | 3.45    |
| 3      | ³Π       | O(¹D₂)  | 1000–1300     | 5.28    |
| 4      | ⁵Σ⁺      | O(¹S₀)  | 900–1300      | 2.49    |

### Notes.

a van Dishoeck & Dalgarno (1984).

### Table 6

| Branch | Direct | Chemical Moderately Dense | Chemical Very Dense | Total Very Dense | N(H) |
|--------|-------|---------------------------|---------------------|-----------------|------|
| 1      | 3.5   | 0.6                       | 0.6                 | 4.1             | 3    |
| 2      | 3.5   | 0.6                       | 2.6                 | 6.1             | 3    |
| 3      | 5.3   | 0.6                       | 2.6                 | 7.9             | 3    |
| 4      | 2.5   | 0.6                       | 2.6                 | 5.1             | 3    |

### Notes.

a Units are eV per photodissociation.
b Total is the sum of direct plus chemical for the very dense case.

### 4. DISCUSSION

Table 7 gives an overview of the estimates of photochemical heating made in the previous section. They have uncertainties that are a good fraction of an eV per photodissociation. The potentially significant variation of the incident FUV flux with wavelength has been ignored, and the rare case of dense gas with n_H > 10¹¹ cm⁻³ has been omitted. The two cases considered here are extreme in the sense that one (moderately dense) is too low for extracting heat by collisional de-excitation and the other (very dense) is high enough for collisional de-excitation to be effective. For intermediate densities, the level populations of the relevant species need to be calculated, including the effects of collisions as well as radiative decay. In the case of atomic C, two values are given corresponding to the destruction of C⁺ by reaction with H₂ and H₂O discussed in Section 3. For OH, a cross-section-weighted average over the four branches in Table 6 was made. In the case of H₂O, a simple average was taken of the two bands in Table 4. The last column gives the average number of H atoms they generate. The associated photochemical heating has been omitted because it is usually included in H₂ formation heating.

### Table 7

| Absorber | Direct | Chemical Moderately Dense | Chemical Very Dense | Total Very Dense | N(H) |
|----------|-------|---------------------------|---------------------|-----------------|------|
| C⁺       | 1.1   | 3.5, 4.7                  | 6.9, 9.5            | 8.0, 10.6       | 5    |
| H₂       | 1.2   | 1.2                       | 11.3                | 12.5            | 2    |
| CO       | 1.4   | 3.6                       | 7.3                 | 8.7             | 3    |
| H₂O      | 1.2   | 0.6                       | 0.9                 | 2.1             | 2.1  |
| OH       | 3.6   | 0.6                       | 1.9                 | 5.5             | 3    |

### Notes.

a Units are eV per photodissociation.
b Total is the sum of direct plus chemical for the very dense case.
c The two values correspond to C⁺ reactions with H₂ and H₂O, respectively.
Some rough generalizations are apparent from Table 7. The three species whose photo-destruction comes from the 912–1100 Å band, i.e., H$_2$, CO, and C, provide little direct heating but a large amount of chemical heating. By contrast, the two species with smaller dissociation energies absorb the FUV band over a wide range of wavelengths and generate roughly comparable amounts of direct and chemical heating. All of the species considered generate a significant amount of total heating for each photodissociation. Because several are abundant in PDRs, photochemical heating has the potential to affect the thermal balance of dense molecular regions.

An important conclusion to be drawn from these estimates of photochemical heating is that the results depend on density (as indicated by columns 3 and 4 in Table 7) and in some cases on temperature (as in the case of atomic C). The present estimates deal only with two extreme density regimes. Because of the dependence on density and temperature, there is no single value for the photochemical heating, even for a given species, except in the special case of a completely uniform model of a molecular gas cloud. More generally, photochemical heating needs to be calculated according to the local physical properties, with special attention given to the collisional de-excitation of the products of the initial photodissociation and the subsequent chemical reactions.

Despite these warnings concerning the limitations of the estimates in Table 7, one can still get a rough idea about the magnitudes in these particular cases by comparing the direct heating in column 2 and the estimated maximum heating for the very dense case in column 5. The values of the direct heating for the five species are all between 1 and 2 eV, except for the rather large value of 3.6 eV for OH, where it tends to dominate the total heating. Thus the total heating for OH in the two limits is 4.2 and 5.5 eV, and so adopting the average value of 4.8 eV for the photochemical heating of OH will lead to errors of only 20%. The water molecule is another special case because the chemical heating is not very different in the two limits in Table 7. A good approximation for the total heating of H$_2$O is the average of 1.8 and 2.1 eV for the moderately dense and the very dense limits, or 2.0 eV. The situation for the three species whose dissociation occurs in the 912–1100 Å band is quite different because the direct heating is small and also because the chemical heating in the moderately dense and the very dense limits are rather different. The exception is CO where the average value of the total heating, 6.8 eV, is a fair approximation in both limits. The important case of H$_2$, and also atomic C, have to be treated in detail, as suggested in the previous paragraph. For applications where other species are of interest, the treatment of the five species in Table 7 should serve as a guide for obtaining preliminary estimates.

The entries in column 5 of Table 7 for the total heating of very dense regions of order 10 eV also illustrate the possibility of the total heating exceeding the initial photon energy. This becomes clear when the energy gain from H$_2$ formation is considered. The photodissociation of CO provides a good example where the dissociation products, C and O, react to reform CO (C + OH → CO + H; Equation (R11)) and H$_2$O (O + 2H$_2$ → H$_2$O + 2H; Equation (15)) and generate 3 H atoms that can form H$_2$ molecules on dust grain surfaces. As discussed in Section 3.1.1 after Table 2, the magnitude of H$_2$ formation heating is quite uncertain but if we use our estimate of 1.3 eV as an example of what might be recovered at very high densities, then the total photochemical heating of CO is ~12.6 eV, which is close to the mean energy of the dissociating photons. The example of CO also shows how, following photodissociation of CO, it may be quickly replaced by the chemical reaction of the product atomic C. When the results of Table 7 are included in a full-scale thermal-chemical model for protoplanetary disks, a steady state in temperature and chemical abundances is reached in which the net production and destruction of every species are balanced and the photochemical heating (and every other heating mechanism) is balanced by gas cooling processes.

One can also see from Table 7 that, with several of the total heating energies of order 10 eV per photodissociation in dense regions, FUV photochemical heating dominates cosmic-ray heating. This is true even in only moderately dense regions. Although cosmic rays generate ~10 eV per ionization (GGP12), there are typically one million fewer cosmic-ray ionizations than FUV dissociations. The situation changes for thick clouds where the photo-transition region becomes optically thick to FUV radiation through absorption by dust and various neutral species.

More relevant than cosmic rays is the comparison between photochemical heating and photoelectric heating by dust and other small particles (e.g., PAHs), generally believed to be the most important heating source for the ISM (Tielens 2005, Section 3.3.3; Draine 2011, Section 30.2). Both of these heating mechanisms are initiated by the broadband FUV flux and yield significant levels of heating per event: ~2 eV for the case of photochemical heating of H$_2$O from Table 7 and ~5 eV for photoelectric heating (Tielens 2005). Other differences can arise from the cross sections for the two processes and abundance factors.

For the photoelectric effect, we use the standard ISM dust cross-section per H nucleus, ~10$^{-21}$ cm$^2$, ~10$^{-21}$ cm$^2$ (Spitzer 1978, Equations (7)–(23)), and an efficiency of ~0.1 for charged grains (Draine 2011, Section 30.2) and obtain an effective photoelectric cross-section for heating of 10$^{-22}$ cm$^2$. For H$_2$O, the mean cross-section for Bands 1 and 2 is ~2.0 × 10$^{-18}$ cm$^2$. With an H$_2$O abundance of ~10$^{-4}$ for very dense regions, the effective cross-section per H nucleus is then ~2 × 10$^{-22}$ cm$^2$. Taking into account the smaller heating per photodissociation from Table 7, H$_2$O photochemical heating can be comparable to photoelectric heating in very dense regions. This result is of course sensitive to assumptions about grain properties and the water abundance, and so the present estimate may not apply in all cases. For example, for those moderately dense regions of the interstellar medium where the H$_2$O abundance is small, the photochemical heating will be reduced and grain photoelectric heating will dominate.

According to the above estimate, photochemical heating may well dominate photoelectric heating in the atmospheres of the inner regions of protoplanetary disks where both the grain surface area and the PAH abundance are likely to be reduced. How these atmospheres are heated is a long standing issue (e.g., Glassgold et al. 2004, henceforth GNI04). Most modeling papers on protoplanetary disks consider a variety of heating mechanisms, and photoelectric heating often plays an important role (e.g., Gorti & Hollenbach 2004, 2009, 2011; Nomura et al. 2007; Woitke et al. 2009; Woods & Willacy 2009; Bruderer 2013). An exception is GNI04 and models derived from that study, most recently AGN14. In this work, standard thin-disk heating,

$$\Gamma_{acc} = \frac{9}{4} \alpha H_{\nu} c^2 \Omega, \quad (22)$$
is generalized to three dimensions, $\Omega$ is the angular rotation speed, $\rho \approx (1 + 4x(\text{He})) n_{\text{H}}M_{\odot}$ is the local mass density of the gas, $c$ is the local sound speed for gas temperature $T$ ($c^2 = kT/m$), and the mean particle mass is

$$m = \frac{1 + 4x(\text{He})}{1 - x(H_2) + x(\text{He}) + x_e} n_{\text{H}}.$$  \hspace{1cm} (23)

Equation (22) can be written in a numerically useful form (units, erg cm\(^{-3}\) s\(^{-1}\)):

$$\Gamma_{\text{acc}} = \frac{1}{3 \sqrt{\pi}} \frac{1}{(2e^3)} \frac{\alpha_h}{M_e} \left( \frac{T}{800 \text{ K}} \right)^{3/2} \left( \frac{\text{AU}}{r} \right)^{3/2}.$$  \hspace{1cm} (24)

$\alpha_h$ is a three-dimensional (3D) phenomenological parameter of the order of unity on the surface of the disk, in contrast to the usual average value of the standard $\alpha$-disk parameter $\sim 0.01$. In addition to the arguments given in Section 3.2 of GNN04, this formulation of accretion heating is supported by recent simulations of the magneto-centrifugal instability by Hirose & Turner (2011) and Bai & Stone (2013).

For purposes of comparison with photochemical heating, we evaluate Equation (24) for a T Tauri star with mass $0.5M_\odot$ and inner disk-atmosphere physical conditions corresponding to the surface region just below the transition between the upper hot atomic and the warm molecular regions: $T = 800$ K, $n_{\text{H}} = 10^{10}$ cm\(^{-3}\), and $\alpha_h = 0.5$, following AGN14. The accretion heating rate per unit volume in this case is then

$$\Gamma_{\text{acc}} = 1.08 \times 10^{-20} \text{ erg s}^{-1} \left( \frac{\alpha_h}{0.5} \right) n_{\text{H}} \left( \frac{T}{800 \text{ K}} \right) \left( \frac{\text{AU}}{r} \right)^{3/2}.$$  \hspace{1cm} (25)

This may be compared with the photochemical heating rate for H\(_2\)O based on Equation (2) for the same conditions at 1 AU and an H\(_2\)O abundance of $10^{-4}$.

$$\Gamma_{\text{phchem}}(\text{H}_2\text{O}) = 1.5 \times 10^{-20} \text{ erg s}^{-1} n_{\text{H}}.$$  \hspace{1cm} (26)

Thus, at 1 AU at the top of the molecular region, the photochemical heating rate from H\(_2\)O is estimated to be about the same as the accretion heating in Equation (25). Photochemical heating is sensitive to the FUV flux level and to the H\(_2\)O abundance, and both of these quantities are varying rapidly at the top of the molecular transition layer, and they also depend on radius. The above estimate was made with a T Tauri star FUV luminosity of $5 \times 10^{31}$ erg s\(^{-1}\). The atlas of Hubble Space Telescope FUV luminosities of T Tauri stars (Yang et al. 2012) shows luminosities that are much larger and mainly much smaller than our choice. Therefore, FUV heating may not be important for T Tauri stars with small FUV luminosities. Because FUV and accretion luminosities correlate, significant photochemical heating may only apply to high accretion sources.

5. CONCLUSION

The main conclusion of this paper is that heating from the absorption of FUV radiation by neutral species in dense molecular gas can be dominated by the energy yield from the chemical reactions induced by the products of photodissociation or photoionization. The total heating, referred to here as photochemical heating, consists of heating from the slowing down of the initial photo-fragments (direct heating) and the energy released by the ensuing chemical reactions (chemical heating). The products from both processes are often excited and, if the density is high enough, some of the excitation energy can be converted into heating by collisional de-excitation and lead to a significant amount of heating. A good example is provided by H\(_2\), where formation on grains produces rovibrationally excited molecules, and FUV absorption yields electronically excited molecules whose fluorescent decay leads to excitation of ro-vibrational levels.

When the reactions of the photo-fragments are considered, atomic H is a likely product, either because it is itself a fragment or another radical such as O or C generates it in reaction with H\(_2\). We have not included the heating obtained when these atoms form H\(_2\) on grains and then, either directly or after collisional de-excitation, contribute to the total photo-chemical heating in dense regions. H\(_2\) formation heating is generally included in thermal-chemical modeling of molecular gas. Instead we have listed the mean number of atoms in Tables 2, 4, and 7. For example, this number is listed in column 6 of summary Table 7, and can then be used to estimate the total heating if the formation heating per newly formed H\(_2\) molecule is known.

The occurrence of collisional de-excitation places demands on modeling the excitation of the species involved in photochemical heating in applications where the gas density varies significantly. In principle, the excitation has to be explicitly calculated and radiative decay and collisional de-excitation treated on an equal footing. Unfortunately, the necessary rate coefficients are not always known. In this paper, directed mainly to demonstrating proof of principle, we made approximate estimates of the photochemical heating in two limits that are either dense enough or not dense enough for collisional de-excitation to play a significant role. Our estimates may also be uncertain because they are restricted to a limited set of chemical reactions.

Another important conclusion of this study is that the magnitude of the total photochemical heating can be significant in the sense that it is comparable to, and even larger than, other familiar heating processes. This result is well illustrated by the case of the dense upper atmospheres of the inner regions of protoplanetary disks. This example also shows how photochemical heating is affected by the attenuation of the FUV radiation. More detailed modeling of the role of photochemical heating in protoplanetary disk atmospheres is underway and will be reported in subsequent publications.

The authors are pleased to acknowledge support from NASA grant NNG06GF88G (Origins of Solar System). They are also grateful for helpful discussions with Maté Adámkovics.

APPENDIX

Table 8 contains a list of the main reactions, and Table 9 gives the chemical energies of the relevant species in terms of the enthalpies $\Delta H$ at STP, i.e., 300 K. They can differ from ground state energies by as much as a few tenths of an eV. The standard unit, kcal mole\(^{-1}\), is used, with 1 eV = 23.06 kcal mole\(^{-1}\) and 1 kcal mole\(^{-1}\) = 4.1854 kJ mole\(^{-1}\). For the neutral species, a good reference is Table 3.1 of Baulch et al. (Baulch et al. 2005, “Evaluated Kinetic Data for
### Table 8
Main Reactions

| No.  | Reaction                        | Rate Coefficient (cm³ s⁻¹) | ΔEchem (eV) | Reference                  |
|------|--------------------------------|----------------------------|-------------|----------------------------|
| (R1) | C⁺ + H₂ → CH⁺ + H               | 7.5 × 10⁻¹⁰ s⁻¹            | −0.35       | (1)                        |
| (R2) | C⁺ + H₂ → CH₂ + hν              | 4.0 × 10⁻¹⁶              | 4.47        | (2)                        |
| (R3) | C⁺ + H₂O → HCO⁺ + H             | 2.1 × 10⁻⁹              | 5.33        | (3)                        |
| (R4) | CH₃ + e → products              | 2.0 × 10⁻⁷ s⁻¹           | 3.24        | (4)                        |
| (R5) | CH₃ + H₂ → CH₄ + H              | 1.80 × 10⁻²¹ s⁻¹        | 7.46        | (5)                        |
| (R6b) | O + CH₃ → CO + 2H               | 2.0 × 10⁻¹⁷ s⁻¹         | 3.22        | (5)                        |
| (R6b) | O + CH₃ → CO + H₂              | 1.4 × 10⁻¹⁰ s⁻¹         | 7.73        | (5)                        |
| (R7) | H + H + Gr → H₂ + Gr*           | §/2 n(H)ν(HνΔ > ½ΔF > ½αJ) | 4.48        | (6)                        |
| (R8) | e + HCO⁺ → CO + H               | 1.8 × 10⁻⁵ s⁻¹          | 7.48        | (7)                        |
| (R9) | O + H₂ → OH + H                 | 6.34 × 10⁻¹² s⁻¹        | −0.065      | (5)                        |
| (R10) | OH + H₂ → H₂O + H               | 3.60 × 10⁻¹⁶ s⁻¹       | 0.63        | (5)                        |
| (R11) | C + OH → CO + H                 | 7.0 × 10⁻¹¹           | 6.48        | (8)                        |

References
1. Herráez-Aguilar et al. (2014), 2. McElroy et al. (2013), 3. Anichich 1993, 4. Thomas et al. (2012), 5. Baulch et al. (2005), 6. Cazaux & Tielens (2004), as discussed in detail by GMN09, 7. Herman et al. (2014), 8. Lin et al. (2008).

### Table 9
Enthalpies (kcal mole⁻¹)

| Neutral | Enthalpy | Ion      | Enthalpy |
|---------|----------|----------|----------|
| H       | 52.1     | H⁺       | 366      |
| H₂      | 0        | H₂⁺      | 356      |
|         |          | H₃⁺      | 265      |
| C       | 171.3    | C⁺       | 431      |
| O       | 59.5     | O⁺       | 374      |
| CO      | −26.4    | CO⁺      | 297      |
| HCO     | 10.4     | HCO⁺     | 198      |
| H₂CO    | −24.9    | H₂CO⁺    | 225      |
| OH      | 8.9      | OH⁺      | 360      |
| H₂O     | −57.8    | H₂O⁺     | 233      |
|         |          | H₃O⁺     | 145      |
| O₂      | 0        | O₂⁺      | 278      |
| O₃H     | 0.5      | O₃H⁺     | 262      |
| CO₂     | −94.0    | CO₂⁺     | 231      |
| O₃      | 34.1     | O₃⁺      | 323      |
| CH      | 142.0    | CH⁺      | 387      |
| CH₂     | 92.4     | CH₂⁺     | 328      |
| CH₃     | 34.8     | CH₃⁺     | 262      |
| CH₄     | −17.9    | CH₄⁺     | 273      |
|         |          | CH₅⁺     | 218      |

Combustion Modeling: Supplement II). Additional information is available at the NIST Chemical Kinetics website.¹ For ions, one needs ionization potentials and/or proton affinities pa. Much of this information is available in the NIST Chemistry WebBook.¹ A useful table for hydrocarbon ions is given by Anichich et al. (1984). For example, the enthalpy of a molecular ion is

\[ \Delta H (MH⁺) = \Delta H (H⁺) + \Delta H (M) - pa (M). \]  

(27)

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¹ http://kinetics.nist.gov/kinetics/welcome.jsp
² http://webbook.nist.gov/chemistry/
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