COSMIC-RAY AND X-RAY HEATING OF INTERSTELLAR CLOUDS AND PROTOPLANETARY DISKS

ALFRED E. GLASSGOLD\textsuperscript{1}, DANIELE GALLI\textsuperscript{2}, AND MARCO PADOVANI\textsuperscript{3}

\textsuperscript{1} Astronomy Department, University of California, Berkeley, CA 94720-3411, USA; aglassgold@berkeley.edu
\textsuperscript{2} INAF-Osservatorio Astrofisico di Arcetri, Largo E. Fermi 5, I-50125, Italy; galli@arcetri.astro.it
\textsuperscript{3} Laboratoire de Radioastronomie Millimétrique, UMR 8112 du CNRS, Ecole Normale Supérieure et Observatoire de Paris, 24 rue Lhomond, F-75231 Paris Cedex 05, France; marco.padovan@lra.ens.fr

Received 2012 May 11; accepted 2012 July 18; published 2012 August 24

ABSTRACT

Cosmic-ray and X-ray heating are derived from the electron energy-loss calculations of Dalgarno, Yan, and Liu for hydrogen–helium gas mixtures. These authors treated the heating from elastic scattering and collisional de-excitation of rotationally excited hydrogen molecules. Here we consider the heating that can arise from all ionization and excitation processes, with particular emphasis on the reactions of cosmic-ray and X-ray generated ions with the heavy neutral species, which we refer to as chemical heating. In molecular regions, chemical heating dominates and can account for 50% of the energy expended in the creation of an ion pair. The heating per ion pair ranges in the limit of negligible electron fraction from \(\sim4.3\) eV for diffuse atomic gas to \(\sim13\) eV for the moderately dense regions of molecular clouds and to \(\sim18\) eV for the very dense regions of protoplanetary disks. An important general conclusion of this study is that cosmic-ray and X-ray heating depends on the physical properties of the medium, i.e., on the molecular and electron fractions, the total density of hydrogen nuclei, and, to a lesser extent, on the temperature. It is also noted that chemical heating, the dominant process for cosmic-ray and X-ray heating, plays a role in UV irradiated molecular gas.

Key words: cosmic rays – ISM: clouds – protoplanetary disks – X-rays: ISM

1. INTRODUCTION

There has been a significant increase of interest in the cosmic-ray ionization rate in both local and distant neighborhoods. Much of it has been spurred by infrared absorption-line measurements of the \(\text{H}_2^+\) ion in diffuse and translucent interstellar clouds (e.g., Indriolo et al. 2007 and references therein). Indriolo & McCall (2012) have extended these measurements to 50 lines of sight dominated by translucent clouds with more than 1 mag of visual extinction, obtaining 21 detections. Their straightforward analysis of the observations yields values of the ionization rate for \(\text{H}_2\) in the range \((2–11) \times 10^{-16}\) s\(^{-1}\), significantly larger than the range of values that had been in use for several decades.\(^4\) This result has led to the reconsideration of how both electron and proton cosmic rays propagate in the interstellar medium (e.g., Indriolo et al. 2009; Padovani et al. 2009; Padovani & Galli 2011; Rimmer et al. 2012; Everett & Zweibel 2011). In the context of the new survey, Indriolo & McCall (2012) reviewed the explanation advanced by Indriolo et al. (2009) and Padovani et al. (2009) that the intensity of low-energy protons is reduced inside dense molecular clouds. The large difference between diffuse/translucent and dense clouds is maintained in Indriolo & McCall (2012), but their sample shows little evidence for a dependence of ionization rate on column density. The value of the cosmic-ray ionization rate for the local interstellar medium remains an open question.

Another topic of interest relating to the interaction of cosmic rays with the interstellar medium is their role in heating. Cosmic rays are an efficient (often dominant) source of heating in various environments, from the dense gas in molecular clouds (Goldsmith & Langer 1978), both in normal and starburst galaxies (e.g., Suchkov et al. 1993), to photodissociation regions (Shaw et al. 2009), and possibly even in the primordial gas (Jasche et al. 2007). In dense, shielded regions like molecular cloud cores, the balance of cosmic-ray heating and gas cooling determines a temperature gradient decreasing inward (Galli et al. 2002) that has been accurately traced by interferometric observations of molecular emission in prestellar cores (Crapsi et al. 2007; Pagani et al. 2007) and dark globules (Pineda & Bensch 2007). The values for the cosmic-ray heating energy per ion pair available in the literature range over a factor of three.

In this paper, we will attempt to clarify this situation for both cosmic-ray and X-ray heating.

The interaction of fast electrons slowing down in molecular gas was first analyzed more than three decades ago by Glassgold & Langer (1973, hereafter GL73), Cravens et al. (1975), and Cravens & Dalgarno (1978). Although GL73 was the first paper to consider cosmic-ray heating in interstellar molecular regions, it suffered from the incompletely known electron cross sections of the early 1970s, a crude energy-loss calculation, and cumbersome notation. Cravens et al. (1975) did a better job on cross sections and energy loss, but restricted themselves to low-energy electrons in order to evaluate the validity of the commonly used continuous slowing down approximation. This limitation was removed by Cravens & Dalgarno (1978).

There are no glaring discrepancies between Cravens & Dalgarno (1978) and GL73. All of these papers considered pure \(\text{H}_2\) regions, i.e., the roles of \(\text{H}^+\) and \(\text{He}^+\) ions in molecular gas were ignored. A more up to date and complete analysis was carried out by Dalgarno et al. (1999, hereafter DYL). DYL considered carefully all of the energy-loss channels for electron energies from 30 eV to 1 keV in various mixtures of \(\text{H}, \text{H}_2\), and \(\text{He}\). They showed how the energy expended to make an ion pair \(W\) is partitioned between elastic and non-elastic processes, but they did not fully treat the heating.

Cosmic rays and X-rays (or the equivalent, fast electrons) produce ions and excited molecules that can interact with the dominant neutral atomic or molecular gas. The products of
these reactions carry away a significant amount of the available energy and heat the gas. We refer to this as chemical heating and quantify it by a quantity $Q_{chem}$ defined per ion pair. Chemical heating by cosmic rays and X-rays occurs in a wide range of applications from diffuse and dense interstellar clouds to pre-stellar cores, protoplanetary disks, and planetary atmospheres. In this paper, we use the results of DYL to inquire how the excited species and ions heat a gas mixture of H, H$_2$, and He. We will show that ~1/2 of the energy of X-rays and cosmic rays can go into heating in dense molecular regions and that chemical heating can be the most important part of the heating. We also note that chemical heating occurs when molecular regions are irradiated by far ultraviolet (FUV) photons.

This paper is organized as follows. In Section 2, we outline the physical basis of our analysis and make quantitative estimates in Sections 3 and 4. We discuss the most important results in Section 5. The paper ends with a short summary in Section 6.

2. THE PHYSICAL BASIS FOR COSMIC-RAY AND X-RAY HEATING

A basic tenet of earlier work on cosmic-ray heating is that proton cross sections can be represented accurately by the corresponding ones for electrons (which are generally more available), at least at sufficiently large energy. Cravens & Dalgararo (1978) discussed this explicitly on the basis of the good agreement between experiments on proton collisional ionization of H$_2$ (Hooper et al. 1961) and the Born approximation, as developed by Bates & Grifling (1953), all the way down to a proton energy of 0.06 MeV. This conclusion stems from the fact that high-energy ionization cross sections are a function of the incident particle’s speed, so proton cross sections are the same as those for electrons with the same speed, i.e., when the electron energy $E$ satisfies the relation $E = (m_e/m_p)E_p$.

An energetic cosmic-ray proton loses energy in cosmic gases in small steps that are characterized by the energy $W$ to make an ion pair, known to be close to 37 eV from extensive experimental and theoretical studies. In their interactions with the hydrogen and helium of the gas, each cosmic-ray (proton) ionization generates a distribution of relatively slow electrons with an average energy of 19 eV (Opal et al. 1971; GL73) and that lead to another “secondary” ionization two-thirds of the time. X-rays with keV energies develop a similar sequence once the initial photon is absorbed by a heavy atom by L- or K-shell electron ejection. The energy of this primary electron is $E = h\nu_X - B - \Delta E$, where $B$ is the binding energy of the K or L shell of the heavy atom and $\Delta E$ is the mean energy of the resulting ion. It is significantly less than the initial X-ray energy, but much of the difference is restored in the form of several prompt supra-thermal Auger electrons with keV energies. There is also some X-ray fluorescence that, by the processes just described, generates more fast electrons. The net effect of X-ray ionization of heavy atoms, accompanied by Auger electrons and fluorescence, is that most of the initial X-ray photon energy is recovered in the form of the primary electron plus several other fast electrons. Thus, once the processes attending the absorption of a keV X-ray have occurred, the main ionization effects of the X-ray are accomplished by the fast electrons that it produces.

The spectra of cosmic rays and X-rays can change from region to region due to proximity to a source or absorption within the cloud of interest. One example is the absorption of low-energy protons in thick clouds, proposed by Indriolo et al. (2009) and Padovani et al. (2009) to explain the reduction of the ionization rate inside dense molecular clouds. Another is the observed variation in the observed spectra of the X-rays emitted by young stellar objects. DYL give results for mono-energetic electrons with energies from 30 to 1000 eV. Their results do not vary by more than 10% for $E > 200$ eV, and if the underlying spectrum does not extend below this energy for electrons or the equivalent energy of 0.4 MeV for protons, the variation of the DYL results at low electron energy can be ignored. Otherwise the results presented in this paper have to be integrated over the appropriate spectrum. Below $E = 30$ eV (or ~60 keV protons), the lowest energy considered by DYL, one can use GL73, but the equivalence between electrons and protons has very likely broken down at this point. In this paper, we focus on electrons with energies greater than 500 eV, corresponding to protons with energies greater than 1 MeV.

We use DYL to analyze all of the outcomes of a fast electron as it slows down by interacting with a cosmic gas mixture dominated by H, H$_2$, and He, ignoring the much less abundant heavy elements. Unlike DYL, we make a comprehensive effort to evaluate how much of the energy expended in each process goes into heating—the primary goal of this paper. For this purpose, the most useful results in DYL are Table 4 (ion production), Table 5 (excitation), and Table 7 (heating efficiency), all for the case of H, He and H$_2$, He gas mixtures.

The energy partitions for a 1 keV electron in an He, H$_2$ mixture in the limit of zero electron fraction are listed in Table 1. The entries are independent of energy above 100–200 eV. If the X-ray spectrum extends below 200 eV or the cosmic-ray spectrum below 400 keV, the full tables in DYL contain the information needed for lower energies. Table 1 has been organized into four parts: ion production, excitation of H$_2$ levels, excitation of He levels, and the heating from elastic scattering combined with the heating from rotational excitation. All energies are expressed in eV. The first column names the process; the second column the energy expended for that process $W_i$; the third column the number of such processes for an electron $N_i$; the fourth column the threshold energy $E_{th}$ for the process; and lastly the energy associated with the process, i.e., the product $NE_{th}$ of the two previous columns (for $E = 1$ keV).

For example, the first four lines of Table 1 show that a keV electron generates 23.9 H$^+$ ions, 1.1 H$^+$ ions, 2.2 He$^+$ ions, and <0.1 He$^{2+}$ ions, for a total of 27.2 ions. This follows from the fact that an incident electron expends on average an energy $W_i$ to make an ion pair of type $i$ ($i = 1$ for H$^+$, $i = 2$ for H$^+$, $i = 3$ for He$^+$, and $i = 4$ for He$^{2+}$). More generally, if $N_i = E/W_i$ is the number of ions generated of type $i$, the total number of ions is $N = \sum_i N_i = \sum_i W_i^{-1}$ and the average energy per ion pair is $E/N = \left(\sum_i W_i^{-1}\right)^{-1}$.

\[ E/N = \left(\sum_i W_i^{-1}\right)^{-1}. \tag{1} \]

According to Table 1, $E/N = 36.8$ eV per ion pair for $E = 1$ keV and zero electron fraction.

The data in DYL account for 96% of the initial electron energy $E = 1$ keV in Table 1. The small deviation from 100% is not significant in light of the uncertainties in the calculations.
The Astrophysical Journal, 756:157 (11pp), 2012 September 10

Glassgold, Galli, & Padovani

Table 1

| Process                      | \( W \) (eV) | \( N \) | \( E_{\text{th}} \) (eV) | \( N E_{\text{th}} \) (eV) |
|------------------------------|--------------|-------|-----------------|-----------------|
| \( \text{H}_2^+ \)         | 41.9         | 23.87 | 15.44           | 369             |
| \( \text{H}^+ \)          | 921          | 1.09  | 18.08           | 20              |
| \( \text{He}^+ \)        | 459          | 2.18  | 24.59           | 54              |
| \( \text{He}^{2+} \)     | 16000        | 0.0625 | 54.43          | 3               |
| **Total ion production**  |              |       |                 | 446             |
| \( B \)                  | 117          | 8.55  | 11.37           | 97              |
| \( C \)                  | 132          | 7.58  | 12.42           | 94              |
| Dissociation\(^a\)       | 92.6         | 10.8  | \(~13\)         | 140             |
| \( \text{He}^+(2p) \)    | 534          | 1.87  | 14.7            | 28              |
| \( \text{He} \)          | \( = \)1     | 7.81  | 0.516           | 66              |
| \( \text{He} \)          | \( = \)2     | 109   | 9.17            | 102             |
| **Total \( \text{H}_2 \) excitation** |          |       |                 | 435             |
| \( \text{He}^2S^c \)     | 15000        | 0.0667| 20.62           | 1               |
| \( \text{He}^2P^c \)     | 1940         | 0.515 | 21.22           | 11              |
| \( \text{He}^2S^c \)     | 34900        | 0.0287| 19.82           | 1               |
| \( \text{He}^2P^c + n > 2^1 \) | 22500        | 0.0444| 21.0            | 1               |
| \( n > 2^1 \)           | 3520         | 0.284 | 23              | 7               |
| **Total \( \text{He} \) excitation** |          |       |                 | 21              |
| Elastic collisions and rotational excitation\(^a\) | |       | 57               |
| **Grand total**          |              |       |                 | 959             |

Notes.

\(^a\) For the case \( x_e = 0 \) and \( E = 1 \) keV.

\(^b\) Dissociation occurs mainly via triplet excitations.

\(^c\) He excitation follows the notation in DYLP.

\(^d\) Based on DYLP “heating efficiency” in their Table 7.

It may be due to the use of the approximate fitting formulae for the parameters \( W \), for which DYLP quote an accuracy of 5%–15%. Another possibility is the omission of triplet states starting near 14 eV that lie above the \( a, b, \) and \( c \) levels, which DYLP refer to as missing “pseudo states.” In addition, most of the cross sections used in the energy-loss process are probably not known to an accuracy of 10%. Approximately 47% of the energy in Table 1 is accounted for by ionization, 47% by excitation, and 6% by direct heating and the collisional de-excitation of \( \text{H}_2 \) rotational levels. Applying this to the 36.8 eV to make an ion pair, elastic scattering and rotational excitation lead to only about 2 eV heating per ion pair in neutral gas. However, as the ionization fraction increases beyond \( x_e = 10^{-4} \), the direct heating increases, largely due to Coulomb collisions with ambient electrons. Most cosmic-ray and X-ray heating in molecular regions comes from the reactive ions and excited states. This is exactly the part of the energy-loss problem that is not treated by DYLP.

3. THE HEATING ENERGY

In general, the heating energy per ion pair \( Q \) consists of contributions from collisions with \( \text{H} \) and \( \text{H}_2 \),

\[
Q = \frac{x(\text{H})Q(\text{H}) + x(\text{H}_2)Q(\text{H}_2)}{x(\text{H}) + x(\text{H}_2)},
\]

where \( x(\text{H}) + 2x(\text{H}_2) = 1 \); the functions \( Q(\text{H}) \) and \( Q(\text{H}_2) \) depend on the abundance of He and especially on the abundance of electrons. The volumetric rate of ion-pair production is \( \zeta_{\text{H}^+} \), where \( \zeta_{\text{H}^+} \) is the ionization rate per \( \text{H} \) nucleus and \( n_{\text{H}} \) is the volumetric density of \( \text{H} \) nuclei. Thus, the volumetric heating rate is given by \( \Gamma = Q(\zeta_{\text{H}^+}) \).

The dominant heating process in atomic regions is elastic scattering. DYLP include Coulomb collisions with ambient electrons, but only for the case where the electron abundance relative to total \( \text{H} \) nuclei is \( \lesssim 0.1 \). For negligible ionization, it is twice that for \( \text{H}_2 \) regions, as can be seen in Table 7 of the Appendix, the analog of Table 1 for atomic regions. It is included in \( Q(\text{H}) \), the first term in the numerator of Equation (2). In the Appendix, we show that chemical heating induced by the atomic ions \( \text{H}^+ \) and \( \text{He}^+ \) reacting with \( \text{H} \) is very small. As shown in Figure 8 of DYLP, the dominant excitation product in atomic \( \text{H} \) is the \( 2p \) level of atomic hydrogen. The resultant Ly\( \alpha \) photons will either escape or be absorbed by and heat the dust, and not the gas.

The heating in molecular regions is the sum of the effects from elastic collisions plus rotational excitation \( Q_{\text{el/rot}} \), excitation of \( \text{H}_2 \) vibrational levels \( Q_{\text{vib}} \), dissociation of \( \text{H}_2 \) \( Q_{\text{diss}} \), and chemical heating \( Q_{\text{chem}} \):

\[
Q(\text{H}_2) = Q_{\text{el/rot}} + Q_{\text{vib}} + Q_{\text{diss}} + Q_{\text{chem}}.
\]

In the following paragraphs we discuss the first three contributions to \( Q(\text{H}_2) \), and then focus on \( Q_{\text{chem}} \) in the next section.

3.1. Elastic Scattering and Rotational Excitation

The critical densities for the rotational levels of \( \text{H}_2 \) depend on the transition and also on the \( \text{H}/\text{H}_2 \) ratio and the temperature (e.g., Le Bourlot et al. 1999). In many situations, the lowest \( S(0) \) and \( S(1) \) rotational levels are collisionally de-excited and most of the rotational excitation goes into heating. GL73 estimated that a density \( n_{\text{H}_2} = 1000 \text{ cm}^{-3} \) would satisfy this condition on density, independent of temperature. We use DYLP for the combined heating due to elastic scattering and rotational excitation,

\[
Q_{\text{el/rot}}(\text{H}_2, e) = Q_{\text{el}}(\text{H}_2, e) + Q_{\text{rot}}(\text{H}_2, e).
\]

This quantity is then expressed in terms of a “heating efficiency” \( \eta \) for an \( \text{H}_2 \) molecule, He gas mixture,

\[
Q_{\text{el/rot}}(\text{H}_2, e) = \eta(\text{H}_2, e)W(\text{H}_2, e),
\]

where \( W(\text{H}_2, e) \) is the average energy to make an ion pair. Both \( \zeta_{\text{H}_2} \) and the heating function \( Q \) are defined in terms of ion pairs. For the \( \text{H}, \text{He} \) gas, there is of course no rotational heating, and the heating is expressed in a similar form where the heating efficiency \( \eta(\text{H}, e) \) now describes only elastic collisions,

\[
Q(\text{H}, e) = \eta(\text{H}, e)W(\text{H}, e).
\]

However, \( W(\text{H}, e) \approx W(\text{H}_2, e) \) to an accuracy of \( \approx 5\% \) for electron energies greater than several hundred eV, and the first term of Equation (3) becomes,

\[
Q_{\text{el}}(\text{H}, e) + Q_{\text{el/rot}}(\text{H}_2, e) \approx \frac{[x(\text{H})\eta(\text{H}, e) + x(\text{H}_2)\eta(\text{H}_2, e)]}{x(\text{H}) + x(\text{H}_2)} \times W(\text{H}_2, e)
\]

with \( W(\text{H}_2, e) \approx 37 \text{ eV} \) asymptotically for \( E \gtrsim 500 \text{ eV} \).

The heating efficiencies \( \eta \) are expressed by the fitting formulae, Equation (14) of DYLP,

\[
\eta = 1 - \frac{1 - \eta_0}{1 + Cx_e^\alpha}.
\]
The two sets of fit parameters are given at the bottom of Table 7 of DYL (“Two-Gas Mixtures”) as a function of electron energy $E$. For example, the $E = 1$ keV values are

$$\eta(H, e) = 0.117, \quad \alpha = 0.678, \quad C = 7.95,$$

for atomic regions, and

$$\eta(H_2, e) = 0.055, \quad \alpha = 0.366, \quad C = 2.17,$$

for molecular regions. These values might be appropriate for the keV X-rays emitted by young stellar objects. These fits have only a modest accuracy $\sim 10\%–15\%$.

According to DYL, see Table 1, $Q_{el/rot}$ accounts for only 57 eV, or $\sim 6\%$ of the energy of the 1 keV incident electron. The rest of the energy is almost equally shared by ionization and excitation of He and H$_2$. Thus, the DYL heating efficiency for molecular regions is only a small part of the total. With $W \sim 37$ eV to make an ion pair, elastic scattering and rotational excitation lead to $Q_{el/rot} = 2.1$ eV heating per ion pair in neutral H$_2$, He gas. This is half of the direct heating in an atomic H, He gas, $\sim 4.3$ eV under the same conditions.

### 3.2. Dissociation Heating

The most important pathway to dissociation is collisional excitation of H$_2$ triplet states that start at 11.9 eV ($a$ and $c$), 13.4 eV ($e$) and possibly above. These levels decay into continuum states of the triplet repulsive potential and have essentially unit probability for dissociation. Unlike the Lyman and Werner transitions to the singlet $B$ and $C$ levels, these spin-flip transitions are forbidden for photon excitation from the singlet ground state $X$. Table 1 indicates that for $E = 1$ keV and $x_e = 0$, there are 10.8 dissociations per keV. Adopting the DYL estimate of 5.4 eV per dissociation, we obtain 58 eV heating per keV, or 2.14 eV per ion pair for a neutral H$_2$, He mixture. More generally, we use Table 5 of DYL for the dissociation heating in Equation (3),

$$Q_{diss} = \frac{x(H_2)}{x(H) + x(H_2)} \frac{D_0}{1 + C x_e^\alpha},$$

where $D_0 = 2.14$ eV, $\alpha = 0.574$, and $C = 22.0$.

### 3.3. Vibrational Heating

Fast electrons can excite the vibrational levels of H$_2$ by direct collisions or by fluorescent de-excitation of electronically excited $B$ and $C$ levels. The excitation energy goes into heating if the densities are high enough for the levels to be collisionally de-excited. Recent calculations of the collisional de-excitation rate coefficients (e.g., Wrathmall et al. 2007 for H; Lee et al. 2008 for H$_2$; Balakrishnan et al. 1999 for He) replace earlier work of Tiné et al. (1997) and Le Bourlot et al. (1999). The rate coefficients are generally much larger for collisions with atomic H than for H$_2$ and He. They are very small below 100 K and increase rapidly above this temperature. Thus, one can expect little quenching of vibrational levels in the cool and moderately dense regions of molecular clouds. By contrast, in the surface layers of the inner regions of protoplanetary disks, where $n_\text{H} \sim 10^{10}$ cm$^{-3}$ and $T \sim 1000$ K, the densities of both H and H$_2$ are large enough to collisionally quench vibrationally excited H$_2$ molecules and provide significant heating. In less dense molecular regions, atomic H collisions may be effective in collisionally de-exciting H$_2$, but this depends on the temperature and the H/H$_2$ ratio as well as the total density $n_{\text{H}}$.

In order to obtain the heating from direct collisional excitation in dense H$_2$ regions, we use Table 5 of DYL for H$_2$, He mixtures which gives the following fit for the energy to excite the $v = 1, 2$ levels:

$$\epsilon_v = W_v \left(1 + C_v x_e^\alpha\right),$$

where $W_v$ is the number of excitations per keV of electron energy, the high-density direct vibrational heating per keV of incident electron energy is

$$\left(\frac{1000}{\epsilon_1} \frac{\Delta E_1}{\epsilon_1} + \frac{1000}{\epsilon_2} \frac{\Delta E_2}{\epsilon_2}\right) \text{eV}.$$  

The vibrational heating per ion pair is obtained by dividing this expression by the number of ion pairs per keV (27.2 for $E \geq 500$ eV), with the result,

$$Q_{diss/vib} \approx \frac{x(H_2)}{x(H) + x(H_2)} 19.0 \text{eV} \left[\frac{1}{\epsilon_1} + \frac{2}{\epsilon_2}\right].$$

In a pure H$_2$ region with negligible ionization, the vibrational heating per ion pair is 2.8 eV for $E \geq 500$ eV, with $v = 2$ contributing about 15%.

Excited vibrational levels are also produced when collisionally excited $B$ and $C$ states decay with the emission of fluorescent photons in the 1500–1600 Å range, with a maximum near 1575 Å. We can calculate the high-density heating that follows the collisional de-excitation of the vibrational levels using the above method for direct collisional excitation based on Equation (12). The necessary parameters again come from Table 5 of DYL for H$_2$, He mixtures.

With roughly 4 eV in vibrational excitation energy and 27.2 ion pairs per keV, the high-density $B, C$ vibrational heating per keV of incident electron energy is

$\frac{1000/\epsilon_B + 1000/\epsilon_C}{27.2} 4.0 \text{eV} = 147 \text{eV} \left[\frac{1}{\epsilon_B} + \frac{1}{\epsilon_C}\right].$

The $B, C$ vibrational heating per ion pair is then

$$Q_{BC/vib} = \frac{x(H_2)}{x(H) + x(H_2)} 147 \text{eV} \left[\frac{1}{\epsilon_B} + \frac{1}{\epsilon_C}\right].$$

If we substitute the values in Table 3 for $x_e = 0$, the result is $2.4 \text{eV}$ per ion pair for a neutral H$_2$, He gas, a small but not negligible contribution to the high-density heating.

As discussed earlier, both Equations (13) and (14) hold only if the density well exceeds the critical density $n_{cr}$ for the de-excitation of the vibrational transitions of the H$_2$ ground level.
They therefore should be multiplied by an appropriate factor $\Theta_{\text{vib}}$, that depends on the ratio $n_{\text{e}}/n_{\text{H}}$, such that $\Theta_{\text{vib}} = 0$ for small $n_{\text{e}}/n_{\text{H}}$ and $\Theta_{\text{vib}} = 1$ for large $n_{\text{e}}/n_{\text{H}}$. Their contribution to the total heating in Equation (3) is now,

$$Q_{\text{vib}} = \Theta_{\text{vib}} (Q_{\text{dir/vib}} + Q_{\text{BC/vib}}).$$

The $B$ and $C$ levels have a $\sim 15\%$ probability to dissociate (e.g., Abgrall et al. 1997), with a yield of approximately 0.25 eV in typical interstellar conditions (Tielens 2000). The small branching ratio for dissociation and the small energy yield mean that the heating per ion pair following dissociation is very small, e.g., 0.02 eV for $E = 1$ keV, and thus negligible.

## 4. CHEMICAL HEATING

Chemical heating derives mainly from reactions instigated by the primary cosmic-ray and X-ray ions, $H^+$, $H^+$, and $He^+$, with neutral species and electrons. It was first considered in the context of EUV heating of Jupiter’s upper atmosphere (Henry & McElroy 1969) and then for cosmic-ray ionization of interstellar molecular clouds (GL73). These authors focused on $H_2^+$ transformation into $H_3^+$, and the destruction of $H_2^+$ by dissociative recombination. In dense molecular regions, however, where $x_e \ll x(H_2)$, dissociative recombination has to compete against ionic reactions with neutral species. Rather than treat all of the ion–neutral reactions that can be traced to the primary ionic reactions with neutral species. Rather than treat all of the ion–neutral reactions that can be traced to the primary ionic reactions to the primary ionization of interstellar conditions (Tielens 2000). The small branching ratio for dissociation and the small energy yield mean that the heating per ion pair following dissociation is very small, e.g., 0.02 eV for $E = 1$ keV, and thus negligible.

### 4.1. Chemical Heating of $H_2$

As discussed in Section 2, the most abundant ion generated by cosmic rays and X-rays in $H_2$ regions is $H_2^+$. We first consider its main destruction routes; $H^+$ and $He^+$ ions will be analyzed later in this section. $H_2^+$ is mainly destroyed by dissociative recombination and by proton transfer with $H_2$,

$$H_2^+ + e^{-}\rightarrow H + H, \quad H_2^+ + H_2\rightarrow H_3^+ + H \quad (17)$$

with rate coefficients, $\beta = 2.0 \times 10^{-7} T^{-1/2} \text{cm}^3 \text{s}^{-1}$ (a rough fit to Schneider et al. 1994) and $k = 2 \times 10^{-9} \text{cm}^3 \text{s}^{-1}$ (Theard & Huntress 1974). The probability for $H_3^+$ production is

$$P(H_3^+, \ H_2^+) = \frac{k_x(H_2)}{k_x(H_2) + \beta x_e} = \frac{x(H_2)}{x(H_2) + 100 T^{-1/2} x_e}, \quad (18)$$

so that,

$$x_e < 0.1 \frac{k}{\beta} x(H_2) = 0.01 \left( \frac{T}{100 \text{K}} \right)^{1/2} x(H_2), \quad (19)$$

the rate of dissociative recombination is less than 10% that for $H_2$ destruction. For regions with considerable $H_2$, this condition is well satisfied, $P(H_3^+, \ H_2^+) \approx 1$, and most of the $H_2^+$ ions are transformed into $H_3^+$.

The destruction pathways for $H_3^+$ are first, dissociative recombination with two branches,

$$H_3^+ + e^{-}\rightarrow H_2 + H (25\%) \quad \text{and} \quad H + H + H (75\%). \quad (20)$$

and total rate coefficient $\beta' = 4.5 \times 10^{-6} T^{-0.65} \text{cm}^3 \text{s}^{-1}$ (Sundström et al. 1994), and second, proton-transfer reactions such as,

$$H_3^+ + CO \rightarrow HCO^+ + \ H_2 \quad k_1 = 1.6 \times 10^{-9} \text {cm}^3 \text{s}^{-1} \quad (21)$$

$$H_3^+ + H_2O \rightarrow H_3O^+ + \ H \quad k_2 = 5.3 \times 10^{-9} \text{cm}^3 \text{s}^{-1} \quad (21)$$

$$H_3^+ + O \rightarrow OH^+ + \ H_2 \quad k_3 = 0.8 \times 10^{-9} \text{cm}^3 \text{s}^{-1} \quad (21)$$

Dissociative recombination, Equation (20), was considered by GL73. It is competitive with the reactions in Equation (21) where the electron fraction is relatively large. Denoting the abundance of the neutral reactants in Equation (21) by $x_i$ with $i = 1, 2, 3$ for CO, $H_2O$, and $O$, respectively, we introduce branching ratios for the main reaction pathways of $H_3^+$,

$$B_e = \frac{\beta' x_e}{\sum k_i x_i + \beta' x_e} \quad B_i = \frac{k_i x_i}{\sum k_i x_i + \beta' x_e} \quad (i = 1, 2, 3). \quad (22)$$

In order for dissociative recombination to compete with ionic reactions at the 10% level, the electron fraction must satisfy the condition,

$$x_e > 0.1 \frac{\sum k_i x_i}{\beta'} = 2.22 \times 10^{-9} T^{0.65} (\sum k_i x_i)_{-13}, \quad (23)$$

where $(\sum k_i x_i)_{-13} = (\sum k_i x_i/10^{-13} \text{ cm}^3 \text{s}^{-1})$ measures the reactivity of $H_3^+$ with abundant neutrals in units determined by neutral abundances of the order of $10^{-4}$ and ionic reactions with rate coefficients of the order of $10^{-9} \text{ cm}^3 \text{s}^{-1}$. Even in cold molecular regions, $(T \sim 10 \text{ K})$ dissociative recombination can still play a role in the presence of neutral reactions. Equation (23) for $H_3^+$ is much less restrictive than Equation (19) for $H_2^+$ because of the reduced abundance of heavy elements compared to hydrogen.

The first reaction in Equation (21) with CO is simple to treat because the product $HCO^+$ is mainly destroyed in one step by dissociative recombination back to $CO + H$, whereas dissociative recombination of $H_3O^+$ in the second reaction has three branches, $H_2O + H, OH + H_2$, and $OH + 2H$. The situation for the reaction with $O$ is similar because $OH^+$ in the third equation is quickly transformed into $H_3O^+$ by hydrogenation reactions with $H_2$. In this sequence, we can ignore dissociative recombination of $OH^+$ and $H_2O^+$ because of conditions similar to Equation (19).
Keeping in mind that the probability for the conversion of $H_2^+$ into $H_3^+$, $P(H_2^+, H_3^+)$, is essentially unity according to Equations (18) and (19), the chemical energy released by the creation of an $H_3^+$ ion can be obtained by consolidating the reactions in Equations (17) and (21) into the equivalent reactions,

$$e + H_2^+ \rightarrow H + H \quad (24)$$

$$e + H_2^+ + H_2O + H_2 \rightarrow H_2O + H_2 + 2H, \; OH + 2H_2 + H, \; OH + H_2 + 3H \quad (25)$$

$$e + H_2^+ + O + 2H_2 \rightarrow H_2O + 4H, \; OH + H_2 + 3H, \; OH + 5H \quad (26)$$

where $\overline{q}_1 = 11.1$ eV, $\overline{q}_2 = 7.8$ eV, and $\overline{q}_3 = 5.7$ eV are the net energy yields for each of the three consolidated reactions of $H_2^+$ (Equations (24)–(26)). The $\overline{q}$ are averages over the outcomes generated by the three branches in the dissociative recombination of $H_2O^+$.

$$H_3O^+ + e \rightarrow H_2O + H \; (25\%); \; OH + H_2 \; (15\%); \; OH + 2H \; (60\%). \quad (27)$$

For example, Equation (24) results from adding the full sequence of reactions that are involved when $H_3^+$ reacts with CO:

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

$$H_3^+ + CO \rightarrow HCO^+ + H_2$$

$$e + H_2^+ \rightarrow CO + H.$$  

The chemical heating due to the reactions of the $H_2^+$ ion is then the rate at which that ion is produced per unit volume multiplied by the probability that it is transformed into an $H_3^+$ ion (Equation (18)) times the heating averaged over the three branches of the latter’s reactions and including the heating from the dissociative recombination of $H_2^+$, all multiplied by the $H_2$ fraction. In terms of the notation of Equation (16), the chemical heating per ion pair stemming from the production of the $H_2^+$ ion is

$$Q_{\text{chem}}(H_2^+) = \frac{x(H_2)}{x(H) + x(H_2)} F(H_2^+) P(H_2^+, H_3^+) \left[ \Sigma_i B_i (H_2^+) \overline{q}_i (H_2^+) + B_e \overline{q}_e (H_2^+) \right] \quad (28)$$

The heating energies $\overline{q}_i$ are given following Equation (26) and the branchings are defined in Equation (22); $q_e(H_2^+) = 7.6$ eV. For the case where ion–molecule destruction prevails over dissociative recombination, we can estimate the value of the chemical heating for the case where the abundances for CO, H$_2$, and O all equal $10^{-4}$. The result is $\Sigma_i B_i (H_2^+) q_i (H_2^+) = 8.4$ eV, but this must still be multiplied by $F(H_2^+) = 0.88$ to yield $Q_{\text{chem}}(H_2^+) = 7.2$ eV.

Examination of Equations (25) and (26) reveals that the products of the ion–molecule reactions for H$_2$O and O involve the radicals OH and H whose further reaction can lead to more chemical heating. For example, OH can be converted to H$_2$O by the exothermic reaction,

$$OH + H_2 \rightarrow H_2O + H \quad (29)$$

and the H atoms can make H$_2$ by formation on dust grain surfaces “gr,”

$$H + H + \text{gr} \rightarrow H_2 + \text{gr} \prime. \quad (30)$$

The energy yield of the OH reaction is 0.65 eV. When this is added to the energy yields of Equations (25) and (26), the chemical heating produced in these reactions is increased slightly, $\overline{q}_2 = 8.4$ eV and $\overline{q}_3 = 6.4$ eV. The previous estimate of $\Sigma B_i \overline{q}_i$ for the case of equal abundances for CO, H$_2$O, and O (all $10^{-4}$) is increased from 8.4 eV to 8.8 eV, and $Q_{\text{chem}}(H_2^+) = 7.7$ eV.

The heating from Equation (30) depends on how much of any of the energy release goes into kinetic energy of the newly formed molecule compared to internal excitation and excitation of the birth grain. Theoretical estimates and guesses in the literature range from 0.5 to 3.0 eV, but laboratory experiments (e.g., Roser et al. 2003) suggest that the H$_2$ molecule thermally accommodates to the temperature of the grain before making its final escape, at least as far as kinetic energy is concerned. In a recent experiment, Lemaire et al. (2010) present evidence that ~30% of newly formed H$_2$ molecules are vibrationally excited for dust temperatures as warm as 70 K. Assuming that the results of Lemaire et al. apply to molecular regions where the density is large enough for vibrationally excited H$_2$ molecules to be collisionally de-excited, the chemical heating for the H$_2$O and O channels would be increased by 1.5 eV. This would then lead to an increase in the heating function by about 1 eV to $Q_{\text{chem}}(H_2^+) \sim 9$ eV. In the numerical estimates below, we ignore this contribution pending the resolution of this long-standing issue regarding H$_2$ formation on grains.

4.2. Chemical Heating of H$^+$ and He$^+$

In principle, the chemical heating of H$^+$ and He$^+$ ions can be treated in a similar way as H$_2^+$, but the outcomes depend on the chemical composition of the molecular region in question. Thus H$^+$ does not react with CO, the most abundant and stable heavy molecule, and its fast charge exchange with O is closely balanced by the reverse reaction. It does react with H$_2$O, which can be very abundant under certain circumstances, and with many organic species that usually have small abundances. In a cold molecular cloud, where H$_2$O may be expected to be frozen out on grains, this route will be shut down. On the other hand, in a dense warm region like those observed in the inner regions of protoplanetary disks, the primary destruction pathway for H$^+$ is

$$H^+ + H_2O \rightarrow H_2O^+ + H, \quad (31)$$

followed by hydrogenation to H$_3$O$^+$,

$$H_2O^+ + H_2 \rightarrow H_2O^+ + H, \quad (32)$$

and destruction of H$_3$O$^+$ by dissociative recombination, according to Equation (27). The energy balance equation is similar to Equation (25) for H$_2^+$ reacting with H$_2$O. The only difference is that H$_2^+$ is replaced by H$^+$ on the left side and H$_2$ is replaced by H on the right side. The net change in exothermic reaction yield (and in the maximum heating) is just the difference between the ionization potentials of H$_2$ and H, or 1.83 eV. Thus, the chemical heating arising from H$^+$ analogous to Equation (28) is

$$Q_{\text{chem}}(H^+) = \frac{x(H_2)}{x(H) + x(H_2)} F(H^+) B_2(H^+) \overline{q}_i (H^+), \quad (33)$$

where $F(H^+)$ is the fraction of H$^+$ ions (0.040 from Table 1), $B_2(H^+) \approx 1$ is the branching ratio for H$^+$ to react with H$_2$O, and $\overline{q}_i (H^+) = \overline{q}_e (H^+) - 1.83$ eV. In principle, $B_2(H^+)$ is given by an expression similar to Equation (22) with $\beta^*$, the dissociative
recombination rate coefficient for H$_3^+$, replaced by the radiative recombination rate for H$^+$. Because the latter is smaller by many orders of magnitude, destruction of H$^+$ by radiative recombination can be ignored. For a completely molecular region, $F(H^+)=0.04$, $B_2 \sim 1$, and $\tau_{\gamma}(H^+)=6.9$ eV, resulting in $Q_{\text{chem}}(H^+) = 0.28$ eV. This estimate includes the energy that can be recovered from the OH radical but not from the conversion of product H atoms to form H$_2$ on grains. It is much smaller than the heating per ion pair for H$_3^+$ because H$_3^+$ is less energetic and because only 4% of the ion pairs involve H$^+$. This estimate is also sensitive to the physical conditions because the H$_2$O abundance can vary, especially due to freeze out on grains, and because reactions with other species may occur such as charge transfer with neutral heavy atoms.

The heating by the He$^+$ ions is more complicated because it reacts with many molecules including H$_2$. Here we consider the dominant reaction to be

$$\text{He}^+ + \text{CO} \rightarrow \text{C}^+ + \text{O} + \text{He}, \quad (34)$$

followed by,

$$\text{C}^+ + \text{H}_2\text{O} \rightarrow \text{HCO}^+ + \text{H}, \quad (35)$$

and then by dissociative recombination of HCO$^+$. A similar analysis to that followed above for H$_2$ gives an energy budget equation,

$$e + \text{He}^+ + \text{H}_2\text{O} \rightarrow \text{O} + 2\text{H} + \text{He}, \quad (36)$$

with an energy yield of 15.0 eV. Including the reactions of the remaining O atom gives another 0.6 eV, or $q(\text{He}^+)=15.6$ eV. On this simplified basis, the heating due to He$^+$ ions is

$$Q_{\text{chem}}(\text{He}^+) = \frac{x(\text{H}_2)}{x(\text{H}) + x(\text{H}_2)} F(\text{He}^+) B_1(\text{He}^+) q(\text{He}^+). \quad (37)$$

Using $F(\text{He}^+)=0.80$, $B_1(\text{He}^+)=1$ (radiative recombination is again unimportant in molecular regions), $Q_{\text{chem}}(\text{He}^+)=1.25$ eV. This may be a slight overestimate because other reactions of He$^+$ have been neglected, e.g., with water.

### 4.3. Summary of Chemical Heating

To summarize this treatment of chemical heating, we have considered the energy that is available for heating due to the reactions of H$_2^+$, H$^+$, and He$^+$ ions, which account, respectively, for 88%, 4%, and 8% of the $\sim 27$ ion pairs per keV produced by high-energy electrons ($E > 500$ eV). The H$_2^+$ ion accounts for 7.7 eV per ion pair, which is most of the chemical heating (84%). This is very close to the heating from the dissociative recombination of H$_3^+$, $\sim 7.6$ eV (GL73). Even the total chemical heating, 9.2 eV per ion pair, is insensitive to the electron fraction because the chemical heating from H$^+$ and He$^+$ are also essentially independent of the electron fraction. There are a number of fine points that could add or subtract 1–2 eV from this result, depending on the physical conditions and on the role of poorly understood processes. For example, this treatment of high-density chemical heating is an overestimate in that no energy is assumed to be lost by vibrationally excited molecules produced in the relevant chemical reactions, on the assumption that the density is high enough for collisional de-excitation to be effective. Similarly, we have ignored the uncertain possibility that $\sim 1.5$ eV of excitation energy of newly formed H$_2$ molecules may be available for heating at high densities.

### 5. RESULTS

In the previous sections we developed a theory for the heating of molecular gases exposed to cosmic rays and X-rays, with detailed consideration of chemical heating. To illustrate the magnitude of the various contributions to the heating, we list in Table 4 the maximum values for the case of zero electron fraction and densities high enough for vibrationally excited molecules to be collisionally de-excited; the electron energy is $E = 1$ keV. The chemical heating in Table 4 is based on somewhat arbitrary choices for the most abundant neutrals: $x(\text{CO}) = x(\text{O}) = x(\text{H}_2\text{O}) = 10^{-4}$. Starting at the bottom, we see that the total maximum heating is $Q = 18.7$ eV per ion pair; close to 50% of the energy expended per ion pair, which in this case is $W = 36.8$ eV. The largest fraction, about one-half, is accounted for by chemical heating (9.3 eV). This value is $\sim 20\%$ larger than the value of 7.6 eV obtained from reactions Equation (17), H$_2^+$ + H$_2$ → H$_3^+$ + H, and Equation (20), H$_2^+$ + e → H$_2$ + H, along the lines of GL73. The next largest contribution, 5.2 eV, comes from vibrationally excited H$_2$ molecules, produced by direct collisional excitation or following the excitation of the B and C states. Elastic scattering, rotational excitation, and dissociation account for the rest, or $\sim 20\%$.

The values in Table 4 are based on several assumptions: the electron fraction is very small, the density is very high, and the abundances of C, H$_2$O, and O all equal to $10^{-4}$. The chemical heating appears to be insensitive to the electron fraction as long as Equation (19) is satisfied. On the other hand, Coulomb collisions with ambient electrons begin to play a significant role in heating wherever $x_e$ approaches the $10^{-4}$ level. This effect is automatically included in Equation (7). The entries for vibrational heating in Table 4 are the most sensitive to density because very high densities are required to collisionally quench vibrationally excited H$_2$ molecules, as discussed in Section 3.3.
H+ chemical heating is dominated by dissociative recombination of species. For example, if instead of the abundances used for the heating also depends weakly on the abundances of the neutral in molecular clouds outside of pre-stellar cores. The chemical estimate for the chemical heating associated with the H+ cloud are too low for vibrational heating. The estimate for ζ is reduced that ionic reactions dominate chemical heating. The densities in this diffuse region of a pre-stellar core, the density may be high enough for vibrational heating, but their low temperatures suggest that the elastic/rotational heating may be somewhat smaller than given in Table 6. The freezeout of volatiles, including some CO, means that the chemical heating will probably be close to the value for dissociative recombination.

Under certain circumstances, such as very low energy cosmic rays or soft X-rays, the considerations of this paper need to be extended to electron energies E < 1 keV. Without attempting to treat this subject in detail, we can obtain a preliminary view of the situation from Table 5, which gives heating functions Q and the energy to make an ion pair as a function of electron energy. Many of the heating functions increase with decreasing energy, especially collisional excitation and dissociation. However, the percentage of the energy to make an ion pair that goes into heating remains close to 50% down to E = 50 eV. Indeed, the following quantities vary by less than 10% for energies greater than 200 eV; total heating Q, energy to make an ion pair \( W \) and the percentage heating.

We can make the implications of the theory in this paper more concrete by estimating the heating for representative examples of interstellar and circumstellar matter that have significant amounts of H2. The estimates in Table 6 are based on the assumption that the electron energy is greater than 0.5 keV, corresponding to cosmic-ray proton energies greater than 1 MeV. For the well-observed line of sight toward ζ Per (\( A_V \approx 1 \)) (an early focus of the H2 observations; Indriolo et al. 2007), we use the modeling results for many observed species by Shaw et al. (2008), who fit the cosmic-ray ionization rate per H2 with \( ζ_2 \approx 8 \times 10^{-16} \) s\(^{-1}\). The densities in this diffuse cloud are too low for vibrational heating. The estimate for elastic/rotational heating may be too high because the density and temperature in this cloud may not be large enough for significant quenching of rotational excitation, according to the discussion in Section 3.1. The chemical heating in this case comes from dissociative recombination because, according to Equation (23), it dominates over ion reactions. All of the heating estimates for \( ζ \) Per have been reduced by 70% to take into account that atomic H has not been fully converted into H2. The entries under H2 destruction in Table 6 indicate whether the chemical heating is dominated by dissociative recombination of H2 (“DR”) or ionic reactions (“I”).

For the case of a molecular cloud clump, dissociative recombination plays a role in the destruction of H2, but ion–molecule reactions are probably more important. Again, clumps are not dense enough for vibrational heating, and they also may not be warm enough to quench rotational excitation. For the inner region of a pre-stellar core, the density may be high enough for vibrational heating, but their low temperatures suggest that the elastic/rotational heating may be somewhat smaller than given in Table 6. The freezeout of volatiles, including some CO, means that the chemical heating will probably be close to the value for dissociative recombination.

The densities in the inner molecular layer of a protoplanetary disk are often in excess of \( 10^9 \) cm\(^{-3}\), and both rotational and vibrational heating should be effective. Because these regions are close to a stellar X-ray source, the X-ray ionization rates are much larger than the cosmic-ray rates for interstellar matter. Thus, the electron fractions are relatively high at the top of the molecular region, \( \sim 10^{-7}−10^{-6} \), and Equation (23) indicates that dissociative recombination still plays a role in the chemical heating of the very dense inner regions. However, for sufficiently large vertical columns, the X-ray ionization is sufficiently reduced that ionic reactions dominate chemical heating.

All of the cases considered in Table 6 contain a significant if not an overwhelming fraction of H2. These rough estimates for the total heating per ion pair increase with the total density, and range from \( \sim 10 \) eV per ion pair for a moderately thick diffuse cloud like ζ Per to \( \sim 18 \) eV per ion pair for the densest regions. Perhaps the most important conclusion from these four examples is that cosmic-ray and X-ray heating are sensitive to the physical conditions, as expressed in the equations presented in Sections 3 and 4. The values of \( Q \) listed in Table 6 for various environments, combined with prescriptions for \( ζ_{\text{HI}} \) as function of the column density of the ambient gas (Padovani et al. 2009) and for the magnetic field intensity (Padovani & Galli 2011), allow the determination of the cosmic-ray heating rate in clouds, cores, and protostellar disks.

6. CONCLUSION

Dalgarno et al. (1999; DYL) made an extensive study of the energy loss of fast electrons in H, He and H2. He gas mixtures. The electrons are at the heart of the interaction of cosmic rays and X-rays with interstellar and circumstellar matter. Although DYL analyzed essentially all excitation and ionization processes, they only discussed the heating from...
elastic collisions and rotational excitation of \( \text{H}_2 \). Starting from the results in DYL, we have extended the scope of cosmic-ray and X-ray heating to include all of the relevant interactions. One of the main conclusions of this study is that heating by fast electrons depends on the physical properties of the gas, i.e., on the abundance of electrons, \( \text{H}_2 \) molecules, and heavy atoms and molecules, and also on the total density of hydrogen nuclei. The electron fraction is important because, once it exceeds a certain level, heating by collisions with ambient electrons becomes important. The electron abundance also determines whether the destruction of the \( \text{H}_2^+ \) ions proceeds by dissociative recombination or ionic reactions, which affects the quantitative amount of chemical heating. Of course the \( \text{H}_2/\text{H} \) abundance ratio is important because the diversity of the energy levels of \( \text{H}_2 \) offers many more channels for energy loss than atomic \( \text{H} \).

The dependence on physical conditions means that X-ray and cosmic-ray heating cannot be specified by a single number. This should be clear from the fact that in neutral atomic regions the heating efficiency is only 12%, whereas in neutral molecular regions it can reach 50% at very high densities.

A wide range of values for the heating per ion pair can be found in the literature on molecular clouds, from 7 eV (Stahler & Palla 2004) to 20 eV (Goldsmith & Langer 1978; Goldsmith 2001), but not necessarily for the reasons given here, e.g., in the above discussion of Table 6. Many authors adopt Goldsmith’s value while others estimate intermediate values of 10–15 eV based on GL73, e.g., Maloney et al. (1996), Yusef-Zadeh et al. (2007), and Krumholz et al. (2011). As shown in Table 4, 13 eV is a good choice for not too dense molecular gas.

Chemical heating also applies to regions exposed to far UV radiation (Dalgarno & Oppenheimer 1974). It was then considered by Barsuhn & Walmsley (1977) and Clavel et al. (1978), who studied the chemical and thermal equilibrium in dark clouds exposed to far UV radiation and cosmic rays. Clavel et al. explicitly included the contribution of every reaction in their chemical network to heating. Chemical heating has also been widely used in the study of planetary atmospheres (e.g., Roble et al. 1987).

The results of this paper are based on the fact that roughly half of the energy generated by cosmic rays and X-rays comes into ionization of the gas and roughly half into its excitation, more specifically according to the way the individual processes are treated by DYL. Roughly half of the gas heating comes from the reactions of various ions with the assumed mainly neutral gas. Potentially, an equal amount of heating can arise from dissociation and from rotational and vibrational excitation, but the yield from excitation depends on whether the physical conditions are conducive to the quenching of the excited levels. If quenching is inefficient, the levels decay with the emission of radiation, which can escape or be absorbed by dust. This possibility is even more important for the excitation of the singlet levels of \( \text{H}_2 \), e.g., the \( B \) and \( C \) levels, and the excitation of the \( n = 2 \) level of \( \text{H} \) in atomic regions. We have not attempted to follow the fluorescent radiation to determine how much escapes and how much is absorbed. This is an important issue when considering the broader thermal properties of the gas.

The treatment of the fluorescent radiation involves radiation transfer and depends on the properties of the dust, i.e., it is application specific. In contrast, our goal has been to treat one relatively well-defined part of the thermal problem of interstellar and circumstellar molecular gas.

In pursuing this goal, we have also ignored the direct interaction of X-rays and cosmic rays with the dust, of some interest because of the possibility that they may release fast electrons from the dust. Although this occurs, it is relatively unimportant. First of all, the dust cross-section per H nucleus for the diffuse ISM is \( 1.6 \times 10^{-21} \text{cm}^{-2} \). For molecular clouds and disk atmospheres, it will be even smaller. The main inelastic cross-sections for a keV electron with \( \text{H}_2 \) are typically several times \( 10^{-17} \text{cm}^{-2} \), so the probability that an incident X-ray or cosmic ray interacts with dust is roughly 1000 times less than with \( \text{H}_2 \). When this rare event does occur, no more than 1% goes into photoelectrons, as shown by Dwek & Smith (1996) for the EUV/X-ray bands.

We are indebted to Máté Ádámkovics for testing the heating terms described in this paper in a thermal-chemical code for protoplanetary disks. A.E.G. acknowledges support from the NASA grant NNG06GF88G (Origins) and the NASA grant 1367693 (Herschel DIGIT). The authors thank the anonymous referee for a careful reading and thoughtful comments.

### APPENDIX

#### CHEMICAL HEATING IN ATOMIC REGIONS

Table 7 provides the same information on the energy partitions for an atomic H, He mixture as Table 1 does for an \( \text{H}_2 \), He mixture. Although less energy is expended in ion production (because of the smaller ionization potential of H compared to that for \( \text{H}_2 \)), the total number of ions is essentially unchanged at 27.2 ion pairs per keV.

The heating of an atomic region is simpler to treat than a molecular region because of the absence of rotational and vibrational excitation. The direct heating by elastic scattering is usually important. We ignore the radiation emitted following the electronic excitation of the levels of H and He in Table 7, and focus here on the chemical heating.

In addition to radiative recombination,

\[
e^+ + \text{H}^+ \rightarrow \text{H} + h\nu, \quad \alpha(\text{H}^+) \simeq 2.12 \times 10^{-10} T^{-0.73} \text{cm}^3 \text{s}^{-1},
\]

#### Table 7

| Process | Dray Energy Partitions for an He, H Mixture, \( x_e = 0 \) and \( E = 1 \text{ keV} \) |
|---------|---------------------------------|
| \( \text{H}^+ \) | 39.8 | 25.1 | 13.60 | 342 |
| He\(^+\) | 487 | 2.05 | 24.6 | 51 |
| He\(2^+\) | 16400 | 0.061 | 54.4 | 3 |
| Total ion production | | | | 396 |
| \( \text{H}_2 \) | 267 | 3.75 | 10.2 | 38 |
| \( \text{He}_2 \) | 33.1 | 30.2 | 10.2 | 308 |
| \( \text{H}_2 \) | 191 | 5.24 | 12.1 | 6 |
| \( \text{H}_2 \) | 236 | 4.24 | 13.2 | 56 |
| Total H excitation | | | | 408 |
| \( \text{He}_2 \) | 17300 | 0.058 | 20.6 | 1.2 |
| \( \text{He}_2 \) | 2080 | 0.481 | 21.2 | 10.2 |
| \( \text{He}_2 \) | 50700 | 0.020 | 19.8 | 0.39 |
| \( \text{He}_2 \) | 30800 | 0.032 | 21.0 | 0.68 |
| \( \text{He}_2 \) | 3790 | 0.264 | 23 | 6.1 |
| Total He excitation | | | | 19 |
| Total excitation | | | | 427 |
| Heating | | | | 117 |
| Grand total | | | | 940 |
H+ can be destroyed by radiative attachment to H to form H2+,
H+ + H → H2+ + hν, \( k_{sa} \approx 2.10 \times 10^{-23} \ T^{1.80} \ \text{cm}^3 \text{s}^{-1} \). (A2)

The rate coefficient for radiative association is especially small, and the probability to form H2+ this way is given by

\[
P(H^+, H_2^+: H) = \frac{k_{ra}x(H)}{k_{sa}x(H) + \alpha x_e} = \frac{x(H)}{x(H) + (\alpha/k_{sa})x_e}. \tag{A3}
\]

In order for radiative recombination to be important, the electron fraction must approach the value,

\[k_s / \alpha \approx 10^{-13} T^{2.53}. \tag{A4}\]

This requirement is relatively easy to satisfy, e.g., \( k_{sa} / \alpha \approx 10^{-8} \) at 100 K and \( \sim 10^{-4} \) at 4000 K.

The energetics of the two processes are different. In both cases the reaction is lost or absorbed by dust grains and will be ignored. In an atomic H region, the newly formed H2+ can charge exchange with H to form H2,

\[H_2^+ + H → H_2 + H^+, \quad k = 6.4 \times 10^{-10} \ \text{cm}^3 \text{s}^{-1}. \tag{A5}\]

This reaction can provide up to \( q(H^+: H) = IP(H_2) - IP(H_2^+) = 1.83 \text{eV} \) in heating, where IP stands for ionization potential, but it has to compete with dissociative recombination, Equation (17), which has a branching ratio,

\[B_e = \frac{\beta x_e}{\beta x_e + kx(H)} = \frac{(\beta/k)x_e}{(\beta/k)x_e + x(H)}. \tag{A6}\]

The ratio \( k/\beta = 5.33 \times 10^{-3} T^{0.4} \) determines the electron fraction where dissociative recombination is important, i.e., in regions where \( x_e \sim 0.01 \).

We follow Section 3 and express the heating per ion pair for atomic regions due to the H+ ion as

\[Q_{chem}(H^+: H) = \frac{x(H)}{x(H) + x(H_2)} F(H^+: H) P(H^+, H_2^+: H) \times \left[ B_{HI} q_{HI}(H^+: H) + B_e q_e(H^+: H) \right], \tag{A7}\]

where \( F(H^+: H) \) is the fraction of all ions that are H+, \( P(H^+, H_2^+: H) \) is the probability that an H+ ion is converted into H2+, \( q_{HI}(H^+: H) = 1.83 \text{eV} \) is the net heating from reactions Equations (A2) and (A5), \( B_{HI} \) is the branching ratio for reaction Equation (A5),

\[B_{HI} = \frac{kx(H)}{kx(H) + \beta x_e} = \frac{kx(H)}{x(H) + (\beta/k)x_e}. \tag{A8}\]

and \( q_e(H^+: H) = 11.0 \text{eV} \) is the net heating from radiative charge exchange, Equation (A2), followed by dissociative recombination, Equation (17). From Table 7, we find that the fraction of H+ ions \( F(H^+: H) = 0.92 \) for the parameters in that table \((E = 1 \text{keV} \text{ and } x_e = 0)\); it increases slowly with decreasing electron energy.

The maximum chemical heating per ion pair coming from H+ depends on how the H2+ it generates is destroyed: 1.7 eV by charge exchange and 10.1 eV by dissociative recombination, with the latter only occurring for relatively large electron fractions. However, in most H1 regions, the dominant factor is the probability of forming H+, \( P(H^+, H_2^+: H) \) in Equation (A7), which can greatly reduce \( Q_{chem}(H^+: H) \), simply because radiative association in this case is such a weak process. Thus, chemical heating in atomic H regions is usually negligible.

In addition to radiative recombination,

\[e + He^+ → He + hν, \quad \alpha(He^+) \approx 2.12 \times 10^{-10} T^{-0.73} \ \text{cm}^3 \text{s}^{-1}. \tag{A9}\]

He+ can be destroyed by radiative charge exchange,

\[He^+ + H → He^++H + hν, \quad k_{che} \approx 1.6 \times 10^{-16} T^{-0.50} \ \text{cm}^3 \text{s}^{-1}, \tag{A10}\]

and by radiative association to form HeH+,

\[He^+ + H → HeH^+ + hν, \quad k_{ra} \approx 1.33 \times 10^{-14} T^{-0.37} \ \text{cm}^3 \text{s}^{-1}. \tag{A11}\]

All of these radiative processes are weak, although the last two are not as weak as the corresponding reactions just discussed that start from H+ + He. These reactions have the potential to provide greater heating because of the larger energy of the He+ ion, except that much of the available energy is lost in radiation. We therefore ignore radiative recombination and focus on radiative charge exchange, Equation (A10), and radiative association, Equation (A11). The former process generates \( IP(He^+) - IP(He) = 11.0 \text{eV} \) in recombination radiation rather than gas heating. The heating from the formation of the HeH+ ion, discussed in the previous section, has a maximum value 1.83 eV. But this value must be reduced by the fraction of He+ which, according to Table 7 for \( E = 1 \text{keV} \), is \( F(He^+, H) = 0.075 \). It may also be reduced by the branching ratio for radiative association,

\[B_{ra}(He^+) = \frac{k_{ra}}{k_{ra} + k_{che} + \alpha x_e}, \tag{A12}\]

which is often less than unity. For example, in warm regions charge exchange is more important than radiative association, and radiative recombination is competitive with the other reactions for \( x_e > 10^{-3} \). Thus, we cannot expect the chemical heating from He+ to be any more than 0.14 eV, and thus negligible, as we found also for the H+ ion.

REFERENCES

Abgrall, H., Roueff, E., Liu, X., & Shemansky, D. E. 1997, ApJ, 481, 557
Balakrishnan, N., Forrey, R. C., & Dalgarno, A. 1999, ApJ, 514, 520
Barsuhn, J., & Walmsley, C. M. 1977, A&A, 54, 345
Bates, D. R., & Griffin, G. 1953, Proc. Phys. Soc., A66, 961
Clavel, J., Viau, Y. P., & Bel, N. 1978, A&A, 65, 435
Crapsi, A., Caselli, P., Walmsley, M. C., & Tafalla, M. 2007, A&A, 470, 221
Cravens, T. E., & Dalgarno, A. 1978, ApJ, 219, 750
Cravens, T. E., Victor, G. A., & Dalgarno, A. 1975, Planet. Space Sci., 23, 1059
Dalgarno, A., & Oppenheimer, M. 1974, ApJ, 192, 597
Dalgarno, A., Yan, M., & Liu, W. 1999, ApJS, 125, 237 (DYL)
Dwek, E., & Smith, R. K. 1996, ApJ, 459, 686
Everett, J. E., & Zweibel, E. G. 2011, ApJ, 738, 60
Galli, D., Walmsley, M., & Gonçalves, J. 2002, A&A, 394, 53
Goldsmith, P. F., & Langer, W. D. 1973, ApJ, 186, 859 (GL73)
Goldsmit, P. F. 2001, ApJ, 557, 736
Goldsmith, P. F., & Langer, W. D. 1978, ApJ, 222, 881
Henry, R. J. W., & McElroy, M. B. 1969, J. Atmos. Sci., 26, 912
Hooper, J. W., McDaniel, E. W., Martin, D. W., & Harmer, D. S. 1961, Phys. Rev., 131, 1123
Indriolo, N., Fields, B. D., & McCaill, B. J. 2000, ApJ, 694, 257
Indriolo, N., Geballe, T. R., Oka, T., & McCaill, B. J. 2007, ApJ, 671, 1736
Indriolo, N., & McCaill, B. J. 2012, ApJ, 745, 911
Jasche, J., Ciardi, B., & Enßlin, T. A. 2007, MNRAS, 380, 417
Krumholz, M. R., Leroy, A. K., & McKee, C. F. 2011, ApJ, 731, 25
Lee, T.-G.,Balakrishnan, N., Forrey, R. C., et al. 2008, ApJ, 689, 1105

Glassgold, Galli, & Padovani
Le Bourlot, J., Pineau des Forêts, G., & Flower, D. R. 1999, MNRAS, 305, 802
Lemaire, J. L., Vidali, G., Baouche, S., et al. 2010, ApJ, 725, L156
Maloney, P. R., Hollenbach, D. J., & Tielens, A. G. G. M. 1996, ApJ, 466, 561
Opal, C. B., Peterson, W. K., & Beatty, E. C. 1971, J. Chem. Phys, 55, 4100
Padovani, M., & Galli, D. 2011, A&A, 530, A109
Padovani, M., Galli, D., & Glassgold, A. E. 2009, A&A, 501, 619
Pagani, L., Bacmann, A., Cabrit, S., & Vestel, C. 2007, A&A, 467, 179
Pineda, J. L., & Bensch, F. 2007, A&A, 470, 615
Rimmer, P. B., Herbst, E., Morata, O., & Roueff, E. 2012, A&A, 537, A7
Roble, R. G., Ridley, E. C., & Dickinson, R. E. 1987, J. Geophys. Res., 92, 8745
Roser, J. E., Swords, S., Vidali, G., Manicò, G., & Pirrónello, V. 2003, ApJ, 596, L55

Schneider, I. F., Dulieu, O., Giusti-Suzor, A., & Roueff, E. 1994, ApJ, 424, 983
Shaw, G., Ferland, G. J., Henney, W. J., et al. 2009, ApJ, 701, 677
Shaw, G., Ferland, G. J., Srianand, R., et al. 2008, ApJ, 675, 405
Stahler, S. W., & Palla, F. 2004, The Formation of Stars (Weinheim: Wiley-VCH)
Suchkov, A., Allen, R. J., & Heckman, T. M. 1993, ApJ, 413, 542
Sundström, G., Mowat, J. R., Danared, H., et al. 1994, Science, 263, 785
Theard, L. P., & Huntress, W. T. 1974, J. Chem. Phys., 60, 2840
Tielens, A. G. G. M. 2000, The Physics and Chemistry of the Interstellar Medium
(Cambridge: Cambridge Univ. Press)
Tiné, S., Lepp, S., Gredel, R., & Dalgarno, A. 1997, ApJ, 481, 282
Wraithmuller, S. A., Gusdorf, A., & Fower, D. R. 2007, MNRAS, 382, 133
Yusef-Zadeh, F., Wardle, M., & Roy, S. 2007, ApJ, 665, L123