

## MOLECULAR CLOUD CHEMISTRY AND THE IMPORTANCE OF DIELECTRONIC RECOMBINATION

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Received 2008 September 25; accepted 2008 November 18; published 2009 March 16

## ABSTRACT

Dielectronic recombination (DR) of singly charged ions is a reaction pathway that is commonly neglected in chemical models of molecular clouds. In this study we include state-of-the-art DR data for He<sup>+</sup>, C<sup>+</sup>, N<sup>+</sup>, O<sup>+</sup>, Na<sup>+</sup>, and Mg<sup>+</sup> in chemical models used to simulate dense molecular clouds, protostars, and diffuse molecular clouds. We also update the radiative recombination (RR) rate coefficients for H<sup>+</sup>, He<sup>+</sup>, C<sup>+</sup>, N<sup>+</sup>, O<sup>+</sup>, Na<sup>+</sup>, and Mg<sup>+</sup> to the current state-of-the-art values. The new RR data have little effect on the models. However, the inclusion of DR results in significant differences in gas-grain models of dense, cold molecular clouds for the evolution of a number of surface and gas-phase species. We find differences of a factor of 2 in the abundance for 74 of the 655 species at times of 10<sup>4</sup>–10<sup>6</sup> yr in this model when we include DR. Of these 74 species, 16 have at least a factor of 10 difference in abundance. We find the largest differences for species formed on the surface of dust grains. These differences are due primarily to the addition of C<sup>+</sup> DR, which increases the neutral C abundance, thereby enhancing the accretion of C onto dust. These results may be important for the warm-up phase of molecular clouds when surface species are desorbed into the gas phase. We also note that no reliable state-of-the-art RR or DR data exist for Si<sup>+</sup>, P<sup>+</sup>, S<sup>+</sup>, Cl<sup>+</sup>, and Fe<sup>+</sup>. Modern calculations for these ions are needed to better constrain molecular cloud models.

*Key words:* astrochemistry – atomic data – atomic processes – dust, extinction – ISM: atoms – ISM: molecules

## 1. INTRODUCTION

Investigating the physics and chemistry of molecular clouds (also known as quiescent cores) is crucial if one is to understand the processes that ultimately lead to star formation. Such studies are also important in the field of astrobiology since these clouds are the birthplace of the first organic molecules.

Chemical models used to describe the evolution of molecular clouds typically include hundreds of species. At molecular cloud temperatures ( $\lesssim 100$  K) these atoms and molecules are either neutral or singly ionized. The abundances of these species are, in turn, governed by thousands of reactions that are highly nonlinear. These derived abundances are sensitive to the accuracy of the rate coefficients involved. The implication of uncertainties in the rate coefficients used in chemical models has been investigated by Roueff et al. (1996), Vasyunin et al. (2004, 2008), Wakelam et al. (2005, 2006), and others. However, these studies cannot account for reaction processes that are not included in the models in the first place.

To the best of our knowledge, the only recombination process of free electrons with atomic ions included in any molecular cloud simulation is radiative recombination (RR). Recent calculations by Badnell (2006)<sup>5</sup> have improved the accuracy of the rate coefficients of these reactions for a number of ions. The alternative pathway of dielectronic recombination (DR) has previously not been included in molecular cloud models. This is largely due to the bulk of published DR calculations and experiments being valid only for plasmas of higher temperature. Recently, however, theoretical calculations by Badnell et al. (2003)<sup>6</sup> have probed DR at the low-temperature regimes of molecular clouds. At these temperatures, the DR rate coefficient

can be a factor of 5 or more greater than the RR rate coefficient for certain systems.

In this paper, we both update the RR data and include DR for the relevant singly charged atomic ions. We do this for several molecular cloud models under a variety of initial conditions. We use Nahoon (Wakelam et al. 2004) to simulate dense clouds and protostars, the OSU gas-grain code (Hasegawa et al. 1992; Garrod & Herbst 2006) to simulate dense clouds, and the Meudon Photodissociation Region (PDR) code (le Petit et al. 2002, 2006) to simulate both diffuse and dense PDRs. We compare the species abundances with those calculated with and without DR included in order to show the effects on the models. The remainder of the paper is organized as follows: in Section 2 we review the recent developments in our understanding RR and DR. Section 3 outlines the chemical models we use to simulate dense clouds, diffuse clouds, and protostars. In Section 4 we present the results of including DR in these chemical models. Concluding remarks are given in Section 5.

## 2. RECOMBINATION DATA

## 2.1. Radiative Recombination

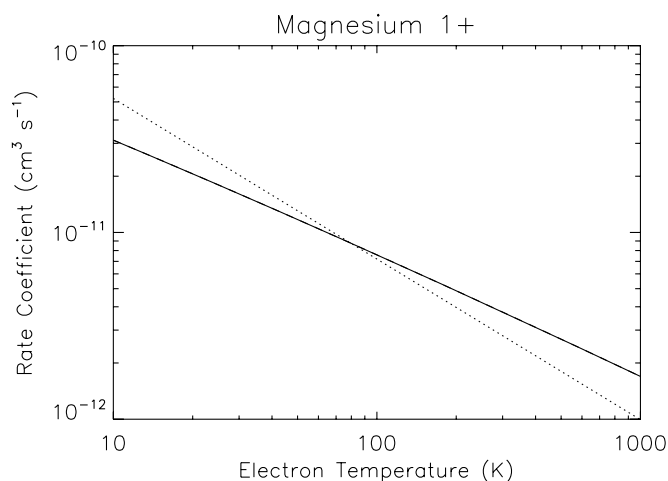
RR is a one-step recombination process that occurs when a free electron is captured by an ion. Energy and momentum are conserved in the process by the simultaneous emission of a photon. At the low temperatures typical of molecular clouds, RR is the dominant ion–electron recombination process for most ions. Until now, the molecular cloud codes that we use in the present work (see Section 3) have used RR rate coefficients from the UMIST database<sup>7</sup> (Woodall et al. 2007). For the most part it is unclear where the RR data in the UMIST database stem from as there is often no reference given; this is the case for the rate coefficients of H<sup>+</sup>, He<sup>+</sup>, Na<sup>+</sup>, Mg<sup>+</sup>, Si<sup>+</sup>, P<sup>+</sup>, S<sup>+</sup>, Cl<sup>+</sup>, and Fe<sup>+</sup>. There is no RR data for F<sup>+</sup>. For C<sup>+</sup> and N<sup>+</sup> the rate

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<sup>5</sup> <http://amdpp.phys.strath.ac.uk/tamoc/RR/>.

<sup>6</sup> <http://amdpp.phys.strath.ac.uk/tamoc/DR/>.

<sup>7</sup> <http://www.udfa.net/>.



**Figure 1.** RR rate coefficient for  $\text{Mg}^+$  forming Mg. The dotted line is the rate coefficient from the UMIST database and the solid line shows the modern calculation of Badnell (2006).

coefficients are those of Nahar & Pradhan (1997) and for  $\text{O}^+$  the rate coefficient is from Nahar & Pradhan (1999). The data of Nahar & Pradhan are actually unified RR+DR calculations using LS-coupling. As a result, they have no DR component at low temperatures of molecular clouds since they do not account for fine structure transitions of the ground term (see Section 2.2).

In recent years there have been attempts to better understand the RR process using state-of-the-art computational techniques. Badnell (2006) has calculated RR rate coefficients for all elements from H through Zn for bare through Mg-like isoelectronic sequences. We have implemented these calculations for the ions included in the chemical networks of the models considered here, namely  $\text{H}^+$ ,  $\text{He}^+$ ,  $\text{C}^+$ ,  $\text{N}^+$ ,  $\text{O}^+$ ,  $\text{Na}^+$ , and  $\text{Mg}^+$ . For the ions that Badnell (2006) has not calculated—namely  $\text{Si}^+$ ,  $\text{S}^+$ ,  $\text{Cl}^+$ , and  $\text{Fe}^+$ —we have used the rate coefficients recommended by Mazzotta et al. (1998). These come from Aldrovandi & Péquignot (1973) for  $\text{Si}^+$  and  $\text{S}^+$ ; an extrapolation of the S-like sequence is used to estimate the  $\text{Cl}^+$  rate coefficient; and the rate coefficient from Schull & van Steenberg (1982; refitted with the Verner & Ferland 1996 formula) is used for  $\text{Fe}^+$ .

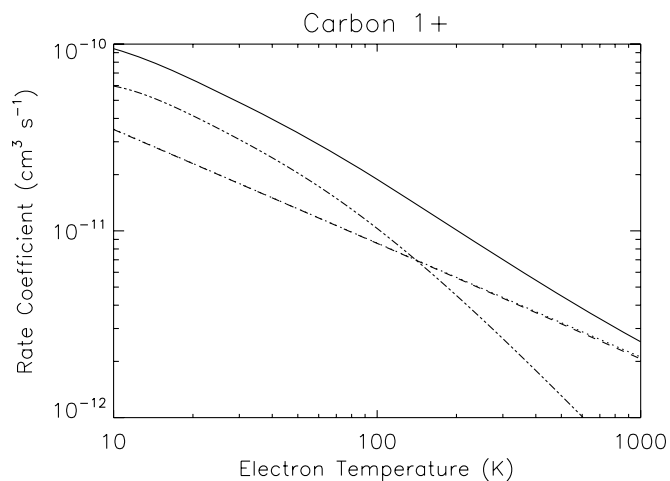
At molecular cloud temperatures, the largest difference found between the RR rate coefficients of the UMIST data set and the Badnell (2006) RR data is for  $\text{Mg}^+$ , as is shown in Figure 1. At a temperature of 10 K, typical of a cold molecular cloud, the UMIST rate coefficient is 60% larger than that of Badnell.

## 2.2. Dielectronic Recombination

DR is a two-step recombination process that begins when a free electron collisionally excites a core electron of an ion and is simultaneously captured. This first step is called dielectronic capture. The core electron excitation can be labeled  $nl_j \rightarrow n'l'_j$ , where  $n$  is the principal quantum number,  $l$  is the orbital angular momentum, and  $j$  is the total angular momentum. The energy of this intermediate system lies in the continuum and the complex may autoionize. The DR process is complete when the system emits a photon, reducing the total energy of the recombined system to below its ionization threshold. Conservation of energy requires that for DR to go forward

$$E_k = \Delta E - E_b. \quad (1)$$

Here,  $E_k$  is the kinetic energy of the incident electron,  $\Delta E$  is the excitation energy of the initially bound electron in the presence



**Figure 2.** DR and RR rate coefficients for  $\text{C}^+$  forming C. The dotted line is the RR rate coefficient from the UMIST database. The dashed line shows the modern RR calculation of Badnell (2006) and lies almost exactly on top of the UMIST data. The dot-dot-dashed line shows the DR calculation of Badnell et al. (2003). The solid line is the total RR+DR recombination rate coefficient of Badnell.

of the captured electron, and  $E_b$  is the binding energy released when the incident electron is captured onto the excited ion. Because  $\Delta E$  and  $E_b$  are quantized, DR is a resonant process occurring for a given channel at energies  $E_k < \Delta E$ .

For a molecular cloud of temperature  $T_{\text{cloud}}$ , the important DR channels are those where  $\Delta E \sim k_B T_{\text{cloud}} \lesssim 0.01$  eV. Thus, from atomic energy structure considerations alone, it is clear that fine structure excitations of the ground term are important in molecular clouds.

However, until recently, the preponderance of DR data has been calculated using the LS-coupling scheme, which does not include these low-energy resonances. To the best of our knowledge, the first work to propose that recombination via fine structure core excitations are important at low temperatures was Watson et al. (1980). However, these authors only considered dielectronic capture and not the complete DR process. A subsequent series of papers by Nussbaumer & Storey (1983, 1984, 1986, 1987) calculated DR rate coefficients for a number of ions using the LS-coupling scheme and introduced a weak interaction approximation to account for core fine structure interactions. However, they only considered temperatures above  $10^3$  K. Badnell (1988) then pioneered explicit intermediate-coupling calculations for some of these DR rate coefficients, but again only for temperatures above  $10^3$  K. Recent state-of-the-art calculations by Badnell et al. (2003), using intermediate coupling, have provided DR rate coefficients for H- through Mg-like ions of all elements from He through Zn at temperatures relevant to molecular clouds.

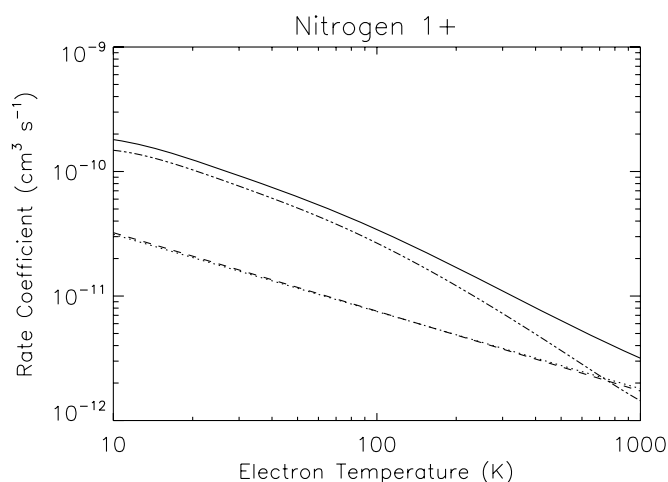
For the singly ionized ions of interest in molecular clouds— $\text{H}^+$ ,  $\text{He}^+$ ,  $\text{C}^+$ ,  $\text{N}^+$ ,  $\text{O}^+$ ,  $\text{F}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^+$ ,  $\text{Si}^+$ ,  $\text{P}^+$ ,  $\text{S}^+$ ,  $\text{Cl}^+$ , and  $\text{Fe}^+$ —one would expect a significant low-temperature DR contribution for  $\text{C}^+$ ,  $\text{N}^+$ ,  $\text{F}^+$ ,  $\text{Si}^+$ ,  $\text{P}^+$ ,  $\text{Cl}^+$ , and  $\text{Fe}^+$  due to their fine structure splitting of the ground term. The other ions either do not undergo DR (i.e.,  $\text{H}^+$ ) or have no such fine structure splitting. Of these five ions with fine structure splitting, Badnell et al. (2003) has calculated DR only for  $\text{C}^+$ ,  $\text{N}^+$ , and  $\text{F}^+$ . Figures 2 and 3 show a comparison of the DR and RR rate coefficients for  $\text{C}^+$  and  $\text{N}^+$ , respectively. At temperatures  $\lesssim 100$  K, typical of molecular clouds, the DR component dominates the electron-ion recombination rate coefficient highlighting the importance of including this recombination process. For the present work

**Table 1**  
Initial Species Abundances Relative to the Total H Nuclei Density, and Physical Conditions for Dense Clouds, Protostars, and Dense and Diffuse PDRs

Parameter	Initial Conditions			
	Dense Cloud	Protostar <sup>a</sup>	Diffuse PDR	Dense PDR
H	...	...	$9.90 \times 10^{-1}$	$9.90 \times 10^{-1}$
He	$1.40 \times 10^{-1}$	$1.40 \times 10^{-1}$	$1.00 \times 10^{-1}$	$1.00 \times 10^{-1}$
N	$2.14 \times 10^{-5}$	$2.14 \times 10^{-5}$	$7.50 \times 10^{-5}$	$7.50 \times 10^{-5}$
O	$1.76 \times 10^{-4}$	$1.76 \times 10^{-4}$	$3.19 \times 10^{-4}$	$3.19 \times 10^{-4}$
F	$6.68 \times 10^{-9}$	$6.68 \times 10^{-9}$	...	...
C <sup>+</sup>	$7.30 \times 10^{-5}$	$7.30 \times 10^{-5}$	$1.32 \times 10^{-4}$	$1.32 \times 10^{-4}$
Na <sup>+</sup>	$2.00 \times 10^{-9}$	$2.00 \times 10^{-9}$	...	...
Si <sup>+</sup>	$8.00 \times 10^{-9}$	$8.00 \times 10^{-9}$	...	...
S <sup>+</sup>	$8.00 \times 10^{-8}$	$8.00 \times 10^{-8}$	$1.86 \times 10^{-5}$	$1.86 \times 10^{-5}$
Mg <sup>+</sup>	$7.00 \times 10^{-9}$	$7.00 \times 10^{-9}$	...	...
P <sup>+</sup>	$3.00 \times 10^{-9}$	$3.00 \times 10^{-9}$	...	...
Cl <sup>+</sup>	$4.00 \times 10^{-9}$	$4.00 \times 10^{-9}$	...	...
Fe <sup>+</sup>	$3.00 \times 10^{-9}$	$3.00 \times 10^{-9}$	$1.50 \times 10^{-8}$	$1.50 \times 10^{-8}$
H <sub>2</sub>	$5.00 \times 10^{-1}$	$5.00 \times 10^{-1}$	$5.00 \times 10^{-3}$	$5.00 \times 10^{-3}$
H <sub>2</sub> O	...	$5.00 \times 10^{-5}$	...	...
H <sub>2</sub> CO	...	$2.00 \times 10^{-6}$	...	...
CH <sub>4</sub> O	...	$2.00 \times 10^{-6}$	...	...
CH <sub>4</sub>	...	$5.00 \times 10^{-7}$	...	...
Temperature (K)	10	100	20	90
H <sub>2</sub> Density (cm <sup>-3</sup> )	$1 \times 10^4$	$1 \times 10^7$	25	$5 \times 10^4$
Cosmic-ray Ionization Rate	$1.3 \times 10^{-17}$	$1.3 \times 10^{-17}$	$5.0 \times 10^{-17}$	$5.0 \times 10^{-17}$
Visual Extinction	10	10	1	10

**Notes.** There is no F included in the OSU gas-grain code.

<sup>a</sup> The elemental abundances are those at the beginning of the simulation, while the molecular abundances (H<sub>2</sub>O, H<sub>2</sub>CO, CH<sub>4</sub>O, and CH<sub>4</sub>) are set to the given values at a model time of  $10^5$  yr.



**Figure 3.** Same as Figure 2 but for N<sup>+</sup> forming N.

we have implemented the DR rate coefficients of Badnell et al. (2003) for He<sup>+</sup>, C<sup>+</sup>, N<sup>+</sup>, O<sup>+</sup>, F<sup>+</sup>, Na<sup>+</sup>, and Mg<sup>+</sup>. No such non-LS coupling calculations exist for Si<sup>+</sup>, P<sup>+</sup>, Cl<sup>+</sup>, and Fe<sup>+</sup>.

### 3. MODELS

#### 3.1. Nahoona

The Nahoona code (Wakelam et al. 2004) is a pseudo-time-dependent chemical model that computes the chemical evolution of gas-phase species for a fixed gas temperature and density. It is suited for modeling dense molecular clouds and protostars. The model includes 452 species with initial conditions being atomic (neutral and singly charged) He, C, N, O, F, Na, Mg, Si, P, S, Cl, and Fe plus molecular hydrogen. Dust grains are included in the

model but are not fully treated; ions are allowed to neutralize by charge exchange with negative grains but accretion of species onto grains is not included, and thus no grain surface chemistry is possible. The code computes the evolution of the abundance of each species as governed by the 4423 included reactions between species. The reaction rate coefficients come from the osu.2005<sup>8</sup> chemical network (Smith et al. 2004). The RR rate coefficients in this network are those from the UMIST database (see discussion in Section 2.1). We have replaced these RR rate coefficients with those of Badnell (2006) for H<sup>+</sup>, He<sup>+</sup>, C<sup>+</sup>, N<sup>+</sup>, O<sup>+</sup>, Na<sup>+</sup>, and Mg<sup>+</sup>. We have also added the DR reactions for He<sup>+</sup>, C<sup>+</sup>, N<sup>+</sup>, O<sup>+</sup>, Na<sup>+</sup>, and Mg<sup>+</sup> using the rate coefficients of Badnell et al. (2003). For the other ions that have not been calculated by Badnell et al. (2003) or Badnell (2006)—Si<sup>+</sup>, S<sup>+</sup>, Cl<sup>+</sup>, and Fe<sup>+</sup>—we have used the RR and DR rate coefficients of Mazzotta et al. (1998). While the elements F and P are present in Nahoona, recombinations of F<sup>+</sup> and P<sup>+</sup> are not included. We have chosen not to introduce these processes and instead concentrate on the effect of the updated RR and DR rate coefficients for those reactions that are already present.

With these new reactions included, we have used Nahoona to simulate the evolution of dense cold clouds and protostars. A dense cold cloud is simulated by assuming a temperature of 10 K, an initial H<sub>2</sub> density of  $10^4$  cm<sup>-3</sup>, a visual extinction of 10 so that the photochemistry driven by external UV photons does not occur, and a fixed cosmic-ray ionization rate of  $1.3 \times 10^{-17}$  s<sup>-1</sup>. These dense cloud conditions are given in Table 1. We use the low-metal elemental abundances of Graedel et al. (1982) as our initial conditions. These are also given in Table 1. For a protostar, we take our initial gas-phase chemical composition as that computed by Nahoona for the above dense cloud conditions at  $10^5$  yr.

<sup>8</sup> [http://www.physics.ohio-state.edu/~eric/research\\_files/osu.2005](http://www.physics.ohio-state.edu/~eric/research_files/osu.2005).

Additionally, we increased the temperature to 100 K, the initial  $\text{H}_2$  density to  $10^7 \text{ cm}^{-3}$ , and set the abundances of  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_4\text{O}$ , and  $\text{CH}_4$  as given in Table 1. This is required because Nahoon does not include the surface chemistry that is needed to form these species, so we artificially increase their abundance in the gas phase to simulate protostar conditions. Results for both dense clouds and protostars are presented in Section 4.

### 3.2. OSU Gas-Grain Code

The OSU gas-grain code (Hasegawa et al. 1992; Garrod & Herbst 2006) is similar to Nahoon in that it follows the evolution of the species abundances as a function of time for a fixed cloud temperature and density. Like Nahoon, it is used to simulate the conditions of dense molecular clouds. However, unlike Nahoon, the OSU gas-grain code includes surface chemistry in addition to gas-phase chemistry. This allows for time-dependent accretion onto grain surfaces as well as thermal and cosmic-ray-induced evaporation from the surfaces. The code assumes a sticking coefficient of unity for neutral species that strike grains. It is unclear whether charged species can also accrete onto grains (Watson 1976). It is assumed here that they do not, with the energy released on neutralization resulting in the species desorbing from the grain surface. This model also includes the new nonthermal evaporation mechanism of Garrod et al. (2007). This process assumes that the energy released by exothermic surface reactions partially evaporates the products.

Species can react on the grain surfaces to form molecules more efficiently than is possible solely in the gas phase. This surface chemistry is an important contributor to the species present in the warm-up phase of hot molecular cores (Garrod & Herbst 2006). Species that form on the grains at earlier times are injected into the gas phase when the dust is heated by a nearby protostar.

The OSU code uses the *osu.2005* chemical network, although there is no F present in the OSU gas-grain code, unlike in Nahoon. With the addition of the surface species to the network used with Nahoon, there are 655 species and 6309 reactions. We added the new RR and DR rate coefficients in the same way as was done in Nahoon (see Section 3.1). With these changes to the chemical network, we have run the OSU code with the same initial conditions as used in Section 3.1 when simulating a dense cold cloud (see Table 1). We present our results in Section 4.

### 3.3. PDR Code

In order to simulate a molecular cloud with a significant impinging radiation field, we use the PDR code of the Meudon group (le Petit et al. 2002, 2006).<sup>9</sup> This code is used to simulate clouds with no rapidly evolving processes occurring. The cloud is treated in steady state as an infinite slab of gas and dust irradiated by an ultraviolet radiation field impinging on both sides of the cloud. While dust is included in the model, there is no surface chemistry other than allowing for the formation of  $\text{H}_2$  which cannot be produced rapidly enough in the gas phase.

Using a standard chemistry file with 120 species we have added the new RR and DR data to the PDR code. The elemental abundances are given in Table 1. We have run the model with physical conditions that simulate a diffuse PDR and, separately, a dense PDR. For diffuse conditions, we set the  $\text{H}_2$  density to  $25 \text{ cm}^{-3}$ , the temperature to 20 K, and the cosmic-ray ionization rate of  $5 \times 10^{-17} \text{ s}^{-1}$ . The radiation field is 1 Draine at the edges of the cloud. For a dense PDR, we simulate the Horse-

head nebula (Pety et al. 2005) with an  $\text{H}_2$  density of  $5 \times 10^4 \text{ cm}^{-3}$ , a temperature of 90 K, and a cosmic-ray ionization rate of  $5 \times 10^{-17} \text{ s}^{-1}$ . For this case the radiation field is 100 Draine at the edge of the cloud. The species abundances are calculated as a function of depth into the cloud. Results are presented in Section 4.

## 4. RESULTS

For the models described in Sections 3.1 and 3.2 we have run the simulation with the original chemical network without any additions, with just the new RR, and again with the new RR and DR rate coefficients included. When running the models with only the new RR data included we find no differences greater than a factor of 2 for any of the models. Only for the OSU gas-grain code do we find abundance differences of greater than 50%. These are found for gas-phase Fe, surface FeH, and surface  $\text{MgH}_2$ , resulting from the change in the  $\text{Mg}^+$  and  $\text{Fe}^+$  RR rate coefficients. The more significant results reported in the remainder of this section can thus be attributed primarily to the effect of DR on the models. For models run using the PDR code described in Section 3.3, we did not perform a similar analysis of the effects of RR alone. When including both RR and DR in the PDR code the only significant difference was in the abundance of C (see later in this section) and, as is evident from Figure 2, this is clearly due to the changes in the DR rate coefficient.

Simulations of a dense, cold molecular cloud of low metallicity were run with the OSU gas-grain code, which computes both gas-phase and surface chemistry. We find that the introduction of DR results in significant differences in certain species evolution. To identify those differences that are most important in the cloud chemistry we consider differences only at times when species have an abundance (either before or after the inclusion of DR) of at least  $10^{-12}$  with respect to the total H nuclei density. This represents those species that are most likely to be detectable. Second, we only consider abundances at times of  $10^4$ – $10^6$  yr in the model evolution as it is during this period in the evolution of the model that observed molecular cloud conditions are best represented. With these criteria, we find 100 species to have a difference in abundance of at least 50% on including DR. We list in Table 2 the 74 species for which we find at least a factor of 2 difference in abundance. Of these 74 species, 48 are attached to the surface of dust grains and 26 are found in the gas phase. The effect of the new DR rate coefficients on species abundances is over 2 orders of magnitude for 16 species. The greatest effect is found for surface  $\text{O}_3$ , with a 3 orders of magnitude difference in abundance. In Figures 4, 5, and 6, we show the evolution of the abundance of surface C, surface  $\text{CH}_3\text{OH}$ , and surface  $\text{O}_3$ , respectively.

We have run the gas-grain model a number of times, including DR for only a single selected ion in each run, and repeated this for every ion. This allows us to determine which ion has the largest effect on the differences we have found. These results indicate that the abundance differences listed in Table 2 are primarily due to the introduction of the  $\text{C}^+$  DR. When the  $\text{C}^+$  DR rate coefficient is not included in the model we find no differences in abundance greater than a factor of 2. The inclusion of DR increases the  $\text{C}^+$  recombination rate, neutralizing C earlier in the model evolution. The model allows neutral species to accrete onto grains but not charged species. Thus, with an increased abundance of neutral C, the surface chemistry is enriched and results in the abundance differences that we observe.

Despite the large increase in the electron–ion recombination rate coefficient for  $\text{N}^+$  (Figure 3), the comparatively small effect

<sup>9</sup> <http://aristote.obspm.fr/MIS/pdr/pdr1.html>.

**Table 2**  
Maximum Abundance Differences Found When Including DR in the OSU Gas-Grain Code Relative to Excluding DR

Species	Phase	Maximum Difference	Time (yr)	Relative Abundance	Gas-Phase Detection <sup>a</sup>	Surface Detection <sup>b</sup>
O <sub>3</sub>	Surface	1440	$1.78 \times 10^4$	$1.06 \times 10^{-8}$	No	No
N <sub>2</sub> H <sub>2</sub>	Surface	59.3	$3.16 \times 10^4$	$1.47 \times 10^{-12}$	No	No
H <sub>2</sub> O <sub>2</sub>	Surface	45.0	$5.62 \times 10^4$	$7.23 \times 10^{-9}$	No	No
HNCO	Gas	38.7	$1.78 \times 10^4$	$6.13 \times 10^{-12}$	Yes	No
HNCO	Surface	37.0	$1.78 \times 10^4$	$2.93 \times 10^{-9}$	Yes	No
NO	Surface	34.9	$3.16 \times 10^4$	$5.44 \times 10^{-12}$	Yes	No
NH <sub>2</sub> CHO	Surface	30.0	$5.62 \times 10^4$	$3.46 \times 10^{-11}$	Yes	No
C <sub>2</sub> H	Surface	27.2	$1.00 \times 10^4$	$1.06 \times 10^{-12}$	Yes	No
C <sub>2</sub> H <sub>4</sub>	Surface	23.1	$1.00 \times 10^4$	$5.64 \times 10^{-10}$	Yes	No
HC <sub>2</sub> O	Gas	18.3	$1.78 \times 10^4$	$2.41 \times 10^{-12}$	No	No
CH <sub>2</sub> CO	Surface	15.0	$1.00 \times 10^4$	$3.10 \times 10^{-10}$	No	No
CH <sub>2</sub> OH	Gas	14.1	$1.00 \times 10^4$	$5.47 \times 10^{-12}$	No	No
CH <sub>3</sub> OH	Gas	13.8	$1.00 \times 10^4$	$3.26 \times 10^{-12}$	Yes	Yes
C <sub>3</sub> H <sub>3</sub> N	Surface	12.8	$3.16 \times 10^4$	$1.98 \times 10^{-12}$	No	No
HC <sub>3</sub> N	Surface	12.5	$3.16 \times 10^4$	$3.77 \times 10^{-11}$	Yes	No
C <sub>2</sub> H <sub>6</sub>	Gas	11.3	$1.00 \times 10^4$	$5.07 \times 10^{-12}$	No	No
CH <sub>2</sub> NH <sub>2</sub>	Gas	9.76	$5.62 \times 10^4$	$1.96 \times 10^{-12}$	No	No
CH <sub>3</sub> NH	Gas	9.76	$5.62 \times 10^4$	$3.65 \times 10^{-12}$	No	No
CH <sub>5</sub> N	Surface	9.55	$5.62 \times 10^4$	$9.48 \times 10^{-9}$	No	No
C <sub>2</sub> H <sub>2</sub>	Surface	8.27	$1.00 \times 10^4$	$1.19 \times 10^{-9}$	Yes	No
CH <sub>3</sub> OH	Surface	7.59	$3.16 \times 10^4$	$2.43 \times 10^{-8}$	Yes	No
N <sub>2</sub> H <sub>2</sub>	Gas	7.44	$1.00 \times 10^5$	$5.57 \times 10^{-12}$	No	No
CH <sub>3</sub> CN	Surface	7.39	$1.00 \times 10^4$	$7.14 \times 10^{-11}$	Yes	No
HCN	Surface	7.37	$1.78 \times 10^4$	$1.24 \times 10^{-8}$	Yes	No
CH <sub>3</sub>	Surface	6.96	$5.62 \times 10^4$	$4.42 \times 10^{-12}$	Yes	No
CH <sub>2</sub>	Surface	6.96	$5.62 \times 10^4$	$4.46 \times 10^{-12}$	Yes	No
HNC	Surface	6.82	$1.78 \times 10^4$	$6.08 \times 10^{-9}$	Yes	No
CH	Surface	6.74	$5.62 \times 10^4$	$3.99 \times 10^{-12}$	Yes	Maybe
C	Surface	6.74	$5.62 \times 10^4$	$4.03 \times 10^{-12}$	No	No
C <sub>2</sub> H <sub>6</sub>	Surface	6.63	$3.16 \times 10^4$	$1.25 \times 10^{-8}$	No	No
N	Surface	6.51	$5.62 \times 10^4$	$1.99 \times 10^{-12}$	No	No
NH	Surface	6.51	$5.62 \times 10^4$	$2.02 \times 10^{-12}$	Yes	No
NH <sub>2</sub>	Surface	6.50	$5.62 \times 10^4$	$2.09 \times 10^{-12}$	Yes	No
O	Surface	6.40	$5.62 \times 10^4$	$1.48 \times 10^{-11}$	No	No
C <sub>4</sub> H <sub>2</sub>	Surface	6.36	$5.62 \times 10^4$	$6.67 \times 10^{-11}$	Yes	No
C <sub>9</sub> H <sub>2</sub>	Surface	6.35	$5.62 \times 10^4$	$1.00 \times 10^{-12}$	No	No
H <sub>2</sub> CO	Surface	6.05	$1.78 \times 10^4$	$3.75 \times 10^{-8}$	Yes	Maybe
H <sub>2</sub> C <sub>3</sub> O	Gas	5.88	$3.16 \times 10^4$	$1.01 \times 10^{-12}$	Yes	No
HC <sub>3</sub> O	Gas	5.88	$3.16 \times 10^4$	$1.90 \times 10^{-12}$	No	No
H <sub>2</sub> C <sub>3</sub> O	Surface	5.86	$3.16 \times 10^4$	$3.53 \times 10^{-10}$	Yes	No
C <sub>3</sub> H <sub>2</sub>	Surface	5.70	$5.62 \times 10^4$	$1.50 \times 10^{-8}$	Yes	No
OH	Surface	5.49	$5.62 \times 10^4$	$1.24 \times 10^{-11}$	Yes	No
C <sub>5</sub> H <sub>2</sub>	Surface	5.43	$5.62 \times 10^4$	$6.92 \times 10^{-12}$	No	No
CH <sub>2</sub> NH	Gas	4.89	$1.00 \times 10^4$	$4.16 \times 10^{-12}$	Yes	No
O <sub>2</sub>	Surface	4.62	$1.78 \times 10^4$	$3.97 \times 10^{-10}$	Yes	No
O <sub>3</sub>	Gas	4.25	$1.00 \times 10^5$	$6.71 \times 10^{-10}$	No	No
H <sub>5</sub> C <sub>3</sub> N	Surface	3.75	$3.16 \times 10^4$	$1.03 \times 10^{-10}$	No	No
N <sub>2</sub> O	Gas	3.48	$1.00 \times 10^4$	$5.05 \times 10^{-11}$	Yes	No
H <sub>2</sub> S	Surface	3.41	$5.62 \times 10^4$	$5.08 \times 10^{-9}$	Yes	No
H <sub>2</sub> O <sub>2</sub>	Gas	3.37	$3.16 \times 10^4$	$9.22 \times 10^{-11}$	No	No
CH <sub>5</sub> N	Gas	3.26	$1.00 \times 10^4$	$2.19 \times 10^{-12}$	No	No
N <sub>2</sub> O	Surface	3.19	$1.78 \times 10^4$	$1.40 \times 10^{-12}$	Yes	No
NO <sub>2</sub>	Gas	3.04	$1.00 \times 10^4$	$2.27 \times 10^{-11}$	No	No
HNO	Gas	2.98	$1.00 \times 10^4$	$2.97 \times 10^{-10}$	Yes	No
HNO	Surface	2.76	$1.00 \times 10^4$	$8.76 \times 10^{-9}$	Yes	No
CH <sub>3</sub> CN	Gas	2.71	$1.00 \times 10^4$	$6.84 \times 10^{-12}$	Yes	No
C <sub>6</sub> H <sub>2</sub>	Surface	2.69	$3.16 \times 10^4$	$1.17 \times 10^{-12}$	Yes	No
NO <sub>2</sub>	Surface	2.62	$3.16 \times 10^4$	$1.05 \times 10^{-12}$	No	No
C <sub>3</sub> H	Surface	2.44	$1.00 \times 10^4$	$1.02 \times 10^{-12}$	Yes	No
CO <sub>2</sub>	Surface	2.23	$1.00 \times 10^4$	$2.08 \times 10^{-10}$	Yes	Yes
CH <sub>3</sub> CO <sup>+</sup>	Gas	2.16	$1.00 \times 10^4$	$2.59 \times 10^{-12}$	No	No
HC <sub>2</sub> NC	Gas	2.09	$1.00 \times 10^4$	$1.51 \times 10^{-12}$	Yes	No
C <sub>3</sub> H <sub>3</sub> <sup>+</sup>	Gas	2.09	$1.00 \times 10^4$	$2.55 \times 10^{-12}$	No	No

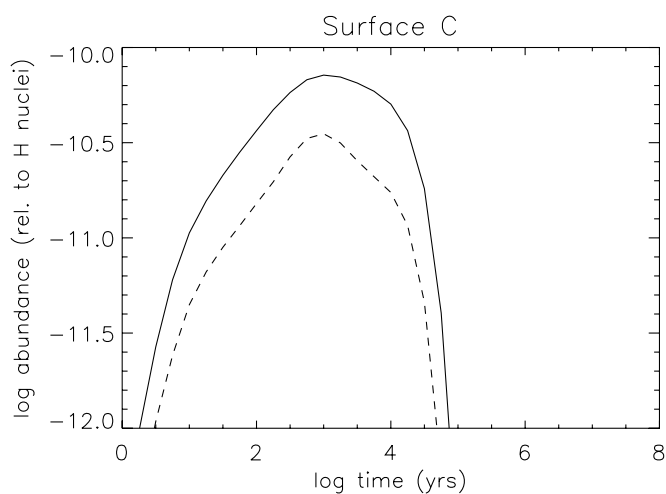
**Table 2**  
(Continued)

Species	Phase	Maximum Difference	Time (yr)	Relative Abundance	Gas-Phase Detection <sup>a</sup>	Surface Detection <sup>b</sup>
HC <sub>3</sub> N	Gas	2.02	$1.00 \times 10^4$	$2.99 \times 10^{-11}$	Yes	No
H <sub>2</sub> CS	Surface	0.141	$1.00 \times 10^4$	$1.93 \times 10^{-12}$	Yes	No
C <sub>2</sub> S	Surface	0.210	$5.62 \times 10^4$	$1.25 \times 10^{-12}$	Yes	No
C <sub>5</sub> H <sub>4</sub>	Surface	0.292	$1.00 \times 10^4$	$2.82 \times 10^{-12}$	No	No
C <sub>3</sub> H <sub>4</sub>	Surface	0.323	$1.00 \times 10^4$	$4.01 \times 10^{-9}$	No	No
CS	Surface	0.325	$1.00 \times 10^4$	$1.71 \times 10^{-12}$	Yes	No
C <sub>6</sub> H <sub>4</sub>	Surface	0.349	$1.78 \times 10^4$	$4.65 \times 10^{-13}$	No	No
HS <sub>2</sub>	Gas	0.384	$5.62 \times 10^4$	$6.88 \times 10^{-12}$	No	No
H <sub>2</sub> S <sub>2</sub>	Gas	0.386	$5.62 \times 10^4$	$6.99 \times 10^{-12}$	No	No
H <sub>2</sub> S	Gas	0.392	$3.16 \times 10^4$	$1.80 \times 10^{-10}$	Yes	No
H <sub>3</sub> S <sup>+</sup>	Gas	0.413	$5.62 \times 10^4$	$7.64 \times 10^{-13}$	No	No

**Notes.** We list the maximum difference factor in abundance when DR is included in the OSU gas-grain code relative to when it is left out. We also list the time in the model evolution when the maximum difference occurs and additionally at this time list the abundance of each species relative to total H nuclei density when DR is included. We also list whether there has been an interstellar detection of the molecule in the gas phase or on dust surfaces.

<sup>a</sup> [http://astrochymist.org/astrochymist\\_ism.html](http://astrochymist.org/astrochymist_ism.html).

<sup>b</sup> Gibb et al. 2004.

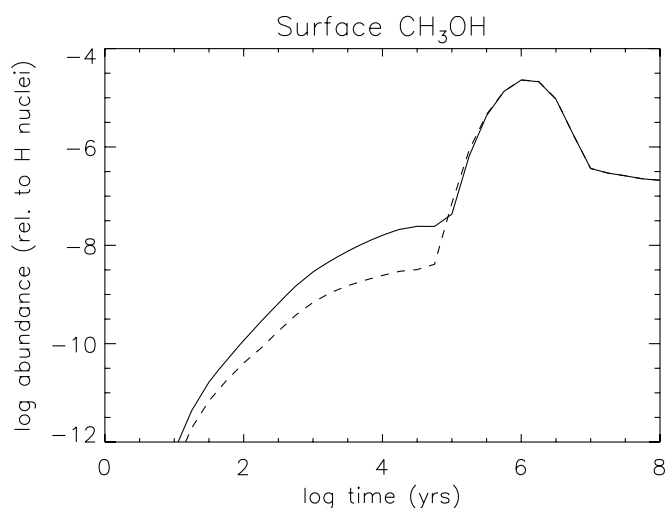


**Figure 4.** Abundance of surface C with respect to the total H nuclei density as a function of time as calculated by the OSU gas-grain code. The solid line is with the new RR and DR data included in the model and the dotted line is without the new RR and DR included.

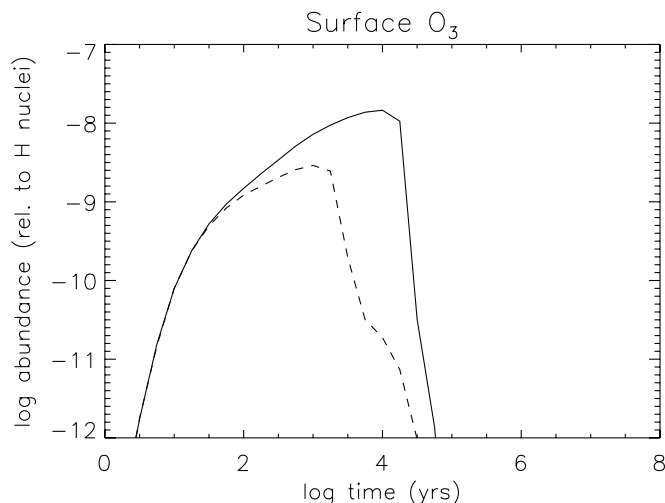
of the inclusion of N<sup>+</sup> DR can be explained by considering the ionization balance of N in the simulation. Initially (see Table 1) all N in the model is in the neutral charge state, so recombination of N<sup>+</sup> with a free electron is not possible. As the model evolves, some N<sup>+</sup> is formed but neutral N remains many orders of magnitude greater in abundance.

In contrast, atomic C, due to its lower first ionization potential, is initially all singly ionized by UV radiation shortward of the 13.6 eV ionization potential of H but above the 11.3 eV ionization potential of C (again see Table 1). Thus, recombination of C<sup>+</sup> is important from the very start of the model evolution and the inclusion of DR greatly increases the electron-ion recombination rate. The increase in the C recombination rate also results in a change in the ionization fraction of the gas as can be seen in the abundance evolution of the sum of all negatively charged species. To show this we plot the free electron abundance in Figure 7. The abundance of all other negatively charged species are negligible in comparison.

To investigate the importance of the surface chemistry on our results, we have run the gas-grain model with no accretion of species onto dust grains allowed. We have compared results with



**Figure 5.** Same as Figure 4 but for surface CH<sub>3</sub>OH.



**Figure 6.** Same as Figure 4 but for surface O<sub>3</sub>.

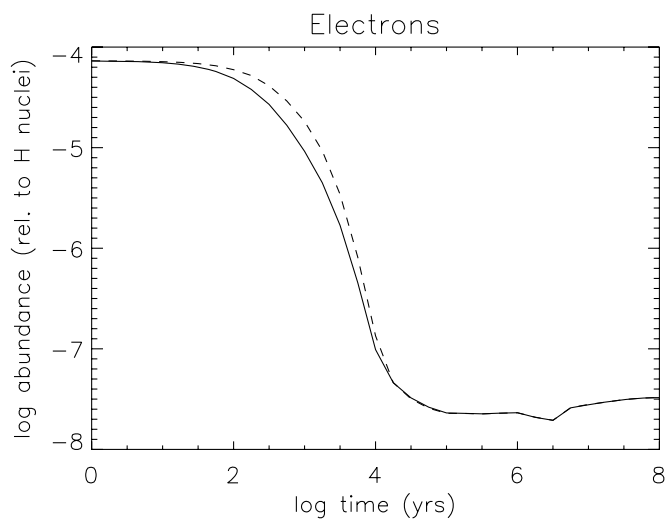


Figure 7. Same as Figure 4 but for free electrons.

and without DR included. With the surface chemistry excluded, we find differences in abundance of 50% for 32 species but a factor of 2 increases for only five species— $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{CO}^+$ ,  $\text{HC}_2\text{NC}$ ,  $\text{C}_3\text{H}_3^+$ , and  $\text{HC}_3\text{N}$ . These five gas-phase molecules had among the smallest changes of the 74 species we identified as having a factor of 2 difference when the surface chemistry was included. Of the 74 species listed in Table 2, 48 are surface species which are unable to form when we do not include the surface chemistry. However, there are also 26 gas-phase species in Table 2. Only the five gas-phase species identified above have differences of a factor of 2 when the surface chemistry is excluded. Of the 21 other gas-phase species in Table 2, 11 have no formation routes without the surface chemistry included. The other 10, whose abundances are greatly enhanced by formation routes on grain surfaces, have changes of less than 50% in a purely gas-phase model. Thus, the majority, and indeed the largest, abundance differences seen when including DR in the OSU gas-grain model are found for species influenced by surface reactions.

Not surprisingly then, we do not find significant abundance differences when running the dense cloud simulation using Nahoon, which does not include grain surface chemistry. All species in Nahoon are in the gas phase. Introduction of the DR data resulted in 20 species having an abundance difference of 50% and only two species,  $\text{OCS}$  and  $\text{C}_2\text{H}_3\text{N}$ , having abundance increases of greater than a factor of 2. When running the protostar simulation using Nahoon, we again find few significant differences when DR is included; 21 species have an abundance difference of 50% or more. The only species with greater than a factor of 2 difference are  $\text{C}_2\text{S}$ ,  $\text{HCN}$ ,  $\text{HNC}$ ,  $\text{C}_2\text{H}_3\text{N}$ ,  $\text{HCOOCH}_3$ ,  $\text{CH}_3\text{OCH}_3$ ,  $\text{H}_2\text{CN}^+$ , and  $\text{CH}_3\text{OCH}_4^+$ , all of which are increased in abundance with DR relative to without.

Simulations of diffuse and dense PDRs were carried out using the Meudon PDR code, allowing us to probe the effect of DR in a molecular cloud with a radiation field present. On introducing the new DR rate coefficients there is a large increase in the total recombination rate of  $\text{C}^+$  and we see a significant effect on the abundance of neutral carbon as a result. This is the case for both diffuse and dense PDRs. The column density of C is shown in Figures 8 and 9 for diffuse and dense regions, respectively, as a function of visual extinction (i.e., depth into the cloud). However, we find no significant abundance differences

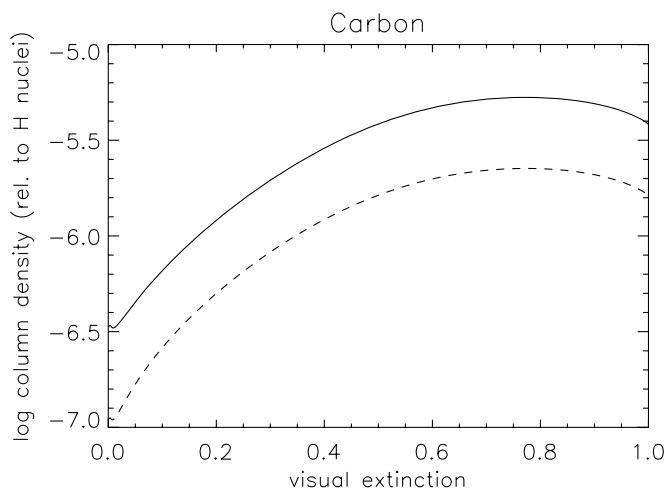


Figure 8. Column density of C relative to the total H nuclei column density as a function of visual extinction (i.e., depth into the cloud) calculated by the Meudon PDR code for a diffuse PDR. The solid line is with the new RR and DR included in the model and the dashed line is without the new RR and DR included.

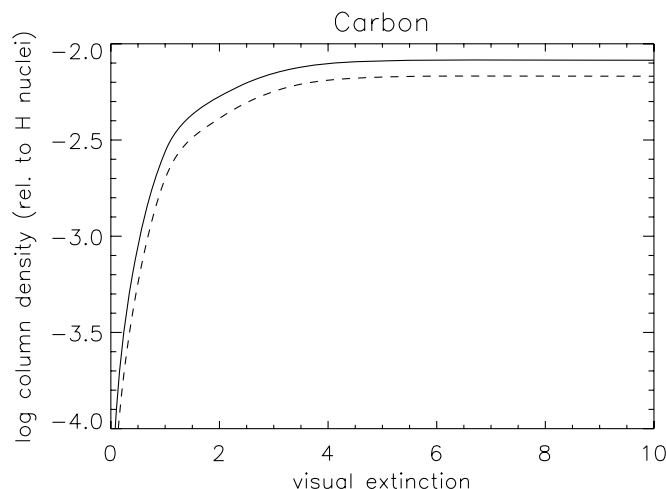


Figure 9. Same as Figure 8 but for a dense PDR.

for any other species in the diffuse case. For a dense PDR, there are only five other species that show an abundance difference greater than 50%— $\text{SO}_2$ ,  $\text{O}_2\text{H}^+$ ,  $\text{HSO}_2^+$ ,  $\text{HOCS}^+$ , and  $\text{C}_4$ . These species all increase in abundance with the introduction of DR but the increases are all less than a factor of 2.

## 5. CONCLUSIONS

This work has investigated the importance of new RR and DR rate coefficients in molecular cloud models. We have updated the RR rate coefficients of  $\text{H}^+$ ,  $\text{He}^+$ ,  $\text{C}^+$ ,  $\text{N}^+$ ,  $\text{O}^+$ ,  $\text{Na}^+$ , and  $\text{Mg}^+$  to the current state-of-the-art in three different molecular cloud chemical models. We have run these models under different conditions and compared the abundances of the species present with and without the new RR rate coefficients. We find that the new RR data have no significant effects on the model results (i.e., less than a factor of 2 effect). We have also included DR for  $\text{He}^+$ ,  $\text{C}^+$ ,  $\text{N}^+$ ,  $\text{O}^+$ ,  $\text{Na}^+$ , and  $\text{Mg}^+$  in the three chemical models, finding some sizable differences (greater than a factor of 2) in the evolution of certain species.

We find that DR has the greatest effect for dense cloud models, particularly when surface chemistry is included. Of the models we ran here, only the OSU gas-grain code includes the extensive surface chemistry that allows species to be accreted onto grains and subsequently react with other surface species. Nahoon does not include this surface chemistry and the Meudon code only allows the formation of  $H_2$  on surfaces. DR has its greatest influence for species that form on grain surfaces. These species may be particularly important in the warm-up phase of molecular clouds when they become desorbed into the gas phase. We find DR of  $C^+$  to be primarily responsible for the abundance changes in the model. This is because charged species are assumed not to accrete onto grains and adding DR increases the gas-phase neutral C abundance available for first accreting onto grains and then participating in the surface chemistry.

We conclude by noting that there are some ions for which no state-of-the-art RR or DR data exist, specifically  $Si^+$ ,  $P^+$ ,  $S^+$ ,  $Cl^+$ , and  $Fe^+$ . Given the fine structure present in the ground terms of  $Si^+$ ,  $Cl^+$ ,  $P^+$ , and  $Fe^+$ , one would expect a significant DR component to the total electron-ion recombination rate coefficient at low temperatures for these ions. These four elements also have first ionization potentials below that of H (13.6 eV). Given that they would thus be ionized in molecular clouds, the effect of increasing their recombination rates may be important. Modern calculations of both RR and DR rate coefficients for these ions are needed for generating reliable molecular cloud chemical models.

P.B., H.K., and D.W.S. were supported in part by the NASA Astronomy and Physics Research and Analysis Program and the NSF Astronomy and Astrophysics Grants Program. E.R. and V.W. were supported in part by the French national program Physique et Chimie du Milieu Interstellaire (PCMI).

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