The Effects of Cosmic Rays on the Chemistry of Dense Cores

Ross O’Donoghue\textsuperscript{1} \textsuperscript{\textcopyright}, Serena Viti\textsuperscript{2,1} \textsuperscript{\textcopyright}, Marco Padovani\textsuperscript{3} \textsuperscript{\textcopyright}, and Tomas James\textsuperscript{1} \textsuperscript{\textcopyright}

\textsuperscript{1} Department of Physics & Astronomy, University College London, Gower Street, London, WC1E 6BT, UK; ross.o.donoghue.19@ucl.ac.uk
\textsuperscript{2} Leiden Observatory, Leiden University, P.O. Box 9513, 2300 RA Leiden, The Netherlands
\textsuperscript{3} INAF-Osservatorio Astrofisico di Arcetri, Largo E. Fermi, 5, I-50125 Firenze, Italy

Received 2022 February 3; revised 2022 June 14; accepted 2022 June 14; published 2022 July 26

Abstract

Cosmic rays are crucial to the chemistry of molecular clouds and their evolution. They provide essential ionizations, dissociations, heating, and energy to the cold, dense cores. As cosmic rays pierce through clouds they are attenuated and lose energy, which leads to a dependency on the column density of a system. The detailed effects these particles have on the central regions still need to be fully understood. Here, we revisit how cosmic rays are treated in the UCLCHEM chemical modeling code by including both ionization rate and \Htwo dissociation rate dependencies alongside the production of cosmic ray induced excited species and we study in detail the effects of these treatments on the chemistry of pre-stellar cores. We find that these treatments can have significant effects on chemical abundances, up to several orders of magnitude, depending on the physical conditions. The ionization dependency is the most significant treatment influencing chemical abundances through the increased presence of ionized species, grain desorptions, and enhanced chemical reactions. Comparisons to chemical abundances derived from observations show the new treatments reproduce these observations better than the standard handling. It is clear that more advanced treatments of cosmic rays are essential to chemical models and that including this type of dependency provides more accurate chemical representations.

Unified Astronomy Thesaurus concepts: Astrochemistry (75); Chemical abundances (224); Cosmic rays (329)

1. Introduction

Cosmic rays (CRs) play a vital role in the chemistry of cold (10–30 K), dense (>10\textsuperscript{3} cm\textsuperscript{-3}) molecular clouds as they can pierce deep into them, unlike interstellar UV radiation (for a review see Indriolo & McCall 2013). These high-energy interstellar particles primarily consisting of protons can be heavier elements and electrons, and have large energy ranges, up to zetaelectronvolt energies (Blandford et al. 2014). Although the energies can be high, it is the lower energy CRs (≤1 TeV) that affect the dense interiors (Viti et al. 2013; Padovani et al. 2020). In these regions, CRs have a wide variety of effects, one of the most important is being a producer of atomic hydrogen through the dissociation of \Htwo (van der Werf et al. 1988; Montgomery et al. 1995; Li & Goldsmith 2003; Goldsmith & Li 2005; Padovani et al. 2018a). Other important effects are being the dominant source of ionization; regulating the degree of coupling of the gas and the magnetic field; having an important role in the dynamics and the collapse timescale of collapsing clouds (e.g., Padovani et al. 2013, 2014); providing heating and energy to dust grains (de Jong & Kamijo 1973; Shingledecker et al. 2018; Kalvàns & Kalnin 2019; Sipilä et al. 2020, 2021; Silsbee et al. 2021) producing internal UV photons (Prasad & Tarafdar 1983); may have a role on the charge distribution on dust grains (Ivlev et al. 2015); influencing disk growth (Kuffmeier et al. 2020); and affecting deuteration (Caselli et al. 2008). For example, each species ionized by a CR releases an electron. This secondary electron can cause further collisions, which in turn, depending on the energy, can induce more ionization and heating (Ivlev et al. 2021). If a secondary electron does not have enough energy to ionize a species, the species may become excited (Shingledecker & Herbst 2018). Excited species produced by CR bombardment have energy levels higher than their base counterparts, allowing these excited species to overcome some reaction barriers that would otherwise be difficult in cold environments. These species have been shown to drive more complex chemistry from reactions that can form interstellar complex organic molecules (Abplanalp et al. 2016).

Although CRs can pierce deep into the molecular clouds, they are still attenuated as they collide and lose energy. The denser the region is, the lower the CR ionization rate becomes (Padovani et al. 2018b). This leads to a dependency of the ionization rate on the density of a region, more precisely on the \Htwo column density passed through by CRs. As the Earth is shielded from the low-energy spectrum of CRs through solar modulation (see Potgieter 2013, for a review on solar modulation), measurements of the CR ionization rate taken from Earth are not indicative of measurements in the interstellar medium (ISM), and are in fact lower. Observations of molecules that are dependent or sensitive to the CR ionization rate (for example, \Htwo is produced from CR ionization of \Htwo) can be used as a tracer for the ionization rate (see Viti et al. 2013, for a review). The typical value for the CR ionization rate is often taken to be around the order of 10\textsuperscript{-17} \text{ s}^{-1} (e.g., Spitzer & Tomasko 1968; Solomon & Werner 1971; Herbst & Klemperer 1973; Li & Goldsmith 2003). It is necessary to note that while this may be known as the typical rate, observations show environments with significantly higher rates. Diffuse clouds have been observed with ionization rates in the order of 10\textsuperscript{-16} \text{ s}^{-1} (Indriolo et al. 2007; Indriolo & McCall 2012) and rates of up to 10\textsuperscript{-14} \text{ s}^{-1} have been observed within the inner 300 pc of the Galactic Center (Oka et al. 2005; Le Petit et al. 2016).

Recently, both Voyager spacecraft passed beyond the heliopause, and have been observing lower energies of the CR spectrum (as low as 3 MeV for both nuclei and electrons).
such as CO for example, the H2 dissociation rate is 1.30 rate in Equation
electrons produced from CR ionization and can be represented
ionization rate. The rate is dependent on the secondary
networks, is not a constant value and is not equal to the
dissociation rate is higher than is often represented in chemical
ionization rate. In chemical networks, however, the rate is often
dissociation, as the UV photons for photodissociation cannot
In high-density regions, this reaction is the only form of H2
and the subsequent reaction

\[ \text{H}_2 + \text{CR} \rightarrow \text{H}_2^+ + e^- + \text{CR}' \]

where \( \text{H}_2 \) ionization is the rate limiting reaction. In dense
clouds, \( \text{H}_2^+ \) can then react via proton transfer with molecules
such as CO (to form HCO+ or HOC+), O (forming OH\( ^+ \)), N2
(forming HN\( ^+ \)), and HD (forming H2D\( ^+ \)). See the review by
Indriolo & McCall (2013) for a more in-depth summary.

CRs also dissociate molecular hydrogen in the ISM through
the reaction:

\[ \text{H}_2 + \text{CR} \rightarrow \text{H} + \text{H} + \text{CR}'. \]

In high-density regions, this reaction is the only form of H2
dissociation, as the UV photons for photodissociation cannot
penetrate deep into the cloud. This reaction depends on the CR
dissociation rate, which is often taken to be equal to the
ionization rate. In chemical networks, however, the rate is often
lower than the typical value. In UMIST (McElroy et al. 2013),
for example, the H2 dissociation rate is \( 1.3 \times 10^{-18} \) s\(^{-1} \). In
Padovani et al. (2018a), it has been shown that the H2
dissociation rate is higher than is often represented in chemical
networks, is not a constant value and is not equal to the
ionization rate. The rate is dependent on the secondary
electrons produced from CR ionization and can be represented
as a function of column density, similar to the CR ionization
rate in Equation (1) (Padovani et al. 2018a).

As discussed, it is clear that CRs are extremely important to
the chemistry of molecular clouds and their evolution, and
hence it is essential that their effects are represented accurately
within modern chemical models. This paper aims to improve
the handling of CRs in gas-grain chemical models, by
introducing both the CR ionization rate and the H2 dissociation
rate as functions of column density and to include the ability to
produce excited species and their reactions on the grain. The
chemical effects of these additions will be tested on models of
collapsing cloud cores. These environments are crucial steps in
the early stages of star formation and the effects of CRs on
these objects where the gas density increases with time and
changes the column density of the core, still need to be
investigated. In Section 2, we discuss the chemical modeling
and details of the CR treatments we have included for this
paper. In Section 3, we describe the effects these treatments
have on the chemical abundances of selected species and
discuss the main processes involved in these changes, while in
Section 4 we summarize our findings.

2. Modeling

The chemical code selected for this paper is UCLCHEM
(Holdship et al. 2017). UCLCHEM is a time-dependent gas-
grain chemical code, written in modern Fortran. UCLCHEM is
an open-source chemical code, freely available for use and
modification. It is diverse in use due to its modular nature.
Specific environments (shocks, cores, and collapses) each have
their own physics module. UCLCHEM uses separate gas and
grain networks. The default gas-phase network used is the
UMIST RATE12\(^4\) network, described in McElroy et al. (2013),
and is used for this paper. The grain network used is described
in Section 2.1.3 below. For more detailed information on
UCLCHEM see Holdship et al. (2017) or visit the UCLCHEM
website.

2.1. Treating CRs in UCLCHEM

2.1.1. CR Ionization Rate

In Padovani et al. (2018b), a polynomial fit was developed to express
the dependency of the CR ionization rate on column
density. We have implemented such a fit into UCLCHEM.

\[
\log_{10} \left( \frac{z}{s^{-1}} \right) = \sum_{k=0}^{9} c_k \log_{10} \left( \frac{N}{\text{cm}^{-2}} \right),
\]

where \( k \) is an integer ranging from 0–9, \( c_k \) is the fitting
coefficient, and \( N \) is the column density.

Equation (1) is used to calculate the ionization rate at each
time step and the calculated rate is used in all chemical
reactions that involve the CR ionization rate.

Table A1 gives two sets of fitting coefficients. One, labeled
as model \( L \), describes the trend of the ionization rate as a
function of the column density obtained by using the Voyager
data; the other, labeled as model \( H \), represents the average
value of the ionization rate in diffuse clouds (Shaw et al. 2008;
Neufeld et al. 2010; Indriolo & McCall 2012; Neufeld &
Wolffire 2017).

2.1.2. H2 Dissociation Rate

Padovani et al. (2018a) evaluated the H2 dissociation rate
based on the same CR interstellar spectra used to compute the
ionization rate. In the following, the dissociation rate is
parameterized as a function of the column density by using
Equation (1) with the coefficients listed in Table A1. Similar
to the CR ionization treatment, the dissociation rate can now
be calculated at each time step of the model. However, this
handling of the dissociation rate can only be activated if the
CR ionization dependency is also activated and is automatically
set to the same model (\( L \) or \( H \)) as the CR ionization
dependency.

Figure 1 shows how the CR ionization rate and H2
dissociation rate differ from the standard handling of
UCLCHEM (i.e., the fixed, user-defined value) under increasing
density. This particular example shows all three models at a
\( \times 1 \) ionization factor. UCLCHEM handles the ionization rate in
multiples of \( 1.3 \times 10^{-17} \) s\(^{-1} \), so an ionization factor of \( \times 1 \) will
correspond to an ionization rate of \( 1.3 \times 10^{-17} \) s\(^{-1} \) and a H2

\(^4\) www.udfa.net
dissociation rate of $1.3 \times 10^{-18} \text{ s}^{-1}$ for the standard handling. UCLCHEM calculates the column density by multiplying the size of the cloud (in parsecs) by the total hydrogen density (per cubic centimeter).

### 2.1.3. Excited Species

UCLCHEM uses a user-defined grain network, separate from the gas-phase network. The default grain network that is provided with UCLCHEM handles some basic CR and photon interactions, freeze-out reactions, and chemical desorption and diffusion reactions. This network was used for this paper, with the additions of excited species production and reactions due to CRs: these excited species are added using the principles described in detail in Shingledecker & Herbst (2018) and used in Shingledecker et al. (2018).

The underlying principles are that CR bombardments of a solid species generally have one of the following outcomes:

$$(\text{R1}) A + \text{CR} \rightarrow A^+ + e^- + \text{CR'}$$
$$(\text{R2}) A + \text{CR} \rightarrow B^* + C^* + \text{CR'}$$
$$(\text{R3}) A + \text{CR} \rightarrow B + C + \text{CR'}$$
$$(\text{R4}) A + \text{CR} \rightarrow A^* + \text{CR'}$$

where A is the target species, B and C are dissociated products and * represents an excited species. The reaction rates for these interactions are defined in Shingledecker & Herbst (2018) and follow the formula:

$$k_{\text{Rn}} = G_{\text{Rn}} \left( \frac{S_e}{100 \text{ eV}} \right) \left( \phi_{\text{ST}} \left[ \frac{\zeta}{10^{-17} \text{ s}^{-1}} \right] \right),$$

where $G_{\text{Rn}}$ is the radiochemical yield for the reaction pathway Rn, (Rn being R1–R4 above), and $S_e$ is the electronic stopping cross section. $\phi_{\text{ST}}$ is the integrated Spitzer–Tomasko CR flux (from 0.3 MeV–100 GeV) and has a value of 8.6 cm$^{-2}$ s$^{-1}$. $\zeta$ is a CR ionization rate scaling factor for the CR flux.

Once produced, an excited species will either react with another solid species, or relax back to the ground energy state. The excited species reaction proceeds at the rate:

$$k_{\text{st}} = f_{br} \left( \frac{v_0 + v_0^*}{N_{\text{site}} n_{\text{dust}}} \right),$$

where $f_{br}$ is the branching ratio, $v_0$ is the vibrational frequency of the species, $N_{\text{site}}$ is the number of physisorption sites on the grain, and $n_{\text{dust}}$ is the dust density.

### 2.2. Modeling Pre-stellar Cores

The effects of these additions will be studied in the cases of pre-stellar cores. Pre-stellar cores represent the early stages of low-mass star formation and have densities in the range of $10^4$–$10^7$ cm$^{-3}$, depending among other things, on their evolutionary stage. The models will be set to mimic these regions; in each case, the model will start at an initial density of $10^2$ cm$^{-3}$. At $\sim 10^5$ yr, the models will collapse in freefall to a specific final density. To cover the density range, the models have four possible final densities: $10^4$, $10^5$, $10^6$, or $10^7$ cm$^{-3}$. After collapsing, the models are set to run with static conditions until a final time of $10^8$ yr is reached, in order to investigate the chemical evolution over time. To determine the influence that temperature and radiation field may have on the CR ionization dependency, each will be varied independently (see Table 1 for values). Note: UCLCHEM assumes 1 Habing to be the Galactic radiation field strength. The chemical species that will be analyzed are H$_2$O, CS, NH$_3$(grain)$^\ddagger$, N$_2$H$^+$, NH$_3$, CO(grain)$^\ddagger$, HCO$^+$, H$_2$O(grain)$^\ddagger$, and CO$_2$(grain)$^\ddagger$. These species are important as some act as tracers of the gas phase of pre-stellar cores, their regions, and physical conditions (CS, N$_2$H) (Lee et al. 1999), and some are key species for grain chemistry and the chemical complexity (NH$_3$, NH$_3$(grain)$^\ddagger$) (Rodgers & Charnley 2001) and others are some of the most abundant species found in these regions (H$_2$O(grain)$^\ddagger$, CO(grain)$^\ddagger$, and CO$_2$(grain)$^\ddagger$) (Öberg et al. 2011).
The CR ionization dependency, H\textsubscript{2} dissociation dependency, and excited species production and reactions will all be tested individually as well as combined. To test the effects of the CR ionization dependency, under each condition, models will be run with the CR ionization dependence turned off and compared to the same conditions with the \(L\) and the \(H\) model dependencies activated. The H\textsubscript{2} dissociation rate dependency can only be activated when the \(L\) or \(H\) ionization model is also selected. To test the influence of the H\textsubscript{2} dissociation rate, \(L\) and \(H\) models with the dissociation dependency disabled will be compared to the same model with the dissociation dependency activated. The excited species can be activated without the CR or H\textsubscript{2} dissociation rate dependencies. As such their effects will be examined independently of the other additions and then combined together. Table 1 shows a summary of the parameters investigated, their values, and their descriptions. In total, a grid of 280 models were run.

### 3. Results

When discussing the influence of the CR ionization rate dependency on the chemistry of pre-stellar cores, our simulated core evolution is split into three phases. The pre-collapse phase covers the period of up to \(\sim 10^5\) \(\text{yr}\) and represents the period of time leading up to the beginning of the cloud collapse (abundances are examined at a time of \(10^5\) \(\text{yr}\)). This phase of the model has a gas density of \(10^2\) \(\text{cm}^{-3}\), until the collapse phase where density begins to increase. The cloud collapse phase represents the time at which the cloud is undergoing collapse in freefall and occurs between \(\sim 10^6\) and \(6 \times 10^6\) \(\text{yr}\), depending on the final density. The density here is increasing over this period from the initial density to the selected final density of the model. The post-collapse phase represents the period of static density, after the cloud collapses to the designated final density. The post-collapse phase will always have a constant density equal to the selected final density parameter of the individual model. In order to assess trends in our simulations, we set a lower limit for observable fractional abundances of \(10^{-13}\), below this fractional abundance, changes across the parameter space will be considered irrelevant. Additionally, any changes in abundances that are below a factor of 3 will not be discussed, as these differences are not likely observable. Any abundance changes that do not obey the following trends are listed in Table 2.

#### 3.1. Density Dependent Ionization Rates

Figure 2 shows the effects of adding the ionization rate density dependency on chemical abundances for a final density of \(10^4\) \(\text{cm}^{-3}\), a temperature of 10 \(\text{K}\), a radiation field strength of 1 Habing, and an un-adjusted ionization rate factor of \(\times 1\). Table A2 summarizes the abundance trends. In the pre-collapse phase, the addition of the ionization rate dependency results in reduced abundances for all our selected species. The same trend is seen for both the \(L\) and \(H\) models with the \(H\) model having enhanced effects (i.e., larger reductions in abundances, up to 3 orders of magnitude, see Table A2). We note that during this phase of the pre-stellar core evolution, the CR ionization rate is indeed higher by almost a factor of \(\sim 20\) compared to the value used for the standard model, which proves to be very destructive in the early stages.

This destruction comes from both the increased presence of ionized species and increased grain desorptions. H\textsuperscript{+} and He\textsuperscript{+} are two ions that play important roles in gaseous destruction. For example, with CS, the main destruction route during the pre-collapse phase under the standard model comes from its photodissociation into S and C with some contribution from photoionization and reactions with ionized species. The increased ionization rates for the \(L\) and \(H\) models result in increased abundances for the H\textsuperscript{+} and He\textsuperscript{+} ions. The H\textsuperscript{+} ion plays a part in the CS destruction through the route

\[
\text{H}^+ + \text{CS} \rightarrow \text{CS}^+ + \text{H}.
\]

The importance of this reaction is enhanced with the \(L\) model and is significantly more dominant for the \(H\) model. The \(H\) model also has higher destruction contributions from the He\textsuperscript{+} ion via the routes

\[
\text{He}^+ + \text{CS} \rightarrow \text{S}^+ + \text{C} + \text{He},
\]

\[
\text{He}^+ + \text{CS} \rightarrow \text{S} + \text{C}^+ + \text{He}.
\]

A second example of this is H\textsubscript{2}O, where the destruction in the standard model has some contributions from C\textsuperscript{+} and H\textsubscript{2}O...
Figure 2. Plot showing the effect of the \(L\) and \(H\) ionization models (short- and long-dashed black lines, respectively) on chemical abundances over time compared to the basic UCLCHEM handling (solid black line). These models have a final density of \(10^4\) cm\(^{-3}\), an initial temperature of 10 K, a radiation field of \(\times 1\), and an ionization rate of \(\times 1\). The red line represents the time at which the final density is reached and the numbers in the legend represent the model number identifier.

Table 2

The Post-collapse Species, Conditions, and the Behavior That Do Not Follow the General Trends of the Ionization Dependency

| Species  | Conditions                  | Ionization rate dependency                                      | Behavior                                           |
|----------|-----------------------------|----------------------------------------------------------------|---------------------------------------------------|
| H\(_2\)O | \(10^6\) cm\(^{-3}\), \(H\) model | Increase in abundance larger than other densities.            |                                                   |
| N\(_2\)H\(^+\) | \(10^5\) cm\(^{-3}\), \(H\) model | Only density to undergo a notable change (increased abundance).   |                                                   |
| NH\(_3\)  | \(10^6\) cm\(^{-3}\), \(H\) model | Only density to undergo a notable change (increased abundance).   |                                                   |
| HCO\(^+\) | \(10^6\) cm\(^{-3}\), \(H\) model | Increase in abundance larger than other densities.              |                                                   |

Ionization rate dependency with parameter variations

| Species  | Conditions                  | Behavior                                                   |
|----------|-----------------------------|------------------------------------------------------------|
| N\(_2\)H\(^+\) | 20 K, \(10^6\) cm\(^{-3}\), \(H\) model | Change in abundance greater than other densities.           |                                                   |
|           | 30 K, \(10^6\) cm\(^{-3}\), \(H\) model | Only condition to undergo a change in abundance at 30 K. Abundance not as reduced as at 20 K. |                                                   |
| NH\(_3\)(grain) | 30 K, \(10^5\) cm\(^{-3}\), \(H\) model | Only condition to undergo a change in abundance at 30 K. Abundance further reduced than at 20 K. |                                                   |
| CO\(_2\)(grain) | 30 K, \(10^5\) cm\(^{-3}\), \(H\) model | Only condition to undergo a change in abundance at 30 K. Abundance further reduced than at 20 K. |                                                   |
| CS       | 100 times radiation field, \(10^5\) cm\(^{-3}\), \(H\) model | Abundance is not as reduced as at 10 times radiation field. |                                                   |
| H\(_2\)O(grain) | 100 times initial ionization rate, \(10^5\) cm\(^{-3}\), \(H\) model | Reduction in abundance is greater than at \(10^4\) cm\(^{-3}\). |                                                   |
reactions but is mostly dominated by H$_2$O photodissociation into OH and H. Similarly to CS, the increased abundances of H$^+$ at higher ionization rates drove the destruction of H$_2$O through the reaction

$$H^+ + H_2O \rightarrow H_2O^+ + H.$$  

While gaseous species undergo reduced abundances due to ions, solid species undergo these reductions via CR-induced desorptions. For example, H$_2$O$_{(grain)}$ in the standard model is primarily destroyed by CR-induced UV desorptions. With the increased ionization rates of the $L$ model, direct CR desorption also begins to take place. The even higher ionization rates of the $H$ model result in both the CR-induced UV desorption and the direct CR desorptions becoming more efficient, resulting in the reduced abundances seen.

During the post-collapse phase, species only undergo notable changes in abundance with the $H$ model. Gas-phase H$_2$O and CS have increased abundances while the solid phase CO$_{(grain)}$ and CO$_2$(grain) show decreased abundances. In this case, the solid phase species tend to undergo more destruction, with CO$_{(grain)}$ and CO$_2$(grain) decreasing in abundance by over 3 orders of magnitude and the gaseous species undergo increases up to a factor of 20. While these large decreases in abundances are mainly caused by CR-induced desorptions, there are also contributions from reduced formation rates. CO freeze-out to CO$_{(grain)}$ is the dominant formation route during the cloud collapse. Under the $H$ model, this formation method is significantly inhibited during the collapse phase, reducing the amount of freeze-out taking place. CO$_2$(grain) is also affected by the CO freeze-out inhibition. The primary formation route for CO$_2$(grain) comes from the diffusion of CO$_{(grain)}$ and OH$_{(grain)}$. Reduced abundances for both of these species with the $H$ model inhibit the amount of CO$_2$(grain) formation. The combination of less formation and more desorption results in these significant decreases seen with the $H$ model. These increased desorptions can also influence the gas-phase species. After the collapse, the primary H$^+$ destruction route for H$_2$O is no longer efficient; this fact coupled with the increased desorptions of H$_2$O$_{(grain)}$, result in the increased post-collapse abundances seen. Other species, like CS, are not as reliant on desorptions. After the collapse, the primary formation route for CS comes from the photodissociation of H$_2$CS into CS and H$_2$. The H$_2$CS molecule also shows increased abundances for the $H$ model and significantly so for the $H$ model, which in turn leads to more efficient photodissociation.

When the final density is increased, this reduces the effects of the addition of ionization dependency. CO$_{(grain)}$ and CO$_2$(grain) are prime examples of this effect, as the large decreases in abundances seen at 10$^3$ cm$^{-3}$ are no longer present at higher densities (changes in abundance are now under an order of magnitude). The reduced ionization rates as density increases are the main cause of this feature through reduced CR desorptions. Also, under these conditions, CO freeze-out
during the collapse is not inhibited by the increased ionization rates. This, along with the lower desorptions, leads to the reduced effects of the ionization dependency.

3.1.1. Effects Due to Temperature Variations

Figure 3 shows the \( L \) and \( H \) models with an increased initial temperature of 20 K, while Table A3 summarizes the effects on the \( L \) and \( H \) models with initial temperatures of 20 K and 30 K. During the pre-collapse phase, when the temperature is increased, only CS and HCO\(^+\) show notable changes. Both still show a reduction in abundance with the ionization dependency, but the reduction is lower at higher temperatures (CS is reduced by over 2 orders of magnitude and HCO\(^+\) is reduced by up to a factor 6 for the \( H \) model). At higher temperatures, only \( \text{H}_2\text{O}, \text{CS}, \text{and HCO}^+ \) have abundances above the set limit of \( 10^{-15} \). For the post-collapse phase, increasing the temperature to 20 K results in larger changes in abundance than in the \( H \) model for solid and gas-phase \( \text{NH}_3 \). However, CS, CO\((\text{grain})\), and CO\(_2\)(\text{grain}) instead undergo less of a change than at 10 K (significant in the cases of CO\((\text{grain})\) and CO\(_2\)(\text{grain}), where the large reduction in abundance at 10 K for the \( H \) model is no longer seen). At 30 K, only CS and \( \text{NH}_3 \) have their abundance change by over a factor of 3 (both by a factor of \( \sim 8 \)) and in both cases, these changes are less than they are at 20 K for the \( L \) model. Increasing the density at these temperatures has a similar effect as that at 10 K (i.e., reduced changes as density increases).

Gas-phase \( \text{NH}_3 \) abundances are strongly influenced by the solid phase \( \text{NH}_3 \) abundances. Gas-phase formation comes completely from grain desorptions. \( \text{NH}_3(\text{grain}) \), however, at 10 K under all models, is formed via \( \text{H}(\text{grain}) \) and \( \text{NH}_2(\text{grain}) \) diffusion. As the temperature increases, this reaction becomes less dominant, particularly during the pre-collapse phase and with the \( H \) model at 30 K. In this case, there is no formation from the diffusion reaction, which results in \( \text{NH}_3(\text{grain}) \) having abundances below the set limit. CO\(_2\)(\text{grain}) at higher temperatures, relies less on CO\((\text{grain}) \) diffusion. During the post-collapse phase, the primary formation rate comes from the diffusion reaction:

\[
\text{H}_2\text{CO}(\text{grain}) + \text{O}(\text{grain}) \rightarrow \text{CO}_2(\text{grain}) + \text{H}_2.
\]

The reduced changes in abundance for CO\(_2\)(\text{grain}) here are a result of the H\(_2\)CO\((\text{grain}) \) abundances. Under the \( L \) model, H\(_2\)CO\((\text{grain}) \) has higher abundances, resulting in more diffusion, which is balanced out by the increased desorption of CO\(_2\)(\text{grain})-leading to little change from the standard model. The \( H \) model on the other hand, still sees a reduction in abundance, which is a result of the increased desorptions, but the reduction is not as severe as it is at 10 K, due to the \( H \) model having increased O\((\text{grain}) \) abundances for more diffusion.
3.1.2. Effects Due to Variations in the Radiation Field Strength

Figure 4 shows the differences between the standard model and the models where the new treatment of the cosmic ionization rate is included, when the radiation field is increased by a factor of 10. Table A3 summarizes the results of enhancing the radiation field by factors of 10 and 100.

In the pre-collapse phase, enhancing the radiation factor by a factor of 10 reduces the changes in abundance produced by the ionization dependency, which are further reduced when the radiation field is increased by a factor of 100 (changes in abundance are up to 1 order of magnitude, see Table A3). During the post-collapse phase, in general, increasing the radiation field enhances the effects of the ionization rate dependency. At a radiation field of 100 Habing, only H$_2$O, CS, NH$_3$, and HCO$^+$ are above the $10^{-13}$ threshold and have increased abundances compared to the standard model. Changes in H$_2$O, NH$_3$, and HCO$^+$ are enhanced by $\sim$1, $\sim$2, and $\sim$1 orders of magnitude, respectively. The large increase in abundance for NH$_3$ comes from desorption from the grains. Under the standard model and the L model, NH$_3$(grain) abundances are below the set limit. This is not the case for the H model. The increased grain abundance here is due to the diffusion of H$_2$(grain) and NH$_2$(grain). Under these conditions, both of these species have significantly higher abundances with the H model than the L or standard model. This increases NH$_3$(grain) formation, which then can desorb into the gas phase. For HCO$^+$, under the increased radiation field, there are two main formation routes, photoionization of HCO and the H$_3^+$ reaction:

$$\text{H}_3^+ + \text{CO} \rightarrow \text{HCO}^+ + e^-.$$

Under the L and H models, both CO and H$_3^+$ have much higher abundances, leading to the increased production of HCO$^+$. When the density is increased above $10^4$ cm$^{-3}$, there are no significant differences between the effects of the ionization dependency at the standard radiation field strength and the effects at increased strengths.

3.1.3. Effects Due to the Variations in the Initial CR Ionization Rate

Figure 5 shows the effects of increasing the ionization rate by a factor of 10 on the chemical abundances with the ionization rate dependency. Table A3 summarizes the results of increasing the rate by factors of 10 and 100.

Increasing the initial ionization rate in this manner proves to be very destructive both with and without the ionization dependency, particularly in the pre-collapse phase. Many species have abundances below the set limit with this increased ionization rate factor. Those that are visible show much larger abundance reductions (up to 2 orders of magnitude, see Table A3) than at an un-adjusted rate. During the post-collapse phase, increasing the ionization rate by factors of 10 and 100, increases the influence of the ionization dependency. Species that had no notable changes under the standard rate now show...
reduced abundances. $\text{CO}_{\text{grain}}$ and $\text{CO}_2{\text{grain}}$ again are particularly affected, showing reductions of up to 7 orders of magnitude. These effects are more enhanced in the $\times 100$ initial ionization rate. As with the other conditions, cores of higher densities show reduced effects from the ionization dependency, even with the enhanced initial CR ionization rate. These trends originate for the same reasons as for the models with a standard initial CR ionization rate but are more pronounced (e.g., increased ions and desorption).

### 3.2. Density Dependent Dissociation Rates

Table A4 summarizes the only cases where the $\text{H}_2$ dissociation rate has any effect. In short, under an enhanced radiation field of 100 times the galactic one, an increase in abundance was seen for the solid species (by a factor of $\sim 4$), at a low density ($10^4 \text{ cm}^{-3}$) and only for the $L$ model. The other notable effect is seen at an increased initial ionization rate of $\times 10$, for $\text{CO}_{\text{grain}}$, and also at $10^4 \text{ cm}^{-3}$ with the $L$ model, where a significant increase in abundance ($\sim 3$ orders of magnitude) is seen. This large increase in abundance can be traced to the diffusion of $\text{H}_{\text{grain}}$ and $\text{CO}_{\text{grain}}$ into $\text{HCO}_2{\text{grain}}$. Under these conditions, this is the dominant destruction route (for $\text{CO}_{\text{grain}}$). Under the $\text{H}_2$ dissociation rate, this reaction pathway is severely inhibited, reducing the destruction of $\text{CO}_{\text{grain}}$ during and after the collapse. Abundances of $\text{H}_{\text{grain}}$ here are also lower for the $\text{H}_2$ dissociation dependency model, which may explain the inhibition.

### 3.3. Excited Species

Table A4 summarizes the only conditions where the inclusion of the excited species had a notable effect on the abundances of the selected species. At an increased temperature of $30 \text{ K}$, $\text{N}_2\text{H}^+$ shows a reduced abundance by a factor of 4 at a density of $10^5 \text{ cm}^{-3}$. Increasing the initial ionization rate by a factor of 10 reduces $\text{CO}_2{\text{grain}}$ abundances at a density of $10^4 \text{ cm}^{-3}$. The most significant effects come from increasing the ionization by a factor of 100. While the higher ionization rates provide more excitations, the increased destruction of the species is not only from their excitation and subsequent reactions. $\text{CO}_{\text{grain}}$, for example, is also heavily affected by the $\text{H}_{\text{grain}}$ and $\text{CO}_{\text{grain}}$ diffusion reaction. The addition of the excited species also produces higher abundances of $\text{H}_{\text{grain}}$, which increased the amount of $\text{CO}_{\text{grain}}$ diffusion.

### 3.4. Density Dependency with Excited Species

In this section, models with both the ionization rate and dissociation rate dependencies activated are compared with and without the inclusion of excited species. Table A5 shows the effects under standard conditions ($10 \text{ K}$ initial temperature, radiation field strength of 1 Habing, and an initial ionization factor of $\times 1$). $\text{CO}_{\text{grain}}$ and $\text{CO}_2{\text{grain}}$ are the main species affected, and have reduced abundances when the excited species are included. These reduced abundances are caused via the same destruction methods discussed in the previous subsection.

Figure 6. Figure showing the upper and lower limits of species in TMC-1, derived from Fuente et al. (2019). The figures compare observed abundances of CS (top left), HCO$^+$ (top right), and $\text{N}_2\text{H}^+$ (bottom) limits to UCLCHEM post-collapse models. The red dotted lines show the upper and lower limits.
3.4.1. Effects Due to Varying the Parameters

When the excited species are included with the CR ionization and H₂ dissociation in the chemical models, the effects of varying the temperature and radiation field strength are reduced, while the effects of varying the ionization factor are increased. As such these effects are quickly summarized here.

Increasing the initial temperature and increasing the radiation field strength both inhibit the effects of including the excited species. Under a higher temperature, including the excited species only has an effect on N₂H⁺ (this is at 30 K and a density of 10⁷ cm⁻³ with the H model only) where the species show an increased abundance. Increasing the radiation field strength only has an inhibitory effect on lower densities. At 10⁵ cm⁻³ and above, there are no differences between 1, 10, and 100 Habing.

Including the excited species with increased initial ionization rates of 10 and 100 times the standard handling has a greater effect than at the ×1 value. The changes in abundance are both larger and seen for more species. At 10 times the standard initial ionization rate, effects are only seen with the H model at 10⁴ and 10⁶ cm⁻³. Under these conditions, most species undergo reduced abundances (several orders of magnitude for CS, CO₂(grain), HCO⁺ and CO₂(grain)). Under an increased rate of 100 times the standard handling, the species undergo larger reductions, under the same densities but with the L model instead. Similar reductions are also seen here at 10⁷ cm⁻³ in both the L and H models.

3.5. Comparison to Observations

In this section, we qualitatively compare our models to a set of observations from the cyanopolyne peak (CP or Core D; Hirahara et al. 1992) of the molecular cloud TMC-1, which is thought to currently undergoing rapid core formation (Choi et al. 2017). This core was chosen as it has been well studied and its density is expected to be around 10⁴ cm⁻³ with a temperature of about 10 K. The density of 10⁴ cm⁻³ is a good candidate for this study, as the effects of the ionization rate dependency are greater due to the low density.

Both von Procházka & Millar (2020) and Fuente et al. (2019) report chemical abundances of the CP region. Fuente et al. (2019) report molecular abundances derived from observations using the IRAM 30 m (3 mm and 2 mm) and the Yebes 40 m telescopes. Depending on the setup, the IRAM 30 m has a spatial resolution of ~29″ and the Yebes telescope has an HPBW of 42″ or 84″. On the other hand, von Procházka & Millar (2020) report a collection of upper and lower abundance limits obtained from ~20 other studies (see Table 2 in von Procházka & Millar 2020), with the emphasis that focusing on upper and lower limits somewhat mitigates the errors in observations and modeling.
Figure 6 shows the data reported in Fuente et al. (2019), compared to the UCLCHEM models at 10 K and a final density of $10^4$ cm$^{-3}$ with and without the inclusion of the CR ionization rate dependency during the post-collapse phase. The standard UCLCHEM model for CS and HCO$^+$ tends to display abundances that are near the lower limit, while the $L$ model is closer to the central values. The $H$ model overpredicts the abundance for CS and underpredicts the abundance for HCO$^+$. With $N_2H^+$, all models underpredict the abundance, with the $L$ model being the closest and the $H$ model underpredicting the most.

Figure 7 shows data reported in von Procházká & Millar (2020), also compared to the UCLCHEM models at 10 K and a final density of $10^4$ cm$^{-3}$ with and without the inclusion of the CR ionization rate dependency during the post-collapse phase. In the cases of HCO$^+$, $N_3H^+$, and NH$_3$, for all models the post-collapse abundances are within the upper and lower limits of the observations. In von Procházká & Millar (2020) only an upper limit is noted for H$_2$O. In this case, the $H$ model exceeds the stated limit while the $L$ and basic models do not.

In the case of this region in TMC-1 and the compared species, the $L$ model of the ionization dependency appears to perform the best out of the three models. The $H$ model overpredicts or underpredicts the abundances on several occasions, suggesting this upper limit for the ionization rate may in fact be too high.

One caveat that must be addressed is how UCLCHEM handles grains. This version of UCLCHEM considers a grain to be a single layer (i.e., no distinction between grain surface and bulk). It is therefore necessary to speculate on the effects a multilayer grain approach may have on these results. Species in the bulk are somewhat shielded from CR impacts and the subsequent desorptions. As CR desorptions are critical to the changes in the abundance seen for species like CO$_{(\text{grain})}$ and CO$_2(\text{grain})$, it is likely the changes in abundance seen with the inclusion of the CR ionization dependency will be less significant. Excited species in the bulk are also more protected. Desorptions from excitations and excited reactions would be reduced with a greater emphasis on relaxations, again reducing the effects we see in our models.

4. Summary

In this paper, we improve the treatment of CRs in the gas-grain time-dependent chemical code UCLCHEM by including the dependency of the CR ionization and H$_2$ dissociation rates on the column density of the gas, as well as the excited species due to the CRs on the grains. We then evaluate the effects of these additions on the chemistry of pre-stellar cores. It is evident that the CR ionization rate dependency on the column density of the core is the most influential of the treatments, with the inclusion of excited species on the grains playing roles only under specific conditions. Our conclusions can be summarized as follows:

1. In the low densities of the pre-collapse phase ($\sim10^4$ cm$^{-3}$) the ionization rate dependency is very destructive due to CR-induced desorptions and the production of chemically important ions.
2. After the core collapses, the inclusion of the dependency of the CR ionization rate on the column density of the core leads to increased grain desorptions, which decrease solid species abundances (and subsequently increases the abundances of gaseous species), and species like H$_2$O, CO$_{(\text{grain})}$ and CO$_2(\text{grain})$ are particularly affected by this. Other gaseous species, like CS show increased abundances from dissociations of larger molecules like H$_2$CS.
3. Changing the physical parameters of the cloud alters the impact of the new treatments in a nontrivial manner. Higher densities have lower ionization rates with the dependency, reducing the changes in abundance seen for all species. Increasing the temperature also has a similar effect on CS, CO$_{(\text{grain})}$, and CO$_2(\text{grain})$ (increased formation rates balance out the destruction from the CRs), while NH$_3$ shows lower abundances due to less NH$_3(\text{grain})$ formation and subsequent desorption. Increasing the radiation field strength enhances the effects of the ionization dependency, which occurs as a result of grain and gas formation routes. NH$_3$, for example, undergoes increased abundances with the $H$ model due to higher NH$_3(\text{grain})$ grain formation and desorption, while HCO$^+$ undergoes larger changes due to formation in the gas via H$_2$ and CO.
4. The H$_2$ dissociation rate dependency and the inclusion of excited species only affect the chemistry of some of the investigated species under specific conditions. The H$_2$ dissociation dependency increases the abundances of some solid species for the $L$ model under two conditions, a $\times10$ ionization rate and a $\times100$ radiation field strength. CO$_{(\text{grain})}$ results in these increases in abundances due to the inhibition of its primary destruction route, from a reduced abundance of the H$_{(\text{grain})}$ reactant. The excited species reduce solid abundances at higher ionization rates, particularly with CO$_2(\text{grain})$ and CO$_{(\text{grain})}$. While the excitations and subsequent reactions reduced the solid abundances, destruction also comes from reactions with H$_{(\text{grain})}$ (which also sees higher abundances under these conditions).
5. Chemical models with and without the ionization dependency were compared to molecular abundances in the TMC-1 cyanopolyne peak from Fuente et al. (2019) and von Procházká & Millar (2020). The comparisons show that the $L$ model of the dependency tends to reproduce abundances more reliably than the standard handling or the $H$ model. All models had more difficulty reproducing $N_2H^+$ abundances (the $L$ model still performed better). The $H$ model predicted abundances outside the Fuente et al. (2019) observational limits for both CS and HCO$^+$ and overpredicted the abundance of H$_2$O compared to that in von Procházká & Millar (2020).

We would like to thank Jonathan Holdship for his contribution to the chemical modeling, particularly with UCLCHEM’s analysis tools. This project has received funding from the European Unions Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 811312 for the project “Astro-Chemical Origins” (ACO). This work is part of a project that has received funding from the European Research Council (ERC) under the European Unions Horizon 2020 research and innovation program MOPPEX 833460.

Appendix

Table A1 details the $c_k$ coefficients used in Equation 1 for the CR ionization rate and the H$_2$ dissociation rate dependencies. Tables A2–A5 summarize all abundance changes seen and their corresponding conditions.
Table A1
Coefficients from Padovani et al. (2018b) and Padovani et al. (2018a) for the Rate Dependencies

| CR Ionization Dependency Coefficients |  |  |
|--------------------------------------|---|---|
| $k$ | $c_f$ (model $L$) | $c_f$ (model $H$) |
| 0  | $1.545456645800 \times 10^7$ | $1.22352965309 \times 10^7$ |
| 1  | $-6.30770626617 \times 10^6$ | $-5.0137664305 \times 10^6$ |
| 2  | $1.14268066041 \times 10^6$ | $9.12015566763 \times 10^5$ |
| 3  | $-1.20593202621 \times 10^5$ | $-9.6654618847 \times 10^4$ |
| 4  | $8.17091335269 \times 10^3$ | $6.576930812109 \times 10^3$ |
| 5  | $-3.686121296079 \times 10^2$ | $-2.979875686226 \times 10^2$ |
| 6  | $1.107203722057 \times 10^1$ | $8.989721355058 \times 10^0$ |
| 7  | $-2.135293914267 \times 10^{-1}$ | $-1.741300519598 \times 10^{-1}$ |
| 8  | $2.399219033781 \times 10^{-3}$ | $1.965081612610 \times 10^{-3}$ |
| 9  | $-1.19664901916 \times 10^{-5}$ | $-9.84420349747 \times 10^{-6}$ |

| CR H$_2$ Dissociation Dependency Coefficients |  |  |
|-----------------------------------------------|---|---|
| $k$ | $c_f$ (model $L$) | $c_f$ (model $H$) |
| 0  | $1.582911005330 \times 10^7$ | $1.217227462831 \times 10^7$ |
| 1  | $-6.465722684896 \times 10^6$ | $-4.989649250304 \times 10^6$ |
| 2  | $1.172189025424 \times 10^6$ | $9.07980825395 \times 10^5$ |
| 3  | $-1.237950798073 \times 10^5$ | $-9.624890825395 \times 10^4$ |
| 4  | $8.393404654312 \times 10^3$ | $6.551161486120 \times 10^3$ |
| 5  | $-3.78881358130 \times 10^2$ | $-2.96897216187 \times 10^2$ |
| 6  | $1.13868455029 \times 10^1$ | $8.959037875226 \times 10^0$ |
| 7  | $-2.197136304567 \times 10^{-1}$ | $-1.73575724445 \times 10^{-1}$ |
| 8  | $2.46984127895 \times 10^{-3}$ | $1.95926727734 \times 10^{-3}$ |
| 9  | $-1.232393620924 \times 10^{-5}$ | $-9.816996707980 \times 10^{-6}$ |

Table A2
Results of the Ionization Rate Dependency on Abundances

| Density Species | Pre-collapse |  |  | Post-collapse |  |  |
|-----------------|--------------|---|---|---------------|---|---|
|                 | $10^2$ cm$^{-3}$ | $10^3$ cm$^{-3}$ | $10^5$ cm$^{-3}$ | $10^6$ cm$^{-3}$ | $10^7$ cm$^{-3}$ |
|                 | $L$ | $H$ | $L$ | $H$ | $L$ | $H$ | $L$ | $H$ |
| H$_2$O          | ... | $-9.5$ | ... | $+5.4$ | ... | $+3.6$ | ... | $+6.1$ |
| CS              | $-6.2 \times 10^1$ | $-1.1 \times 10^3$ | ... | $+2.4 \times 10^4$ | ... | $+1 \times 10^4$ | ... | $+1.2 \times 10^4$ |
| NH$_3$ (grain)  | ... | ... | ... | ... | ... | ... | ... | ... |
| N$_3$H$^+$      | <limit | <limit | ... | ... | ... | ... | ... | ... |
| NH$_4^+$        | ... | ... | ... | ... | ... | ... | ... | ... |
| CO$_2$ (grain)  | <limit | <limit | ... | $-4.4 \times 10^6$ | ... | ... | ... | ... |
| HCO$^+$         | $-4.2$ | $-2.4 \times 10^1$ | ... | ... | ... | $+4.8$ | ... | $+8.2$ |
| H$_2$O (grain)  | ... | $-6.8$ | ... | ... | ... | ... | ... | ... |
| CO$_2$ (grain)  | <limit | <limit | ... | $-5.3 \times 10^3$ | ... | $-6.1$ | ... | $-5.7$ |

Note. The values shown represent an increase (+) or a decrease (−) in abundances compared to the basic model and by what factor the abundances differed. This table only shows changes in abundance greater than a factor of 3 and any value marked “< limit” is below the lower abundance limit of $10^{-13}$.
### Table A3

Results of the Ionization Rate Dependency on Abundances with Varying Parameters

| Temperature (K) | Density: Species | Pre-collapse | Post-collapse |
|-----------------|------------------|--------------|--------------|
|                 | $L$ (10$^7$ cm$^{-3}$) | $H$ | $L$ (10$^7$ cm$^{-3}$) | $H$ | $L$ (10$^8$ cm$^{-3}$) | $H$ | $L$ (10$^9$ cm$^{-3}$) | $H$ | $L$ (10$^{10}$ cm$^{-3}$) | $H$ |
| 20              | H$_2$O           | ···           | ···           | +7.2   | ···           | +6.8   | ···           | +5.5   | ···           | ···   |
| 20              | NH$_3$(grain)    | <limit       | <limit       | ···     | <limit       | ···     | ···           | ···     | ···           | ···   |
| 20              | N$_2$H$^+$       | <limit       | <limit       | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 20              | NH$_3$          | <limit       | <limit       | ···     | +1.3 x 10$^4$ | ···     | +6.1 x 10$^4$ | ···     | +1.2 x 10$^4$ | ···   |
| 20              | CO$_2$(grain)    | <limit       | <limit       | ···     | −6.1 x 10$^4$ | ···     | ···           | ···     | ···           | ···   |
| 30              | H$_2$O           | ···           | ···           | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 30              | NH$_3$(grain)    | <limit       | <limit       | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 30              | N$_2$H$^+$       | <limit       | <limit       | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 30              | HCO$^+$          | ···           | ···           | ···     | 3.8 x 10$^4$  | ···     | 7.6 x 10$^4$  | ···     | 8.8 x 10$^4$  | ···   |
| 30              | H$_2$O$_2$(grain)| <limit       | <limit       | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 30              | CO$_2$(grain)    | <limit       | <limit       | ···     | ···           | ···     | ···           | ···     | ···           | ···   |

Radfield

| 10              | H$_2$O           | ···           | −3.8 x 10$^4$ | ···     | +3.8 x 10$^4$ | ···     | +3.6 x 10$^4$ | ···     | +6.1 x 10$^4$ | ···   |
| 10              | CS              | −7.7          | −1.3 x 10$^4$ | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 10              | NH$_3$(grain)   | <limit       | <limit       | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 10              | N$_2$H$^+$      | <limit       | <limit       | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 10              | NH$_3$        | ···           | ···           | ···     | +1.3 x 10$^4$ | ···     | ···           | ···     | ···           | ···   |
| 10              | CO$_2$(grain)   | <limit       | <limit       | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 100             | H$_2$O          | ···           | ···           | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 100             | CS              | ···           | ···           | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 100             | NH$_3$(grain)   | <limit       | <limit       | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 100             | N$_2$H$^+$      | <limit       | <limit       | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 100             | NH$_3$        | ···           | ···           | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 100             | CO$_2$(grain)   | <limit       | <limit       | ···     | ···           | ···     | ···           | ···     | ···           | ···   |

Zeta

| 10              | H$_2$O           | ···           | −4.7          | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 10              | NH$_3$(grain)   | <limit       | <limit       | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 10              | N$_2$H$^+$      | <limit       | <limit       | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 10              | NH$_3$        | ···           | ···           | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 10              | CO$_2$(grain)   | <limit       | <limit       | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 10              | H$_2$O$_2$(grain)| <limit       | <limit       | ···     | ···           | ···     | ···           | ···     | ···           | ···   |
| 10              | CO$_2$(grain)   | <limit       | <limit       | ···     | ···           | ···     | ···           | ···     | ···           | ···   |

**Note.** The values shown represent an increase (+) or a decrease (−) in abundances compared to the basic model and by what factor the abundances differed. This table only shows changes in abundance greater than a factor of 3 and any value marked “< limit” is below the lower abundance limit of 10$^{-13}$. 


Table A4
The Only Conditions Where the Inclusion of the Dissociation Rate Dependency or the Inclusion of Excited Species Had Any Notable Effect on Abundances

| Radfield | Density: | Dissociation Dependency | Excited Species |
|----------|-----------------|--------------------------|-----------------|
|          | Species        | L 10^6 cm⁻³ | H 10^6 cm⁻³ | L 10^7 cm⁻³ | H 10^7 cm⁻³ | L 10^8 cm⁻³ | H 10^8 cm⁻³ | L 10^9 cm⁻³ | H 10^9 cm⁻³ | L 10^10 cm⁻³ | H 10^10 cm⁻³ |
| 100      | NH₃(grain)     | +4.6         | ...         | ...         | ...         | ...         | ...         | ...         | ...         | ...         | ...         |
| 100      | CO(grain)      | +4.5         | ...         | ...         | ...         | ...         | ...         | ...         | ...         | ...         | ...         |
| 100      | H₂O(grain)     | +4.5         | ...         | ...         | ...         | ...         | ...         | ...         | ...         | ...         | ...         |
| 100      | CO₂(grain)     | +4.2         | ...         | ...         | ...         | ...         | ...         | ...         | ...         | ...         | ...         |
| Zeta     | CO(grain)      | +1.4 × 10³   | ...         | ...         | ...         | ...         | ...         | ...         | ...         | ...         | ...         |
| 10       | CO₂(grain)     | −6.5         | ...         | ...         | ...         | ...         | ...         | ...         | ...         | ...         | ...         |
| 100      | H₂O            | ...         | +3.7       | ...         | ...         | ...         | ...         | ...         | ...         | ...         | ...         |
| 100      | CS             | ...         | −7 × 10¹⁰ | −1.8 × 10¹³ | −7.1       | ...         | ...         | ...         | ...         | ...         | ...         |
| 100      | N₂H⁺           | ...         | ...         | +3.5       | +3.4       | ...         | ...         | ...         | ...         | ...         | ...         |
| 100      | NH₃            | ...         | +4.6       | +3.9       | ...         | ...         | ...         | ...         | ...         | ...         | ...         |
| 100      | CO₂(grain)     | ...         | −1.7 × 10⁶ | −8.1 × 10⁹ | −2.2 × 10⁷ | ...         | ...         | ...         | ...         | ...         | ...         |
| 100      | HCO⁺           | ...         | −2.3 × 10² | −4.9 × 10³ | −2.9 × 10⁴ | ...         | ...         | ...         | ...         | ...         | ...         |
| 100      | H₂O₂(grain)    | ...         | −3.9       | ...         | ...         | ...         | ...         | ...         | ...         | ...         | ...         |
| 100      | CO₂(grain)     | ...         | −2.2 × 10² | −1 × 10⁸   | −3.8 × 10¹⁰| ...         | ...         | ...         | ...         | ...         | ...         |

Note. The values shown represent an increase (+) or a decrease (−) in abundances compared to the basic model and by what factor the abundances differed. This table only shows changes in abundance greater than a factor of 3 and any value marked “< limit” is below the lower abundance limit of 10⁻¹³.
### Table A5

Results of the Combined Dissociation Rate Dependency and Excited Species on Abundances under Standard Conditions and with Varying Parameters

| Species            | Density (10^8 cm⁻³) | Post-collapse (10^7 cm⁻³) | Temperature (K) |
|--------------------|----------------------|---------------------------|-----------------|
|                    | L        | H        | L        | H        | L        | H        | 30     | N₂H⁺  | <limit | <limit | +5.8    |
| CO₂(grain)         | ...      | −3.3     | ...      | −5.4     | ...      | −6.1     | ...    | ...   | ...    | ...    | ...      |
| HCO⁺               | ...      | ...      | ...      | ...      | ...      | ...      | ...    | ...   | ...    | ...    | ...      |
| H₂O(grain)         | ...      | −4.1     | ...      | −6.7     | ...      | −5.9     | −3.7   | −5.4  | −7.4   | ...    | ...      |
| CO₂(grain)         | ...      | −3.6     | ...      | −6.8     | ...      | −5.9     | −3.7   | −4.9  | −7.4   | ...    | ...      |

#### References

Abplanalp, M. J., Gozem, S., Krylov, A. L., et al. 2016, PNAS, 113, 28
Blandford, R., Simeon, P., & Yuan, Y. 2014, NatPhy, 256, 9
Caselli, P., Vastel, C., Ceccarelli, C., et al. 2008, A&A, 492, 703
Choi, Y., Lee, J.-E., Bourke, T. L., & II, N. J. E. 2017, ApJS, 229, 38
Cummings, A. C., Stone, E. C., Heikila, B. C., et al. 2016, ApJ, 831, 18 de Jong, T., & Kamijo, F. 1973, A&A, 25, 363
Fuente, A., Navarro, D. G., Caselli, P., et al. 2019, A&A, 624, A105
Gloeckler, G., & Fisk, L. A. 2013, ApJL, 806, L27
Goldsmith, P. F., & Li, D. 2005, ApJ, 622, 938
Herbst, E., & Klemperer, W. 1973, ApJ, 185, 505
Hirahara, Y., Suzuki, H., Yamamoto, S., et al. 1992, ApJ, 394, 539
Holdship, J., Viti, S., Jiménez-Serra, I., Makrymallis, A., & Priestley, F. 2017, AJ, 154, 38
Indriolo, N., & McCall, B. J. 2013, ChiRv, 42, 7763
Ivlev, A. V., Padovani, M., Galli, D., & Castelli, P. 2015, ApJ, 812, 135
Indriolo, N., & McCall, B. J. 2012, ApJ, 745, 91
Indriolo, N., & McCall, B. J. 2013, ChiRv, 42, 7763
Ivlev, A. V., Sliseck, K., Padovani, M., & Galli, D. 2021, ApJ, 909, 107
Kalvins, I., & Kalnin, I. R. 2019, MNRAS, 486, 2050
Kuffmeier, M., Zhao, B., & Castelli, P. 2020, A&A, 639, A86
Le Petit, F., Ruaud, M., Bron, E., et al. 2016, A&A, 585, A105
Lee, C. W., Myers, P. C., & Tafalla, M. 1999, ApJ, 526, 788
Li, D., & Goldsmith, P. F. 2003, ApJ, 585, 823
McElroy, D., Walsh, C., Markwick, A. J., et al. 2013, A&A, 550, A36
Montgomery, A. S., Bates, B., & Davies, R. D. 1995, MNRAS, 273, 449
Neufeld, D. A., Goicoechea, J. R., Sommerrunder, P., et al. 2010, A&A, 521, L10
Neufeld, D. A., & Wolfire, M. G. 2017, ApJ, 845, 163
Öberg, K. I., Boogert, A. C. A., Pontoppidan, K. M., et al. 2011, in Proc. IAU Symp. 280, Ices in Starless and Starforming Cores. (Cambridge: Cambridge Univ. Press), 65
Oka, T., Geballe, T. R., Goto, M., Usuda, T., & McCall, B. J. 2005, ApJ, 632, 882

Note. The values shown represent an increase (+) or a decrease (−) in abundances compared to the basic model and by what factor the abundances differed. This table only shows changes in abundance greater than a factor of 3 and any value marked “< limit” is below the lower abundance limit of 10⁻¹³.
