CHEMICAL MODELING OF YOUNG STELLAR OBJECTS. I. METHOD AND BENCHMARKS

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ABSTRACT

Upcoming facilities such as the Herschel Space Observatory or Atacama Large Millimeter Array will deliver a wealth of molecular line observations of young stellar objects (YSOs). Based on line fluxes, chemical abundances can then be estimated by radiative transfer calculations. To derive physical properties from abundances, the chemical network needs to be modeled and fitted to the observations. This modeling process is however computationally exceedingly demanding, particularly if in addition to density and temperature, far-UV (FUV) irradiation, X-rays, and multi-dimensional geometry have to be considered. We develop a fast tool, suitable for various applications of chemical modeling in YSOs. A grid of the chemical composition of the gas having a density, temperature, FUV irradiation and X-ray flux is pre-calculated as a function of time. A specific interpolation approach is developed to reduce the database to a feasible size. Published models of AFGL 2591 are used to verify the accuracy of the method. A second benchmark test is carried out for FUV sensitive molecules. The novel method for chemical modeling is more than 250,000 times faster than direct modeling and agrees within a mean factor of 1.35. The tool is distributed for public use. Main applications are (1) fitting physical parameters to observed molecular line fluxes and (2) deriving chemical abundances for two- and three-dimensional models. They will be presented in two future publications of this series. In the course of developing the method, the chemical evolution is explored: we find that X-ray chemistry in envelopes of YSOs can be reproduced by means of an enhanced cosmic-ray ionization rate with deviations less than 25%, having the observational consequence that molecular tracers for X-rays are hard to distinguish from cosmic-ray ionization tracers. We provide the detailed prescription to implement this total ionization rate approach in any chemical model. We further find that the abundance of CH⁺ in low-density gas with high ionization can be enhanced by the recombination of doubly ionized carbon (C++) and suggest a new value for the initial abundance of the main sulfur carrier in the hot core.

Key words: astronomical data bases: miscellaneous – ISM: molecules – methods: data analysis – methods: numerical – molecular processes – stars: formation

Online-only material: color figures

1. INTRODUCTION

There is an interesting but little explored phase in star formation when the cloud core collapses, but the protostar is still deeply embedded. In this phase, the temperature of the interior envelope exceeds 100 K, outflows are observed, protoplanetary disks form, and the protostar begins to radiate in UV and X-rays. These physical processes can best be observed in low temperature lines, some atomic but most molecular. A wealth of new line data of young stellar objects (YSOs) will be available soon by upcoming facilities like the Herschel Space Observatory or Atacama Large Millimeter Array (ALMA; e.g., van Dishoeck & Jørgensen 2008 for a recent review). Two steps are necessary to constrain physical parameters by molecular line observations: (1) radiative transfer calculations are applied to estimate the abundance of the observed molecule, and (2) modeling the chemical network relates the abundance to physical parameters such as age, density, temperature, far-UV (FUV), and X-ray irradiation by the protostar. Although the present knowledge of these networks is still limited by unknown reactions on grain surfaces, in some cases it is possible to derive chemical abundances from a set of initial physical parameters. The abundances form the bases for radiative transfer calculations. The resulting line fluxes can then be compared to the observed fluxes. Finally, the input physical parameters for the chemical modeling are changed until the derived line fluxes fit the observed ones, for instance producing a minimum in a $\chi^2$ test. Chemical modeling simulates a network of molecular species reacting with each other (e.g., Doty et al. 2002). Contrary to an atomic gas, molecular abundances are not conserved, but depend on local physical parameters. In chemical simulations, the abundances of different species are related to the change of one species in a set of nonlinear coupled differential equations. Solving these equations is a time-consuming task for a chemical network consisting of several hundred species connected by thousands of reactions.

While early astrochemical models of envelopes of YSOs assumed a fixed density and temperature (e.g., Leung et al. 1984), more recent models considered space-dependent chemistry (e.g., Caselli et al. 1993 or Millar et al. 1997b). So far, chemical models have only been fitted to observations under the assumption of spherically symmetric, one-dimensional physical parameters (Doty et al. 2002; Stäuber et al. 2005). This is a questionable assumption as YSOs have inherently two-dimensional or three-dimensional geometries with outflow cavities, disks etc. For such geometries the number of cells for which chemical modeling has to be performed increases from about 100 to $10^4$ and more. Fitting requires repetition of many similar calculations. It becomes inefficient and beyond present resources for two-dimensional or three-dimensional geometries and for a large sample of sources.

In a dynamical situation, the “chemical age” (evolution time since the start from an initial composition) may be different from the age of the YSO. The chemistry in a gravitationally
collapsing envelope has been studied by Rodgers & Charnley (2003) and Lee et al. (2004). Doty et al. (2006) have constructed a model including infall as well as the evolution of the central stellar object. They conclude that the chemical evolution of an ice-evaporated hot core appears to be younger than the time since the formation of the YSO by a factor of 4 to 10. “Pseudo time-dependent” models keep the physical structure constant with time, while the chemical abundances evolve. Such models nevertheless are reasonable approximations if the chemical composition evolves rapidly compared to the change of the relevant physical parameters, like for example in regions with strong FUV irradiation.

Undoubtedly, the ionization of molecular hydrogen, $H_2$, followed by fast ion–molecule reactions involves extremely rapid processes. Ionized molecules are a driving force of the chemistry in the envelope of YSOs (Dalgarno 2006). Cosmic rays account for ionizations mainly in the outer part of the envelope. In the inner part, high-energy radiation from the YSO may be the dominant source of ionization. Accretion phenomena and shocks may account for FUV radiation in low-mass stars, while hot high-mass stars emit copious FUV photons mostly from their hot photosphere. Direct photoionization through FUV photons leads to a particular chemistry as observed in photodissociation regions (PDRs). FUV radiation is attenuated by dust (e.g., Montmerle 2001). Unless a low-density region allows FUV radiation to escape from the innermost region of the envelope, its influence on the chemistry is restricted to a small volume behind the irradiated surface (Stäuber et al. 2004). The observations of Stäuber et al. (2007) revealed a much larger amount of several FUV sensitive molecules than predicted by their spherically symmetric models. These authors suggested outflows acting as paths for FUV photons to escape and penetrate the high-density gas in the border region between the outflow and the envelope. A multidimensional geometry is needed to model these “outflow walls.”

In addition to FUV, young stars are known to be strong emitters of X-rays with luminosities up to $10^{32}$ erg s$^{-1}$ in the 1–100 keV band (e.g., Preibisch & Feigelson 2005). Magnetic activity is believed to be the origin of the X-rays, but the exact mechanism remains unclear. X-ray photons have a smaller absorption cross section than FUV ($\propto \lambda^2$) and penetrate deeper into dense material than FUV. X-ray ionization thus decreases mostly by geometric dilution, $\propto r^{-2}$ with distance $r$ to the source. Various studies on the influence of X-ray irradiation on the chemistry of molecular clouds have been carried out (Krolik & Kallman 1983; Maloney et al. 1996; Lepp & Dalgarno 1996; Yan 1997; Stäuber et al. 2005). For low-mass YSOs, the presence of X-rays has implications on the disc and thus planet formation (e.g., Ilgner & Nelson 2008; Meijerink et al. 2008). In an early stage of star formation, FUV and X-ray radiation are absorbed by the large opacity of the envelope and are therefore not directly observable. The point of evolution when FUV and X-ray activity sets in is unknown.

The goal of our work is to provide a fast and simple method for chemical modeling. A large set of pre-calculated abundances for different ages and physical conditions (density, temperature, etc.) is used to quickly interpolate the chemical abundances for individual conditions in a model with physical conditions that change with position. The main problem is to reduce the high-dimensional space of physical parameter to a size that fits current hardware resources, but keep the accuracy of the interpolation at an acceptable level. Based on this new method for chemical modeling, observed data can be quickly fitted to physical parameters such as the chemical age or the X-ray luminosity. Also detailed two-dimensional or three-dimensional models may be constructed quickly allowing to study the influence of the geometry on observable parameters (Bruderer et al. 2009; S. Bruderer et al. 2009, in preparation)

This paper is organized as follows: in the first section, we describe the grid approach. We discuss the relevant parameters for the chemical composition and the similarity between X-ray and cosmic-ray-induced chemistry. In Section 3, the chemical model (network and reaction rates) used for this work is briefly described. Two benchmark tests on realistic applications are carried out and discussed in the following section. Section 5 describes the application of the method. In the following parts of this series of papers, we will present a detailed multidimensional chemical model of a high-mass star-forming region applied to the enigmatic CO$^+$ molecule and a parameter study of two-dimensional effects on the interpretation of line observations as expected to be observed with Herschel and ALMA.

2. A GRID OF CHEMICAL MODELS

Chemical models solve for the molecular abundances using the rate equations

$$\frac{dn(i)}{dt} = \sum_j k_{i,j} \cdot n(j) + \sum_{j,k} k'_{i,j,k} \cdot n(j) \cdot n(k) + S(i) \quad (1)$$

which relate the temporal evolution of a species, labeled by $i$, to the number density $n(j)$, $n(k)$ (cm$^{-3}$) of some species $j$ and $k$. The constants of proportionality $k_{i,j}$ (s$^{-1}$) and $k'_{i,j,k}$ (cm$^3$ s$^{-1}$) depend on physical properties such as temperature, cosmic-ray ionization rate, or FUV flux. Some applications require an additional source term $S(i)$ to account, e.g., for molecules evaporating from dust grains or spatial flows.

Many of the reactions relevant in the interstellar environment at low temperature are difficult or impossible to measure in terrestrial conditions. In standard networks for astrochemical applications, a majority of reaction rates are thus only known to within a factor of 2 (Woodall et al. 2007). Furthermore, uncertainties in the rate coefficients may grow due to the nonlinear nature of the rate equations (Equation (1)). Studies on the quantitative uncertainty of the chemical abundances have been carried out only recently by Wakelam et al. (2005, 2006) and Vasyunin et al. (2008). Considering their results, it seems reasonable to require the interpolated abundances to agree within a factor of 2 with the fully calculated values.

The basis of our method is to interpolate abundances from a grid of physical parameters relevant for the chemical composition. These physical parameters form a multidimensional space, where the dimensions correspond to temperature, density, cosmic-ray ionization rate and several parameters for the impact of high-energetic radiation (X-rays and FUV irradiation). For each grid point and all molecules in the chemical network, the temporal evolution is stored in a database. Therefore, time enters as an additional dimension. In order to explore a wide range in parameter space, we assume a rectangular grid: for every grid point along one axis, all possible combinations of grid points along all other axes are calculated. The total number of models is obtained by multiplying the number of grid points along each dimension. Thus, it is crucial to keep the number of dimensions and grid points as low as possible, while it must still be sufficient to guarantee the required interpolation accuracy.

As an example for problems to be met by the interpolation, we show the water fractional abundance with respect to $H_2$ in
Figure 1. Fractional abundance of different species depending on physical properties (temperature, density). The arrows indicate the positions of the interpolation points. The red lines show the results of the interpolation in log–log space. (a) Water in a region with X-ray irradiation vs. temperature for three different densities. (b) Density dependence of four selected species related to the ionization fraction. (c) Sulfur bearing species in the temperature range of the grid. (d) X-ray irradiated points. The red lines show the results of the interpolation in log–log space.

Figure 1(a): A parcel of gas and dust at a gas density between \(10^5\) cm\(^{-3}\) and \(10^8\) cm\(^{-3}\) irradiated by X-rays has been modeled in a similar way as Stäuber et al. (2007). For this figure, the fractional abundances are given at the time (the so called chemical age) of \(5 \times 10^4\) yr according to the age of the high-mass protostellar object AFGL 2591 (Stäuber et al. 2005).

The presentation of Figure 1 with logarithmic scales in both dimensions suggests the use of linear interpolation of the fractional abundance in log–log space. The straight (red/gray) lines in the figure show interpolated fractional abundances. The temperatures marked by arrows at the top of the figure act as interpolation points. Two temperatures close to 100 K have been used, since water is assumed to evaporate at this temperature from dust grains. For an accurate interpolation in the temperature range between \(\approx 200\) and \(400\) K, a couple of interpolation points is required. The reaction \(\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}\) with high activation energy becomes important in this temperature range, leading to little net variation in the water abundance at \(T > 400\) K, while at lower temperature \(\text{H}_2\text{O}\) is destroyed by X-rays (Stäuber et al. 2006).

2.1. Temperature and Density Dependence

The dependence of abundance on parameters can be much simpler than the temperature sensitivity of water: the fractional abundances of \(\text{H}_3^+\), \(\text{HCO}^+\), \(\text{H}_2\text{O}\), and \(\text{H}_2\text{CO}\) depending on the total gas density are shown in Figure 1(b). For that plot, a temperature slightly above the water evaporation temperature of 100 K has been assumed. No X-ray or FUV irradiation is considered, but cosmic rays ionize \(\text{H}_2\) and account for the production of \(\text{H}_3^+\). A cosmic-ray ionization rate \(\zeta_{\text{cr}} = 4 \times 10^{-16}\) s\(^{-1}\), found by Doty et al. (2004) in IRAS 16293-2422 is used for this plot. Higher values than the “standard” value of a few times \(10^{-17}\) s\(^{-1}\) have also been suggested by van der Tak & van Dishoeck (2000). This shows the necessity to include the cosmic-ray ionization rate as a dimension for the interpolation approach. The rate of ionizations by cosmic-ray particles and thus the density of \(\text{H}_3^+\) is independent of the \(\text{H}_2\) density. Therefore, the fractional abundance of \(\text{H}_3^+\) is approximately inversely proportional to the density. The same effect is found for \(\text{HCO}^+\), produced by the reaction \(\text{H}_3^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{H}_2\). In contrast, water and formaldehyde are not directly related to the ionization rate and their fractional abundances do not vary more than an order of magnitude in the explored density range.

As can be seen in Figures 1(a) and (b), the fractional abundance is a much stronger function of temperature than of density. This is due to the exponential dependence of some reaction rates on temperature. Reactions between neutrals that do not involve radicals or atoms often have considerable activation barriers. Their reactions rate is proportional to the Boltzmann factor...
exp\(-E_a/k_B T\) in the usual Arrhenius expression, where \(E_a\) denotes the activation energy, \(k_B\) is the Boltzmann constant and \(T\) the kinetic temperature of the gas.

Selecting grid points in temperature is most important for the accuracy of the interpolation. In addition to water, sulfur-bearing species also pose problems: many reactions have large activation energy and their fractional abundance is thus expected to be especially dependent on temperature. Indeed, Figure 1(c) shows a strong dependence of \(H_2S, CS, SO_2\) and atomic sulfur on temperature. Again, we overplot interpolated abundances onto the fully calculated results. For temperatures below 100 K, only a small number of grid points is needed, but the hot-core regime of \(T > 100\) K requires a much larger amount in order to keep deviations small.

How can we select the grid points along the temperature axis of the grid? Two methods have been tested: (1) an unbiased method and (2) hand-placed points. For method (1), the grid points are chosen based on the number of reactions with activation temperature in a certain temperature range. The activation temperature of a reaction is obtained by scaling to the activation energy of the very important reaction \(OH + H_2 \rightarrow H_2O + H\) which proceeds at a gas temperature above \(\approx 250\) K (Figure 1(a) and Stäuber et al. 2006). The grid points are then placed to properly sample temperature ranges with higher activation temperatures. For method (2), the grid points are placed by hand based on parameter studies like Figure 1(a). The selection of species given by Stäuber et al. (2005) and other important molecules are considered at different chemical ages.

The interpolation quality of the two methods has been tested using the technique presented in Section 4.1. We find a considerably better interpolation accuracy using the grid with hand-placed grid points for the following reason: the unbiased approach does not take into account the relative importance of different reactions: e.g., the reaction between \(OH\) and \(H_2\), despite its substantial influence on the chemical network since the key molecule water is involved. As Figure 1(a) shows for this reaction, it is not sufficient to put two grid points near 250 K in order to obtain a good interpolation quality. The temporal evolution of the water abundance reveals another difficulty in the selection of the grid points (Figure 1(d)): for chemical ages between a few times \(10^3\) and \(5 \times 10^3\) yr, the fractional abundance cannot be interpolated well using the same set of grid points: the gradient of the water abundance for 100 < \(T < 250\) K and \(T > 250\) K changes with the chemical evolution. Thus, the base point for the connection between the low and high water abundance shifts from 100 K to 250 K.

A similar effect is also observed in Figure 1(a), where different total densities lead to different timescales of the water destruction. While the fractional abundance of water varies by approximately two orders of magnitude, species connected to the network may be affected even stronger. For example, the fractional abundance of \(H_2S\) has its main destroyer (HCO+) in common with \(H_2O\) increases by many orders of magnitude between 250 K and 600 K (Figure 1(c)). We finally decided to implement 23 hand picked points at 8, 12, 17, 40, 59.9, 60.1, 99.9, 100.1, 120, 180, 230, 250, 300, 400, 600, 800, 1000, 1400, 1800, 2200, 2600, 3000, and 3400 K for our work. This range thus covers conditions from cold dark clouds to hot PDR-like regions, heated by FUV photons.

The selection of the grid points for the density axis is less critical due to the smooth abundance profile along this dimension. We implement one grid point per order of magnitude in density. The density is taken to be within \(10^4\)–\(10^9\) cm\(^{-3}\), sufficient to model envelopes of low-mass and high-mass YSOs (Jørgensen et al. 2002; Maret et al. 2002; van der Tak et al. 2000).

### 2.2. FUV Driven Chemistry

Reaction rates for photodissociation or ionization of molecules by FUV radiation can be written as (e.g., van Dishoeck et al. 2006)

\[
k = \int_{E_{\text{min}}}^{E_{\text{max}}} J(E) \sigma(E) dE \quad (\text{s}^{-1}).
\]

The mean intensity of the FUV radiation field \(J(E)\) (cm\(^{-2}\) s\(^{-1}\)) times the cross section for photoabsorption and ionization \(\sigma(E)\) (cm\(^2\)) is integrated between the average dust work function \(E_{\text{min}} \approx 6\) eV and the ionization energy of hydrogen \(E_{\text{max}} = 13.6\) eV. For these photon energies, photodissociation proceeds through line absorption and absorption of the continuum by dust. Line absorption occurs by other species or by the considered species itself (the so-called self-shielding). In principle, the exact shape of the spectra is thus required to calculate the chemical rates. As an approximation, van Dishoeck (1988) used the spectral shape of the interstellar radiation field (ISRF; e.g., Habing 1968 or Draine 1978) and fitted rate coefficients to the equation

\[
k = G_0 \cdot C \cdot \exp(-\gamma \cdot \tau) \quad (\text{s}^{-1}),
\]

where \(G_0\) is a scaling factor to the interstellar radiation field and \(\tau = A_v/1.086, A_v\) being the extinction at visual wavelengths due to dust. It is calculated from the total hydrogen column density by the conversion factor \(N(H_\text{tot}) = 2N(H_2) + N(H) \approx 1.87 \times 10^{21} \cdot A_v\) cm\(^{-2}\) (Bohlin et al. 1978 for a dust reddenning of \(R_\text{V} \approx 3.1\)). The values of the constants \(C\) and \(\gamma\) in Equation (3) depend on the spectrum, used for the fitting. For hot FUV sources with \(T > 20000\) K, it is safe to use fits to the interstellar radiation field, dominated by O and B stars. \(G_0\) is then scaled with respect to the average interstellar flux of \(1.6 \times 10^{-3}\) erg cm\(^{-2}\) s\(^{-1}\) at photon energies between 6 and 13.6 eV. For colder sources such as accretion hot spots, the intensity of the spectra decreases at lower wavelengths, and \(C\) and \(\gamma\) should be adjusted (see van Dishoeck et al. 2006). The value of \(\gamma\) depends furthermore on the adopted dust model as well as on the range of \(A_v\) used for the fitting.

Stäuber et al. (2004) studied the influence of FUV radiation on the chemistry in envelopes of YSOs and found CO\(^+\) to be a good tracer in high-temperature regions. Observations of that molecule by Stäuber et al. (2007) revealed a surprisingly high abundance which cannot be explained in terms of their spherical models. The second part of this series of papers will thus present a detailed chemical model in two dimensions using the interpolation approach introduced in this work. The dependence of the fractional abundance of CO\(^+\) on the radiation field \(G_0\) and the attenuation \(\tau\) is presented in Figure 2. The fractional abundance peaks at radiation strengths of \(10^3\) to \(10^4\) times the ISRF for low extinction (\(\tau \approx 0.1\)). Self-shielding can lead to a high H\(^2\) abundance at extinctions \(\tau < 0.1\). We restrict the range of our chemical grid to values \(\tau > 0.1\), since for the planned applications, the uncertainty in the geometry can easily account for errors of \(\tau\) on the order of 0.1. At high extinction, with \(\tau > 20\), the influence of the FUV radiation is negligible even for field strengths of \(10^7\) times the ISRF. In absence of any attenuation, this FUV field corresponds to an early B star with a temperature of \(30,000\) K and a luminosity of \(2 \times 10^6 L_\odot\) at a distance of about \(1000\) AU.
An implementation of the chemical grid using $\tau$ and $G_0$ as interpolation axes would lack sufficient interpolation accuracy. Another approach was therefore developed: contour plots of FUV sensitive molecules (e.g., C$^+$, C, CO, and hydrocarbons C$_x$H$_y$) similar to Figure 2 are calculated for different temperature regimes. The contour lines are then used to fit a curvilinear coordinate system as indicated by (red/grey) dots in Figure 2. A unique function relates the physical units of $\tau$ and $G_0$ to arbitrary units of a coordinate system denoted by $\alpha$ and $\beta$. In this way, the interpolation quality can be greatly improved while the number of grid points is kept constant (Table 1). One grid point is placed at very high extinction and no FUV irradiation to represent a model without any influence of FUV irradiation.

### 2.3. X-ray Driven Chemistry

Rates for the direct photoionization by X-ray photons can be evaluated in a similar way as for FUV radiation using Equation (2). The local intensity of the X-ray emission of thermal plasma is approximated by

$$J(E, r) \approx \frac{L_X}{4\pi r^2} \cdot \frac{N}{E} \cdot \exp \left( -\frac{E}{kT_X} \right) \cdot \exp \left( -\sigma_{\text{photo}}(E) \cdot N(\text{H}_\text{tot}) \right),$$

where $E$ is the photon energy, $r$ the distance to the X-ray source, $T_X$ the temperature of the X-ray emitting plasma and $N(\text{H}_\text{tot})$ the attenuating column density. The normalization factor $N$ is evaluated from the luminosity of the X-ray source $L_X$ (erg s$^{-1}$) using $L_X = 4\pi r^2 \int L_{\text{matt}}(E, r) dE$, where $L_{\text{matt}}$ denotes Equation (4) without attenuation ($N(\text{H}_\text{tot}) \equiv 0$). The photoionization cross section $\sigma_{\text{photo}}$ is obtained by summing up the contributions of all species including heavy elements in the solid phase (Stäuber et al. 2005). For a photon energy above 10 keV, inelastic Compton scattering (described by $\sigma_{\text{Compton}}$) governs the total X-ray cross section ($\sigma_{\text{tot}} = \sigma_{\text{photo}} + \sigma_{\text{Compton}}$). The influence of elastic Compton scattering and line emission in the X-ray spectra to the chemical composition can be neglected (Stäuber et al. 2005).

### Notes.

The parameters are defined and described in the text.

Unlike FUV radiation, secondary processes are more important for the chemistry than direct photoionization (e.g., Maloney et al. 1996; Stäuber et al. 2005): fast photoelectrons and Auger electrons can ionize other species very efficiently. The rate of ionization per hydrogen molecule due to the impact of secondary electrons can be written as

$$\zeta_{\text{H}_2} = \int_{E_{\text{min}}}^{E_{\text{max}}} J(E, r) \sigma_{\text{total}}(E)(E/W(E)\chi(\text{H}_2)) dE,$$

where $x(\text{H}_2) \approx 0.5$ denotes the fractional abundance of H$_2$ with respect to the total hydrogen density. The mean energy per ion pair is given by $W(E)$. Like cosmic rays, secondary electrons can excite H$_2$, hydrogen, and helium atoms. The electronically excited states decay back to the ground state by emitting FUV photons. Mostly photons of the Lyman–Werner bands of H$_2$ contribute to this internally generated FUV field. This field can also photodissociate and photoionize other species, and hence influence the chemistry.

In a straightforward implementation, three different parameters are required to parameterize the impact of X-rays on the chemistry: (1) the X-ray flux, as defined by $F_X \equiv L_X/4\pi r^2$, with the X-ray luminosity $L_X$ and the distance to the X-ray source $r$. (2) The attenuating column density $N(\text{H}_\text{tot})$ and (3) the temperature $T_X$ of the X-ray emitting plasma. The relevant range for each grid dimension is given in Table 1. It is chosen to cover the range of high-mass and low-mass (class 0/1) sources as modeled by Stäuber et al. (2005, 2006). The required number of 14 grid points in the dimension of the X-ray flux can be explained referring to the example of the very strong dependence of the water fractional abundance on this parameter. In Figure 5(g), the H$_2$O abundance for a gas temperature of 120 K is shown: at an X-ray flux of $10^{-4}$ erg s$^{-1}$ cm$^{-2}$, the abundance drops by about two orders of magnitude. As discussed by Stäuber et al. (2006), this drop depends on X-ray irradiation and the chemical age. Thus, many grid points along the dimension of $F_X$ are required to sufficiently sample this drop.

### Table 1

Parameters for the Grid of Chemical Models, their Physical Range in the Envelope of YSOs, and the Required Number of Models to Achieve a Good Interpolation Accuracy ($\approx$ a Factor of 2 for Most Species/Physical Conditions)

| Parameter | Range         | Grid points |
|-----------|---------------|-------------|
| Density n | $10^3$–$10^6$ cm$^{-3}$ | 6           |
| Temperature $T$ | 8–3400 K | 23          |
| X-ray flux $F_X$ | $10^{-6}$–$10$ erg cm$^{-2}$ s$^{-1}$ | 14          |
| Plasma temperature $T_X$ | $10^7$–3 $\times$ $10^8$ K | 4           |
| X-ray Attenuation $\tau$ | $10^{-1}$–$10^{24}$ cm$^{-2}$ | 6           |
| Cosmic-ray ionization rate $\zeta_{\text{ris}}$ | $10^{-17}$–$10^{-15}$ s$^{-1}$ | 5           |
| FUV flux $G_0$ | 0 $\leftrightarrow$ $10^7$ ISRF | 9           |
| FUV attenuation $G_0$ | 0.1–10 Av | 10          |

**Straightforward Implementation:**

- Density: $10^3$–$10^6$ cm$^{-3}$
- Temperature: 8–3400 K
- X-ray flux: $10^{-6}$–$10$ erg cm$^{-2}$ s$^{-1}$
- Plasma temperature: $10^7$–$10^8$ K
- X-ray Attenuation: $10^{-1}$–$10^{24}$ cm$^{-2}$
- Cosmic-ray ionization rate: $10^{-17}$–$10^{-15}$ s$^{-1}$
- FUV flux: $G_0$ = 0 $\leftrightarrow$ $10^7$ ISRF

**Improved Implementation:**

- Density: $10^3$–$10^6$ cm$^{-3}$
- Temperature: 8–3400 K
- X-ray flux: $10^{-6}$–$10$ erg cm$^{-2}$ s$^{-1}$
- Plasma temperature: $10^7$–$10^8$ K
- X-ray Attenuation: $10^{-1}$–$10^{24}$ cm$^{-2}$
- Cosmic-ray ionization rate: $10^{-17}$–$10^{-15}$ s$^{-1}$
- FUV flux: $G_0$ = 0 $\leftrightarrow$ $10^7$ ISRF

### Figure 2

Fractional abundance of CO$^+$ for different FUV fluxes ($G_0$) and FUV attenuation ($\tau$). The solid contour lines and gray scale give the fractional abundance of the molecule. The gas density was chosen to be $10^6$ cm$^{-3}$, while the temperature is fixed at 550 K. The curvilinear coordinate system ($\alpha$, $\beta$) given in dotted line is used for the interpolation in the ($G_0$, $\tau$) plane. The grid points are given by gray/red dots.

(A color version of this figure is available in the online journal.)
Together with five points along the dimension for the cosmic-ray ionization rate \( \zeta_{\text{cr}} \) (s\(^{-1}\)), we would obtain \( 1.7 \times 10^7 \) grid points for a straightforward implementation (Table 1). This large number can be reduced by a factor of 100 using the following approximation. Instead of the X-ray model described in Stäuber et al. (2005), we make use of the fact that direct photoionization processes due to X-rays can be neglected for the chemical abundances; instead of the X-ray model, the H\(_2\) ionization rate \( \zeta_{\text{H}_2} \) is calculated by Equation (5) and the parameter for the cosmic-ray ionization rate is increased by this rate. A virtually enhanced cosmic-ray ionization rate thus acts as a proxy for the total ionization rate:

\[
\zeta_{\text{tot}} = \zeta_{\text{cr}} + \zeta_{\text{H}_2}(F_x, N(\text{H}), T_x).
\]

The “standard” cosmic-ray ionization rate \( \zeta_{\text{cr}} \approx 5.6 \times 10^{-17} \) s\(^{-1}\) and the ionization rate of H\(_2\) due to the impact of secondary electrons \( \zeta_{\text{H}_2}(F_x, N(\text{H}), T_x) \) form together the total ionization rate, which enters the chemical model as effectively increased cosmic-ray ionization rate. In this vein, Doty et al. (2004) used an increased cosmic-ray ionization rate as a proxy for an additional, internal source of ionization. Our approach treats the photodissociation reactions due to internally produced FUV photons exactly in the same way as the X-ray model by Stäuber et al. (2005); rates by Gredel et al. (1989) for cosmic-ray-induced FUV reactions are implemented therein with the same total ionization rate.

This approach provides a simple recipe to include X-ray induced reactions with an arbitrary X-ray spectrum into chemical models: the average energy per ion pair \( W(E) \) and X-ray cross sections \( \sigma_{\text{photo}} \) and \( \sigma_{\text{Compton}} \) are given in Appendix A. Using Equation (5) the total ionization rate \( \zeta_{\text{H}_2}(F_x, N(\text{H}), T_x) \) can be calculated. Pre-calculated ionization rates for a thermal X-ray spectrum (Equation (4)) are given in the same appendix.

### 2.4. Total Ionization Rate versus X-rays

The approach to use a total ionization rate instead of the previous X-ray model is tested with a spherical model of AFGL 2591 as given in Stäuber et al. (2005). In this model, temperature and density vary with distance to the central source. The density structure is given in the form of a power law in radius (van der Tak et al. 1999) and the temperature structure is taken from the detailed thermal balance calculations of Doty et al. (2002). The temperature and density distributions are given in Figure 3. The model is divided into 30 shells of approximately constant column density in radial direction. In this way, more shells are placed in the warm, chemically active part of the envelope. To resolve the water evaporation properly, assumed to be at 100 K, an additional shell is set to the corresponding position. Fewer positions are needed in the outer, colder, and thus chemically less active region. Calculations with more shells show insignificant differences in observable quantities derived from the models. More points may be necessary for other temperature/density profiles as presented in Figure 3. When the interpolation method for chemical abundances is used to construct such a spherical model, the number of points can be easily increased due to the gain in speed using that approach. For the implementation, we suggest to bisect the points until the derived observable quantities converge.

Figure 4 shows the radial dependence of the abundances for the main molecules CO, H\(_2\)O, CO\(_2\) as well as for those 10 molecules predicted to be the best X-ray tracers by Stäuber et al. (2005; HCN, HNC, H\(_2\)S, CS, CN, SO, HCO\(^+\), HCS\(^+\), H\(^+_2\), and N\(_2\)H\(^+\)). The ionized hydrides CH\(^+\), SH\(^+\), and NH\(^+\), discussed later in this section, are given in addition. The X-ray models are indicated by black lines. Results from the model with a total ionization rate \( \zeta \) given by Equation (6) are presented by thick (gray/red) lines. A model without protostellar X-ray radiation and models with X-ray luminosity \( L_X = 10^{30}, 10^{31}, \) and \( 10^{32} \) erg s\(^{-1}\) are shown. Protostellar FUV radiation is included in the same way as Stäuber et al. (2005) assuming a flux of \( G_0 = 10 \) at 200 AU. The agreement between the model including X-rays and with a total ionization rate is very good for the shown set of species, with deviations less than 25% in the fractional abundance.

This very good agreement between X-ray models and models with a total ionization rate has observational consequences: in order to use molecular lines as tracers for protostellar X-ray radiation, the effects of cosmic-ray ionization and X-ray induced ionizations have to be disentangled by spatial or excitation information on the abundance. This can be obtained from high-\( J \) lines with a high critical density (e.g., observed by the upcoming HIFI spectrometer onboard the Herschel Space Observatory) or by comparing visibility amplitudes from high angular resolution interferometer observations (e.g., Benz et al. 2007).

What are the limits of this approach? The X-ray flux \( F_X = L_X / 4\pi r^2 \) at a distance of 20 AU from a source with an X-ray luminosity of \( 10^{32} \) erg s\(^{-1}\) is about 90 erg s\(^{-1}\) cm\(^{-2}\). Meijerink & Spaans (2005) used similar field strengths when modeling X-ray-dominated regions (XDRs) in galactic nuclei. Thus, we explored the validity of the ionization rate approximation up to X-ray fluxes of 100 erg s\(^{-1}\) cm\(^{-2}\). All molecules in the chemical network have been tested for significant deviations between the two approaches in the range from 0 to 100 erg s\(^{-1}\) cm\(^{-2}\). Excellent agreement as in the example of water (Figure 5(g)) was found for most species. For our application in envelopes of YSOs, the ionization rate approach thus can be safely used.

A small set of species revealed discrepancies between the two approaches under certain conditions. They are presented in Figure 5. There are different reasons for deviation. They are discussed in the following paragraphs.
Figure 4. Abundances in a spherical AFGL 2591 model calculated by the X-ray model of Stäuber et al. ("X-ray," black lines) compared to a model with a total ionization rate given by Equation (6) ("\( \zeta \)," gray/red lines). Four different models are shown for X-ray luminosities of 0, \( 10^{30} \), \( 10^{31} \), and \( 10^{32} \) erg s\(^{-1}\).

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

The negatively charged species H\(^{-}\), OH\(^{-}\), and CN\(^{-}\) significantly deviate since the X-ray approach does not include a path for the formation of H\(^{-}\) by the ionization of H\(_2\) (Figure 5(a)). The UMIST database lists the reaction H\(_2\) + c.r. \( \rightarrow \) H\(^{+}\) + H\(^{-}\) for this process, resulting in a much higher abundance of this species. Subsequently, the abundances of OH\(^{-}\) and CN\(^{-}\) also increase. The X-ray approach only includes H\(^{-}\) formation by radiative association (H + e\(^{-}\) \( \rightarrow \) H\(^{+}\) + \( \gamma \)). Thus, our total ionization rate approach is an improvement.

At low X-ray fluxes the abundance of O\(^{+}\) is higher in the X-ray model than in the total ionization rate approach (Figure 5(b)). In the X-ray approach, direct photoionization CO \(+\) \( \gamma \) \( \rightarrow \) C\(^{+}\) + O\(^{+}\) + 2e\(^{-}\) can compete with the relatively inefficient formation of O\(^{+}\) through the reaction of He\(^{+}\) with CO\(_2\), OCS, or SO. The fractional abundance of O\(^{+}\) thus increases due to the presence of X-ray photons. However, it remains below a few times \( 10^{-12} \) insignificant for our applications (Section 4.1). At higher X-ray fluxes, O\(^{+}\) is formed in the charge exchange reaction of H\(^{+}\) with O, and the two approaches agree well.

For the hydride ions SH\(^{+}\) and CH\(^{+}\) at low density and high X-ray flux, the X-ray approach predicts higher abundances than the ionization rate approach. This discrepancy can be explained by doubly ionized atoms added by Stäuber et al. (2005) to the chemical network, but not included in the UMIST database. Thus, doubly ionized atoms lack in the total ionization rate approach. At high densities, doubly ionized atoms are not
important because \( X + H^+_2 \rightarrow \text{XH}^+ + H_2 \) dominates \( \text{XH}^+ \) formation. Abel et al. (2008) found the branching ratio of \( S^{++} + H_2 \) to be important for the efficiency of \( \text{SH}^+ \) production through doubly ionized atoms. Stäuber et al. (2005) only included \( X^{++} + H_2 \rightarrow X^+ + H_2^+ \) with rate coefficients taken from Yan (1997) \((k \lesssim 10^{-13} \text{ cm}^3 \text{s}^{-1})\). However, in the later version of their code used here, they implemented the formation of hydride ions as the main product with a rate coefficient of \( 10^{-9} \text{ cm}^3 \text{s}^{-1} \) (Yan 1997), similar to the value of Abel et al. (2008) for \( \text{SH}^+ \), but about an order of magnitude higher for \( \text{CH}^+ \).

Doubly ionized atoms become important for low densities and high irradiation. For a given X-ray flux, the number of ionization processes per volume is constant, independent of the total gas density. The electron density at a high X-ray flux of \( 10^6 \text{ erg cm}^{-2} \text{s}^{-1} \) varies only by a factor of about 2 between a density of \( 10^4 \) and \( 10^6 \text{ cm}^{-3} \). The amount of \( O^+ \) is large, accounting for a short destruction timescale of \( H_2 \) in the reaction \( H_2 + O^+ \rightarrow \text{OH}^+ + H \). \( H_2 \) is however the precursor of \( H^+_2 \) which is subsequently also reduced (Figure 5(h)). In this regime, the main production of \( \text{SH}^+ \) and \( \text{CH}^+ \) is through \( X^{++} + H_2 \rightarrow \text{XH}^+ + H^+ \).

\( \text{NH}^+ \) enhancement in the X-ray approach is due to another effect. The charge exchange reactions of oxygen and nitrogen with \( H_2 \) have rate coefficients of \( 3 \times 10^{-11} \text{ cm}^3 \text{s}^{-1} \) and \( 10^{-9} \text{ cm}^3 \text{s}^{-1} \), much faster than for sulfur and carbon. The chemical network of Stäuber et al. (2005) follows Yan (1997) and thus assumes the formation of \( \text{OH}^+ \) and \( \text{NH}^+ \) through doubly ionized species to be negligible. The slightly enhanced abundance of \( \text{NH}^+ \) in the X-ray approach compared to the total ionization rate approximation is explained by the larger amount of \( N^+ \) at low density, since its production by the reaction of \( N^{++} + H \rightarrow N^+ + H_2 \) is faster than the reaction between \( N^{++} \) and \( H_2 \).

In conclusion, the total ionization approach should not be used for low densities where the X-ray fluxes exceed \( 10 \text{ erg s}^{-1} \text{cm}^{-2} \) X-ray flux. For \( \text{SH}^+ \) and \( \text{CH}^+ \), the X-ray flux limit is lower (Figure 5).

We note that the X-ray approach is also incomplete in this regime as, e.g., the important vibrationally excited \( H_2 \) with a high energy deposition of X-rays per density \( H_2 / n > 10^{-25} \text{ erg cm}^3 \text{s}^{-1} \) (Yan 1997) is not included. Nevertheless, the total ionization rate approach is well applicable for models of YSO envelopes, since density models by Jørgensen et al. (2002) or van der Tak et al. (2000) predict a gas density larger than \( 10^6 \text{ cm}^{-3} \) close to the protostar where X-ray irradiation is significant (i.e., exceeding the cosmic ray effects). Indeed, the derived abundances of \( \text{SH}^+ \), \( \text{CH}^+ \), and \( \text{NH}^+ \) in Figure 4, show no difference between the two approaches. For our application, the total ionization approach is not only more elegant, but adequate.

### 2.5. Multidimensional Interpolation

The relevant physical parameters for the molecular/atomic fractional abundance evolution are the temperature \( T \), the density \( n \), two parameters for the FUV flux, and the total ionization rate. The implemented grid thus consists of five dimensions and a total of about \( 1.1 \times 10^5 \) grid points in the improved implementation. The range and number of points for each dimension are given in Table 1. For the interpolation of the abundance at a specific physical condition \( \vec{x} \equiv (\lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5) \), a multidimensional interpolation in logarithmic space is used: the neighboring interpolation points of \( \vec{x} \) are found in each dimension \( d = \{1, 2, \ldots, 5\} \), such that \( \lambda_{d, a} < \lambda_{d, b} < \lambda_{d, m} \). Then, the abundances at the interpolation points, \( x_{\{i,j,k,l,m\}} \) are read out of the grid for all combinations of \( i, j, k, l, m = \{a, b\} \).

The interpolated abundance \( x \) is obtained from

\[
\log_{10}(x) = \sum_{i,j,k,l,m} \alpha_i^a \alpha_j^a \alpha_k^a \alpha_l^a \alpha_m^a \cdot \log_{10} \left( \frac{x_{\{i,j,k,l,m\}}}{\alpha_i^a \alpha_j^a \alpha_k^a \alpha_l^a \alpha_m^a} \right)
\]
The weights $\alpha_d^i$ along each dimension are defined by $\alpha_d^i = 1 - \beta$ and $\alpha_d^i = \beta$. The position within the hypercube, normalized to the interval between 0 and 1 is given by $\beta = \left[ \log_{10}(\lambda_d^i) - \log_{10}(\lambda_d^{a_i}) \right] / \left[ \log_{10}(\lambda_d^{a_i}) - \log_{10}(\lambda_d^{b_i}) \right]$. The most time-consuming step of the interpolation is the calculation of the total ionization rate by the integral of Equation (3) and the inversion of the coordinate transformation $(\alpha, \beta) \rightarrow (G_0, \tau)$. Both functions are given in tabulated form in the interpolation routine. This allows to obtain approximately 10,000 fractional abundances per second on a standard personal computer. Using the full chemical model, the calculation of the same number of abundance evolutions would require about 80 hr of CPU time.

3. CHEMICAL MODEL

For our work, we start from the chemical model introduced by Doty et al. (2002, 2004) and Stäuber et al. (2004, 2005). Thus, we describe only changes to their model in this section: the chemical network has been updated from the UMIST 97 (Millar et al. 1997a) to the UMIST 06 database for astrochemistry (Woodall et al. 2007). We implement the standard UMIST 06 database without the dipole-enhanced rates. For technical reasons, fluorine-bearing species have not been included. Appendix B gives details of the implementation of the new chemical network. The rates for cosmic-ray- and X-ray-induced FUV reactions implemented in Stäuber et al. (2005) were a factor of 2 too high due to an error in the previously used database (compare comment by S. Doty in Woodall et al. 2007) and are now at their correct values. Charge exchange on PAH or small grains can be important for the ionization balance (Wakelam & Herbst 2008; Maloney et al. 1996). FUV irradiation enhances the number of positively charged grains. The rates for this process were accidentally divided by the total density in the implementation of Stäuber et al. (2005) and are now at the correct value. The influence on the chemical abundance in their applications is however small. Grain surface reactions are not taken into account except for the formation of H$_2$, where the rate given in Draine & Bertoldi (1996) is used.

We have extended the chemical model with self-shielding of CO and H$_2$ using the shielding factors given in Lee et al. (1996) and Draine & Bertoldi (1996), respectively. They depend on the column densities $N$(H$_2$) and $N$(CO) between the FUV source and the modeled parcel of gas. Since we do not include any "non-local" parameter as dimension in the chemical grid, an approximation is needed: prior to the calculation of a model, the optical depth dependence of the H$_2$ abundance at the given physical conditions (density, temperature, and FUV irradiation) is calculated for a simple steady-state model considering only the H$_2$ photodissociation and formation on dust with a fixed density and temperature. The column density can be read out of this toy model and shows good agreement with the examples given in Draine & Bertoldi (1996). As a rough approximation of the CO column density, we assume a fixed ratio of $N$(CO)/$N$(H$_2$) = 2 $\times$ 10$^{-4}$.

In the papers of Doty et al. /Stäuber et al., the system of stiff ordinary differential equations (Equation (1)) is solved using the DDRIV3 algorithm. This solver is numerically unstable for chemical networks involving reactions with short timescales, e.g., evaporation from dust or photodissociation at high values of $G_0$. The DVODE solver proved to be more robust and much faster.

3.1. Initial Conditions

In order to solve the first-order differential rate equations (Equations (1)), initial conditions for the abundances have to be assumed. If the chemical evolution were traced starting from diffuse cloud conditions, a purely atomic composition would have to be assumed and the physical conditions such as FUV irradiation or density would have to be changed during the evolution (e.g., Lintott & Rawlings 2006). Here, we follow the approach of Doty/Stäuber et al., who started at dark cloud conditions with a molecular composition (Table 6 in the appendix). In this way, uncertainties of the physical evolution during this first phase and/or reactions on dust grains less affect the chemical composition. The evaporation of species frozen out on ice is not taken explicitly into account with evaporation-type reactions but approximated with different sets of initial abundances as in the models of Doty/Stäuber et al. Evaporation and freeze-out reactions are implemented in the model. However, they slow down the calculation significantly due to short timescales at high temperature and are not activated for this work.

3.2. Sulfur Bearing Species

Various sulfur bearing molecules are predicted by Stäuber et al. (2005) to be good tracers of X-ray radiation. Despite the large uncertainty in many of the reaction rates involving sulfur-bearing species (Wakelam et al. 2004), these molecules might be important for applications of the grid. To better constrain the initial molecular conditions, we use the multitude of observed sulfur-bearing species found toward AFGL 2591 by van der Tak et al. (2003), van der Tak et al. (1999), and Stäuber et al. (2007). Spherical models of AFGL 2591 (compare Section 2.4) are calculated for different sets of initial abundances, main sulfur carriers, and chemical ages. The abundances are used as input for a full non-LTE radiative transfer calculation using the RATRAN code (Hogerheijde & van der Tak 2000) to model line fluxes. A $\chi^2$ test is carried out to compare the modeled line fluxes with the observations. For this work we adopt $S$ ($T < 100$ K) and H$_2$S ($T > 100$ K) to be the main initial sulfur carriers. The abundance for the cold part follows Aikawa et al. (2008) to be 9.1 $\times$ 10$^{-9}$ relative to the total hydrogen density. For the hot core, the abundance of SO is chosen to reproduce the jump in the abundance between the cold and hot part as observed by Benz et al. (2007). The adopted sulfur abundance is about the solar abundance (compare Snow & Witt 1996 and Asplund et al. 2005) indicating no or only minor sulfur depletion on dust grains in the hot core. Goicoechea et al. (2006) modeled a PDR with a relatively low FUV irradiation of $\chi = 60$ ISRF (Draine) and reported a sulfur abundance of about a factor of 4 lower than the value adopted in this work to reproduce their observations. It may be caused by the massive impact of FUV irradiation in the vicinity of AFGL 2591, raising the temperature severely and resulting in an even higher sulfur abundance in the gas phase.

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3. http://www.netlib.org/slatec
4. http://www.netlib.org/ode
Figure 6. Abundances of major species, X-ray/UV tracers and problem cases in a spherical model of AFGL 2591. The plots show a comparison between results calculated by the chemical model (solid line) and interpolated from the grid of chemical models (dashed line). The gray region shows a deviation of a factor of 2 from the chemical model. Note the different vertical scales of individual panels. The thick lines correspond to a model with a stellar X-ray luminosity of $10^{32}$ erg s$^{-1}$ calculated by the chemical model (solid line) and interpolated from the grid of chemical models (dashed line). The gray region shows a deviation of a factor of 2 from the chemical model. The thin line to a model without X-rays. All abundances are given for a chemical age of 5 $\times$ 10$^4$ yr, except for HCNH$^+$ (3 $\times$ 10$^5$ yr).

4. BENCHMARKS

In this section, the accuracy of the interpolation method is verified. For two realistic problems—possible applications of the chemical grid—the interpolated abundances are compared to abundances calculated using the chemical model. The results are considered satisfactory if they agree within a factor of 2 of each other for the reasons noted in Section 2.

4.1. A Spherical Model of AFGL 2591

A first test of the chemical grid is performed using the spherical model of AFGL 2591 as introduced in Section 2.4. Figure 6 shows the radial dependence of the abundances for the main molecules CO, H$_2$O, CO$_2$ as well as for those 10 molecules predicted to be the best X-ray tracers by Stäuber et al. (2005) (HCN, HNC, H$_2$S, CS, CN, SO, HCO$,^+$, HCS$^+$, H$_3^+$, and N$_2$H$^+$). CO$^+$ which will be addressed in the next paper of this series and the two molecules, C$_6$H and HCNH$^+$, having the largest deviation are shown in addition. Solid lines give the results of the chemical model, while interpolated abundances are shown by dashed lines. Models with no protostellar X-ray radiation and an X-ray luminosity of $L_X = 10^{32}$ erg s$^{-1}$ (Stäuber et al. 2005) are given in thin and thick lines, respectively. We assume a chemical age of 5 $\times$ 10$^4$ yr. The shaded region indicates a
range of a factor of 2 compared to the fully calculated model and marks the goal of our interpolation approach. Indeed, most molecules comply with the aimed accuracy for the models with and without X-rays.

To provide an unbiased check for a larger set of molecules, a statistical approach is used. The goal of chemical modeling is to obtain characteristics which can be compared with observations. In the following, we check the column density of all molecules in the chemical model for agreement between the grid and full calculation. The radial column density, \( N_{\text{radial}} = \int n(r) dr \), with the radial distance \( r \), gives a measure for molecules observed in absorption. For molecules observed in emission, the beam-averaged column density is more appropriate. It is defined by

\[
N_{\text{beam}} = \frac{\int \int \int n(z, p) G(p) 2\pi p dp dz}{\int \int \int G(p) 2\pi p dp},
\]

with \( z \) being the coordinate along the line of sight and \( p \) the impact parameter perpendicular to \( z \). \( G(p) \) is a beam response function (e.g., a Gaussian). This approach using column densities does not incorporate the molecular excitation. Thus, it cannot be used to compare models directly with observations. Computationally much more demanding radiative transfer calculations would have to be carried out instead. For our benchmark purposes however, column densities are sufficient.

Four different spherical models of AFGL 2591 without protostellar X-rays and with X-ray luminosity of \( L_x = 10^{30}, 10^{31}, \) and \( 10^{32} \) erg s\(^{-1}\) are compared. Three different chemical ages of \( 3 \times 10^3, 5 \times 10^4, \) and \( 3 \times 10^5 \) yr are considered to trace possible deviations due to the temporal evolution of the fractional abundances. For these 12 models, the radial \( (N_{\text{radial}}) \) and beam averaged \( (N_{\text{beam}}) \) column density are obtained for all molecules in the chemical network. We assume a 14\(^{\circ}\) beam corresponding approximately to a James Clerk Maxwell Telescope or Herschel beam and adopt a distance of 1 kpc to the source. To compare grid results to fully calculated models, the factorial deviation \( Y \equiv \max (N_{\text{grid}}/N_{\text{full}}, N_{\text{full}}/N_{\text{grid}}) \) is introduced. The fraction of molecules having a factorial deviation larger than a certain value is shown in Figure 10. Only molecules with a column density larger than \( 10^{11} \) cm\(^{-2}\) and a frequency of 350 GHz is about 40 mK km s\(^{-1}\), a lower limit for observations with current and upcoming facilities. Compared with the H\(_2\) column density of order \( 10^{15} \) cm\(^{-2}\), it corresponds to a fractional abundance of about \( 10^{-12} \) which marks approximately the possible limit of a detection within an observation time of a few hours.

Table 7 in Appendix D lists the molecules with the largest deviations. The largest disagreement is found in the radial column density of OH\(^-\) with a factorial deviation up to a factor of 9.6. This deviation is explained by the different paths for H\(^-\) formation in the two models (Section 2.4). It is thus an improvement of the total ionization approach. A problematic disagreement larger than a factor of 5 is found however for HCNH\(^+\) (\( Y = 5.4 \)) and C\(_6\)H (\( Y = 5.2 \)). Figure 6 shows the radial dependence of the fractional abundances for these two species at the chemical age and X-ray luminosity where the largest deviation occurs.

How can such large deviations be explained? In the case of C\(_6\)H at low X-ray fluxes, it is surprisingly an effect of the ionization rate. Figure 7 presents the fractional abundance of C\(_6\)H versus total ionization rate obtained from the chemical model and interpolated from the chemical grid. Three different chemical ages are given. For \( 5 \times 10^4 \) yr, we find a deviation of about a factor of 5 due to the interpolation over a sharp peak in the fractional abundance (bold vertical bar), which is not resolved by the grid. This peak shifts to higher ionization rates with time. A proper sampling would thus require a large number of grid points to cover all chemical ages. At ionization rates below this peak, C\(_6\)H is formed by the reaction C + C\(_5\)H\(_2\) \( \rightarrow \) C\(_6\)H. C stems from the X-ray- or cosmic-ray-induced dissociation of CO. At an older chemical age (or higher ionization rate), the “late-phase” molecule SO\(_2\) is photodissociated to SO and O. Reaction of C\(_6\)H + O then decreases the fractional abundance of C\(_6\)H. At very high ionization rate, the bulk of C\(_6\)H is produced by the electron recombination of C\(_6\)H\(^+\).

Most contribution to the radial column density of HCNH\(^+\) is from the innermost part of the model. In this region, HCNH\(^+\) is mainly formed by the reaction of HCN with H\(_2\)O\(^-\). Both molecules are enhanced by X-rays and FUV irradiation at temperatures above 250 K, where water is not destroyed due to X-ray irradiation (Stauber et al. 2006). An X-ray luminosity higher than \( 10^{30} \) erg s\(^{-1}\) is sufficient to dominate the effect of FUV enhancement. At lower X-ray luminosities however, the FUV flux dominates the HCNH\(^+\) abundance. Due to the particular shape of the contour lines of its fractional abundance depending on \( G_0 \) and \( \tau \), this molecule is difficult to interpolate. Figure 8 shows the fractional abundance of HCNH\(^+\) in the \((G_0, \tau)-\)plane along with the coordinate system used for the gridding and interpolation (Section 2.2). Physical conditions of the innermost region of the AFGL 2591 model and a chemical age of \( 3 \times 10^3 \) yr were chosen for this figure.

In general, the agreement between the grid results and the fully calculated abundances is excellent. The mean deviation of \( \langle Y_{\text{beam}} \rangle = 1.12 \) for the beam-averaged column densities.
and \( \langle Y_{\text{radial}} \rangle = 1.28 \) for the radial column densities indicate agreement for the majority of the species. A total number of 1661 (\( N_{\text{radial}} \)) and 1563 (\( N_{\text{beam}} \)) column densities are considered for the means, respectively. The slightly higher mean deviation of the radial column density is explained by the larger weight of the chemically active hot-core region. The mean deviation does not vary by more than 0.04 with chemical age.

4.2. FUV Driven Chemistry

In the spherically symmetric models of AFGL 2591, protostellar FUV radiation cannot penetrate further into the envelope than a few hundred AU (Stäuber et al. 2004). This is, however, not the case when an outflow cavity allows FUV photons to escape and irradiate a larger volume of gas. This two-dimensional situation will be addressed in the second and third parts of this series of papers. Here, we carry out the following benchmark test. A (plane parallel) region with a fixed temperature of 80, 100, and 550 K and a density of \( 10^6 \) cm\(^{-3} \) is considered. The incident radiation field is assumed to be 1, 10, 10\(^2 \), 10\(^4 \), and 10\(^6 \) times the ISRF and no geometrical dilution (i.e., \( G_0 \propto r^{-2} \)) is taken into account. The dust column density, however, attenuates the FUV radiation. It is given by the optical depth \( \tau \) using the conversion factor introduced in Section 2.2. Figure 9 shows the fractional abundance versus the optical depth \( \tau \). The main molecules CO, H\(_2\)O, CO\(_2\), several PDR related species, and the molecules showing the largest deviations are selected for Figure 9. For most species only the results for a temperature of 550 K are shown, since FUV irradiation can considerably heat the gas through the photoelectric effect on dust grains. For reasons of clarity not all fractional abundances are given in this plot.

A value reflecting observable quantities is needed for the statistics comparing interpolated to fully calculated abundances (Figure 10). We use the column density of a molecule \( i \) between \( \tau = 0.1 \) and \( \tau = 15 \) calculated by

\[
N_i = 1.87 \times 10^{21} \int_{0.1}^{15} x_i(\tau) \, d\tau \, (\text{cm}^{-2}),
\]

where \( x_i(\tau) \) is the fractional abundance relative to the total gas density of the species \( i \) depending on the optical depth \( \tau \). All molecules in the chemical network are considered at five different values of \( G_0 \) and three temperatures. Only column densities larger than \( 10^{11} \) cm\(^{-2} \) are selected following the argument given in Section 4.1. A total of 2096 column densities are taken into account. The mean deviation for this benchmark is found to be \( \langle Y_{\text{FUV}} \rangle = 1.35 \), and thus higher than the values in the previous section, but well within the goal of a factor of 2.

Table 7 in Appendix D lists species, for which large factorial deviations in the column density between the grid and the fully calculated model were found. HSO\(^+\) shows the largest deviation amounting to a factor of \( Y \approx 5.6 \) for a high FUV flux of \( G_0 = 10^8 \) times the ISRF at a temperature of 100 K. The deviations can be explained by the sharp peak in fractional abundance at \( \tau \approx 11 \). It is a result of the formation through SO + H\(_2\) → HSO\(^+\) + H\(_2\) or SO + HCO\(^+\) → HSO\(^+\) + CO. The peak in the abundance is also found in the fractional abundance of SO due to the competition of two FUV related reactions; at \( \tau < 11 \), SO is formed by the photodissociation of SO\(_2\) and destroyed by the reaction with OH leading to SO\(_2\). At larger \( \tau \) however, SO dissociation becomes more important and its abundance thus decreases. This peak is not resolved by the current implementation of the grid as can easily be seen in a plot of the fractional abundance depending on \( G_0 \) and \( \tau \) (Figure 14 in Appendix D). While large deviations of HSO\(^+\) occur at high \( \tau \), the O\(_3\)\(^+\) fractional abundance disagrees at low optical depth (Figure 15).

What is the reason for these peaks in fractional abundance? Abundances in FUV irradiated regions are controlled by rate coefficients of the form \( k \propto \exp(-\gamma \cdot \tau) \), where the product of the optical depth times a coefficient enters (see Equation (3)). Photodissociation rates thus drop exponentially with \( \tau \). They become unimportant for the chemical abundance in a narrow interval of \( \tau \). It should be noted, however, that \( \gamma \) is also affected by uncertainties at a level of at least 10% due to the dust model used for fitting the rate and the range of \( \tau \) over which the rates have been fitted (van Dishoeck et al. 2006).

To reveal areas in the \((G_0, \tau)\) plane where deviations occur, the mean factorial deviation for all three temperatures and all species is shown in Figure 11. It shows that large areas agree well with \( Y < 2 \), while other regions show a larger disagreement, however still mostly within a factor of 4. A narrow region in the \((G_0, \tau)\) plane is found to have mean deviations larger than a factor of 10. It coincidences with the values of \( G_0 \) and \( \tau \) where a large deviation of HSO\(^+\) has been found in a previous paragraph. As the statistics in Figure 10 and the low mean deviation of the column density show, this local deviation is, however, sufficiently averaged out when observable quantities are derived from the grid.

5. UTILIZING THE GRID OF CHEMICAL MODELS

The grid of chemical models is accessible through Abundance Modeling of young stellar Objects Under protostellar Radiation (AMOUR) available for public use at http://www.astro.phys.ethz.ch/chemgrid.html. The page provides an online form to retrieve interpolated fractional abundances from the grid of chemical models. This form also calculates the X-ray ionization rate \( \dot{N}_{\text{H}} \), for a particular X-ray flux \( F_X \), X-ray attenuation \( N(H_{\text{tot}}) \), and plasma temperature \( T_X \). For large modeling tasks or to include the interpolation method in other codes, the page also offers a FORTRAN code and the necessary
molecular data tables in binary and ASCII format for download. Documentation is available at the website which describes the input/output parameters, the technical implementation, the format of the data tables, and shows example input/output data.

There exist a number of restrictions for the currently provided implementation which must be kept in mind when applying the method: the chemical composition in the molecular data table has been calculated for a specific chemical network (the UMIST 2006 database, Woodall et al. 2007) using one set of initial conditions (Table 6). The current implementation does not include grain surface reactions except for H2 formation on dust. The medium is assumed to be static and physical conditions (e.g., temperature or density) have been assumed to be constant over time. These are however only restrictions of the currently distributed molecular data tables. Further tables for other chemical networks, initial conditions, time-dependent parameters, etc. can be obtained from the authors on a collaborative basis.

6. CONCLUSIONS AND OUTLOOK

Starting from the chemical model of Doty et al. (2002, 2004) and Stäuber et al. (2004, 2005), we have introduced a new method to simulate the chemical evolution of YSO envelopes based on interpolation in a pre-calculated grid. The chemical model has been revised and the relevant physical parameters for the chemical composition of the gas are discussed. Benchmark tests have been carried out to verify the accuracy of the interpolation method. We conclude the following.

1. Accurate chemical modeling of a multidimensional envelope of YSOs is possible using a fast, grid-based interpolation method (Section 4). Comparison of observable quantities (beam averaged line fluxes) yields a mean factorial deviation between fully calculated and interpolated values of 1.35. This is more accurate than the uncertainties introduced by observations and chemical rate coefficients. Our method is more than five orders of magnitude faster than the full calculation (Section 2.5).
2. The X-ray models by Stäuber et al. (2005) can be reproduced using an enhanced cosmic-ray ionization rate as a proxy for X-ray irradiation (Section 2.4). In the relevant physical range for the application in YSO envelopes, the agreement in the fractional abundance is within 25%. The implementation of this approach is described in detail in Appendix A and allows to include the effect of X-ray irradiation to chemical models in a simple way.

3. Ionization by X-rays and cosmic rays cannot be easily distinguished by molecular tracers. Spatial information on the abundance is thus needed to disentangle protostellar X-ray and cosmic-ray ionization (Section 2.4).

4. For the formation of CH\(^+\) in low density gas (10\(^4\) cm\(^{-3}\)) with high X-ray irradiation (> 1 erg cm\(^{-2}\) s\(^{-1}\)) recombination of...
doubly ionized carbon with H$_2$ (C$^{++}$ + H$_2$ → CH$^+$ + H$^+$) is important.

5. Increasing the initial abundance in the hot-core region ($T > 100$ K) of the main sulfur carrier improves the agreement between models and observations in a high-mass star-forming region (Section 3.2).

6. Exploring the parameter space, we find regions with high gradients in molecular abundances. This is where small changes in the physical parameters yield large variations in abundance. As an example, interpolation of fractional abundances of an FUV irradiated region is difficult because photodissociation rates depend exponentially on the optical depth (Section 4.2). We have compensated for this by adopting a curvilinear coordinate system and a high number of grid points (Section 2.2).

The current grid method is limited by the assumption of the initial composition and fixed chemical rates. For different assumptions, the database needs to be recalculated. Using this fast chemical interpolation method, the radiative transfer calculation becomes the bottleneck in computing time to interpret data. Recently introduced escape probability methods, such as the exact method by Elitzur & Asensio Ramos (2006) or an approximate multidimensional code by Poelman & Spaans (2005) can speed up this step of the modeling.

This paper shows the possibility of interpolation for chemical modeling. In future publications, we will demonstrate major applications in multidimensional chemical modeling of YSOs and fast data-fitting to interpret observations. The gain in speed allows to carry out parameter studies on the influence of the geometry on the interpretation of observations. Furthermore, it will be possible to apply detailed chemical models to a large set of sources and draw conclusions on physical properties based on statistics.

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APPENDIX A

CALCULATION OF THE IONIZATION RATE

For the calculation of the X-ray ionization rate using the equation

$$\zeta_{H_2} = \int_{E_{\min}}^{E_{\max}} J(E, r) \sigma_{\text{total}}(E) \frac{E}{W(E) \lambda(H_2)} dE, \quad (A1)$$

we provide the Compton and photoionization cross sections as well as the mean energy $W(E)$ of an ion pair in a tabulated form. The cross sections are calculated using the X-ray model of Stäuber et al. (2005) to which we refer for the source of the atomic and molecular constants and the exact implementation. We use the elemental composition given in Appendix C. Since the photoionization cross section of a molecule is approximated by adding the cross sections of the contained atoms, the total photoionization cross section does not depend on the abundance of the molecular species as long as the elemental composition does not change.

The cross sections are shown in Figure 12 for a photon energy between 100 and 10$^7$ eV. The photoionization cross section, given by the solid line is approximated using a power law, defined piecewise for an energy range between $E_{\text{min}}$ and $E_{\text{max}}$. Table 2 gives the cross sections at the boundaries of each energy interval. The cross section at an energy $E \in [E_{\text{min}}, E_{\text{max}}]$ can then be calculated using

$$\sigma_{\text{photo}}(E) \approx 10^{\log_{10}(\sigma_{\text{max}})(1-\alpha)+\log_{10}(\sigma_{\text{max}}) \alpha}, \quad (A2)$$

with $\alpha = (\log(E) - \log(E_{\text{min}}))/\log(E_{\text{max}}) - \log(E_{\text{min}})$. The deviation of the fit to the calculated cross section is less than 5%
Table 2
Fitting Parameters for the X-ray Cross Section

| E_min (eV) | E_max (eV) | σ_min (cm^2) | σ_max (cm^2) |
|-----------|------------|--------------|--------------|
| 100       | 291        | 6.02(−20)    | 2.71(−21)    |
| 291       | 404.7      | 3.03(−21)    | 1.15(−21)    |
| 404.7     | 538        | 1.27(−21)    | 5.29(−22)    |
| 538       | 724        | 1.79(−22)    | 3.59(−22)    |
| 724       | 857        | 3.99(−22)    | 2.54(−22)    |
| 857       | 870        | 2.59(−22)    | 2.48(−22)    |
| 870       | 1311       | 2.89(−22)    | 9.75(−23)    |
| 1311      | 1846       | 1.06(−22)    | 4.13(−23)    |
| 1846      | 2477       | 4.61(−23)    | 2.03(−23)    |
| 2477      | 3203       | 2.23(−23)    | 1.09(−23)    |
| 3203      | 4043       | 1.11(−23)    | 5.76(−24)    |
| 4043      | 5996       | 5.89(−24)    | 1.89(−24)    |
| 5996      | 7124       | 1.91(−24)    | 1.15(−24)    |
| 7124      | 8348       | 2.24(−24)    | 1.45(−24)    |
| 8348      | 8890       | 1.50(−24)    | 4.24(−26)    |
| 8890      | 100000     | 4.24(−26)    | 1.04(−27)    |

Notes. a(b) means a × 10^b. The columns give values for different plasma temperatures (K) and the rows correspond to column densities between 10^{20} and 10^{28} cm^-2.

Table 3
The Ionization Rate ζ(T) in s^-1 at F_X = 1 erg s^-1 cm^-2

| N(H_2) cm^-2 | 3(6) K | 1(7) K | 3(7) K | 1(8) K | 3(8) K |
|--------------|--------|--------|--------|--------|--------|
| 1(20) cm^-2  | 4.8(−11)| 2.4(−11)| 1.0(−11)| 3.4(−12)| 1.2(−12)|
| 1(21) cm^-2  | 4.2(−12)| 4.5(−12)| 2.5(−12)| 9.8(−13)| 3.7(−13)|
| 1(22) cm^-2  | 6.9(−14)| 3.7(−13)| 4.0(−13)| 2.2(−13)| 1.0(−13)|
| 1(23) cm^-2  | 6.9(−17)| 9.6(−15)| 3.9(−14)| 4.5(−14)| 3.3(−14)|
| 1(24) cm^-2  | 6.8(−22)| 4.5(−17)| 2.0(−15)| 9.4(−15)| 1.4(−14)|
| 1(25) cm^-2  | 1.8(−30)| 8.6(−22)| 1.7(−17)| 1.4(−15)| 6.4(−15)|

Notes. a(b) means a × 10^b. The columns give values for different plasma temperatures (K) and the rows correspond to column densities between 10^{20} and 10^{28} cm^-2.

in the given energy range. Interpolation intervals are indicated by ticks at the bottom of the figure.

The cross section for inelastic Compton scattering is dominated by H_2 and H. This process does not contribute to the total cross section at low energy. We therefore use the fit from Stäuber et al. (2005) to the XCOM database (NIST) for the energy above 1 keV. With x = log_{10}(E [eV]), the cross section reads

\[ \sigma_{\text{Compton}} = 2.869674 \times 10^{-23} - 2.6364914 \times 10^{-23} \cdot x + 7.931175 \times 10^{-24} \cdot x^2 - 7.74014 \times 10^{-25} \cdot x^3 \quad (E \leq 10 \text{ keV}) \]

\[ \sigma_{\text{Compton}} = -2.374894 \times 10^{-24} + 1.423853 \times 10^{-24} \cdot x - 1.70095 \times 10^{-25} \cdot x^2 \quad (E > 10 \text{ keV}). \] (A3)

Finally, the mean energy per ion pair \( W(E) \) is constant above 1 keV, \( W(E > 1\text{keV}) = 20.95 \text{ eV} \), and can be approximated by

\[ W(E) = 23.65 - (\log_{10}(E[eV]) - 2) \times 2.7 \quad (\text{eV}) \]

between 100 and 10^3 eV, following Dalgarno et al. (1999).

A.1. The Ionization Rate of a Thermal Spectrum

As an important example, we calculate the ionization rates \( \xi \) (s^-1) for a thermal X-ray spectrum. The photo- and Compton ionization cross sections are implemented in the way described before and Equation (A1) is evaluated. Figure 13 shows \( \xi \) depending on the attenuating column density. The “standard” cosmic-ray ionization rate of 5.6 × 10^{-17} s^-1 is given by a dotted line. The top panel gives the ionization rate for three different plasma temperatures at a fixed flux of 10^{-2} erg s^{-1} cm^{-2}. A hotter spectrum results in a larger number of photons at high energy which can penetrate further into the envelope. Most photons of a cold spectrum (≈10^6 K) however are quickly absorbed. For the bottom panel, the plasma temperature has been fixed to 7 × 10^7 K. Since the X-ray intensity depends linearly on the flux \( F_X \), the ionization rates scale in the same way. The difference in the ionization rate, when the integral in Equation (A1) is evaluated between 1 and 100 keV (solid line) and 0.1 and 100 keV (dashed line) is small at column densities larger than 10^{21} cm^{-2}, except for a small difference due to the normalization \( N \) (Equation (4)). Up to column densities of a few times 10^{21} cm^{-2}, photons with an energy below 1 keV can however contribute significantly to the ionization rate.

Table 3, the ionization rate for an X-ray flux of 1 erg s^{-1} cm^{-2} is given. The columns correspond to different plasma temperatures and the rows to different attenuating column densities. These ionization rates can be scaled linearly to an
arbitrary value of the X-ray flux. For a point-like X-ray source, the flux at a distance \( r \) from the source is obtained from the X-ray luminosity by \( F_X = L_X / 4\pi r^2 \).

**APPENDIX B**

**IMPLEMENTATION OF THE UMIST 06 NETWORK**

The UMIST 06 database for astrochemistry (Woodall et al. 2007) lists an interval \([T_{\text{min}}, T_{\text{max}}]\) for the recommended temperature range for each reaction rate. For some reactions, different rates are given for distinct temperature ranges. The paper lists several rates for which no extrapolation to low temperatures of \( \approx 10 \) K should be done. We switch off those reactions for temperatures below \( T_{\text{min}} \).

All other reaction rates are extrapolated to lower temperatures with a few exceptions: some reactions of the collider type (“CL” in Woodall et al. 2007) have a negative activation energy. To stabilize the chemical network, we keep their rates constant at temperatures below 500 K or 1000 K, or switch the reaction entirely off below 500 K (compare Table 4).

Other reactions involve significant extrapolation, i.e., \( T_{\text{min}} > 300 \) K, and the rates do not decrease from 100 K to 10 K. Certain reactions are thus switched off outside their temperature range as given in the database. The reaction \( \text{OH} + \text{CN} \rightarrow \text{OCN} + \text{H} \) is not switched off, since the OSU database (Smith et al. 2004) lists this reaction with the same rate description. The reaction \( \text{OCN} + \text{H} \rightarrow \text{CN} + \text{H}_2 \) was introduced in UMIST 99 and has severe consequences for the abundance of formaldehyde: it is mainly destroyed by this reaction and the abundance drops by about two orders of magnitude compared to observations by (Tak 2000) of a spherical model of AFGL 2591, is short by about two orders of magnitude at steady-state conditions.

| Species | \( n_{\text{rad}}(X)/n_{\text{tot}} \) | Remark |
|---------|---------------------------------|--------|
| \( \text{H}_2 \) | 0.5 (–) |        |
| \( \text{CO} \) | 1.8 (–) |        |
| \( \text{CO}_2 \) | \( \ldots \quad T < 100 \) K | \( a \) |
| \( \text{H}_2\text{O} \) | \( \ldots \quad T < 100 \) K | \( a \) |
| \( \text{O} \) | \( \ldots \quad T < 100 \) K | \( a \) |
| \( \text{H}_2\text{S} \) | \( \ldots \quad T < 100 \) K | \( a \) |
| \( \text{S} \) | 2 (–) | \( T > 100 \) K | \( b \) |
| \( \ldots \quad T > 100 \) K | \( a \) |
| \( \text{N}_2 \) | 3.5 (–) |        |
| \( \text{CH}_4 \) | 5 (–) |        |
| \( \text{C}_2\text{H}_4 \) | 4 (–) |        |
| \( \text{C}_2\text{H}_6 \) | 5 (–) |        |
| \( \text{H}_2\text{CO} \) | \( \ldots \quad T < 60 \) K | \( a \) |
| \( \ldots \quad T > 60 \) K | \( d \) |
| \( \text{CH}_3\text{OH} \) | \( \ldots \quad T < 60 \) K | \( a \) |
| \( \ldots \quad T > 60 \) K | \( a \) |
| \( \text{He} \) | 8.5 (–) |        |
| \( \text{He}^* \) | 2 (–) |        |
| \( \text{H} \) | 5 (–) |        |
| \( \text{H}^* \) | 3 (–) |        |
| \( \text{H}_2^* \) | 2 (–) |        |
| \( \text{HCO}^+ \) | 3 (–) |        |
| \( \text{H}_2\text{O}^+ \) | 5 (–) |        |
| \( \text{Grain}^{-} \) | 1.9 (–) |        |
| \( \text{e}^{-} \) | 7.5 (–) |        |

**Notes.** \( a(b) \) means \( a \times 10^b \).  

\( a \) Assumed to be frozen-out onto dust grains at cold temperatures or to be not abundant in hot regions.  
\( b \) See Section 3.2.  
\( c \) Aikawa et al. (2008).  
\( d \) Evaporation temperature from Doty et al. (2004).  
\( e \) Stübler et al. (2004, 2005).  
\( f \) Negatively charged grains (Maloney et al. 1996).
van der Tak et al. (1999). Thus, we switch this reaction off below the recommended temperature range of 1750 K–2575 K. Furthermore, reactions with a rate more than an order of magnitude faster at 10 K than at 100 K are kept constant below their minimum temperature, \( k(T < T_{\text{min}}) = k(T_{\text{min}}) \).

**APPENDIX C**

**INITIAL CONDITIONS**

The total elemental abundances in Table 5 are used for the calculation of the photoionization cross section, where heavy elements locked into dust grains are also taken into account. The values are taken from Yan (1997), except for helium, where the values assumed by Stäuber et al. (2005) have been adopted. The values are taken from Yan (1997), except for helium, where elements locked into dust grains are also taken into account.

**calculation of the photoionization cross section, where heavy**

**APPENDIX D**

**SPECIES WITH LARGE DISAGREEMENT**

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