The KOSMA-\(\tau\) PDR Model

I. Recent updates to the numerical model of photo-dissociated regions

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ABSTRACT

Numerical models of Photodissociation Regions (PDRs) are a valuable tool to model their chemical and thermodynamic structure and to simulate their line and continuum emission. Few mature PDR models are available and the Cologne KOSMA-\(\tau\) PDR model is the only sophisticated model that uses a spherical cloud geometry thereby allowing us to simulate clumpy PDRs. We present the current status of the code as reference for modelers and for observers that plan to apply KOSMA-\(\tau\) to interpret their data. For the numerical solution of the chemical problem we present a superior Newton-Raphson stepping algorithm and discuss strategies to numerically stabilize the problem and speed up the iterations. The chemistry in KOSMA-\(\tau\) is upgraded to include the full surface chemistry in an up-to-date formulation and we discuss a novel computation of branching ratios in chemical desorption reactions. The high dust temperature in PDRs leads to a selective freeze-out of oxygen-bearing ice species due to their higher condensation temperatures and we study changes in the ice mantle structures depending on the PDR parameters, in particular the impinging UV field. Selective freeze-out can produce enhanced C abundances and higher gas temperatures resulting in a fine-structure line emission of atomic carbon \(\text{C}^+\) enhanced by up to 50\% if surface reactions are considered. We show how recent ALMA observations of HCO\(^+\) emission in the Orion Bar with high spatial resolution on the scale of individual clumps can be interpreted in the context of non-stationary, clumpy PDR ensembles. Additionally, we introduce WL-\(\tau\)-PDR, a simple plane-parallel PDR model written in Mathematica to act as numerical testing environment of PDR modeling aspects.

Key words. (ISM:) photon-dominated region (PDR) — Astrochemistry — ISM: molecules — ISM: kinematics and dynamics — ISM: abundances — Methods: numerical

1. Introduction

Numerical models of Photodissociation Regions (PDRs) are an essential tool to quantitatively understand observations of massive star forming regions through simulations. Few mature PDR models are available and the Cologne KOSMA-\(\tau\) PDR model is the only sophisticated model that uses a spherical cloud geometry thereby allowing us to simulate clumpy PDRs. We present the current status of the code as reference for modelers and for observers that plan to apply KOSMA-\(\tau\) to interpret their data. For the numerical solution of the chemical problem we present a superior Newton-Raphson stepping algorithm and discuss strategies to numerically stabilize the problem and speed up the iterations. The chemistry in KOSMA-\(\tau\) is upgraded to include the full surface chemistry in an up-to-date formulation and we discuss a novel computation of branching ratios in chemical desorption reactions. The high dust temperature in PDRs leads to a selective freeze-out of oxygen-bearing ice species due to their higher condensation temperatures and we study changes in the ice mantle structures depending on the PDR parameters, in particular the impinging UV field. Selective freeze-out can produce enhanced C abundances and higher gas temperatures resulting in a fine-structure line emission of atomic carbon \(\text{C}^+\) enhanced by up to 50\% if surface reactions are considered. We show how recent ALMA observations of HCO\(^+\) emission in the Orion Bar with high spatial resolution on the scale of individual clumps can be interpreted in the context of non-stationary, clumpy PDR ensembles. Additionally, we introduce WL-\(\tau\)-PDR, a simple plane-parallel PDR model written in Mathematica to act as numerical testing environment of PDR modeling aspects.

Astrochemical models of the ISM chemistry date back to the early 1950s (Bates & Spitzer 1951) and have been used to explain the abundance of early observed molecules. They have been constantly extended since then and most modern astrochemical ISM models also simulate chemical kinetic processes on dust-grain surfaces with various degrees of complexity (Tielens & Hagen 1982; Hasegawa & Herbst 1993; Garrod 2013). The first species that has been recognized as almost exclusively formed in space on grain surfaces is molecular hydrogen \(\text{H}_2\). This is particularly relevant, since “all neutral atomic hydrogen gas and a large fraction of the molecular gas in the Milky Way Galaxy and external galaxies lie in PDRs” (Hollenbach & Tielens 1997).

The transition from the atomic to the molecular phase in the interstellar medium (ISM) is controlled by the balance between photo-dissociation by far-ultra-violet radiation (FUV) and the recombination of atomic hydrogen on grain surfaces. Due to its nature as a line absorption process (Federman et al. 1979), photo-dissociation of \(\text{H}_2\) is subject to efficient shielding that leads to a sharp transition from H to \(\text{H}_2\). This is particularly true for dense gas \((n > 10^5 \text{ cm}^{-3})\). This transitions has also been studied analytically and compared with corresponding numerical results (Sternberg 1988, Krumholz et al. 2008, 2009, McKee & Krumholz 2010, Sternberg et al. 2014, Bialy & Sternberg 2016, Bialy et al. 2017, Sternberg et al. 2021).

Numerical models of the physical and chemical conditions of the ISM compute the balance between formation and destruction of the considered chemical species. The respective reaction rates depend on the local temperature which is the result of balancing local heating and cooling processes. Cooling is predominantly done by spectral line emission of energetically excited states of atomic and molecular species. In PDRs the heating is dominated by photo-electric heating, vibrational de-excitation of electronically excited \(\text{H}_2\) and cosmic ray heating. Both, heating and cooling, depend on the chemical abundances of the relevant species, which numerically asks for an iterative solution.

The first PDR models were presented almost 50 years ago to explain fine-structure emission observed with sub-millimeter instruments (Melnick et al. 1979; Russell et al. 1980, 1981, Stacey et al. 1983, Crawford et al. 1985). The earliest models (Glassgold & Langer 1974, 1975, 1976, Langer 1976, Black & Dalgarno 1977, Clavel et al. 1978, de Jong et al. 1980) have been applied to low gas density \(n < 10^3 \text{ cm}^{-3}\) illuminated by the ambient UV radiation. Higher gas density models...
with more intense radiation have been performed by Tielens & Hollenbach (1985b); Sternberg & Dalgarno (1989); Le Bourlot et al. (1993a); van Dishoeck & Black (1986); Black & van Dishoeck (1987); van Dishoeck & Black (1988); Sternberg & Dalgarno (1995); Draine & Bertoldi (1996). Some of these models have been further developed since then reaching a high level of sophistication. Here, we can only name a few prominent ones: The PDR Toolbox (Kaufman et al. 1999, 2006; Pound & Wolfire 2008; Hollenbach et al. 2009) provides an extensive set of computed model grids and user friendly tools to apply the model results to data. The Meudon PDR code (Le Petit et al. 2006; Goicoechea & Le Bourlot 2007; Le Bourlot et al. 2012; Bron et al. 2014) is a plane-parallel code with a particular focus on a detailed treatment of physical and chemical processes, in particular radiative transfer and shielding processes. It computes the line intensities of tens of atomic and molecular species. The chemistry includes hundreds of species with reactions in gas phase and on surfaces. The code is publicly available together with an extensive online database of model grids and analysis tools. The KOSMA-τ group collaborates with both teams to integrate the model results into their online databases and tools.

The CLOUDY code is a spectral synthesis code designed to simulate conditions in interstellar matter under a broad range of conditions (Ferland et al. 2013, 2017). With an initial focus on the ionized gas it has been extended to other regimes including PDRs (van Hoof et al. 2004; Shaw et al. 2005; Abel et al. 2006; Abel & Ferland 2006; Abel 2006). PDR model physics has also been included in a number of other numerical models, ProDiMo, a model of protoplanetary disks including gas phase, X-ray and UV-photo-chemistry, gas heating and cooling balance, disk structure and (dust and line) radiative transfer, is actively developed and extended (Woitke et al. 2009; Kamp et al. 2010; Kamp et al. 2016; Kamp et al. 2017; Thi et al. 2019; 2020). Other disk model are for instance DALI, a thermo-chemical models of protoplanetary disk atmospheres (Bruderer et al. 2009b; 2010; 2012; Bruderer 2013). A general model for the thermo-chemical structure of disks presented by Gorti & Hollenbach (2004; 2008) was recently updated to include the effects of gas-grain chemistry in protoplanetary disks using a three-phase approximation (Rau & Gorti 2019). Agúndez et al. (2018) developed a generic model of protoplanetary disk, with a focus to the photochemistry, and applied it to a T Tauri and a Herbig Ae/Be disk.

UCL_PDR is a publicly available, one-dimensional and time-dependent PDR model (Bell et al. 2005; 2006; Priestley et al. 2017) that has been extended into the first 3-dimensional PDR code 3DPDR (Bisbas et al. 2012; Gaches et al. 2019). The KOSMA-τ team used their clumpy PDR model as building blocks for KOSMA-τ-3D, to model arbitrary 3-dimensional geometries (Cubick et al. 2008; Andree-Labsch et al. 2017; Yanitski 2022).

Most numerical models assume stationary conditions and do not solve the time-dependence, however the importance of dynamical effects in the ISM lead to a number of new non-stationary models. A first approach was to couple (magnetohydro-dynamical (MHD)) models with PDR models to post-process their output (e.g. Levrier et al. 2012; Bisbas et al. 2015) and as sub-grid models (Li et al. 2018). With the recent growth of computing power MHD models started to numerically solve PDR physics and small chemical networks in parallel (Nelson & Langer 1997; Glover et al. 2010; Grassi et al. 2014; Walch et al. 2015; Seifried & Walch 2016; Girichidis et al. 2016; Valdivia et al. 2016; Seifried et al. 2017; Francke et al. 2018; Inoue et al. 2020; Bisbas et al. 2021). Some PDR codes solve the PDR physics and chemistry self-consistently with the dynamics but in

1 http://dustem.astro.umd.edu/
2 https://ism.obspm.fr/
3 https://gitlab.nublado.org/cloudy
4 https://www.astro.rug.nl/~prodimo/
5 https://uclchem.github.io/ucl_pdr/
6 https://uclchem.github.io/3dpdr/
a reduced dimensionality \cite{Kirsanova2009,Akimkin2015,Akimkin2017,Bron2018,Kirsanova2020}.

Because of the high model complexity, the large variety in model assumptions and numerical approximations it remains difficult to compare results of different PDR model codes. The PDR benchmark was a first attempt to cross-calibrate different PDR model codes against each other \cite{Rolfig2007}. The KOSMA-\tau model is one of the models that participated in the benchmark study. It is the only PDR model employing a spherical model geometry and has been applied to a large variety of studies in the recent 20 years.

PDR models are constantly improved and calibrated against observations of Galactic and Extragalactic PDRs. Major constraints were obtained in the last years by a growing number of observations of the main PDR cooling lines, in particular the fine-structure lines of \[\text{[C II]}\] and \[\text{[O I]}\]. Modern instruments such as (up)GREAT (German REceiver for Astronomy at Terahertz Frequencies \cite{Heyminck2012, Risacher2018} on board the Stratospheric Observatory for Infrared Astronomy (SOFIA, \cite{Young2012}) allow to observe Galactic PDRs with high spatial and very high spatial resolution showing complex line profiles due to source kinematics, optical thickness effects, and foreground absorption \cite[e.g.][]{Pabst2019, Kirsanova2019, Schneider2021, Kabanovic2022}.

Similar studies for the Large Magellanic Clouds (LMC) \cite{Okada2019a} together with the first detection of velocity resolved \[^{13}\text{CII}\] emission in the LMC \cite{Okada2019b} show the potential of these observations for Extragalactic studies \cite[e.g.][]{Rolfig2016, Cornier2019, Madden2020, Bigiel2020, Tarantino2021}. Future PDR models may also be applied to ALMA observations of protostars and hot cores and corinos which reveal a rich complex organic chemistry (COM) that current PDR models have yet to explain. Data from future instruments such as the James Webb Space Telescope (JWST, \cite{Gardner2006}) and FYST \cite{Parshley2018}, will challenge present PDR model predictions. The near- and mid-infrared (IR) instruments on board of JWST allow for very detailed studies of the hot gas and dust on PDR surfaces and the detailed knowledge of the \[\text{H}_2\] excitation and the PAH energetics \cite{Okada2013} will help to further calibrate these models \cite{Berne2022}. Consequently, an active development of sophisticated PDR models is essential to deal with the wealth of data from current and near-future observations. The KOSMA-\tau model will try to contribute with its particular strengths.

In this paper we report on recent major developments of the model and give an updated overview over the model properties. In particular, we present an upgrade of the model chemistry in KOSMA-\tau to account for the full grain-surface chemistry in a quasi three-phase model allowing us to study the interplay between ice formation on grains and PDR physics.

2. Models of PDRs - General properties

Figure 1 shows the general structure of a PDR. Attenuation of FUV photons produces a chemical stratification with the more stable chemical species more abundant closer to the surface of the PDR, while species that are easily dissociated can only survive if sufficiently shielded from the FUV field. The chemical stratification is accompanied by a strong temperature gradient from the surface to the shielded parts of the PDR because the main heating takes place via ejection of photo-electrons from dust grains and subsequent collisional energy transfer from the ejected hot electrons to the gas particles \cite{Bakes1989}.

A decreased FUV flux reduces the photo-electric heating (PEH) significantly and results in lower temperatures. FUV attenuation similarly affects heating by vibrational de-excitation of \[\text{H}_2\] which dominates over PEH at higher densities \cite{Rolfig2006}. In this paper we denote total FUV field strength with \(\chi\) in units of the Drain field \(\chi_D = 2.6 \times 10^{-3} \text{ erg s}^{-1} \text{ cm}^{-2}\) (integrated from 91.2 to 200 nm) \cite{Draine1978}.

Fig. 2 shows the numerical scheme any PDR model has to solve. It can be divided into four distinct problems (gray boxes). Three of them are local but the fourth one couples them non-locally, asking for a multi-layer iteration scheme. The local problems are: 

1a) the local chemical problem, i.e. solving the chemical balance equations at a given position in the PDR,

1b) the local excitation, i.e. solving the energy level population of all species relevant for cooling and for comparison with observations at a given position in the PDR,

1c) the local energy balance, i.e. computing the gas and dust temperature at a given position in the PDR.

Those problems are mutually coupled asking for an iterative local solution. As they have to be solved at every spatial point of the model, they are embedded in a spatial loop.

The fourth problem is 2), the solution of the radiative transfer (RT) equation. This step provides quantities such as the photo-dissociation rates of important species, the FUV intensity across the model cloud, and others. Step 2) non-locally couples all positions within a model PDR. Each individual point requires the solution of all other points. Hence a global iterative solution is needed. Problems 1a)-1c) are solved iteratively at every spatial location in the cloud. Using this set of solutions the radiative transfer problem 2) is solved over the whole cloud geometry.

As a consequence, the local physical conditions computed in the previous iteration will be updated due to revised absorption and emission of IR and UV photons, which results in modified local cooling and heating capabilities leading to a new temperature solution and therefore a new chemical solution. Global iteration of the scheme (1a)-1c) - 2) is then performed until a predefined convergence criterion is met. An exception to this scheme are semi-infinite plane-parallel models. In these models, radiation can only enter and escape from one side of the cloud. As a consequence, the UV transfer is computed as the code advances along the spatial grid without the need for separate loops.

Any other model geometry with the possibility of radiation entering and escaping from different directions requires repeated iterations on the spatial grid. The global as well as the local numerical iterations are stopped after predefined convergence criteria are met.

Typical input quantities of PDR models are:

- model geometry, e.g. maximum visual extinction \(A_{V,\max}\), total radius \(R_{\max}\), disk size, directed or isotropic illumination, inclination angle, etc.
- thermodynamic properties of the gas, e.g. isobaric or isochoric conditions with fixed or variable density profile
- macro-physical parameters, e.g. total gas density \(n\), pressure \(p\), illuminating FUV spectrum and intensity \(\chi\), cosmic ray (CR) and X-ray (XR) ionization rate \(\zeta_{\text{CR,XR}}\)
- heating and cooling processes to be used \cite[e.g.][]{Goldsmith2012}
- dust properties, e.g. composition, distribution, optical properties. Common choices are described by \cite{Mathis1977} and \cite{Weingartner2001}.

\cite{Habing1968} provided an alternative description which is taken as the reference with scaling factor \(G_0\) in some models. To convert between the two descriptions use \(\chi_0 = 1.7G_0\).
Fig. 2: General numerical scheme that needs to be solved in KOSMA-τ. Local iterations (red) are performed on every spatial grid point, spatial iterations (green) are performed over all spatial grid points in the model, and global iterations (blue) repeat the spatial loop if necessary until numerical convergence is reached.

- chemical composition and elemental abundances (e.g. Simón-Díaz & Stasinska 2011)
- set of chemical reaction rates. Common databases include KIDA\(^8\) (Wakelam et al. 2015), UdFA\(^9\) (Woodall et al. 2007) and OSU\(^10\) (Garrod et al. 2008).
- micro-physical parameters, e.g. H\(_2\) formation efficiency, grain surface binding energies, turbulent Doppler line width and velocity distribution, magnetic pressure
- atomic and molecular data, e.g. collision rates, level energies, transition frequencies, Einstein A values. Good starting points are the LAMDA Database\(^11\) and the Cologne Database for Molecular Spectroscopy CDMS\(^12\) (Endres et al. 2016; Schöier et al. 2005). H\(_2\) can be treated either with full rotational-vibrational level structure, simplified vibrational level structure only or using parameterized approximations (Röllig et al. 2006 and forthcoming paper).

Typical output quantities of PDR models are

- spatial structure of the model cloud per cloud position
  - physical conditions: gas and dust temperature, local FUV radiation field strength, local photo-dissociation and photo-ionization rates, heating and cooling rates, energy level population of species of interest
  - chemical conditions: gas phase abundances of all included chemical species, possibly grain surface abundances and ice mantle composition, local chemical formation and reaction rates
- integrated quantities of the model cloud
  - spectral line emission: IR and FIR line emission (either spatially resolved or averaged over an assumed telescope beam), possibly UV and FUV emission
- continuum emission: dust continuum emission (spectrally resolved or total), possibly UV continuum emission
- spectral line optical depths
- possibly time evolution of the model cloud

A comparison with experimental data is usually limited to integrated model quantities, such as intensities or emission line ratios. The limited spatial resolution of IR and FIR telescopes and the generally long distance to massive star forming regions allows only in very few cases to directly compare the modeled PDR structure to real observations. In terms of model calibration this is a substantial complication.

In the following we will present the KOSMA-τ code. Section 3 lays out the details of the code structure and the implemented physics. Section 4 discusses the details of the numerical solution of the chemical problem. Section 5 discusses the energy solution and the occurrence of multiple solutions. Section 6 presents the new model predictions of the surface chemistry and compares with predictions by other models and with observations. Section 7 finally demonstrates the practical value of the clumpy PDR modeling approach.

### 3. The KOSMA-τ Code

The KOSMA-τ PDR model is based on the plane-parallel PDR code by Sternberg\(^{13}\). The spherical KOSMA-τ model has been developed at the University of Cologne in collaboration with Tel Aviv University and the first results have been published by Gierens et al.\(^{14}\) and Störzer et al.\(^{15}\) 1996, 2000. Historically, the model geometry was driven by the finding that observations showed molecular clouds to be clumpy, porous or fractal (e.g. Stutzki et al.\(^{16}\) 1988). The fractal properties of many clouds can be described by a fractional Brownian motion structure and such a structure can be reproduced by an ensemble of clumps with a well defined power-law mass spectrum and mass-size relation (Stutzki et al.\(^{17}\) 1998 Zielinsky et al. 2000).

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\(^{8}\) http://kida.astrophy.u-bordeaux.fr/

\(^{9}\) http://udfa.ajmarkwick.net/

\(^{10}\) http://faculty.virginia.edu/ericherb/research.html

\(^{11}\) https://home.strw.leidenuniv.nl/~moldata/

\(^{12}\) https://cdms.astro.uni-koeln.de/

\(^{13}\) Sternberg (1988).

\(^{14}\) Gierens et al. (1992) and Störzer et al. (1996, 2000).

\(^{15}\) Gierens et al. (1992) and Störzer et al. (1996, 2000).

\(^{16}\) Stutzki et al. (1988).

\(^{17}\) Stutzki et al. (1998) Zielinsky et al. 2000.
Theory and numerical simulations of the ISM also show that turbulent flows naturally lead to a highly fragmented structure (e.g., Gammie et al. 2003; Gong & Ostriker 2011) and Gong & Ostriker (2015) showed that dense cores form from supersonic turbulent converging flows and Guszejnov et al. (2018) argue that the observed power-law scaling is the generic result of scale-free structure formation where the different scales are uncorrelated. For a review on clump formation see Ballesteros-Paredes et al. (2020). Consequently it is necessary to include the effect of clumpiness and fragmented structures in any PDR modeling as far as possible.

The fundamental difference between the spherical model geometry and plane-parallel models is the higher ratio of surface to mass (or volume). The infinite extent of plane-parallel models parallel to the surface is not real but a necessity of the 1-D setup. Two-sided plane-parallel models slightly improve on that aspect but have to introduce an additional model parameter, the cut-off $A_V$. The simplest possible model with a finite configuration is the spherical clump, but as for the two-sided models, it comes at the cost of an additional model parameter, the clump mass. The spherical model is also a strong simplification since molecular clouds are never spherical but it allows for a better description of the clumpy structure of the ISM with a large fraction of internal surfaces. By matching the parameters to the observed clump-mass spectra we can approximate the fractal structure in PDRs, something that is impossible with plane-parallel configurations.

The model geometry naturally explains some observations that are hard to explain otherwise. Bolatto et al. (2006) and Röllig et al. (2006) showed that the observed metallicity influence on the emission ratio of $[C\,\text{II}]$/CO and $[C\,\text{II}]$/H$^\text{12}$CO can be explained by a spherical (i.e. finite mass) cloud model. Izumi et al. (2021) observed unusually high ratios of $[C\,\text{II}]$ to $P_1 \rightarrow 2P_0$ to $^{12}$CO(1-0) emission at high extinction that can not be explained by standard plane-parallel PDR models and suggests highly clumpy gas. Schneider et al. (2021) performed a detailed PDR multi-line model analysis of a globule in Cygnus X and showed that the observed line emission can only be explained with a two-component PDR: a clumpy internal and a non-clumpy external PDR. Other studies that used KOSMA-$\tau$ model predictions to successfully analyze and interpret PDR observations include Mookerjea et al. (2006), Schulz et al. (2007), Kramer et al. (2008), Pineda et al. (2008), Cubick et al. (2008), Sun et al. (2008), Röllig et al. (2011, 2012), Schneider et al. (2016), Röllig et al. (2016), Schneider et al. (2018), Garcia et al. (2021), Nayak et al. (2021), Mookerjea et al. (2021). Andreae-Labsch et al. (2017) investigated the spatial variations of PDR emission lines across the Orion Bar and showed that the observed spatial profiles can be explained by dense PDR clumps embedded in a thinner inter-clump medium.

The spherical geometry requires more computational power due to the need of angular averaging and the additional mass parameter. The clump ensemble approach requires the computation of large parameter grids with the consequence of a high computational effort. To compensate for this, physical complexity was reduced in certain calculations, for instance the full ro-vib structure of H$_2$ was approximated by 15 virtual vibrational levels only. As computing power becomes more readily available, we are gradually increasing the model complexity again.

The general model iteration is preceded by the model setup and the pre-computation of the FUV continuum radiative transfer. Using the multi-component dust radiative transfer code MCDRT (Szczerba et al. 1997) we compute the spectrally resolved FUV radiation field in the model clump together with the dust temperature (fully resolved for all dust components and dust sizes) (Röllig et al. 2013). In a post-processing step following the global model convergence, we then compute the detailed line & continuum emission, spatially resolved as well as model clump averaged (Gierens et al. 1992).

3.1. Geometry

KOSMA-$\tau$ is a 1-dimensional model with spherical geometry using the cloud depth $z = R_{\text{tot}} - r$ as spatial coordinate, with the total radius $R_{\text{tot}}$ and the radius $r$ from 0 to $R_{\text{tot}}$. We usually represent the spatial coordinate by the optical extinction $A_V$, along this coordinate. The total gas density $n$ is described by

$$\n = n_0 \left( \frac{r}{R_{\text{tot}}} \right)^{-\alpha} R_{\text{core}} \leq r \leq R_{\text{tot}} \leq 1$$

\[ n_{\text{ext}} = \left( \frac{R_{\text{core}}}{R_{\text{tot}}} \right)^{\alpha} \text{const.} \]

where $n_0$ is the total gas density at the surface ($r = R_{\text{tot}}$) in cm$^{-3}$. The standard parameters are: $\alpha = 1.5$, $R_{\text{core}} = 0.2$, approximating the structure of Bonnor-Ebert spheres with a density contrast from edge to center of 11.2. Therefore the assumption of an isotropic FUV illumination is approximately true for the average ambient FUV field in the Galaxy and for nearby FUV sources if the PDR is embedded in a diffuse medium because of the strong scattering of the interstellar dust in the FUV range. With albedos between 0.3 and 0.4 (Weingartner & Draine 2001b) and the FUV extinction being about three times stronger than at visible wavelengths, a dust column providing an $A_V \leq 1$ is sufficient to convert a directed FUV field into an isotropic field. Observations and corresponding models seem to support this assumption. Choi et al. (2015) showed that the FUV emission of the H II region around ζ Oph is dominated by dust grain scattering. Similar findings have been reported for the Spica nebula (Choi et al. 2013), the Orion–Eridanus Superbubble (Jo et al. 2011, 2012), and the Taurus-Perseus-Auriga Complex (Lim et al. 2013). A similar scattering effect has been proposed for diffuse H$^\text{II}$ emission outside of bright H II regions (Seon & Witt 2012). Therefore the assumption of an isotropic FUV illumination is a good approximation for low to intermediate mass (size) clumps. It becomes questionable for very large model clumps where the radiation would have to be redistributed over parsec scales. However, the very massive clumps are actually a good approximation to the common plane-parallel setup. In Röllig et al. (2007) we could show that for these cases our spherical model agrees well with predictions from plane-parallel PDR codes with a perpendicular FUV irradiation producing comparable PDR structures. This is due to the fact that the emission of very massive structures typically arises from a thin surface layer due to optical thickness effects. This layer itself is dominated by the FUV radiation falling perpendicular onto it. Radiation from other directions and the backside is quickly absorbed in the large columns of material. Even if the approximation of the...
isotropic illumination breaks down in those cases it has no measurable effect because only the perpendicular contribution affects the large-clump model.

To assure a sufficient numerical resolution of the dissociation front and the transition from atomic carbon to CO we do not assume a fixed spatial model grid. Instead we rely on an adaptive spatial gridding using the Bulirsch-Stoer method [Press et al. 2007, Sect. 16.4] to determine the next step width during each spatial iteration.

### 3.1.1. Radiative transfer

Solving the radiative transfer (RT) problem is one of the key aspects in any PDR model. The local FUV photon density determines the heating efficiency as well as the strength of the local photo-chemistry. The problem is complicated by the fact that some of these processes are affected primarily by the FUV continuum dust shielding, while others depend on the combination of dust and spectral line shielding (e.g. [Weingartner & Draine 2001c, Heays et al. 2017]). Solving the RT fully self-consistently is very time-consuming and many PDR codes compromise on certain aspects of the RT to reduce the computational efforts. The RT in KOSMA-τ is currently divided into 3 parts.

1. The dust RT is done in a pre-processing step using the MCRT-code (details described in Röllig et al. 2013). MCRT computes the continuum RT within the spherical clump for a given dust composition based on the respective optical properties of the dust components and an assumed dust size distribution. The result of this computation is the internal FUV field, the emitted continuum spectrum, and the dust temperature distribution in the clump. These are used as input quantities for the KOSMA-τ calculation. MCRT doesn’t know the gas structure of the clump yet and can not account for FUV absorption by H₂ or CO.

2. During the KOSMA-τ iterations the line RT to compute the local photo-processes (dissociation and ionization) are computed during each iteration via a ray tracing scheme that is described below. The line cooling is computed per cooling line based on the local energy level excitation using a spherical escape probability formalism.

3. The final clump line emission is computed in a post-processing step based on the final chemical and physical structure of the clump using the spherical RT code ONION fully accounting for non-LTE (local thermal equilibrium) effects (Gierens et al. 1992). These computations are performed per line ignoring any line overlap or line-pumping between different molecules. The error due to the inconsistent treatment of line cooling and final line emission is small and can be ignored (example [C ii] 158μm: median ΔT_{ex}/T_{ex} = 3.1% over full parameter grid).

MCRT uses the Mie theory ([Bohren & Huffman 1983]) to compute the extinction efficiency Q_{ext} and albedo ω for each dust component, assuming the scattering properties of spherical grains. For silicates and graphite we use the dielectric constants from [Draine 2003], while for very small grains we followed the approach given by [Li & Draine 2001a]. Scattering by dust particles is currently assumed to be isotropic. More details are given in Röllig et al. 2013.

Computing the continuum radiative transfer only once in a pre-processing step is a reasonable approximating due to the weak thermodynamic coupling between gas and dust. The same approach is not possible for the FUV-line radiative transfer because the chemical structure changes during the iterations. Therefore, KOSMA-τ calculates the line radiative transfer for all relevant line transitions. This includes all absorption processes where spectral line absorption is important, i.e. the photo-dissociation of H₂ ([van Dishoeck 1987], Sternberg & Dalgarno 1989), atomic carbon C, and all isotopologues of CO (van Dishoeck & Black 1988, Visser et al. 2009). Line shielding might be important for other species as well, e.g. for N₂ (Heays et al. 2017), but is not yet implemented into KOSMA-τ.

For all photo-processes, the relevant physical quantity is the local photon flux above critical energy available for the respective process. The flux is determined by the initial unattenuated FUV field and the column of absorbing material which the photons penetrated. Given the spherical geometry and the isotropic radiation field the column density of absorbing material is a function of local position and direction of the incoming photons. The final local flux is the result of the angular average over the full solid angle. To compute the attenuation along all directions we use the method described in [Gierens et al. 1992].

Sternberg et al. 2014 showed that the absorption of UV photons in Werner and Lyman H₂ lines can dominate the continuum absorption under certain circumstances. Treating these cases fully self-consistently requires a re-computation of the dust continuum radiative transfer and all dust properties after each iteration. During each iteration we compute the pumping of H₂ lines and its dissociation as well as the dissociation of carbon monoxide. We use the local dust column densities as function of angle and the effective UV continuum absorption cross section σ_D (Sternberg & Dalgarno 1989) to compute the continuum absorption in all directions and integrate over all angles (see Sect. 3.1.2). σ_D depends on the current dust size distribution and is computed by MCRT.

KOSMA-τ computes the self-shielding of all CO isotopologues using the shielding function provided by Visser et al. 2009 (accounting for self-shielding, mutual shielding (line-overlap) and shielding by atomic and molecular hydrogen. The shielding factors f_{ab}(N(X)) are parameterized as function of H₂ and CO column densities. The CO shielding varies with the assumed Doppler line width and Visser et al. 2009 report a 26% increase of the CO photodissociation rate for an increase in the Doppler broadening b_{CO} from 0.3 to 3 km s⁻¹. We use CO shielding functions computed for b_{CO} = 3 km s⁻¹, T_{ex}(CO) = 20 K, and a 12C/13C ratio of 69 and neglect variations with b_{CO}. The H₂ self-shielding for the radiative pumping by FUV photons is computed line by line based on the shielding prescription by Federman et al. 1979 (accounting for the Voigt profile absorption lines, [Draine & Bertoldi 1996] provided H₂ shielding functions that account for line overlap but do not allow for a line-by-line treatment. KOSMA-τ offers the option to use their shielding prescription for the computation of the H₂ photodissociation rate instead.

In this study we do not resolve the rotational energy levels of H₂ but only consider transitions between vibrational levels in the ground state X^1Σ⁺_g (15 levels) and the electronically excited Lyman B Σ_u^+ (24 levels) and Werner C^1Π_u (10 levels) bands. The vib-level population in the ground state is computed from the balance between collisions, spontaneous decay and UV pumping ([Allison & Dalgarno 1969], Dalgarno & Stephens 1970, Stephens & Dalgarno 1972, 1973, Abgrall et al. 1992). The photodissociation rate is computed from decay of Lyman and Werner states, excited by UV pumping, to an unbound state (Sternberg 1988).

Continuum processes that depend on the local FUV intensity, such as the photoelectric heating, are computed based on the intensity results of MCRT and neglect the effect of line ab-
from \( t_{\min} = -N + q - 1 \) to \( t_{\max} = N - q + 1 \). Using the transfer equation we can recursively compute the intensities along a given ray \( q \)

\[
I_{q,t} = \begin{cases} 
  I_{q,t-1}e^{-\kappa_{t-1}l} + S_1 [1 - e^{-\kappa_{t-1}l}], & t = t_{\min} \\
  S_{\text{bg}} & t_{\min} < t \leq t_{\max}
\end{cases}
\]

with \( t = -N + q - 1, \ldots, N - q + 1 \) and \( s, s' \) the corresponding shell indices. \( S_{\text{bg}} \) is the background intensity. Accordingly, the intensity at left surface points in Fig. 3 is \( I_{q,t} = S_{\text{bg}} = B_0(T_{\text{bg}}) \) with Planck’s radiation law \( B_0 \) at the background temperature \( T_{\text{bg}} = 2.73 \text{ K} \), while for the rest of the points we have a step-wise integration of the radiative transfer equation. The detailed energy level population of a species is obtained from the corresponding set of non-LTE rate equations which are solved with a generalized Newton-Raphson technique. We derive the line source function \( S_j \) from the corresponding excitation temperatures. \( S = S_j + S_c \), where \( S_c \) is the continuum contribution from the local dust temperature also contributing to the pumping of the quantum levels. Similarly, we compute the total opacity from their line and continuum contributions \( \kappa = \kappa_c + \kappa \). Contributions from external dust continuum are not considered. We use 16 frequency points to resolve the (Gaussian) line profile and apply a Gauss-Hermite quadrature for the frequency integral. Collision rates, A-values and line frequencies are taken from the Leiden Atomic and Molecular Database (Schöier et al. 2005; van der Tak et al. 2020).

The final result is the emergent intensity for each ray and the intensity inside the cloud for all shell-ray intersections. For any given cloud depth, i.e. shell, this allows us to compute the angular average over intensities coming from all directions:

\[
J_s = \frac{1}{2} \int_0^\pi I(r_s, \theta) \sin(\theta) d\theta \text{ or } \int_0^\pi J_s \sin(\theta_s) d\theta
\]

where \( I(r_s, \theta) \) are the intensities across the shell \( s \) (e.g. at all blue points in Fig. 3) and \( \theta_{s,t} \) are the angles at the points \( s, t \), \( \theta_{s,t} = \arccos(r_{s,t}/|r_s|) \).

A similar ray-tracing scheme is also used to compute the \( H_2 \) and CO self-shielding of the UV absorption lines and the corresponding \( H_2 \) pumping along each ray (Störzer et al. 1996). In our model geometry column densities are functions of the angle \( \theta_{s,t} \). We compute \( N(X_{s,t}) \), the column density of species \( X \) at point \( s, t \), using a simple trapezoidal rule. Equivalent to Eq. 2 we compute the attenuation of all photo-reactions in the chemistry by using the angle-dependent columns in the attenuation factor \( \exp(-\gamma A_V) \) from Eq. 2.2 where we expressed column density by \( A_V \) in order to compute the reaction-specific local photo-rate. To compute the clump averaged emission we compute:

\[
I_{\text{clump}} = \frac{2}{R_{\text{clump}}} \int_{R_{\text{clump}}} I(p) r dp
\]

For more details on the radiative transfer scheme see Gierens et al. (1992). Note, that Eq. 2 and 3 have to be computed for all relevant radiative transitions. For species with many transitions this introduces a significant numerical complexity. In particular the solution to the full rotational-vibrational structure of the \( H_2 \) molecule, including the UV transitions, involves almost 30000 radiative transitions: Thus, the described scheme has to be solved for 30000 transitions along several hundred rays at each spatial step. In the past this was a prohibitive effort, but
we recently extended the code to include the full H\(_2\) problem. This will be described in detail in a subsequent paper (Röllig & Ossenkopf-Okada 2022).

### 3.2. Gas Phase Chemistry

The chemistry in KOSMA-\(\tau\) is modular. Chemical species can easily by added or removed from the chemistry and the code selects all participating reactions from the chemical database in use. The standard database is based on the 2012 edition of the UMIST Database for Astrochemistry (UDfA12) (McElroy et al. 2013)\(^\text{14}\), including a number of modification and updates:

- isotopologues including \(^{13}\)C and \(^{18}\)O have been added (Röllig & Ossenkopf 2013)
- new branching ratios from Chabot et al. (2013) are used
- addition of l-type isomers (UDfA only contains c-type)
- updated fractionation reaction rates (Mladenovic & Roueff 2014)
- refitted low-temperature rates (Röllig 2011)

From the list of reactions KOSMA-\(\tau\) constructs a set of ordinary differential equations (ODE):

\[
\mathcal{F}_i = \frac{dn(i)}{dt} = \sum_{j,k} k_{ij} n(j) n(k) + \sum_j k_{ini} n(m) + \sum_k k_{nim} \tag{7}
\]

The two first terms sum over all two-body processes forming species \(i\) and all photo-processes and/or cosmic-ray processes leading to the formation of species \(i\), respectively. The final two terms are the equivalent sums over all processes leading to the destruction of species \(j\) by two-body reactions (index \(n\)) and photo-processes (index \(m\)). The pre-factor \(k\) is called the rate coefficient and tabulated in parameterized form in chemical databases. We use lower-case \(k\) and upper-case \(K\) to distinguish gas-phase and surface reaction rate coefficients, respectively. We list the implemented gas-phase reaction types in the Appendix D.

The set of \(N\) rate equations (Eq. 7), one for each of the \(N\) chemical species is complemented by a set of conservation equations per chemical element \(M\):

\[
n(M) = \sum_i n(i) c_i^M \tag{8}
\]

where \(c_i^M\) is the number of atoms of element \(M\) in species \(i\). Analogously we also find a charge conservation equation:

\[
n(e^-) = \sum_i n(i) c_i^e \tag{9}
\]

where \(c_i^e\) is the charge of species \(i\) in units of the elemental charge where \(c_i^e\) can be negative in contrast to \(c_i^M\). Charge exchange between grains and gas is currently not considered.

### 3.3. Surface chemistry

A large number of observations of star formation regions show that observed gas-phase abundances of species other than H\(_3\) such as NH\(_2\), N\(_3^+\) and CH\(_3\)OH can not be explained with pure gas phase chemistry (e.g. Geppert et al. 2005) Garrod & Herbst 2006, Herbst & van Dishoeck 2009, Bottinelli et al. 2010, Oberg et al. 2011, Boogert et al. 2015). The freeze-out of gas-phase species in the dark region of molecular clouds also removes important tracer species from the observable content of the ISM and modifies the IR/FIR line emission of the clouds.

Historically, the only grain surface chemistry included in PDR models was the formation of H\(_2\) followed by direct desorption to the gas-phase. Based on measurements in the diffuse medium a mean H\(_2\) formation rate of \(3 \times 10^{-17}\) \(\text{cm}^2\text{s}^{-1}\) was found (Jura, 1974). This formation rate or comparable temperature dependent parametrizations (e.g. Tievens & Hollenbach 1985b, Sternberg & Dalgarno 1995) was implemented in astrochemical models as gas phase reaction simulating the surface process. Later, other prescriptions have been suggested to simulate the formation of H\(_2\) more precisely, including considering Langmuir-Hinshelwood and Eley-Rideal processes (e.g. Le Bourlot et al. 2012), physisorption and chemisorption of H\(_2\) (Cazaux & Tievens 2002, 2004), as well as stochastic treatment of dust temperatures and grain populations (e.g. Barzel & Bihamb 2007, Bron et al. 2014). KOSMA-\(\tau\) implements the H\(_2\) formation formalism described by Cazaux & Tievens (2002, 2004). Details are described in Röllig et al. (2013).

It is yet unclear whether surface chemistry takes place on very small particles such as polycyclic aromatic hydrocarbons (PAHs) (Böschman et al. 2015, Andrews et al. 2016, Foley et al. 2018). To estimate the chemically active grain surface we use the H\(_2\) formation rate observed in the diffuse medium. Cazaux et al. (2016) derive the grain surface per H-atom that is available to H\(_2\) formation as \(4 \times 10^{-21}\) \(\text{cm}^2\text{H-atom}\). We use this value to compute the minimum grain radius for surface chemistry, integrating over the dust size distributions from Weingartner & Draine (2001b) that apply to diffuse gas conditions. Assuming that the limiting factor is the thermal stability of the dust grains, carbonaceous dust can be approximately 20% larger than corresponding silicate grains (Li & Draine 2001b). From these two conditions we find minimum radii of 24\(\AA\) and 29\(\AA\) for silicate and carbon dust by integrating over dust size distributions suitable for diffuse gas. This is comparable to a threshold of 20\(\AA\) given by Hollenbach et al. (2009). Using this as lower integration limit we find total surface areas \(A_{\text{sil}} = 2.6 \times 10^{-21}\) \(\text{cm}^2\text{H-atom}\) and \(A_{\text{carb}} = 1.4 \times 10^{-21}\) \(\text{cm}^2\text{H-atom}\) for silicate and carbonaceous grains, respectively.

Other surface reactions have been introduced to numerical PDR models with a primary focus on formation routes of chemical species observed in PDRs, such as H\(_2\)O and H\(_2\)CO (for example Hollehanbc et al. 2009, Gazmán et al. 2011, Le Bourlot et al. 2012, Esplugues et al. 2016, Putaud et al. 2019). The updated chemistry in KOSMA-\(\tau\) now includes all relevant surface processes in a quasi-three-phase model (gas + surface + inert ice bulk). For the surface chemistry we follow the rate equation approach as described in Hasegawa et al. (1992), Hasegawa & Herbst (1993) including the competition between different processes as described by Chang et al. (2007) and Garrod & Pauly (2011). In our quasi-three-phase model we limit the mobility of surface species to the top surface layer following Cuppen et al. (2017) and desorption to the top two ice mantle monolayers (MLs) (see Eq. D.17). For surface reactions with an activation energy barrier we account for competing processes such as diffusion and desorption following Garrod & Pauly (2011). Including surface chemistry increases the number of chemical species in the network because gas-phase species and surface species must be considered as two different chemical species for all mathematical aspects involved. In the following, the symbol \(n_i\) de-

\(^{14}\) http://udfa.ajmarkwick.net/
extend the gas-phase chemistry Eq. 7 is extended and modified. We get notes chemical species on grain surfaces. The rate equations of

\[ \frac{dn}{dt} = \sum_{j,k} K_{j,i} n_j(i)n_k(k) + \sum_n K_{n,i}(i) - n_s(i) \left[ \sum_m K_{m,i}(m) + \sum_n K_n \right] + k_{acc,i} n(i) - K_{des,i} n_s(i) \]

where \( K_i \) and \( K_{j,k} \) denote the surface reaction rate coefficients for one-body and two-body reactions, respectively. We also have to extend the gas-phase chemistry Eq. 7 by the additional accretion and desorption terms:

\[ \frac{dn}{dt} = (-) - k_{acc,i} n(i) + K_{des,i} n_s(i) \]

where \((-)\) corresponds to the right hand side of Eq. 7. Here \( K_{des} \) describes all thermal and non-thermal desorption processes, i.e. a conversion of a surface species to a gas-phase species while \( k_{acc} \) is the rate coefficient for accretion (freeze-out) which converts gas-phase species into their surface equivalent.

We assume a surface density of binding sites on the grains \( n_{site} = 1.5 \times 10^{15} \text{cm}^{-2} \) (Tielens & Allamandola 1987). For tunneling through activation energy barriers we assume an energy barrier width of \( a = 2A \) (Garrod & Pauly 2011). For the desorption (or binding) energies \( E_d \), we use values provided by KIDA (Wakelam et al. 2017) with the modifications given in Table 1. Typically, \( E_d \) is given for species bound to a H₂O ice surface as the most abundant ice component. Desorption energies for other surfaces may differ significantly (Esplugues et al. 2016) and we include different desorption energies for species bound directly to a carbonaceous surface if they are known (see Table 2). For a more thorough discussion on desorption energy choice and the resulting model sensitivity we refer the reader to e.g. Penteado et al. (2017) and Kamp et al. (2017). We use the notation \( J(X) \) to distinguish surface species from their gas-phase counterpart X.

| species | \( E_d \) [K] |
|---------|---------------|
| C, ¹²C | 14000         |
| O, ¹⁶O | 1440          |
| N       | 400           |

Table 2: Modified desorption energies used in the surface chemistry.

References. [Esplugues et al. (2016)]

In Appendix D.2 we summarize all surface reactions that are currently implemented in KOSMA-\( \tau \). Here, we only report the new chemical desorption framework that we included in the surface chemistry.

H₂ ice A significant population of H₂ ice in the ISM has been proposed already almost 30 years ago based on early astrochemical models (Sandford & Allamandola 1993). However, no clear observational evidence could be detected to date. In the context of numerical models, freeze-out of gas-phase H₂ is potentially problematic because it can lead to a catastrophic freeze-out of all molecular gas onto dust grains. Several physical processes have been discussed to prevent nonphysical H₂ ice populations and we include encounter desorption for J(H) and J(H₂) as suggested by Hincelin et al. (2015). The underlying idea is based on the significantly lower desorption energy for hydrogen on an H₂ substrate compared to other substrates (e.g. Vedantam et al. 1999), Cuppen & Herbst (2007), Das et al. (2021). For J(H) or J(H₂) located next to a H₂ molecule we decrease \( E_d \) from its canonical value to \( E_d = 23 \text{ K} \) (Cuppen & Herbst 2007), greatly enhancing the possibility for a desorption of J(H) and J(H₂). As a consequence, the further accretion of H₂ ice is strongly suppressed after the build-up of the first ML.

Dust model The dust properties are computed by MCDRT assuming a dust composition and dust size distribution, for example as given by Mathis et al. (1977) or Weingartner & Draine (2001b). The dust radiative transfer and dust properties are computed per dust size bin together with corresponding mean values, e.g. for dust temperature, dust surface area and dust density. Details are described in Röllig et al. (2013). Presently, KOSMA-\( \tau \) uses a single surface weighted average grain temperature \( T_{d} \) for all types of grains independent of size and grain composition.\(^{15}\) For the KOSMA-\( \tau \) computations presented in this paper we assume the dust model #7 from Weingartner & Draine (2001b) consisting of 4 dust types: carbonaceous silicates, SIS, PAHs and ionized PAHs. In this model the average radii for silicates and carbon grains (including VSGs and PAHs) are \( \langle a \rangle_{sil} = 4.5 \mu \text{m} \) and \( \langle a \rangle_{carb} = 4.0 \mu \text{m} \), when \( \langle a \rangle \) indicates a surface weighted average. For the photo-electric heating and grain recombination cooling we use the prescription from Weingartner & Draine (2001a) corresponding to the assumed dust size distribution. This implicitly includes the computation of the grain charge distribution. We neglect any feedback of line UV absorption on the dust temperature.

Cosmic-ray induced desorption Cosmic rays (CR) hitting dust grains deposit an energy of \( E_{CR} \approx 0.4 \text{ MeV} \) into dust particles heating an average grain of 0.1 \( \mu \text{m} \) radius (Leger et al. 1985) to approximately \( T_{\text{CR max}} = 70 \text{ K} \) (Hasegawa & Herbst 1993), sufficiently hot to induce significant thermal desorption. Cooling of the grain takes place via radiative cooling \( E_{rad} \) and via evaporation cooling \( E_{sub} \) due to the sublimation of bound ice particles. The cooling time scale of a grain in s is given by

\[ \tau_{\text{cool}} = \frac{E_{CR}}{E_{\text{rad}} + E_{\text{sub}}} \]

\[ \tau_{\text{cool}} \]

\[ \tau_{\text{cool}} \]

\[ \tau_{\text{cool}} \]

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\[ \tau_{\text{cool}} \]

\[ \tau_{\text{cool}} \]

In a future update we will split the surface chemistry computation into dust size bins with individual values of \( T_{d} \) and surface area for each bin.
where the cooling rate due to sublimation is given by:

$$E_{\text{subl}} = \frac{f_{\text{des}}}{\langle n_{\text{dust}} \rangle} \sum_i E_b(i) n_i v(i) \exp \left( -\frac{E_b(i)}{T_{\text{CR,max}}} \right)$$  \hspace{1cm} (13)

where the sum includes all ice species, $\langle n_{\text{dust}} \rangle$ is the average number density of the dust particles, and $f_{\text{des}}$ gives the fraction of surface species that are candidates for desorption so that $f_{\text{des}} n_i(j)/(\langle n_{\text{dust}} \rangle)$ gives the number of desorbable molecules of species $i$ per dust grain. $v(i) \approx 3 \times 10^{-12}$ s$^{-1}$ is the desorption attempt frequency given by the surface vibrations (Hasegawa & Herbst 1993). Radiative cooling is computed by $E_{\text{rad}} = 4\pi q_{\text{abs}}(A\lambda) \sigma T_{\text{CR,max}}^4$ with the Stefan-Boltzmann constant $\sigma$ and $q_{\text{abs}} = 0.13$ K$^{-2}$cm$^{-1}$ for silicate grains. Cooling is always fast compared to the frequency of CR hits for any dust grain.

Assuming that most desorption occurs at about $T_{\text{CR,max}} = 70$ K we can approximate the CR-induced desorption rate coefficient as:

$$K_{\text{CR-des,i}} = f_{\text{CR}} K_{\text{exp}}(T_{\text{CR,max}})$$ \hspace{1cm} (14)

where $f_{\text{CR}} = \tau_{\text{cool}}/\tau_{\text{heat}}$ is the fraction of time spent by grains at the temperature $T_{\text{CR,max}}$, given by the cooling time relative to the frequency of CR hits. $K_{\text{exp}}(T_{\text{CR,max}})$ is the thermal desorption rate coefficient of species $i$ at $T_{\text{CR,max}}$. Assuming $\tau_{\text{heat}} = 3.16 \times 10^3$ s (Hasegawa & Herbst 1993) find $f_{\text{CR}} = 3.16 \times 10^{-19}$ assuming $\epsilon_{\text{CR}} = 5 \times 10^{-11}$ s$^{-1}$. To use this formalism we can distribute the total available dust surface in our model across virtual average grains of radius $(\mu g) = 0.1$ mm and find an average grain density of $\langle n_{\text{dust}} \rangle = 3.17 \times 10^{17}$ per H-atom. Using the same description of 0.1 mm grains (Spilis et al. 2021) published an updated estimate based on time-dependent computations of the heating and cooling due to CRs. Their heating depends on $\epsilon_{\text{CR}}$ and the local Av and can be approximated in the range $\epsilon_{\text{CR}} = [1.3 \times 10^{-17}, 10^{-16}]$ s, and Av = [0, 100] mag by:

$$\log_{10} \epsilon_{\text{heat}} = 0.19 \text{Av} - 1.6 - 10^{-4} \text{Av}^2 + 0.017 \text{Av} + 0.045 \text{Av}^2$$ \hspace{1cm} (15)

where $z = \log_{10} \epsilon_{\text{CR}}$. Energy deposition by CRs directly into the ice mantle (Wakelam et al. 2021) is not considered but will be implemented in a future code update.

Chemical desorption (Minissale et al. 2016) and Cazaux et al. (2016) presented an analytical expression for an additional desorption mechanism using the released binding energy from exothermic reactions in the ice phase to desorb species $i$ to the gas-phase first presented by Dulieu et al. (2015). They fitted a set of experimentally measured desorption rates through a probability that the reaction product has an energy higher than the desorption energy $E_{D_{ij}}$:

$$\mathcal{P}_{\text{CD}} = \exp \left( -\frac{E_{D_{ij}}}{\epsilon_i \Delta H_R / d_j} \right)$$ \hspace{1cm} (16)

where $\Delta H_R$ is the exothermicity of the formation of the product(s) and $d_j$ specifies the degrees of freedom that the energy is distributed among. A good fit was obtained when using an expression with a grain mass of $M = 120$ amu where the energy fraction obtained by the product is $\epsilon_i = (M - m_j)^2/(M + m_i)^2$. This approach, however, is not applicable if multiple reaction products are generated that can desorb. In this case the released energy $\Delta H_R$ must be distributed over all reaction products. A modification of Eq. (16) is needed which accounts for the energy distribution between multiple reaction products:

$$\mathcal{P}_{\text{CD,i}} = \exp \left( -\frac{E_{D_{ij}}}{\epsilon_i \Delta H_R / d_j} \right)$$ \hspace{1cm} (17)

where $\eta_i$ specifies the fraction of $\Delta H_R$ that is available to species $i$. Unfortunately, no laboratory data seem to be available for the desorption rate in case of more than one reaction product so that $\eta_i$ cannot be determined from a fit to the experimental data. (Wakelam et al. 2021) used an equal split between all atoms within the reaction products, assigning equal energy fractions to all atoms within the molecules. We propose a different approach based on the nature of the chemical reaction that produces the exothermicity. We assume that the fraction $\eta_i$ of the binding energy that is transferred to the individual products is proportional to the number of open shell electrons $e_i$ that contribute to the formation of each product (ignoring closed shells). Taking for example the reaction $J(O) + J(HCO) \rightarrow CO_2 + H$ this gives the following $e_i$: $e_{H} = 1$, $e_{C} = 2$, $e_{O} = 4$.

$$\eta_i = \frac{e_i}{\sum_j e_j}$$ \hspace{1cm} (18)

where the sum is over all atoms involved in the reaction. For each product this quantifies the probability for desorption $\mathcal{P}_{\text{CD,i}}$ and for remaining on the surface $(1 - \mathcal{P}_{\text{CD,i}})$. In the general case of two reaction products we can compute the branching ratios for all 4 possible reaction branches:

$$P_{r_{1}, +} + P_{r_{2}, -} \rightarrow \mathcal{P}_{\text{CD,1}} \times (1 - \mathcal{P}_{\text{CD,2}})$$
$$P_{r_{1}, +} + P_{r_{2}, -} \rightarrow \mathcal{P}_{\text{CD,2}} \times (1 - \mathcal{P}_{\text{CD,1}})$$
$$P_{r_{1}, +} \rightarrow \mathcal{P}_{\text{CD,1}} \times (1 - \mathcal{P}_{\text{CD,2}})$$
$$P_{r_{2}, +} \rightarrow \mathcal{P}_{\text{CD,2}} \times (1 - \mathcal{P}_{\text{CD,1}})$$ \hspace{1cm} (19)

where $r_{1,2}$ stands for two reactants and products respectively, and the subscript $s$ denotes species on the surface or in the ice mantle. Take for example the reaction $J(O) + J(HCO) \rightarrow CO_2 + H$: we find $\eta_H = 1/11$, $\eta_{CO} = 10/11$ and $\mathcal{P}_{\text{CD,H}} = 0.695$, $\mathcal{P}_{\text{CD,CO}} = 0.1188$. Following Eq. (19) gives the branching ratios (Values in parenthesis would result from the application of Eq. (16) to all products, this means a value of $\eta_i = 1$ for all products): $J(O) + J(HCO) \rightarrow CO_2 + H$ $BR = 0.08 (0.14)$ $J(O) + J(HCO) \rightarrow J(CO_2) + H$ $BR = 0.61 (0.82)$ $J(O) + J(HCO) \rightarrow J(CO_2) + J(H)$ $BR = 0.04 (0.01)$ $J(O) + J(HCO) \rightarrow J(CO_2) + H$ $BR = 0.27 (0.03)$

The final reaction rate coefficient for the chemical desorption of $i$ resulting from the reaction between species $j$ and $k$ is:

$$K_{\text{chem-des,i}} = K_{jk} \times \mathcal{P}_{\text{CD,i}}$$ \hspace{1cm} (20)

with $K_{jk}$ from Eq. (D.8). For the computation of the BR we always use the $E_{D_{ij}}$ for a H$_2$O substrate. Tests have shown that the chemistry is not very sensitive to variations in the assumed desorption energies. The list of all chemical desorption reactions and their branching ratios is given in Appendix D.2, Table D.4.

### 3.4. Thermal Balance

Thermal balance is the local balance between all cooling $\Lambda_k$ and heating $\Gamma_k$ processes:

$$E_{\text{tot}}(T) = \sum_h \Gamma_h(i_h) - \sum_k \Lambda_k(i_k) = 0$$ \hspace{1cm} (21)
where the efficiency of any individual process depends on the local conditions \( \xi \equiv (\vec{n}, \vec{N}(\vec{d}), T_{g,d}, 1_{\text{FUV}}, 1_{\text{CR}}, \ldots) \), such as the chemical vector \( \vec{n} = (n_1, \ldots, n_N) \), the column density vector \( \vec{N}(\vec{d}) \) which is a function of direction \( \vec{d} \), gas and dust temperature \( T_{g,d} \), FUV intensity \( I_{\text{FUV}} \) (in units of the Draine field \( \text{Draine}(1978) \)), the cosmic ray ionization rate \( 1_{\text{CR}} \), and possibly others. The superscript \( i \) is the global iteration counter, the subscript \( x \) enumerates the positions.

Eq. [27] is coupled to the problems of chemical balance, local excitation and radiative transfer (see Fig. [2]). The importance of various heating and cooling mechanisms as a function of position in the PDR has been widely discussed in the past (e.g. \cite{Tielens1985b, Hollenbach1991, Bakes1994, Sternberg1995, Röllig2006}). Below we introduce a few of these mechanisms.

### 3.5. Local convergence

Solving the local problem is equivalent to finding a local gas temperature such that the local chemistry and all the local thermodynamics are in equilibrium. To solve the chemistry as well as the heating and cooling we need to compute the local radiation field, the dust temperature and the local photon escape probability (see Local iteration loop in Fig. [2]). In plane-parallel PDR models this can usually be achieved by assuming exponential attenuation along the line of sight. In spherical PDRs this is complicated by the fact that we assume an isotropic FUV irradiation and that absorbing columns of gas and dust depend on the direction. To compute the local intensity in a spherical cloud we then need to average over all directions:

\[
I(\vartheta) = \frac{1}{4\pi} \int_{0}^{\pi} I_{\nu}(\vartheta) \exp(-\gamma_{\nu} A_{\nu}(z, \vartheta)) \, d\vartheta \tag{22}
\]

Along any given line-of-sight the attenuation of radiation at a given frequency can be described in terms of \( \exp(-\gamma_{\nu} A_{\nu}) \). \( \gamma_{\nu} \) relates the attenuation at a frequency \( \nu \) to the visual extinction. Using the relation \( A_{\nu} = 1.086\tau_{\nu} \), it is common practice to use the visual extinction \( A_{\nu} \) as 'optical' coordinate. A quantity such as the local optical depth \( \tau_{\nu} = \sigma_{\nu} N \) \( \text{Sternberg & Dalgarno}(1989) \), with frequency \( \nu \) dependent cross section \( \sigma_{\nu} \) and the related column density of the absorber \( N \), has to be considered for all directions \( \vartheta \):

\[
\tau_{\nu}(\vartheta) = \sigma_{\nu} N(\vartheta) \tag{23}
\]

The flow of the local iteration is summarized in Algorithm: Local iteration.

### Algorithm: Local iteration 1

**Initial values:**

\[
z \leftarrow z_{\text{old}}, \quad T_{g} \leftarrow T_{g,\text{old}}
\]

Compute \( T_{\nu}(z) \) - angular average of radiative quantities

\[
\text{Compute } I_{\text{FUV}}(z) \quad \text{reaction specific dust attenuation } \text{self shielding CO } \text{H}_2 \text{ UV shielding and pumping}
\]

Compute \( T_{\nu}(z) \)

while \( E_{\text{tot}} \neq 0 \) do

\[
T_{g} \leftarrow T_{g}
\]

solve level population: \( H_2, CO, O, C, \ldots \)

solve chemistry

compute local heating & cooling \( \Gamma(T), \Delta(T) \)

\[
E_{\text{tot}} \leftarrow \Gamma(T) - \Delta(T)
\]

choose root finding algorithm

\[
T \leftarrow \arg \min \{ E_{\text{tot}}(T) \}
\]

end while

\[
T_{g}(z) \leftarrow T
\]

### 3.6. Spatial loop

The physical and chemical conditions in a PDR are subject to non-linear effects such as the photo-dissociation of \( H_2 \) and \( CO \).
and their respective shielding. The photo-dissociation rates show a sudden drop once the absorption lines become optically thick. As a consequence, we find a steep density gradient of $H_2$ and CO in these transition regions covering many orders of magnitude in volume density. To avoid numerical problems it is important to use a sufficiently dense spatial grid across these transition regions and the method described below performs well across the full parameter range.

During each spatial iteration KOSMA-$\tau$ performs an adaptive spatial gridding using the Bulirsch-Stoer method [Press et al. 2007, Sect. 16.4] to determine the next step width such that the numerical solution of the set of $N$ coupled first-order differential equations for the functions $y_i; i = 1, 2, \ldots, N$, having the general form

$$\frac{dy_i(z)}{dz} = f(z, y_1, y_2, \ldots, y_N)$$

is sufficiently accurate. In the context of solving the PDR structure we identify $y_i(z) = N_i(z)$ as the perpendicular column density of species $i$ from the surface to depth $z$ in the cloud so that $dy_i(z)/dz = n_i(z)$. This extends to the column densities of energy level populations of species of interest, in particular CO, C$^+$, CO, and H$_2$. From a given position and column density vector, the Bulirsch-Stoer stepper routine returns the next step-width $\Delta h$ together with the respective values for $n_i(z + \Delta h)$ and $N_i(z + \Delta h)$ as well as an estimate of which step-width to attempt next. This successively propagates the solution into the cloud until the cloud center is reached.

### 3.6.1. Global convergence

KOSMA-$\tau$ uses the final column density vector, i.e. the column density of all species measured from the edge of the cloud to the cloud center, $N$ to test for convergence. Global convergence is met if

$$\frac{N_i^{\text{old}} - N_i^{\text{new}}}{N_i^{\text{new}}} < \epsilon_{\text{iter}} \forall i \text{ with } N_i^{\text{new}} > 10^{12} \text{ cm}^{-2}$$

The standard value applied is $\epsilon_{\text{iter}} = 0.01$. The minimum number of iterations is 2. We also specify a maximum number of iterations (default of 60) before stopping further iterations (Most models converge within less than 30 iterations). If more than 40 iterations are needed we incrementally relax the 0.01 criterion in steps of 0.01 to 0.1. We try another 10 iterations with $\epsilon_{\text{iter}} = 0.1$. If no convergence is found in 60 iterations the result of the last iteration is stored because for certain applications the results might still be sufficient. It is for example in some cases numerically difficult to find a stable solution for massive dense clouds. There, the low $J$ transitions of CO are the only cooling options for the gas in the central parts because of the low gas temperatures. The respective optical depths however are so high that Eq. (21) becomes strongly non-linear and small changes in $T_P$ lead to large differences in the CO population numbers that can produce oscillating solutions for the population column density vector. However, this happens for such high optical depths that the effect is not observable and has no impact on the total CO emission of the model cloud.

In general, we find that for a given number of chemical species the code converges faster for low densities, low masses (i.e. low optical depths) and not too high FUV fields. The total computation time for one cloud model, i.e. one specific set of model parameters range between few minutes and 10-20 hrs on an Intel Core i7 CPU.

### 3.6.2. Chemical time scales

To assess the limits of the model assumption of stationary chemistry we have to compare the involved chemical time scales with other relevant time scales, such as the dynamical time scale of the clump or its total lifetime. The model loses predictive power if those times are comparable or larger than the time the chemistry needs to reach steady-state. We derive chemical times from the total formation or destruction rate of a species divided by its total number density. Taking the inverse is the relevant formalism for the population column densities of $\text{cm}^{-2}$, i.e. the solution to the system

$$\frac{dN_i}{dt} = 0$$

using the Newton-Raphson method with the Jacobi matrix $Q$. This is a locally convergent method that is guaranteed to converge for a starting point sufficiently close to the root. The elements of $Q$ are:

$$Q_{ij} = \frac{dF_i}{dn(j)}$$

#### 4.1. Solving the chemical equations

KOSMA-$\tau$ computes an equilibrium solution to Eq. (7) and Eq. (11) i.e. the solution to the system

$$F_i = \frac{dn(i)}{dt} = 0$$

and

$$Q_{ij} = \frac{dF_i}{dn(j)}$$

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For the unknown densities \( n_i \) of \( N \) species built up from \( M \) elements we find an over-determined set of \( N + M + 1 \) equations. The default method in KOSMA-\( \tau \) is to replace \( M + 1 \) equations from the set of chemical rate equations (7 and 11) with the corresponding elemental and charge conservation equations (8 and 9). This can always be justified because the conservation equations should be strictly fulfilled while all rate equations are in any way only approximately known. Moreover, it improves the numerical stability of the iterative solution.

The Newton-Raphson method approaches the solution by using an (old) approximate solution (or initial guess) \( n^{\text{old}} \) to compute an (new) improved approximate solution \( n^{\text{new}} \) in the next step:

\[
\sum_j Q_{i,j}^{\text{old}} (n(j)^{\text{new}} - n(j)^{\text{old}}) = F_j^{\text{old}} \tag{28}
\]

This is a linearized system of the form \( Q \cdot \delta \vec{n} = \vec{F} \). To solve Eq. (28), we need to invert \( Q \) in order to determine the new density vector \( n^{\text{new}} \). In standard Newton-Raphson algorithms, the new solution-step is computed as \( n(i)^{\text{new}} = n(i)^{\text{old}} + \delta n_i \) and used as updated \( n(i)^{\text{old}} \) value in the subsequent iteration step. The steps can be expressed as relative changes: \( \eta = \delta n_i / n(i)^{\text{old}} \). KOSMA-\( \tau \) solves Eq. (28) by LU decomposition but has alternative solvers implemented.

4.2. Newtonian stepping strategies

The Newton-Raphson algorithm is guaranteed to provide fast convergence if one is close to solution, but depending on the starting values and the overall topology of the Newtonian vector field \( \delta \vec{n} \), i.e. the solution to the system \( Q \cdot \delta \vec{n} = \vec{F} \), the Newton-Raphson algorithm may also diverge or become trapped in a local minimum leading to infinite oscillations. Adaptive stepping strategies may prevent this.

We can express the step in the Newton-Raphson algorithm, \( n(i)^{\text{new}} = n(i)^{\text{old}} + \delta n_i \), as a relative change, so that \( n(i)^{\text{new}} = n(i)^{\text{old}} : f_{\text{step}} \) with

\[
f_{\text{step},\text{N}}(\eta) = (1 + \eta) \quad \text{with} \quad \eta = \frac{\delta n_i}{n(i)^{\text{old}}} \tag{29}
\]

For large steps, this approach can be problematic because it does not prohibit negative solutions, i.e. negative densities. In general, Newton stepping through the negative domain is not problematic as long as we can guarantee that the steps will finally provide positive densities. However, this is problematic because the algorithm may converge on a local minimum involving negative \( n_i \). One way to avoid this is to prevent the Newton steps from producing sign switches in \( \vec{n} \).

The \( \tanh() \) allows for a convenient construction of such a new stepping function whose symmetry and limits can be controlled with few numerical parameters:

\[
f_{\text{step},\text{Tanh}}(\eta) = \begin{cases} 
(1 + (\omega_+ - 1) \cdot \tanh(-\eta / \omega_+))^{-1} & \text{if } \eta < 0 \\
(1 + (\omega_- - 1) \cdot \tanh(1 / \omega_- \cdot \eta))^{-1} & \text{if } \eta \geq 0
\end{cases} \tag{30}
\]

\( \omega_+ > 1 \) and \( \omega_- > 1 \). For small \( \eta \) Eq. (30) approaches Eq. (29) and levels off for large arguments preventing too large steps. We implement an adaptive choice of \( \omega_+, \omega_- \), and \( \eta \), with details described in the Appendix C.1

5. Energy Solution

The numerical results presented in this section have been computed with WL-PDR, a simplified, plane-parallel PDR model written in Mathematica (Wolfram Research Inc. 2020). WL-PDR is designed to act as numerical testing environment of PDR modeling aspects. A brief explanation of the code is given in Appendix G.

5.1. Numerical Iteration Scheme

The key part in Fig. 2 is the local solution module. A local solution in this context is the local balance between all cooling \( \Lambda_k \) and heating \( \Gamma_k \) processes (Eq. 21), where the efficiency of any individual process depends on the local conditions \( \epsilon_i \). Eq. 21 is coupled to the problems of chemical balance, local excitation and radiative transfer (see Fig. 2). Figure 4 shows an idealized form of Eq. 21. At any given position in the PDR, every point on the curve \( E_{\text{sol}}(T) \) corresponds to a different chemical vector and a different temperature. At the solution \( E_{\text{sol}}(T_{\text{sol}}) = E_{\text{sol}} = 0 \) heating and cooling are balanced. If \( E_{\text{tot}} > 0 \) (gray rectangle left of \( T_{\text{sol}} \), i.e. heating dominate) we have heating excess \( \Gamma > \Lambda \). In the opposite case \( E_{\text{tot}} < 0 \) (gray rectangle right of \( T_{\text{sol}} \)) we have a cooling excess \( \Gamma < \Lambda \). Physics ensures that \( \lim_{T \to T_{\text{sol}}} E(T) > 0 \) because all cooling process become inefficient at very low temperatures and heating is less dependent on \( T \). Conversely, it is also ensured that \( E(T_{\text{high}}) = \lim_{T \to T_{\text{high}}} E(T) < 0 \). Here \( T_{\text{max}} \) corresponds to the upper temperature at which is considered reasonable in a PDR and which depends on the parameter range that the model needs to cover. Typical values are \( T_{\text{max}} \approx 10000 \) to 20000 K. Even though many coolants are inefficient at very high temperatures – CO and H\(_2\) for instance are chemically destroyed – other cooling processes become strong. Typical candidates are Lyman \( \alpha \), 6300 Å cooling (Bakes & Tielens 1994; Spitzer 1978) and gas-grain collisional cooling. These processes ensure that \( E(T_{\text{high}}) < 0 \). If \( E_{\text{tot}} \) is a continuous function the intermediate value theorem states that at least one root must lie in the interval \([0, T_{\text{max}}]\) and a physical solution of the problem exists.

\( T_{\text{sol}} \) is a stable solution if \( \partial E_{\text{sol}}/\partial T < 0 \). Imagine the gas at \( T_{\text{sol}} \) is slightly perturbed towards higher temperatures, e.g. toward \( E_{\text{B}} \). In this regime, the cooling exceeds the heating and drives the temperature back to \( T_{\text{sol}} \). The same happens for per-
We find a high temperature solution \( T_{\text{PDR}} \). In Fig. 5 we sketch such a scenario. At low values of the initial starting temperature and the temperature range where the root is searched. Which one depends on the choice of the algorithm, the initial gridding is fine enough, we expect the temperature to change slowly between subsequent numerical steps. However, this strategy is doomed to always find the solution \( T_j \) and will not reach \( T_1 \) (or \( T_2 \)).

If we continue the computation steps at even higher \( A_V \) we have to find a significantly lower root at \( T_{\text{low}} \). In this three-step picture we have a large temperature jump from \( T_j \) to \( T_{\text{low}} \). In real PDR model computations this is a sudden transition from temperatures of a few thousand K to few hundred K across a small spatial range, especially in models with high gas density and high FUV illumination. Depending on the search range of the applied temperature finding algorithm this sudden temperature jump can lead to severe numerical instabilities and prohibit global convergence.

5.3. Physics of multiple PDR temperatures

The described multiple temperature solutions were first reported by Burton et al. (1990) for \( n = 10^6 \text{ cm}^{-3} \) and \( G_0 = 10^3 \). They described two temperature solutions with different heating and cooling balances. We find similar effects for even higher FUV fields. It is important to include this behavior in the PDR code to evaluate knock-on effects for the chemical structure and the observable line intensities. Fig. 6 summarizes the model results (computed with WLPDR) for the benchmark case V4 (\( n = 10^{3.5} \text{ cm}^{-3}, \chi = 10^7 \)). In panel a) we show the temperature and chemical abundance profiles. The dashed curves correspond to the HAM solution, the solid curves to the WMM. In panel b) we plot the total energy balance vs. the gas temperature. At low \( A_V \) values we find a strong contribution by vibrational H\(_2\) de-excitation heating (pump heating) and H\(_2\) line cooling. They inherit the non-monotonous temperature dependence from the H\(_2\) abundance with a weak maximum around 5000 K. H\(_2\) formation heating is also strong and even remains so at much higher temperatures while the pump heating and line cooling drops off beyond 7000-8000 K.

Moving even deeper into the PDR, H\(_2\) cooling becomes stronger and starts to suppress the roots at temperatures higher than the WMM solution \( T_{\text{sol}} = 910 \text{ K} \). In the case \( A_V = 0.75 \) (only shown in panel b) as red curve) we find that \( E_{\text{sol}}(T) > 0 \).
910 K) < 0. Looking at Fig. 6(b) shows that at 6000 K the energy is almost balanced with $E_{\text{tot}} = -5.5 \times 10^{-20}$ erg s$^{-1}$ cm$^{-3}$.\footnote{Numeric root search algorithms may find a root here depending on their numerical parameters even though this is mathematically not a root.}

In Röllig et al. (2006) we discussed how the dominant heating and cooling at the surface of PDRs changes with gas density $n$ and with FUV intensity $\chi$. The energetic behavior described above is associated with the cooling (and heating) capabilities of molecular hydrogen H$_2$. However, we note, that this is not due to increased cooling in the high density case. The important point is that the cooling needs to be balanced by a sufficiently strong heating in order to produce a temperature solution ($E_{\text{tot}} = 0$).

In case of low FUV or low density we don’t have an efficient heating process in this regime and accordingly we will not find multiple solutions. Adding additional or stronger heating to the model can possibly alter this behavior.

Such phase transitions result from physical processes that become effectively inefficient once they cross an energetic threshold. The main difficulty is that even though such transitions are physically possible, their prescription in numerical models suffers from inherent uncertainties: 1) numerical approximations of complex physics, 2) unknown or inaccurate material constants (e.g. collision rates, spectroscopic constants, binding energies), 3) unavoidable model simplification (e.g. geometry, numerical resolution), 4) numerical inaccuracies. Any of these can either lead to a phase transition or prevent it.

In the model V4 at $A_V = 0.75$ we noted in Fig. 6 that $E_{\text{tot}}(T)$ is smaller but close to zero between 5000 and 7000 K. This is because the total cooling is only slightly stronger in that temperature range than the total heating. In Fig. 7 we show how changing a single heating process can change the situation. The orange line shows $E_{\text{tot}}$ in case of a 20% enhanced H$_2$ formation heating. This would result in two additional temperature solutions, i.e. a possible temperature solution about 7 times higher than in the case of standard H$_2$ formation heating.

Predicting the effect of the two different temperature solutions on observable line intensities is not straight forward because excitation conditions and column density effects are mixed. We found up to 20% higher CO emissivities for the upper lines and up to 70-80% higher CH$^+$ line intensities for higher transitions when selecting the HAM solution instead of the WMM solution.

The final choice between WMM and HAM depends on the modeled physical scenario as already described by Burton et al. (1990). An initially hot and fully atomic (or ionized) medium that becomes subject to significant lower FUV illumination will settle down at lower temperatures coming from a much higher temperature. This clearly prefers the HAM solution. In the opposite case, where the gas starts from cold and molecular conditions at the onset of FUV illumination, the WMM solution is favored because the gas is gradually transitioning from lower to higher temperatures. A scenario for the second case is the onset of massive star formation in the vicinity of the model cloud while the first scenario could occur in case of some shielding due
to cloud motions or sudden changes in the illuminating source due to supernova events.

6. New model results

The most important surface reaction in the ISM is the formation of molecular hydrogen (Cazaux & Tielens 2002, 2004, Le Bourlot et al. 2012, Bron et al. 2014, Wakelam et al. 2017a, Thi et al. 2020), and all PDR models already account for it with various degrees of complexity. Other surface reactions were typically not included until sufficient computing power became available. (Woitke et al. 2009) presented the disk PDR model ProDiMo with surface chemistry and (Hollenbach et al. 2009) published a plane-parallel PDR model with a small surface network to study the chemistry of H2O and O2 and (Guzmán et al. 2011) studied the chemistry in the Horsehead using an updated version of the Meudon code (Le Petit et al. 2006). Recently, (Esplugues et al. 2016, 2019) presented PDR model results including (time-dependent) surface chemistry. In a more recent work, they expanded their chemical desorption scheme to include partial desorption of the products (Esplugues et al. 2019). We compare our model computations with their results and in addition we investigate how the revised description of CR induced desorption affects the structure of the PDR. As shown by (Sipilä et al. 2021) Eqs. 12 and 15 result in higher values of the dust temperature due to optical thickness. This leads to an increase in gas temperature until it approaches \( T \approx 200 \) K, almost 20 K warmer compared to the model without freeze-out. This effect also occurs in case of the more efficient CR induced desorption model CR2.

We compare how the structure of a strongly illuminated PDR (\( n = 10^4 \text{ cm}^{-3}, M = 10^3 \text{ M}_\odot, \chi = 10^4 \)) depends on the surface chemistry. Fig. 9 shows the gas and dust temperatures of a PDR model cloud as function of \( \chi \). The dust temperature does not alter with adding surface chemistry. The gas temperature reaches a minimum at \( \chi = 5 \). At this depth, the FUV radiation is sufficiently attenuated and does not dominate the gas heating any more. Other processes, such as heating by gas-grain collisions start to dominate. Deeper in the cloud it becomes increasingly more difficult for cooling line photons to escape the model cloud due to optical thickness. This leads to an increase in gas temperature until it approaches \( T_{\text{dust}} \). This effect is enhanced by any process that further limits the cooling capacity of the gas, for instance freeze-out of relevant line cooling species. Figure 9 shows how the gas temperature increase is stronger if surface chemistry is included and reaches \( T_{\text{gas}} \approx 40 \text{ K} \), almost 20 K warmer compared to the model without freeze-out. This effect also occurs in case of the more efficient CR induced desorption model CR2.

Fig. 10 shows the corresponding chemical structure excluding (left panel) and including (two right panels) surface chemistry. The incident FUV field in this particular case is strong leading to the typical transition from \( \text{C}^+ \rightarrow \text{C} \rightarrow \text{CO} \) at \( \chi = 3 \). In the center of the model cloud without surface chemistry the majority of the carbon is bound in \( \text{CO} \) with a temperature slightly above 20 K. The atomic carbon density peaks at \( \chi = 2 \). In the models with surface chemistry we find the same behavior up to an \( \chi = 7 \). At higher visual extinction, the CO abundance decreases while other gas phase species have higher abundances, e.g. \( \text{C} \) and \( \text{CH} \).

Note, that the dust is too warm to host a significant J(CO) population. Under these conditions the ice consists mainly of J(CO2) which locks up most of the available C and O atoms in the ice mantle. This renders the main destruction reactions of
Table 5: Model parameter for models discussed in Sect. 6.

| parameter | value | comment |
|-----------|-------|---------|
| $n_0$     | $10^7$ cm$^{-3}$ | surface density |
| $M$       | $50,1000M_\odot$ | clump mass |
| $\chi$    | $1 - 10^6$ | FUV in units of Draine (1978) |
| $\alpha$  | 1.5 | density power law index |
| $R_{\text{core}}$ | 0.2 | constant density core fraction |
| FWHM      | 1 km s$^{-1}$ | micro-turbulent line width |
| $\xi_{\text{CR}}$ | $10^{-16}$ cm$^{-1}$ | CR ionization rate |
| dust composition | WD01-7 | (Weingartner & Draine 2001b, entry 7 in their Table 1) |
| $\Gamma_\text{e}$ | PEHWD01-4 | photo electric heating rate (Weingartner & Draine 2001a, entry 4 in their Table 2) |
| $R_{\text{H}_2}$ | H$_2$ formation described in (Röllig et al. 2013), formation on PAHs larger than $\alpha_{\text{carb}} = 29\AA$ |
| $f_{\text{OH}^+}$ | [He]/[H] | He elem. abundance (Simón-Díaz & Stasińska 2011) |
| [Cl]/[H]   | $2.34 \times 10^{-4}$ | C elem. abundance (Simón-Díaz & Stasińska 2011) |
| $[^{13}\text{C}]/[\text{H}]$ | $3.52 \times 10^{-6}$ | $^{13}$C elem. abundance (Simón-Díaz & Stasińska 2011) |
| [O]/[H]    | $4.47 \times 10^{-4}$ | O elem. abundance (Simón-Díaz & Stasińska 2011) |
| [N]/[H]    | $8.32 \times 10^{-5}$ | N elem. abundance (Simón-Díaz & Stasińska 2011) |
| [Si]/[H]   | $3.17 \times 10^{-6}$ | Si elem. abundance (Simón-Díaz & Stasińska 2011) |
| [S]/[H]    | $7.41 \times 10^{-6}$ | S elem. abundance (Simón-Díaz & Stasińska 2011) |

Fig. 10: Influence of the surface chemistry on the chemical structure of a PDR. The results are for the same model as in Fig. 9. Solid (black) lines in the central(right) panel correspond to CR$_1$ while dashed(red) lines are for CR$_2$.

Table 6: Condensation temperatures for some relevant species in K derived from the balance between accretion and desorption.

| element | $T_{\text{dust}}$ |
|---------|------------------|
| H       | 11               |
| CO      | 21               |
| H$_2$O  | 85               |
| CH$_4$  | 25               |
| N$_2$   | 14               |
| HCN     | 36               |
| O$_2$   | 18               |
| CO$_2$  | 48               |
| H$_2$O$_2$ | 100        |
| SO$_2$  | 95               |
| NO      | 29               |
| CH$_3$OH | 66             |

atomic carbon C, e.g. by collisions with O$_2$ and SO$_2$, inefficient. These reactions would otherwise replenish the CO population after destruction by H$_3^+$ and He$^+$. Instead, the carbon remains locked in atomic form and the oxygen is converted to ice species. That affects related species like HCO$^+$ and OH. The higher C abundance leads to an enhanced abundance of light carbon hydrides CH$_n$. As a consequence CO is not available as coolant any more and the gas temperature rises by 15-20 K compared to the pure gas-phase model as shown in Fig. 9. This effect is more pronounced in models with lower FUV illumination where the additional warm C core is visible through 50 - 100% stronger [C i] emission at 610 and 370 μm.

For $\chi = 10^4$ the relatively high $T_{\text{dust}}$ prevents most ices to remain on the surface. Comparing the frost temperatures from Table 6 with $T_{\text{dust}}$ from Fig. 8, shows that I(CO$_2$) is the only visible carbon reservoir in the ice mantle that could survive temperatures above 40 K. CH$_3$OH condensation temperatures would be sufficiently high, but the formation in the ice is prevented because the relevant precursor species do not survive long enough in the solid phase. There are no efficient chemical formation routes for CO$_2$ → H$_2$O available, which prevents the formation of significant amounts of H$_2$O ice.

The influence of surface chemistry on the CO abundance has already been described by Hollenbach et al. (2009). They modeled a significantly simpler chemistry and are mainly focused on the predictions for the H$_2$O and O$_2$ gas-phase abundance but we find a similar formation and destruction behavior for CO when we compare with our $\chi = 10^3$ results. For the higher FUV field shown in Fig. 10 we find that for $A_V \gtrsim 5$ CO is mostly destroyed in gas-phase models by H$_3^+$ → HCO$^+$ + H$_2$ and He$^+ +$ CO → O + C$^+$ + He. Adding surface chemistry does...
not introduce fundamental different channels with the exception of freeze-out.

The increasing C density at high visual extinction can also be understood by looking at the respective formation/destruction rates. Surface chemistry suppresses the dominant destruction channel of C at high $A_V$: C + O$_2$ → CO + O because most of the oxygen is locked up in J(CO$_2$) and J(SO$_2$) ice. This reaction can no longer replenish the CO population leading to a strong increase in C abundance and a decrease in CO in the dark cloud portion of the model cloud.

### 6.2. Illumination effects on the surface chemistry

For a more systematic analysis, we investigate how the additional surface chemistry affects individual species depending on the FUV field strength $\chi$ and whether the chemical desorption reactions discussed in Sect. 5.3 changes the overall chemistry.

The gas temperature remains mostly unaffected for $\chi > 10^2$ as shown in Fig. 11a. In Fig. 12, we show how different values of $\chi \approx 1, 10^2, 10^6$ affect the chemistry for C, HCO$^+$, and O$_2$. The high FUV case $\chi = 10^6$ shows no significant effect of the surface chemistry. All relevant coolants remain abundant in the gas-phase due to the warm grain surfaces. For lower FUV field strengths we find that the gas temperature increases above the pure gas-phase case once the dominant coolant CO starts to deplete from gas-phase (see Fig. 11b). A dominant CO gas-phase population survives until the dust temperature falls below $T_{\text{dust}} \lesssim 20$ K (see Fig. 9), and desorption becomes too weak to replenish gas-phase CO. At lower $\chi \approx 1, 10^2$ this occurs at: $A_V \approx 0.2, 1$, respectively. At higher FUV this requires significantly higher values of $A_V$. Any effect that desorbs J(CO) more efficiently will thus result in a lower gas temperature. This can be seen in Fig. 11b which compares the CO gas-phase abundance between the CR$_1$ and CR$_2$ models. In the CR$_2$ model, the energy injected per grain as well as the grain cooling time are enhanced which effectively corresponds to a higher $T_{\text{dust}}$. As a result we find that CO freeze-out sets deeper in the cloud if $\chi < 10^2$ and consequently we see a somewhat lower $T_{\text{gas}}$.

A general trend is that most carbon bearing species show enhanced abundances at high $A_V$ while most oxygen-bearing species have lower densities compared to the pure gas-phase chemistry. This is because ice composition is dominated by oxygen-bearing species, which locks-up a significant fraction of the available oxygen in the ice mantles. For models with significant CO freeze-out we find C to be the main carbon reservoir in the gas-phase. As a consequence, the CR induced ionization of atomic carbon can significantly contribute to the electron formation. Thus, we observe the same enhancement for the electron density. This strongly affects all species that form via dissociative recombination, such as for instance CH. We note similar inherited effects in Fig. 12 where HCO$^+$ follows the abundance change of CO. The selective freeze-out of oxygen-bearing ice species also leads to a significantly decrease gas-phase abundance of O$_2$. This is in agreement with observations having difficulties to confirm high molecular oxygen abundance predictions from pure gas-phase models.

Enhanced cosmic ray induced desorption in the CR$_2$ models allows for a higher gas-phase abundance of certain species with lower binding energies, such as CO and CH$_4$. The corresponding ice mantle composition is shifted towards tighter bound ice species, e.g. J(CO$_2$) and J(H$_2$O). A weaker dominance of overall depletion over gas-phase abundances seems to be in agreement with observations of e.g. S bearing species in PDRs that do not show signs of significant freeze-out (Riviere-Marichalar, P. et al. 2019). However, our current implementation of CR induced desorption (CR$_1$ vs. CR$_2$) remains a crude approximation with large uncertainties. Nevertheless, it might be feasible to use observations of low FUV source as calibrators for more detailed models of CR induced desorption.

Chemical desorption does affect the formation and destruction of some species at various cloud depths. For instance, J(O) + J(O) → O$_2$ takes over as the dominant O$_2$ formation channel for $2 < A_V < 5$ so that we observe an enhanced O$_2$ density before oxygen freeze-out starts to become important (Fig. 12g). Another example is the reaction J(O) + J(H) → OH which contributes approximately 10% to the total OH formation rate for $A_V > 30$.

Figure 14 shows how the ice composition changes with cloud depth. Each panel in the Fig. correspond to a different FUV illumination (assuming CR$_2$). In the low FUV cases $\chi \lesssim 10$ the ice forming closest to the cloud surface consist mainly of J(CO) (60-80%) up to a few $A_V$. Deeper into the cloud the ice is converted to water ice ($\sim 50\%$) as well as methanol ice J(CH$_3$OH) ($\sim 20-25\%$). Under increasing FUV conditions the ice composition shows some significant changes. For $\chi = 10^2$, $10^3$ we find J(H$_2$O) ice closer to the cloud surface. J(CO) becomes less abundant (10-25%) and forms only deeper in the clump ($A_V > 2$). For FUV strengths $\chi \geq 10^3$ the dust temperatures prohibit large amounts of J(CH$_4$) and CO ice and the carbon ice consists to 50-90% of J(CO$_2$), J(SO$_2$) and water ice. For $\chi = 10^2$ the ice is dominated by H$_2$O ice and J(CO$_2$) at $A_V > 50$. The deeply embedded J(CO$_2$) population vanishes at $\chi = 10^6$ and water ice remains the dominant ice component.

The most obvious conclusion is that adding or removing some surface species from the chemical network may result in significantly different ice structures. The same is of course true for different sets of binding energies in use. Even so, another main effect of (any) existing surface chemistry is to open up new formation & destruction channels that become active below certain grain temperatures and will therefore significantly alter the gas-phase abundances. The freeze-out of CO is a good example for this effect. In terms of typical PDR tracers it is important that they are removed from the gas-phase and not so much whether they end up forming J(CO) or J(H$_2$O) ice.

The effective dust temperature is the most important factor in determining the ice structure. Fig. 8 shows that assuming very low dust temperature for deeply embedded parts of the model PDR is not always justified. High FUV models may show enhanced dust temperatures and selectively prevent certain ice species to form. This modifies the overall ice composition on the grain surfaces also affecting the gas-phase abundances. As an example we showed how gas-phase CO is diminished in the dark cloud even though no explicit J(CO) ice is formed.

### 6.3. Coupling between chemistry and line excitation

The previous section showed that the removal of CO from the gas-phase results in a reduced cooling capacity of the gas and an increase in gas temperature. In terms of observable line intensities the higher gas temperatures may partially compensate the reduced abundance of CO. Nevertheless, the general behavior is that $^{12}$CO and $^{13}$CO line intensities are lower in models with surface chemistry due to the freeze-out of CO. This is shown in Fig. 15 where we plot the CO line emission of the transition $J_{\text{up}} \rightarrow (J_{\text{up}} - 1)$ as function of the angular momentum quantum number $J_{\text{up}}$ for pure gas-phase and surface chemistry models. We find the same behavior across the full density range.
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\[ \chi = 1 \quad \chi = 10^2 \quad \chi = 10^4 \quad \chi = 10^6 \]

\[ \text{gas-phase} \quad \text{gas+surface CR}_1 \quad \text{gas+surface CR}_2 \]

\[ \text{CO} \]

(a) \( T_{\text{gas}} \) profile.
(b) CO gas-phase abundance.

**Fig. 11:** Left: Temperature profile changes with FUV strength (\( n = 10^4 \text{ cm}^{-3} \)). Solid lines show pure gas-phase results, dashed lines correspond to gas+surface chemistry. Right: Influence of the surface chemistry on the CO gas-phase abundance for the same parameters as in Fig. 11. CR\(_1\) and CR\(_2\) indicate the different models for the CR induced desorption.

\[ \text{(a) C density profile.} \quad \text{(b) HCO}^+ \text{ density profile.} \quad \text{(c) O}^2 \text{ density profile.} \]

**Fig. 12:** Chemical structure changes with FUV strength. \( n = 10^4 \text{ cm}^{-3} \). Solid lines indicate pure gas-phase chemistry, dashed lines correspond to the gas+surface chemistry using the CR\(_2\) model.

Table 7 lists the clump averaged emission of the fine-structure lines. The selective freeze-out of O bearing species that leads to a dominant gas-phase population of C at large \( A_V \) results in enhanced fine-structure emission for models with low to intermediate values of \( \chi \). This effect is \( \sim 20\% \) stronger in the CR\(_2\) models due to the slightly enhanced gas-phase abundance of atomic carbon. The enhancement of the \([\text{C} \, \text{i}] \left[ 3P_1 \rightarrow 3P_0 \right] \) and the \([\text{C} \, \text{i}] \left[ 3P_2 \rightarrow 3P_1 \right] \) lines. The same effect does not occur for the \([\text{C} \, \text{ii}] \left[ 2P_{3/2} \rightarrow 2P_{1/2} \right] \) transition. The same holds for the \([\text{O} \, \text{i}] \) lines at 63 and 145\,\text{µm}.

Altogether, the surface chemistry in KOSMA-τ has a small effect on the total CO cooling budget, raising the gas temperatures by typically less than a few K (with some exceptions visible in Fig. 11a). The \([\text{C} \, \text{ii}] \) and \([\text{O} \, \text{i}] \) cooling lines are rather insensitive to the modified chemical and temperature profile while the \([\text{C} \, \text{i}] \) fine-structure lines may be affected depending on the effectiveness of overall desorption, which makes the atomic carbon an interesting tracer of surface chemistry in PDRs. Note, that
Table 7: Comparison of model fine-structure emission (in units of $K \text{km s}^{-1}$).

| transition                  | $\chi = 1$ | $\chi = 10^2$ | $\chi = 10^3$ | $\chi = 10^4$ | $\chi = 10^5$ |
|-----------------------------|------------|---------------|---------------|---------------|---------------|
| $[\text{C} \text{ii}]^2P_{3/2} \rightarrow \text{2}P_{1/2}$ | 0.559/0.562 (0.622) | 9.79/10.2 (10.5) | 61.3/62.6 (63.5) | 139/140 (142) | 226/227 (229) |
| $[\text{C} \text{i}]^4P_{1} \rightarrow \text{4}P_{0}$ | 8.55/11.1 (6.07) | 10.7/13 (8.06) | 11.4/15.7 (9.82) | 15/14.1 (11.5) | 16.5/16.7 (15.7) |
| $[\text{C} \text{i}]^2P_{2} \rightarrow \text{2}P_{1}$ | 2.16/2.78 (1.42) | 3.9/4.6 (2.99) | 5.39/7.03 (4.65) | 7.59/7.29 (5.97) | 9.32/9.52 (8.58) |
| $[\text{O} \text{ii}]^4P_{2} \rightarrow \text{4}P_{1}$ | 0.018/0.005 (0.006) | 1.4/1.45 (1.46) | 7.8/80.4 (82) | 283/280 (279) | 500/495 (500) |
| $[\text{O} \text{ii}]^2P_{1} \rightarrow \text{2}P_{0}$ | 0/0 (0) | 0.128/0.134 (0.135) | 32.7/34 (35) | 160/158 (158) | 317/316 (317) |

Notes. $\text{C}_{}^1$ and $\text{C}_{}^2$ model results are shown as $\text{C}_{}^1/\text{C}_{}^2$; models without surface chemistry are given in parenthesis. The columns give results for models with different FUV strength $\chi$ assuming $n = 10^4 \text{ cm}^{-3}$, $M = 10^3 \text{ M}_\odot$.

Fig. 13: Ice thickness in ML for the model clump center as a function of total gas density $n_0$ and FUV strength $\chi$, using CR$_2$. The numbers give the threshold for the formation of one monolayer of ice in $A_V$.

in diffuse and translucent clouds gas-phase PDR models notoriously over-predict $[\text{C} \text{i}]$ abundances (the so-called $[\text{C} \text{i}]$ problem (Gong et al. 2017)). However, column densities are not a direct observable and therefore comparing model column densities to column densities derived from observations introduces additional uncertainties. Here, we are more concerned with denser clouds where PDR model prediction can over- and under-predict $[\text{C} \text{i}]$ intensities depending on the detailed modeling approach. Standard chemical models are not able to reproduce the described $[\text{C} \text{i}]$ enhancement because they do not solve the temperature self-consistently with the chemistry and the non-local radiative transfer through the model cloud.

The line intensities in Table 7 and Fig. 15 were computed for a model with $n = 10^4 \text{ cm}^{-3}$, $M = 10^3 \text{ M}_\odot$. Many observations of PDRs show significantly brighter emission lines. Examples are the Orion Bar and NGC 7023 (Joblin et al. 2018) and the Carina Nebula (Wu et al. 2018). They require significantly higher gas densities ($n = 10^4 - 10^5 \text{ cm}^{-3}$) to explain the observed intensities. At those high densities rotational lines of CO up to $J > 20$ can be excited; this is not possible for $n = 10^3 \text{ cm}^{-3}$. For comparison we provide plots of the CO SLED for higher densities in the appendix.

6.4 Comparison with other models

Even though inter-model comparison tends to be difficult (compare for e.g. Röllig & Ossenkopf-Okada (2007) we try to compare our results to other computations.

Hollenbach et al. (2009) added surface chemistry to their PDR model (Kaufman et al. 1999, 2006) to study H$_2$ and O$_2$ abundances observed in the gas-phase. They added only a small surface network to their chemistry and used significantly different desorption energies. In particular the values for C and OH are very different significantly affecting the ice composition. Nevertheless we find that H$_2$O peaks at $A_V \approx 5$ with $n$(H$_2$O) $\approx 10^{-3} \text{ cm}^{-3}$ and drops to $10^{-9} - 10^{-10} \text{ cm}^{-3}$ deeper in the clump, comparable to their result. We also see a corresponding increase of the water ice density at $A_V \approx 3 - 5$ locking-up most of the oxygen atoms in the ice mantle. On the other hand, they find a significantly different carbon ice structure, except for J(CO). For $A_V > 6$ they find the carbon atoms locked-up in J(CH$_4$) which does not occur in our models. They do not report details of their carbon surface network but the most likely reason for this is the assumed binding energies. Using comparable values we also find a dominant J(CH$_4$) population. They discuss the threshold $A_V$ for ice formation (ML=1) and we provide the corresponding numbers in Fig. 13. For conditions applicable to the Taurus cloud ($n_0 = 10^3 \text{ cm}^{-3}$ and $\chi \sim 1$) they find a value of 2 almost identical to our result of 2.1. For $n_0 = 10^4 \text{ cm}^{-3}$ and $\chi \sim 100$ they find approximately 3 where we have about 2.3 which can be explained by our increasing total gas density profile, which shifts the ML=1 threshold closer to the surface.

Esplugues et al. (2016) presented a significantly improved version of the Meijerink PDR code (Meijerink & Spaans 2005) including an up-to-date surface chemistry. Unfortunately, they computed their models only up to $A_V = 10$. More importantly, they used a simple approximation for their dust temperature that produces much too low $T_{\text{dust}}$ (compared to detailed computations) and is not valid for $A_V > 10$. Therefore, their model is not able to selectively freeze-out particular ices only and thus could not produce the dark cloud C population we find. Their C density profile for $n = 10^4 \text{ cm}^{-3}$, $G_0 = 10$ at $A_V < 10$ (Esplugues et al. 2016) was very similar to our results (see Fig. 12a). Note, that typical plane-parallel PDR computations often do not cover deeply embedded regions with $A_V > 10$ and therefore miss out the strong peaks in, e.g. C and CH. The common argument that beyond a certain visual extinction no significant chemical variation takes place is not necessarily valid any more once we include surface reactions to the chemical network and account for higher dust temperatures due to diminishing cooling efficiencies. Looking at their Model 1 results ($n = 10^4 \text{ cm}^{-3}$, $G_0 = 10^4$) (Esplugues et al. 2016) we note that their ice composition is dominated by J(CO)$_2$ for $A_V > 3$. Our models show J(CO)$_2$ as major ice component for slightly larger values of $A_V$. They find water ice as second most abundant ice component for $A_V > 3$. Our results indicate that water ice is dominating the ice composition at $A_V > 5$ with a J(SO$_2$) peak around $A_V = 5$ which is not included in the model chemistry of Esplugues et al. (2016). J(CO)$_2$ is dominating the ice composition at $A_V > 5$. Fig. 13 shows how the ice thickness (in MLs) in the center of our model clumps depends on the gas density and the FUV illumination. The number of MLs decreases with $\chi$ as well as with $n_0$. The same is true for the depth where ML $= 1$. For $n_0 = 10^4 \text{ cm}^{-3}$
Fig. 14: Percentile ice composition as function of $A_V$ for $n = 10^4$ cm$^{-3}$, $M = 10^3 M_\odot$ assuming CR$_2$. 
and $\chi = 10^4$ we find that the first ML builds at $AV = 5.2$ roughly consistent with Esplugues et al. (2016) who find 0.6 ML at that extinction. However, our density increases with depth and therefore we have a slightly earlier onset of ice formation.

In a recent update Esplugues et al. (2019) present computations with a modified dust temperature formulation (Hocuk et al. 2019) allowing for higher central dust temperatures. Comparing their dust temperatures with the detailed results from MCDT shows a factor two lower values at the edge of the cloud but a factor ~ 2 higher central dust temperatures (except for $\chi = 10^6$). At $AV = 10$ their $T_{\text{dust}}$ is consistently ~ 10 K hotter except for $\chi = 1$ where they have 8.8 K compared to our 3.6 K. As a result they also see a preferentially oxygen-bearing ice composition but with a different spatial behavior and a different ice composition because of their dust temperature exceeding the sublimation temperatures of CO and CH$_3$. They present three models with different values for density and FUV strengths compared to Esplugues et al. (2016). A comparison with their results for the OH density profiles shows a similar behavior for $AV < 5-6$. The density peak shifts closer to the surface for increasing $n$ and $G_0$ and we observe the same trends. For $n = 10^6$ cm$^{-3}$ they show a peak density of $n_i/n_H \sim 10^{-4} - 10^{-7}$. We find similar OH densities for $\chi = 10^4$. For the lower FUV illumination we find peak OH abundances of $n_i/n_H \sim 10^{-6}$. Their model 3 ($n = 10^6$, $G_0 = 10^9$) shows a much higher peak density for $AV < 1$ of a few $10^{-5}$ and we find similar values at $AV \sim 0.2$. However, all their models show a high OH density at their maximum $AV = 10$ of $2 - 3 \times 10^{-8}$. Our models show a significantly lower central OH density of a few $10^{-10}$ in for $n_0 = 10^4$ models. We find comparably high central densities only for $\chi = 10^6$ which is consistent with our lower dust temperatures for $\chi < 10^6$. Our results for their model 3 configurations shows similar densities at $AV = 10$ but differs significantly in shape and drops to $10^{-10}$ in the center of our cloud. For $O_2$ we find significantly different results. At $\chi = 10^2, 10^4$ we find peak relative densities of a few $10^{-6}$ at $AV = 3-5$. Our central $O_2$ density drops with $n_0$ to $n_i/n_H < 10^{-12}$ for $n_0 = 10^5$ cm$^{-3}$ compared to values above $10^{-6} - 10^{-5}$ for their models 1 and 2. Such high values seem to be in conflict with observations (e.g. Goldsmith et al. 2011; Wiström et al. 2016 and references therein). Only for $\chi = 10^4$ are we finding a strong central $O_2$ population of larger than $10^5$. A similar difference is also visible for H$_2$O that has lower central and higher peak values in our results. Nagy et al. (2017) gives relative H$_2$O densities for the Orion Bar of $1 - 5 \times 10^{-12}$. The closest parameter set from Esplugues et al. (2019) is their model 3 with peak/center abundances of $\sim 10^{-11}$. Within the same $AV$ range we find factor 10 lower values with central densities of $3 \times 10^{-11}$ for $n_0 = 10^6$ cm$^{-3}$ and $\chi = 10^6$. Our total H$_2$O column densities at $AV = 5$ are $2 \times 10^{13}$ cm$^{-2}$ for $n_0 = 10^6$ cm$^{-3}$ and $7 \times 10^{13}$ cm$^{-2}$ for $n_0 = 10^8$ cm$^{-3}$, which is of the same order as the observed values of $2 \times 10^{13}$ to $2 \times 10^{14}$ cm$^{-2}$ (Nagy et al. 2017). Within their computations, changing the dust temperature prescription gave $j$(CH$_3$) abundances at $AV = 10$ that differed by a factor $10^4$! Given their different dust temperature behavior and a significant different set of assumed $E_D$ they find a very different ice composition and we conclude that a detailed comparison with our results is difficult. Qualitatively, we find comparable amounts of J(CH$_3$) and J(CO) ice for low values of $\chi$ but significantly lower abundances for higher FUV fields.

Guzmán et al. (2011) presented observations of H$_2$CO emission from the Horsehead together with surface chemistry computations from the Meudon PDR code (Le Petit et al. 2006). H$_2$CO is interesting because it can be efficiently formed in the gas-phase and on the surface of grains. They showed that adding the surface network leads to an increase of HCO densities by 1-2 orders and a pronounced density peak of HCO densities by 1-2 orders and a pronounced density peak of HCO densities by 1-2 orders.

6.5. Comparison with observations

citetboogert2015 summarizes observed ice abundances based on column density derivations. The dust temperature variations along the observed lines of sight have a major effect on the ice but remain unknown which makes a direct comparison of the model ice composition with observations not trivial. Secondly, the limited number of chemical species included in the presented computations limits the predictive power for some of the ice species, e.g. for J(NH$_3$). Boogert et al. (2015) give ice abundances for different environments: massive young stellar objects (MYSOs), low mass young stellar objects (LYSOs) and BG stars. Naturally, they correspond to different local physical environments.
conditions, but we will focus on general trends only. All abundances in this section will be relative to J(H$_2$O) column densities $X_{H_2O}$. The median of all models with $\chi = 1 - 10^2$ and $M = 50, 1000 M_\odot$ is shown.

The securely observed ices are in descending order: J(CO$_3$) and J(CO) with 20-30% abundance each, J(CH$_3$OH) with 6-10%, J(NH$_3$) with ~ 6% and J(CH$_4$) with ~ 5%. J(H$_2$CO) is likely identified with a few % abundance. In Fig. [16] we show our model ice predictions where we average over a range of FUV strengths $\chi = 1 - 10^3$ and clump mass $M = 50, 1000 M_\odot$ and plot $X_{H_2O}(i)$ as function of the gas density $n_0$. J(H$_2$O) is the most common ice across the whole density range and J(CO) varies 20-30% only for $n_0 \sim 10^3$ cm$^{-3}$. Our J(H$_2$CO) predictions recover the observed values in the lower density range of Fig. [16]. Given the crude averaging over the physical parameters and our small chemical network we find our model predictions to be in reasonable agreement with observations.

### 7. Clumpy ensemble model

Interstellar clouds are neither a plan-parallel slab nor of perfect spherical shape and results from these kind of models will always be a rough approximation to reality, a reality where the ISM is clumpy/fractal, turbulent, organized in filaments or fibers, and most importantly not in equilibrium. PDR models with more complex geometries have been designed to address this deficiency, but the higher complexity always comes with the price of much higher computation costs (Bisbas et al. 2012; Levrier et al. 2012; Grassi et al. 2014; Girichidis et al. 2016; Bisbas et al. 2021). The spherical setup of KOSMA-$\tau$ offers the attractive option of modeling clumpy clouds as a superposition of differently sized clumps following a well-defined clump-mass spectrum. This has been described in detail in Zielinsky et al. (2000), Cubick et al. (2008) and Andree-Labsch et al. (2017).

Clumpiness has frequently been invoked to explain certain emission characteristics of the ISM in spatially unresolved observations. The main driver was always that clumpy gas has a higher surface to volume ratio and therefore shows an excess of emission primarily produced in the PDR surface regions of molecular clouds. A typical example is the [C II] emission, which is produced by strong FUV illumination and a good tracer of PDRs, this means a surface tracer. Conversely, rotational CO line emission is a good volume tracer because CO requires shielding from intense FUV illumination, which is effective only for extinctions $A_V > 1$. Non-clumpy PDR models were not able to explain the observed excess in e.g. the [C II]/CO(1-0) line ratio in active star forming regions (Stutzki et al. 1988; Spaans & van Dishoeck 1997; Dedes et al. 2010; Graf et al. 2012) but the observed ratios asked for models with a larger surface-to-volume ratio. A similar explanation has also been presented by Meixner & Tielens (1999); Hogerheijde et al. (1999); Zielinsky et al. (2000) to explain variations in observed line ratios of several different PDR and molecular cloud tracers through clumpy ensembles of PDRs. Cubick et al. (2008) showed that the global far-infrared (FIR) emission of the Milky Ways can be explained in terms of clumpy PDR emission.

This has been supported by observations of clump spectra in molecular clouds. Based on molecular line observations Heithausen et al. (1998) measured the scaling relations for one source over several orders of magnitude and Kramer et al. (1999) measured the clump-mass distribution in various sources confirming a common power-law across all sources with power-law index 1.6 to 1.8, extending down to the resolution limit and clump masses as low as $10^{-3} M_\odot$ for at least two of the sources. These findings have been put at question by models that managed to explain the observed line ratios from high-pressure PDR models (e.g. Marconi et al. 1998; Joblin et al. 2018) showed that the pure line intensities in the Orion Bar can be explained from a plane-parallel PDR model. Their high-pressure models however, do not reproduce the observed spatial stratification of the different tracers but predict a very thin PDR layering. The key information on the clumpiness comes from the spatially resolved structures. Andree-Labsch et al. (2017) showed that the observed spatial stratification within the Orion Bar is in disagreement with any simple plane-parallel model but that some kind of clumpiness had to be invoked. Andree-Labsch et al. (2017) presented KOSMA-$\tau$-3D, where individual volumetric elements (voxel) are populated with unresolved clumpy PDR ensembles. They modeled the 3-dimensional structure of the Orion Bar and found a good agreement of their results with a multi-line data set from Herschel and Caltech Submillimeter Observatory (CSO) observations.

Velocity-resolved observations from Herschel, SOFIA and ALMA confirm the dynamical nature of PDRs (Goicoechea et al. 2016; 2017; Joblin et al. 2018; Wu et al. 2018; Luisi et al. 2021; Kabanovic et al. 2022). Photo-evaporation flows from globules and other dense clumps are ubiquitous (Mookerjea et al. 2012, 2017; Joblin et al. 2018; Wu et al. 2018; Luisi et al. 2021; Bron et al. 2018). Theoretical papers have predicted for a long time that dense clumps are carved out from their parental cloud by UV irradiation (Lefloch & Lazareff 1994; Henney et al. 2009; Bisbas et al. 2011). The inter-clump medium is then fed by the photo-evaporation flows from the PDR surfaces. The observations confirm the theoretical predictions that the inter-clump medium density is lower than the clump density by at least two orders of magnitude (Arkhipova et al. 2013; Mookerjea et al. 2019; Schneider et al. 2021). The photo-evaporation from the clumps provides a continuous low-density mass flow from the surfaces with velocities of 1–2 km s$^{-1}$ (Makai 2015; Mookerjea et al. 2012; 2019; Sandell et al. 2015; Goicoechea et al. 2020). The inter-clump medium inherits the chemical properties of the PDR surfaces. Despite of the strong density differences their chemistry is rather similar because it is dominated by the FUV radiation rather than collisions. However, in principle this constitutes a non-stationary scenario due to the constant

![Figure 16: Ice abundances relative to the H$_2$O ice column density. The median of all models with $\chi = 1 - 10^2$ and $M = 50, 1000 M_\odot$ is shown.](image-url)
mass loss to the inter-clump medium [Bertoldi & Draine 1996
Störzer et al. 1997] Störzer & Hollenbach 1998, 1999
[Maillard et al. 2021]. It violates the assumption of a constant mass in
Könyves et al. 2020]. For an overview of how different clump
size constraints a clump in the lower left corner (radius
3′′) (Heithausen et al. 1998). The flux of
HCO+ 4-3 emission lines of
HCO+ 4-3 data presented by Goicoechea et al. (2016). The comparison
with the size of a 0.01 M⊙ clump in the lower left corner (radius
1.44′′) shows a match of the typical structure size. Most of the
emission at lower levels is not spatially resolved but forms an
extended structure, mainly behind the Orion Bar. If we assume that this is due to smaller clumps, well below the beam size and
not removed by photo-evaporation yet, we can also model them through KOSMA-τ. When following the original clump mass spectrum clumps with a mass of 0.001 M⊙ have a radius of 0.53″
and a clump averaged HCO+ 4-3 intensity of 39 K km s−1. For
the comparison, we also include dashed contours for 40 K km s−1 in
Fig. [17]. Comparing the areas within the two contours we can
count the required clumps to produce the observed emission and compare the ratio with our standard clump ensemble scaling.

Our standard clump ensemble setup approximately repro-
duces the properties of this HCO+ intensity map without any
further fitting. Table [8] lists the parameters of the corresponding
discrete clump ensemble. Here, we use just the two clump
masses of m1 = 0.001 and m2 = 0.01 M⊙ depicted in Fig. [17]
and assume the standard scaling laws for the clump mass distribution
(power law index α = 1.8) and the mass-size relation
(power law index γ = 2.3) (Heithausen et al. 1998). The flux of the
0.01 M⊙ clumps fully explains the 57 K km s−1 contour if we ignore
higher intensities within the area. This is an obvious over-
simplification since the map shows few smaller condensations with
HCO+ > 80 K km s−1. The low mass clumps explain the
outer contours to about 50%. This is a remarkably good match
given the fact that we did not perform any numerical fitting.

To fully explain the intensity area it would take about twice as
many clumps with M = 0.001 M⊙ (numbers in parenthesis in Table [8]. Consequently, this results in a steeper clump-mass distribution with a power-law index of α ≈ 2.1 or contributions from more even smaller clumps that were ignored in this simple picture. A steeper clump-mass distribution would agree with previous studies showing that denser regions, in particular in Orion A, tend to have steeper clump-mass indices α comparable to what we find [Bally et al. 1987, Maddalena et al. 1986
Nagahama et al. 1998, Schneider & Brooks 2004].

We can also compare the model column densities. For the
model clumps from Table [8] we compute the mean column density of a species averaged over the projected clump area. The contour area filling factor of approximately unity allows to directly compare the column densities. Table [8] gives the observed values and our clumpy results. The observed column densities are mostly consistent with a clumpy PDR ensemble. The CO column density predicted by the model is higher than the value derived from 3-2 observations by Goicoechea et al. (2016). This

7.1. Example: Orion Bar - spatial structure
High-resolution ALMA data of the Orion Bar directly resolve the
larger clumps in our description. Goicoechea et al. (2016)
presented ALMA observations of HCO+ 4-3 emission lines of the
Orion Bar resolving the structure of the ionization and disso-
sociation front with ~ 1″. Their data show fragmented clumps with sizes in the order of 2″ (see Fig. [17]). This corresponds roughly to a clump mass of about 0.1 M⊙ at densities of n ≈ 4 × 106 cm−3 and χ = 1.44″. KOSMA-τ computes I(HCO+ 4-3) = 57 K km s−1 clump averaged emission for such a clump assuming a FUV field of χ = 10⁴. For a detailed discussion on suitable PDR model parameters for the Orion Bar we refer to [Andree-Labsch et al. 2017]. For a qualitative discussion we overlay in Fig. [17] contours for 60 K km s−1 to the HCO+ 4-3 data presented by Goicoechea et al. (2016). The comparison with the size of a 0.01 M⊙ clump in the lower left corner (radius 1.44″) shows a match of the typical structure size. Most of the
emission at lower levels is not spatially resolved but forms an
extended structure, mainly behind the Orion Bar. If we assume that this is due to smaller clumps, well below the beam size and
not removed by photo-evaporation yet, we can also model them through KOSMA-τ. When following the original clump mass spectrum clumps with a mass of 0.001 M⊙ have a radius of 0.53″
and a clump averaged HCO+ 4-3 intensity of 39 K km s−1. For
the comparison, we also include dashed contours for 40 K km s−1 in
Fig. [17]. Comparing the areas within the two contours we can
count the required clumps to produce the observed emission and compare the ratio with our standard clump ensemble scaling.

Our standard clump ensemble setup approximately repro-
duces the properties of this HCO+ intensity map without any
the clump-averaged intensity. The area of the 39 K km s$^{-1}$
for 40 K km s$^{-1}$
Notes.

2002). Goicoechea et al. (2016) find a dynamical crossing time
compression, and a thin interclump medium (Gorti & Hollenbach
enhanced density contrasts with dense clumps, subject to ero-
Compression by this wave and photo-evaporation lead to en-
moving through the molecular cloud (Goicoechea et al. 2016)
The structure in Fig. 17 is the result of a high-pressure zone
intensity distribution.

PDR ensemble are consistent with observed values. 4) The fact
to a significant degree. 3) The column densities from a clumpy
rect depletion (Fuente et al. 2016). The total column densities
are also higher than the values given by Goicoechea et al. (2016)
are consistent with observed values in the map (excluding inner contours).

\[ M_{\text{env}} = 1 M_\odot, (n_{\text{env}}) = 5 \times 10^6 \text{ m}^{-3}, \chi = 10^4, \alpha = 1.8, y = 2.3 \]

Table 8: Properties of a simple discrete Orion Bar ensemble.

| $M_i$ (M$_\odot$) | $N_i$ (cm$^{-3}$) | $n_i$ (pc) | $R_i$ (pc) | $\Omega_i$ (2) | $\Omega_i$ (3) | $\Omega_i$ (4) | $\Omega_i$ (5) | $n_\Omega_i/O_{\text{HCO}^+}$ |
|-----------------|-----------------|----------|----------|-------------|-------------|-------------|-------------|------------------|
| 0.001           | 387(794)        | 8.1 x 10^6 | 0.0011   | 0.53       | 0.88        | 39.4        | 1097        | 0.48(1.0)        |
| 0.01            | 61              | 4.0 x 10^6  | 0.0029   | 1.44        | 6.52        | 57.2        | 385         | 1.0              |

Notes. (1) $N_i$: clump number in the ensemble. The numbers in parenthesis give the clump number to completely fill the intensity contour area for 40 K km s$^{-1}$ $\leq I \leq 60$ K km s$^{-1}$. (2) $n$: average clump density. (3) $R_i$ and $\Omega_i$ denote radius and solid angle of a single clump. $I_i$ corresponds to the clump-averaged intensity. (4) $I$: clump averaged intensity. (5) $\Omega_i$ denotes the solid angle enclosed by the respective intensity contour including the solid area of all inner contours. The area of the 39 K km s$^{-1}$ contour is exclusive of the 57 K km s$^{-1}$ contour listed in the second line. In the last column $N_\Omega_i/O_{\text{HCO}^+}$ gives the ratio between the solid angle covered by the model clumps with the matching intensity and the corresponding observed solid angle in the map (excluding inner contours).

Table 9: Observed column densities vs. model results.

| $N_{\text{obs}}$ (cm$^{-3}$)$^{(1)}$ | $N_{\text{ens}}$ (cm$^{-3}$)$^{(2)}$ |
|---------------------------------|----------------------------------|
| CO                             | 1 x 10^8                        |
| HCO$^+$                         | 5 x 10^3                        |
| H$^1$CO$^+$                     | (5 - 20) x 10^3                 |
| HCO$^+$                         | (3 - 9) x 10^4                  |
| SO$^+$                          | (2 - 4) x 10^12                 |
| SO$^+$                          | (5 - 10) x 10^3                 |
| H + 2 H$_2$                     | 2 x 10^2                        |

Notes. (1) Reference: Goicoechea et al. (2016, 2017). (2) Column densities are given for the ensemble clumps from Table 8.

is easily explained by the fact that the derivation used there is not sensitive to CO at temperatures below 120 K so that a large fraction of cool CO was not accounted for. The major discrepancy in the SO abundance may be attributed to some large uncertainties in the sulfur chemistry due to the unknown roles of vibrationally excited H$_2$ (Goicoechea & Cuadrado 2021) and direct depletion (Fuente et al. 2016). The total column densities are also higher than the values given by Goicoechea et al. (2016) but closer to estimates by Hogerheide et al. (1995) who derived $N_{\text{H}_2} = 6.5 \times 10^{22}$ cm$^{-2}$ at the peak of molecular emission.
The simple numerical experiment shows that 1) the HCO$^+$ 4-3 intensity levels predicted by KOSMA-$\tau$ clumps are consistent with the observations of the Orion Bar. 2) The total flux predicted by a clumpy ensemble covers the observed flux values to a significant degree. 3) The column densities from a clumpy PDR ensemble are consistent with observed values. 4) The fact that we do not resolve the smallest ensemble clumps is consistent with their filling factor which leads to roughly homogeneous intensity distribution.

7.2. Non-stationary clumpy PDR evolution

The structure in Fig. 17 is the result of a high-pressure zone moving through the molecular cloud (Goicoechea et al. 2016) forming a fragmented and dynamically moving PDR surface. Compression by this wave and photo-evaporation lead to enhanced density contrasts with dense clumps, subject to erosion, and a thin interclump medium (Gorti & Hollenbach 2002). Goicoechea et al. (2016) find a dynamical crossing time for the wave front of a few 10$^4$ yr. 10$^4$ yr corresponds to the photo-evaporation destruction time for clumps with $M < 0.01$ M$_\odot$ (Decataldo et al. 2017) and the chemical time-scale for HCO$^+$ formation or destruction in the clumps from Table 8. Consequently, we do not expect the survival of any smaller clumps after the passage of the PDR zone. This is consistent with the fact that Fig. 17 shows almost no 40 K km s$^{-1}$ emission on the side facing the ionization front ($\delta x \leq 15''$). Clumps with $M < 0.01$ M$_\odot$ did not survive the passage of the pressure front. The regions in Fig. 17 with $\delta x \gtrsim 20''$ shows volumes which have not yet been affected by the front and where the lower mass clumps are still surviving. They may already be subject to some evaporation but their embedded HCO$^+$ population is not yet diminished. This picture also explains the emission peaks with levels above 60 K km s$^{-1}$ at the PDR front in Fig. 17. Clumps with original masses above 0.01 M$_\odot$ are brighter than 70 K km s$^{-1}$ but may have been partially eroded so that we only see their larger fragments. We conclude, that the findings by Goicoechea et al. (2016) are consistent with a clumpy medium with a mass spectrum that changes from the original distribution by photo-evaporation during the passage of the PDR. The observed gas dynamics and the related life times of such clumps explain the spatial distribution of the observed emission.

8. Conclusion

We present the current status of the numerical PDR model code KOSMA-$\tau$, which solves the coupled chemical and physical state of the ISM in a spherical model cloud under isotropic FUV illumination. KOSMA-$\tau$ has been thoroughly tested in the last 20 years and has been subject to a number of significant updates and improvements. In this paper, we provide a detailed description of the geometric and numerical setup of the code as a reference for comparison with other model codes. Details of adaptive stepping and numerical convergence are discussed and recommendations for application in other codes are derived. We discuss a series of numerical modifications of the code to improve convergence stability and overall performance. The implementation of a time-dependent chemical solver allows for an efficient fall-back algorithm in case regular steady-state solvers do not converge. Finally we present a publicly available sandbox PDR model realized in the programming language Mathematica by Wolfram Research.

KOSMA-$\tau$ now includes a complete surface chemistry network fully coupled to the gas-phase chemistry via all relevant accretion and desorption processes. In particular chemical desorption has been added to KOSMA-$\tau$. We extended the prescription presented by Minissale et al. (2016) and included all possible reaction branches also including partial desorption. We implemented the surface chemistry in a fully modular way analog
to the gas-phase chemistry, allowing for simple addition or removal of chemical species. Adding surface chemistry to a PDR model can produce unexpected results. In particular the detailed treatment of the dust temperature is important because PDRs can sustain large amounts of warm dust particles at very large extinctions strongly affecting the ice chemistry. We discuss how higher dust temperatures lead to a selective freeze-out of oxygen-bearing species compared to carbon-bearing species due to their higher condensation temperature. For high FUV models the reduction in CO column density due to selective freeze-out of oxygen-bearing species onto grain surfaces produces a surplus of atomic carbon leading to a significantly enhanced [C II] line emission that could explain the difficulties of previous generations of PDR models in fitting observed levels of [C II] emission. The composition of the ice mantles changes in a complicated, not always intuitive way as a function of the FUV irradiation. This applies e.g. to the non-monotonous production of methanol that is suppressed at elevated FUV fields. We discuss the clumpy PDR model assumptions. Performing a simple numerical experiment shows that the PDR structure as well as the observed flux values can consistently described with the assumption of a clumpy ensemble of PDR clumps. Clumps with masses below 0.01 $M_\odot$ are eroded in the dynamical evolution of the the PDR explaining the asymmetry of the observed profile along the high-pressure zone when taking the observed time scales into account.

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Appendix A: New model results

We show the spectral line energy distribution (SLED) of $^{12}$CO and $^{13}$CO lines as function of the FUV field strength $\chi$ for $n_H = 10^2, 10^3, 10^4$ cm$^{-3}$ in Figs. A.3, A.4, A.5, and A.6. The effect of the surface chemistry on the line emission is most prominent for high density and higher-J transitions. We also show the density profile of selected species affected by the surface chemistry.

Appendix B: Numerical details

Sect. A.2 described the spatial loops over the adaptive cloud depth grid. Input to the Bunach-Stoer stepper are the dependent variables $y_i = x_i + N x_i$ (and its derivative $d_i, d_i/dt = x_i + N x_i$) at the starting value of the independent variable $\tau = 0$. Also input are the step size to be attempted, $h_{\text{try}}$ (we start with $10^6$ cm), the required accuracy, eps, and the vector $\text{yscal}(1:N)$ against which the error is scaled to give the desired accuracy $\delta_0 = \text{eps} \times \text{yscal}$. On output, $N$ and $\tau$ are replaced by their new values. $h_{\text{did}}$ is the step size that was actually accomplished, and $h_{\text{next}}$ is the estimated next step size. By default KOSMA-t uses $\text{eps} = 0.01$ and $\text{yscal} = \{1\} \times [\text{htry} \times n+1 \times 10^{-21} \text{cm}^{-3}] \times \text{htry}$ (see Press et al. 2007) for details. It is also possible to alter the value of htry depending on local conditions to influence the performance of the iteration in terms of accuracy and total computation time.

A disadvantage of the adaptive stepping is that testing for global convergence is not straightforward. In contrast to models with fixed spatial grids one cannot easily compare densities and population numbers between each iteration and check whether a given equilibrium is met because the spatial grid changes between iterations. One obvious solution is of course to define a spatial reference grid and interpolate the resulting structure of each iteration to this grid. However, this introduces the additional error of the interpolation to the numerical uncertainty of the solution. We nevertheless offer this option in a coming version of the code.

B.1. Steady-state chemistry details

KOSMA-t offers a variety of solution approaches to solve Eq. 25 such as the DLSODA (Hindmarsh 2019) and the DVODPK from the ODEPACK package (Hindmarsh 1988). We also implemented the option to use other numerical solvers, such as the DLSODA (Hindmarsh 2019) and the DVODPK from the ODEPACK package (Hindmarsh 1988). Some low J transitions show signs of level inversion that are unlikely to appear in practice. Some low J transitions show signs of level inversion that are unlikely to appear in practice. The variable temperature models show a larger variation in CPU times. In general, the time to find a stable solution is 10-1000 times longer compared to the “F” models. For almost all problems, allowing the code to use a time-dependent solution as fallback as in case of convergence difficulties decreases the total CPU time by a significant factor. This was the case for the V1 problem using DGSV. The choice of linear system solver moderately affects CPU times. Using DGSV yields CPU times up to a factor 2 longer compared to the DLSODES solver in case the local chemical solution did not converge. The variable temperature models show a larger variation in CPU times. In general, the time to find a stable solution is 10-1000 times longer compared to the “F” models. For almost all problems, allowing the code to use a time-dependent solution as fallback as in case of convergence difficulties decreases the total CPU time by a significant factor. This was the case for the V1 problem using DGSV. The choice of linear system solver moderately affects the total CPU times. Using DGSV yields CPU times up to a factor 2 longer compared to the DLSODES solver in case the local chemical solution did not converge. We can summarize that the approach of using the DLSODES as fallback solver in case the linear solvers fail is successful and leads to a stabilization of the system, in particular if one considers the additional non-linearity introduced by the choice of the chemical network, as described in Sect. B.2. It is also surprising that it is difficult to predict solve the 8 benchmark problems from (Röllig et al. 2007) and compare the individual results against each other and against the PDR benchmark results. We use the set of model parameters as described in (Röllig et al. 2007) and the same chemical database with the addition of state-to-state formation rates of CH$^+$ and SH$^+$ (Agúndez et al. 2010; Nagy et al. 2013). Changes to the past KOSMA-t setup are the updated UV radiative transfer and dust temperature computation (Röllig et al. 2013), H$_2$ self-shielding according to Drouart & Berthold (1998), CO self-shielding according to Visscher et al. (2009), updated heating and cooling computations and improved numerics. Surface chemistry is ignored and H$_2$ formation is simplified as described in (Röllig et al. 2007).

Table B.1 shows the total CPU time used by the different model setups for the 8 benchmark problems. The numbers in parenthesis give the results for runs where the time-dependent solver DLSODES was used as fallback of the stationary solver in case the local chemical solution did not converge. For the models with fixed temperatures, the choice of the steady-state solver does not significantly affect the total CPU time; all models finish with in about half a minute. The fast model convergence results from removing the requirement of a self-consistent temperature solution for the problem. Fig. 2 shows that this simplifies the “Local iteration” to solving the chemistry and the energy level populations. As a result the global iteration reaches convergence after about 4 iterations. Computing the time-dependent approximation to the steady-state solution converges also after 4-6 iterations. Models F1, F3, and F4 required about $10^4$ total chemical iterations while F2 required $>10^5$ iterations.

We also implemented the option to use other numerical solvers, such as the DLSODA (Hindmarsh 2019) and the DVODPK from the ODEPACK package (Hindmarsh 1988). Some low J transitions show signs of level inversion that are unlikely to appear in practice.

During the first global iteration and for every first spatial step in all subsequent iterations we use a relaxed value of $\text{eps} = 0.05$. DGSV fails primarily when the matrix $\text{Q}$ is rank deficient, which is usually an effect of a stiff system of ODEs together with problematic numerics from other parts of the computation.

We also implemented the option to use other numerical solvers, such as the DLSODA (Hindmarsh 2019) and the DVODPK from the Netlib library dvodpk (http://www.netlib.org/ode/) and MA28, the advance solver of sparse systems of linear equations from the HSL library (http://www.hsl.rl.ac.uk/).

Algorithm: Chemistry 1 Solution

\[
\begin{align*}
T_{\tau} & \rightarrow T_{\tau,\text{int}} \\
\text{while iterationcounter} & < 600 \text{ do} \\
& \text{compute } f^2 \\
& \text{compute } Q \\
& \text{apply preconditioning} \\
& \text{Solve } Q \cdot \delta i = f^2 \text{ for } \delta i \\
& \text{converged } \leftrightarrow \text{ TRUE} \\
& \text{forkeach species } i \text{ do} \\
& \text{if } n(i) > 10^{-3} \text{ cm}^{-3} \text{ then} \\
& \quad \delta n(i) \leftarrow \delta n(i) \text{ if } \eta_i > 0.05 \text{ AND } n(i) > 10^{-15} \text{ cm}^{-3} \text{ then} \\
& \quad \text{converged } \leftrightarrow \text{ FALSE} \\
& \text{end if} \\
& \text{if } n(i)_{\text{new}} \leftrightarrow n(i)_{\text{shift}}(\eta_i) \text{ then} \\
& \quad \text{end if} \\
& \text{end if} \text{ if converged then return } n_{\text{new}} \\
& \text{end if} \text{ end while} \\
& \text{Apply fallback strategy, e.g. call DLSODES} \\
& \quad \text{not converged} \\
& \quad \text{not converged}
\end{align*}
\]

B.1.1. Benchmark of the chemical solver

In this section we compare how the different approaches to solve the chemical network perform in terms of total CPU time and overall solution accuracy. We

18 Some low J transitions show signs of level inversion that are unlikely to appear in practice.

19 During the first global iteration and for every first spatial step in all subsequent iterations we use a relaxed value of $\text{eps} = 0.05$.

20 DGSV fails primarily when the matrix $\text{Q}$ is rank deficient, which is usually an effect of a stiff system of ODEs together with problematic numerics from other parts of the computation.

21 We also implemented the option to use other numerical solvers, such as the DLSODA (Hindmarsh 2019) and the DVODPK from the Netlib library dvodpk (http://www.netlib.org/ode/) and MA28, the advance solver of sparse systems of linear equations from the HSL library (http://www.hsl.rl.ac.uk/).

22 Computed by the Intel FORTRAN routine cpu_time. The time returned is summed over all active threads. The result is the sum (in units of seconds) of the current process’s user time and the user and system time of all its child processes, if any.
computation times depending on the parameter regime especially across different numerical solvers.

B.2. Numerical aspects of solving the chemical problem

Few publications on numerical details of solving the chemical network in the astrochemical context are available in the scientific literature. Nejad (2005) gives an extensive overview over available numerical solvers and methods to improve stability and speed of the solution. An important quantifier is the computational complexity of the solving algorithm, i.e. the number of computational operations necessary to solve the problem. In terms of solving Eq. (28), we need to invert \( \mathbf{Q} \) in order to determine the new density vector \( \mathbf{δ} \). Inverting a \( N \times N \) matrix using classical Gaussian elimination can be done in \( O(N^3) \) steps. Note, that this is also the cost of classically multiplying two \( N \times N \) matrices. More advanced algorithms can perform matrix multiplications in fewer steps. For example, Strassen (1969) presented an algorithm that performs matrix multiplication with complexity \( O(N^{\log_2 7}) \). For large problems this is a non-negligible improvement.

For the LU decomposition applied in the routines DGEYS and DGESVX we find an approximate complexity of \( O(3N^3) \). Please note, that the number of chemical reactions does not influence the time to solve the problem, but it does influence the time to set up the system Eq. (28). Since the rate coefficients involve expensive operations such as exponential functions and fractional powers, increasing the number of reactions might lead to increased CPU running times of the code. This can be partially compensated by pre-computing and storing computationally expensive expression that don’t change during the chemical iteration.

In the following we will discuss various strategies to reformulate the chemical problem in a mathematically equivalent but numerically more favorable way.

B.2.1. Preconditioning of the Jacobi matrix

Matrix preconditioning in the context of solving stiff systems of ODEs is a wide and technical topic. Nejad (2005) gives an extended discussion on preconditioning. Here, we would like to present a simple yet sometimes helpful preconditioning strategy that can be used in KOSMA-\( \tau \) if numerical convergence is problematic, e.g. due to round-off errors. With preconditioning, we mean a transformation of the system from Eq. (28) to the following form (Viallet et al. 2016):

\[
- (L^{-1} Q R) (R^{-1} δ) = (L^{-1} F)
\]

where \( δ \) = \( (d^{\text{new}} - d^{\text{old}}) \) and \( L \) and \( R \) are the left and right preconditioning matrices. Various choices for \( L \) and \( R \) are possible and KOSMA-\( \tau \) employs the following definition: \( L = R = \text{diag}(d^{\text{old}}) \) where \( \text{diag}(\cdot) \) specifies a diagonal matrix with vector \( \cdot \) as diagonal elements and all other elements set to zero. In index notation we can write:

\[
\tilde{F}_j = F_j / L_j = F_j / n_j
\]

with the row index \( j \) of the right hand side vector \( F \) and \( L_j \) the non-zero element in row \( j \) of \( L \). The tilde denotes the preconditioned version of the original vector/matrix. The Jacobi matrix is computed with:

\[
\tilde{Q}_{i,j} = Q_{i,j} / L_j = \tilde{Q}_{i,j} / n_j
\]
where $R_j$ the non-zero element in row $j$ of $R$. The new system Eq. (B.1) solves for $R^{-1} \delta n$ and we have to multiply the solution with $R$ to get the final solution. Another strategy discussed in Nejad (2005) is to perform a row-reorder in the system Eq. (28). The idea is to make use of the sparsity of the problem, which is common in astrochemical computations because most chemical species react with few reaction partners and because many reaction rates are effectively zero in many circumstances. It is numerically favorable if large sub-matrices of the Jacobi matrix are null matrices. Modern solvers of systems ODEs and linear problems are often optimized to invert sparse matrices efficiently.

If we reorder the rows for example by the descending count of zero elements per row in the Jacobi matrix we get a new matrix with large sub-matrices with zero elements which might improve solution speed. KOSMA-τ allows to perform a row reordering such that rows of $Q$ with the most zero elements are at the top and the densest rows at the bottom. The inverse scheme would also be an option and we advice any interested modeler to experiment with either scheme. Because of the high magnitude difference in chemical densities of the involved species we find a large variance in the magnitudes of the Jacobi matrix entries. This might reduce efficiency of the solution and re-scaling the system is an option to somewhat assist the algorithms. We offer the option to re-scale every row in Eq. (25) such that the maximum entry in the respective Jacobi matrix row is unity.

In cases where KOSMA-τ tries to approximate a steady-state solution by solving the time-dependent system for a sufficiently long time $t_{\text{equil}}$, we apply the additional heuristic scaling factor $1/(10^{-2}t_{\text{equil}})$ to the row scaling. We mention this here as experimental approach and invite other groups to perform additional tests.
Fig. A.5: Chemical structure changes with FUV strength. \( n = 10^4 \) cm\(^{-3} \). Solid lines indicate pure gas-phase chemistry, dashed lines correspond to the gas+surface chemistry using the CR\(_2\) model.

Table B.1: Total PDR benchmark CPU time (in units of s) with different chemical solvers.

| Model | DGESV | DGESVX | DSGESV | DLSODES |
|-------|-------|--------|--------|---------|
|       | Fixed temperature models |       |        |         |
| F1    | 21    | 22     | 21     | 129     |
| \((n = 10^3, \chi = 10)\) | (24)  | (24)   | (23)   |          |
| F2    | 34    | 36     | 33     | 131     |
| \((n = 10^3, \chi = 10^5)\) | (32)  | (35)   | (30)   |          |
| F3    | 9     | 8      | 14     | 90      |
| \((n = 10^5, \chi = 10)\) | (10)  | (10)   | (10)   |          |
| F4    | 10    | 9      | 9      | 210     |
| \((n = 10^5, \chi = 10^5)\) | (11)  | (11)   | (11)   |          |
|       | Variable temperature models |       |        |         |
| V1    | 17449 | 17090  | ~      | 3285    |
| \((n = 10^3, \chi = 10)\) | (466) | (621)  | (492)  |          |
| V2    | 1897  | 4816   | 3371   | 3743    |
| \((n = 10^3, \chi = 10^3)\) | (514) | (645)  | (599)  |          |
| V3    | 1524  | 2488   | 4414   | 9803    |
| \((n = 10^5, \chi = 10)\) | (1686) | (3026) | (1411) |          |
| V4    | 1664  | 1912   | 1812   | 23592   |
| \((n = 10^5, \chi = 10^5)\) | (179) | (1303) | (1489) |          |

Notes. The numbers in parenthesis give the results for runs where a time-dependent solver was used as backup approach after the stationary solver failed. The last column corresponds to runs where DLSODES was immediately used instead of a steady-state solver. (\sim\) indicates jobs stopped after 60 iterations. All computations were done on a 8-core Intel(R) Xeon(R) CPU E5-2630 v3 2.40GHz with 64 GB memory. No parallelization was applied. Densities \( n \) are given in units of cm\(^{-3} \).

Results. A performance analysis of the introduced numerical tweaks in full detail is beyond the scope of this paper. Their performance and their applicability depends on detailed model parameters. We performed test computations against a reference model of \( n_0 = 10^6 \) cm\(^{-3} \) with pure gas-phase chemistry solving for the steady-state without any preconditioning. The following scenarios have been tested:

1. pre-conditioned Jacobian as described in Sect. [B.2.1],
2. Jacobian and r.h.s vector re-scaled to unity first AND precondition the re-scaled Jacobian,
3. the (already) pre-conditioned Jacobian and r.h.s vector re-scaled to unity,
4. resorted Jacobian with dense rows first,
5. re-scaled AND resorted Jacobian with dense rows first,
6. re-scaled AND resorted Jacobian with sparse rows first,
7. adaptive choice of elemental conservation rows in \( Q \), replacing the most abundant species,
8. adaptive choice of elemental conservation rows in \( Q \), replacing the least abundant species.

In Table B.2 we summarize the number of global iterations for each of the described variations plus the total computation time. The first row shows the reference computation applying no preconditioning. Preconditioning the Jacobian with \( L \) and \( R \) (strategy 1) shows the strongest impact in terms of performance while all others lead to comparable computation times or even a much worse performance. This will also depend on the detailed chemical network used and the parameter regime. It demonstrates though that the computational effort to solve the chemical problem depends strongly on the detailed numerical approach even though they are all mathematically equivalent. From the CPU times shown in Table B.2 we conclude that the LR-preconditioning outlined in Sect. [B.2.1] performs best. Currently, the standard setup in KOSMA-\( \tau \) is no preconditioning until a more systematic parameter study for typical PDR model parameter ranges has been performed.

Appendix C: Newton-Raphson stepping

Historically, KOSMA-\( \tau \) used the following ArcTan stepping:

\[
f_{\text{step}, \lambda}(\tau) = 1 + \lambda \frac{2}{\pi} \arctan \left( \frac{\pi}{2} \tau \right)
\]

with \( \lambda = 0.9 \). The scaling by \( (2/\pi) \) limits the second term to the range \( \pm 1 \) and the pre-factor of \( \lambda = 0.9 \) limits \( f_{\text{step}, \lambda} \) to the range 0.1, ..., 1.9 and damps the slope.
around the origin to 0.9. The stepper in Eq. C.1 has several advantages over the linear stepper in Eq. B.2: it prohibits steps into the negative domain and ensures positive densities; it is almost Newtonian for small relative steps \( \eta \) and therefore converges fast once it is sufficiently close to the root; it prohibits too wide and too small steps because \( 1 - \lambda \leq f_{\text{step,}\eta}(\eta) \leq 1 + \lambda \eta \) (see Fig. C.1).

An alternative approach is a modification of Eq. B.2 to only prevent Newton steps through the negative domain:

\[
f_{\text{step,N}}(\eta) = \begin{cases} 
(1 - \eta)^{-1} & \text{if } \eta < 0 \\
1 + \eta & \text{if } \eta > 0
\end{cases}
\]  

(C.2)

By construction \( f_{\text{step,N}}(\eta) = f_{\text{step}}(\eta) \) guarantees a positive stepping factor. Eq. B.2 converges to zero for large negative steps \( \eta \ll -1 \). It is also symmetric in the log-domain, e.g., for \( \eta = 1 \) we find \( m(y)^{10} = 2 \times 10^{y} \), and conversely \( \eta = -1 \) returns \( m(y)^{-10} = m(y)^{1/2} \). However, this stepper diverges for large positive steps, \( \eta \gg 1 \) and the symmetry between negative and positive steps may lead to oscillations around the actual solution.

Inheriting from both approaches we construct a more general stepping function \( f_{\text{step,Tanh}} \) (see Eq. B.3), whose symmetry and limits can be controlled with few numerical parameters. The min/max values of \( f_{\text{step,Tanh}} \) are given by

\[
\lim_{\eta \to -\infty} f_{\text{step,Tanh}}(\eta) = \begin{cases} 
(1 + \lambda(\omega_{\eta} - 1))^{-1} & \text{if } \eta < 0 \\
1 + \lambda(\omega_{\eta} - 1) & \text{if } \eta \geq 0
\end{cases}
\]  

(C.3)

Consequently, \( \omega_{\eta} \) controls the maximum factor to increase \( n(y) \) and \( \omega_{\lambda} \) controls the minimum factor for decrease. Choosing slightly different values for \( \omega_{\eta} \) and \( \omega_{\lambda} \) avoids oscillations in symmetric problems.

The slope \( f_{\text{step,Tanh}}(\eta) \) for small \( \eta \), i.e., close to the solution, is given by \( \lambda \). A value close to unity guarantees the quadratic convergence behavior of the Newton-Raphson method for small values of \( \eta \). However, far from the minimum of a function \( f \), a full Newton-Raphson step not necessarily decreases the function. We only know that the stepping direction initially decreases \( f \). Reducing the step width by a damping parameter \( \lambda < 1 \) then limits non-convergent steps (Fig. C.2).

Figure C.2 compares the discussed \( f_{\text{step}} \) variants. The log-lot inset shows the symmetry of \( f_{\text{step,Tanh}} \) that can be controlled by \( \omega_{\eta} \) and \( \omega_{\lambda} \). We see how the Tanh remains closer to the linear Newton behavior for larger \( \eta \) compared to the ArcTan. Note, that the ArcTan stepper \( f_{\text{step,ArcTan}} \) can be reasonably well approximated with \( \omega_{\eta} = 11, \omega_{\lambda} = 2 \), and \( \lambda = 0.9 \).

C.1. Choosing efficient stepping strategies

Ideally, one would like to find a single optimal stepping strategy to reliably solve the Newton-Raphson scheme. In the numerical PDR context this turns out to be a demanding task. We tested a large variety of different steppers and compound stepping strategies. We computed a small grid of models with 107 species including surface species (see Table 4). The model density (constant), mass and FUV strength. There is no clear correlation with the density and with model FUV strength. There is no clear correlation with the density and with model FUV strength.

However, the values from Table C.1 do not generally confirm this assumptions. At first glance the total number of steps shows no clear correlation with \( \lambda \) but we note that missing models distort the row totals, e.g., (10, 5, 0.5) and (10, 0.6) did not converge for high density models each. These models typically took significant number of steps to reach the true solution. There is no clear correlation with the model mass.

As \( \lambda \) determines the slope of the stepping function for small arguments one would assume that solutions are found more quickly for \( \lambda \) closer to unity. However, the values from Table C.1 do not generally confirm this assumptions, we find many counterexamples. At first glance the total number of steps shows no clear correlation with \( \lambda \) but we note that missing models distort the row totals, e.g., (10, 5, 0.5) and (10, 0.6) did not converge for high density models each. These models typically took significant number of steps to finish and are not included in the row total. When approximately accounting for the missing models there is a slight performance improvement with increasing \( \lambda \) excluding the case of \( \lambda = 1 \). Generally, symmetric choices of \( \omega_{\eta} = \omega_{\lambda} \) tend to perform worse than runs with \( \omega_{\eta} > \omega_{\lambda} \).

A general conclusion from Table C.1 is that for low to intermediate densities the details of the Newton-Raphson stepping are hardly affecting the number of steps with the exception of a few cases that failed to converge. The high density model performance shows a much higher variance with stepping, with some models performing up to 10 times worse than others and some even more extreme cases.

Computations where we did not discard the density vector after the last Newton-Raphson step even if convergence was not yet reached (subscript \( \text{new} \)) led to non-converging models overall but successfully reached convergence in some cases where the standard approach failed. In particular the choice of \( \omega_{\eta} = 11, \omega_{\lambda} = 2 \), and \( \lambda = 0.9 \) seems to perform better in the \( \text{new} \) case.

For a given set of PDR parameters it is possible to find an optimized set of stepping parameters \( \omega_{\eta}, \omega_{\lambda}, \lambda \) that will minimize the computing time. Changing the PDR parameters may significantly change the topography of the Newtonian vector field \( \delta \) and consequently may require a modified stepping strategy to succeed. To mitigate these complications we tested a compound strategy, named adaptive 1 in Table C.1. In this approach we change the stepping parameters along the Newton search to find a chemical solution. Our general approach is to use a relatively robust stepping strategy for the first 100 Newton-Raphson steps. Typically, 99.99% of all solution attempts require less than 30-40
steps. If the standard stepper is not successful after 100 steps, it will most likely not converge at all, e.g. because of oscillating or global non-convergent behavior. If the standard stepper is not successful after 100 steps, it will most likely not converge at all, e.g. because of oscillating or global non-convergent behavior. If the more careful stepping is unable to escape a local minimum we allow for large values of $ω$ for the next 100 steps, followed by stronger damping by reducing $λ$. If the more careful stepping is unable to escape a local minimum we allow for large values of $ω$ for the next 100 steps, followed by stronger damping by reducing $λ$.

adapt 1

if $start ≤ 100$

use $s_{new}$

else if $101 ≤ # steps ≤ 200$

use $s_{new}$, $n=0$

> start again from $s_{new}$

else if $201 ≤ # steps ≤ 400$

use $s_{new}$, $n=0$

else if $401 ≤ # steps ≤ 500$

use $s_{new}$, $n=0$

> start again from $s_{new}$

end if

In its final stepping attempt, adapt 1 applies a more aggressive stepper setup. In addition, it restarts the root search from the initial density after 100 and again after 400 steps. The large number of Newton steps computed in some models highlights the importance of the stepper choice. Comparing the adapt 1 and the single step strategies shows better performance for the adapt strategy across all PDR parameters. adapt 1 performs well with 1/2 total Newton steps for the whole grid compared to the reference stepper $s_{ref}$. From Table C1, we conclude that adapt 1 is the most successful algorithm.

Appendix D: Chemical network

D.1. Gas-phase chemistry

The gas-phase chemistry in KOSMA-τ is based on the UDFA12 database with updates listed in Table D1. It contains the following reaction types: For two-body reactions the Arrhenius form for the rate coefficient is

$$k = \frac{a}{r^6} \exp(-\gamma r)$$

with the parameters $a, \beta, \gamma$ tabulated in the database. UDFA12 distinguished between the following two-body reactions: neutral-neutral, ion-neutral, charge exchange, ion-neutral, ion-neutral, dissociative recombination, radiative recombination, associative electron detachment and radiative ionization. In addition it contains two direct photo-processes: photo-dissociation and photo-ionization both described by

$$k = f_s n_0 \exp(-\gamma A)$$

and the extinction by interstellar dust at visible wavelengths $\alpha$. The unit-less (self-)shielding factor $f_s$, and the extinction by interstellar dust at visible wavelengths $\alpha$.

Table D1: Changes and addition to the UDFA12 reaction network

| Reaction | $a$ ($\times 10^{10}$) | $\beta$ | $\gamma$ | Ref. |
|----------|--------------------------|-------|-------|------|
| $CH_5 + H → CH_3 + CH_2$ | 1.74 | 0.00 | 0.3 | (1) |
| $N_2 + H → N_2H + e^-$ | 1.70 | 0.00 | 4.3 | (2) |
| $H_2 + F → H_2F^+$ | 4.80 | 0.00 | 0.0 | (3) |
| $CH_4 + O → OH + H,CO$ | 0.06 | 0.00 | 0.0 | (4) |
| $CH_5 + O → CH_4 + CH_2$ | 0.13 | 0.00 | 0.0 | (5) |
| $CH_5 + O → CH_3 + CH_2$ | 0.160 | 0.00 | 2.4 | (6) |
| $CH_5 + OH → H + CH_3$ | 2.00 | 0.00 | 0.0 | (7) |
| $CH_3OH + OH → H_2O + CH_3$ | 0.006 | -1.02 | 0.0 | (8) |
| $CH_3OH + H_2O → CH_3 + H_2O$ | 3.88 | 0.00 | 0.0 | (9) |
| $CO + CO → CO_2 + H_2$ | 0.26 | 0.00 | 0.0 | (10) |
| $CO + HCO → CO + CH_3$ | 1.50 | 0.00 | 0.0 | (11) |
| $CO + H → H + HCO$ | 0.30 | 0.00 | 0.0 | (12) |
| $CO + H_2 → H + HCO$ | 0.04 | 0.00 | 0.0 | (13) |
| $CO + CH_3 → H + CH_3CO$ | 0.04 | 0.00 | 0.0 | (14) |
| $CO + C → CO + CH_3$ | 0.04 | 0.00 | 0.0 | (15) |
| $CH_3OH + CH_3 → CO + CH_4$ | 1.14 | 0.00 | 0.0 | (16) |
| $CH_3OH + CH_3 → CO + CH_4$ | 1.18 | 0.00 | 0.0 | (17) |
| $CH_3OH + CH_3 → CO + CH_4$ | 2.00 | 0.00 | 0.0 | (18) |

References:
(1) Grosch et al. (2015); (2) Keller-Rudek et al. (2013); (3) Cook et al. (1968); (4) Neufeld et al. (2005); (5) Raad et al. (2015); (6) Hebrard et al. (2009); (7) Baulch et al. (2005); (8) Atkinson et al. (2006)
Direct cosmic-ray ionization is described by

\[ k = \epsilon_H \]  

and cosmic-ray induced photo-processes with a rate

\[ k = \epsilon_H (T/300K)^\gamma (1 - \omega) \]  

where \( \epsilon_H \) is the CR ionization rate per \( H_2 \). \( \gamma \) describes the probability per CR ionization that a photo-process takes place and \( \omega \) is the dust grain albedo in the FUV [McEwen et al. 2013]. We assume \( \omega = 0.5 \).

For reactions with isotopes we use the same rate coefficients as for the standard isotopologue with the addition of the fractionation reactions listed in Table D.2. Reaction rates for the reactions \( c - C_2H_2 + \) HE, \( c - C_2H_2 + \) CH, \( c - C_2H_2 + \) H, and \( c - C_2H_2 + \) HE have been replace with rate coefficients from KIDA [Wakelam et al. 2015]. New reactions involving the linear isomers \( 1 - C_2H_2, 1 - C_2H_3, 1 - C_2H_5, 1 - C_2H_2 \) have also been taken from KIDA.

Table D.2: Updated fractionation reactions

| reaction | \( \alpha \times 10^{-10} \) | \( \beta \) | \( \gamma \) |
|----------|----------------|---------|---------|
| \( ^{13}C^1C + CO \rightarrow C^1 + ^{13}CO \) | 4.42 | -0.29 | 0.0 |
| \( ^{13}C^2C + CO \rightarrow C^2 + ^{13}CO \) | 4.42 | -0.29 | 34.5 |
| \( ^{13}C^2C + CO \rightarrow C^1 + ^{13}CO \) | 4.42 | -0.29 | 0.0 |
| \( ^{13}C^2C + CO \rightarrow C^2 + ^{13}CO \) | 4.42 | -0.29 | 35.4 |
| \( HCO^+ + CO \rightarrow H^1CO + CO \) | 2.83 | -0.26 | 0.0 |
| \( HCO^+ + CO \rightarrow H^2CO + CO \) | 2.83 | -0.26 | 17.8 |
| \( HCO^+ + ^{13}CO \rightarrow H^1CO^+ + ^{13}CO \) | 2.83 | -0.26 | 0.0 |
| \( HCO^+ + ^{13}CO \rightarrow H^2CO^+ + ^{13}CO \) | 2.83 | -0.26 | 17.8 |
| \( HCO^+ + CO \rightarrow H^1CO + CO \) | 2.83 | -0.29 | 0.0 |
| \( HCO^+ + CO \rightarrow H^2CO + CO \) | 2.83 | -0.29 | 6.4 |
| \( HCO^+ + ^{13}CO \rightarrow H^1CO^+ + ^{13}CO \) | 2.83 | -0.29 | 0.0 |
| \( HCO^+ + ^{13}CO \rightarrow H^2CO^+ + ^{13}CO \) | 2.83 | -0.29 | 6.4 |
| \( HCO^+ + CO \rightarrow H^1CO + CO \) | 3.14 | -0.27 | 0.0 |
| \( HCO^+ + ^{13}CO \rightarrow H^1CO^+ + ^{13}CO \) | 3.14 | -0.27 | 24.2 |
| \( HCO^+ + CO \rightarrow H^1CO + CO \) | 2.87 | -0.22 | 0.0 |
| \( HCO^+ + CO \rightarrow H^1CO + CO \) | 2.87 | -0.22 | 11.4 |

References: [Mladenović & Roueff 2014]

D.2. Surface chemistry

We follow the rate equation approach as described in [Hasegawa et al. 1992], [Hasegawa & Herbst 1993] and account for competing surface processes (Garrod & Paully 2011) and chemically inactive bulk ice. The species on the surface need to be mobile in order to scan the surface for a suitable reaction partner. The thermal hopping time scale to move between adjacent binding sites on the surface is given by [Hasegawa et al. 1992] as

\[ t_{hopp} = v_{ij} \exp (E_B / T_d) \]  

with the characteristic vibration frequency for the adsorbed species

\[ v_{ij} = (2\pi \hbar k_B E_D / \sigma_i n_i m_i)^{1/2} \]  

where \( n_i \) is the surface density of binding sites and \( m \) is the mass of the particle and \( k_B \) is the Boltzmann constant. We assume \( n_i = 1.5 \times 10^{14} \text{cm}^{-2} \) [Tieler & Allamandola 1987]. \( E_D \) is the desorption energy for physical desorption, \( E_{Dj} \) is the energy barrier between binding sites. Note, that in this section all energies \( E_D, E_B, E_a \) are given in units of K. Following [Hasegawa et al. 1992] we assume \( E_D = 0.3E_{Dj} \). For H and H2 tunneling might also be a more rapid migration process compared to thermal hopping with a tunneling time:

\[ t_{tunnel} = v_{ij} \exp \left( 2\alpha_i \hbar / (2\pi m_i k_B E_{Dj}) \right) \]  

where \( \alpha_i = \Delta \) is the energy barrier width assuming a rectangular barrier [Garrod & Paully 2011]. Note, that Eq. (D.7) is not valid for particles heavier than H2. The time for an adsorbed particle to sweep over a number of binding sites is \( t_{diff} \), and the diffusion rate \( R_{diff} \) is defined as the inverse of the diffusion time

\[ t_{diff} = N^S \times \text{max}(t_{hopp}, t_{tunnel}) \]  

where \( N_S \) is the total number of surface sites per grain. The surface reaction rate coefficient can then be written as:

\[ k_j = f_{diff} (R_{diff} + R_{tunnel}) \]  

where \( f_{diff} \) is the number density of dust grains. The denominator gives the total number of surface binding sites. The probability that a reaction occurs is given by \( f_{diff} \) and is assumed to be unity for an exothermic reaction without activation energy \( \epsilon \). For an exothermic reaction between surface species \( i \) and \( j \) with activation energy \( E_{ij} \), the probability of reaction during a single collision between the reactants can be expressed as a Boltzmann factor \( \exp \left( -E_{ij}/T_d \right) \) or using the quantum mechanical tunneling probability. Later probability is only relevant for light species and we apply it only if one of the reactants is H(0) or H(1).

\[ k_{ij} = \max \left( \exp \left( -E_{ij}/T_d \right), \exp \left( -2a/h(2\mu_j k_B E_{ij})^{1/2} \right) \right) \]  

where \( \mu_i = m_i/n_i/\sigma_i \) and \( \mu_j = m_j/n_j/\sigma_j \) is the reduced mass. During the collision between \( i \) and \( j \) overcoming the activation energy barrier is in competition with the migration of either reactant to a neighbor site and with desorption of either reactant. We use the reaction probability \( f_{diff} \) as described by [Chang et al. 2007], Garrod & Paully [2011] to account for the competing processes in case an activation energy barrier exists

\[ f_{diff} = \mu_{ij} + \mu_{ij} + \mu_{ij} + \mu_{ij} \]  

with \( \mu_i = \max(n_i, \nu_i) \) and \( \mu_j = \max(n_j, \nu_j) \) and the species dependent diffusion rate coefficient \( K_{ij} = \mu_{ij} \) is a placeholder for species \( i \) and \( j \). \( K_{ij} \) is the sum of all desorption probabilities.

Accretion

The adsorption or accretion rate coefficient depends on the thermal velocity of the incoming particles \( \nu_{ij} \), the total effective cross section area of all target grains \( \sigma_{dust} \), and the sticking coefficient \( S(T, T_d) \) as:

\[ \nu_{ij} = \sigma_{dust} \nu_i S(T, T_d) \]  

with the mean thermal velocity

\[ \nu_i = \sqrt{8k_BT_i/\pi m_i} \]  

For the sticking of H we use the coefficient provided by [Hollenbach & McKee 1979] their Eq. (3.7), in case of H2 we assume \( S(T, T_d) = 0.5 \) [Acharyya 2014] and for any other species we assume \( S(T, T_d) = 1/3 \) [Willacy & Williams 1993].

Thermal desorption

Species on the grain surface are removed depending on the grain surface and the their binding energy \( E_{Dj} \), which is itself a function of the grain material and ice composition. The rate coefficient is given by

\[ K_{cormqj} = \nu_{ij} \exp (-E_{Dj}/T_d) \]  

where \( \nu_{ij} \) is from Eq. (D.5).

H2 formation induced desorption

The H2 binding energy of 4.48 eV is released during the formation process. It is commonly assumed that the energy is distributed evenly between internal energy and kinetic energy of the desorbed molecule and lattice energy of the surface. This local "hotspot"-heating of the surface may be sufficient to desorb additional species. Following [Willacy et al. 1994] we apply this only for species with a binding energy of less than 1210 kJ/mol [Roberts et al. 2007]. The rate coefficient is:

\[ K_{H2des} = \epsilon R_{ij} n_i \nu_{ij} \]  

where \( R_{ij} \) is the desorption rate from the grain [Röllig et al. 2013] and \( \epsilon \) measures the number of atoms and molecules that are desorbed by this process. The value of \( \epsilon \) is uncertain and we assume a low efficiency of \( \epsilon = 0.01 \). Division by the total density of all surface species \( n_i = \sum n_i \) distributes the binding energy across all species on the grain. Depending on the value of \( \epsilon \) this process can dominate other desorption processes and we found it to significantly contribute to the overall desorption. For a more detailed analysis see [Roberts et al. 2007] and more recently [von Procházka & Millar 2021].
Table D.3: Photo-desorption yields

| species | $Y_i$ | Ref |
|---------|-------|-----|
| O$_3$N$_2$O | 10$^{-4}$ | (1) |
| H$_2$O$_2$+H$_2$O | 10$^{-3}$(1.3 + 0.032 $T_J$)(1 - $e^{-x(T)}$) | (2) |
| H$_2$O $\rightarrow$ OH + H | 2 $\times$ 10$^{-3}$ | (3) |
| CO$_{18}$CO,CO$_{13}$CO,CO$_{13}$CHO | 10$^{-2}$ | (4) |

Notes. $Y_i = 10^{-3}$ for all other species. x is the ice thickness in ML, $h(T)$ = 0.6 + 0.24$f_T$.

References. (1) Hollenbach et al. [2009]. (2) Oberg et al. [2009]. (3) Andersson & van Dishoeck [2008]. (4) Fayolle et al. [2011].

Photo-desorption

The absorption of UV photons at the dust surface can sufficiently increase the internal energy of the surface species to induce desorption. Following [Cuppen et al. [2017]] we write the rate coefficient for photo-desorption as:

$$K_{ph\text{-}}des = \frac{1}{n_{i\text{tot}}} \sigma_{	ext{dust}} Y_i F_{Draine} (f_{\text{exp}} \exp(-\gamma A_T)) \text{s}^{-1} \quad (D.15)$$

where $Y_i$ is the photo-desorption yield per UV photon. Experimental data on $Y_i$ is available only for very few species and we assume a general value of $Y_i = 10^{-3}$ (molecules/photon) except for the species listed in Table D.3 For H$_2$O we use the expressions given by [Oberg et al. 2009] accounting for ice thickness and gas and dust temperature (see also Aikawa et al. 1996; Woitke et al. 2009). $F_{Draine}$ is the fraction of all surface species that are considered candidates for desorption. $f_{\text{exp}} = f_{\text{dust}}$, where $f_{\text{dust}}$ is the fraction of particles that can undergo surface reactions. Note, that the effects of ice opacity to FUV radiation and the fact that photo-desorption only occurs from the top few monolayers of the ice is implicitly included in the photo-desorption yields [Cuppen et al. 2017].

Total desorption

The total desorption rate coefficient is the sum of all individual desorption rate coefficients:

$$K_{des} = K_{\text{des}} + K_{\text{chem\text{-}}des} + f_{\text{surf}} K_{\text{chem\text{-}}des} \quad (D.16)$$

where $f_{\text{surf}}$ describes the fraction of all surface species that are considered candidates for desorption:

$$f_{\text{surf}} = \frac{1}{2} \frac{\sum n_{\text{surf}}}{\sum n_{\text{site}}} \quad (D.17)$$

where $\sum n_{\text{surf}}$ gives the total number of all grain surface binding sites per volume summed over all grains (see also [Aikawa et al. 1996]). In Eq. D.17 we make the assumption that surface species from the top two layers of the ice mantle can desorb to the gas phase [Aikawa et al. 1996]. For the chemical desorption we assume $f_{\text{surf}} = f_{\text{dust}}$, where $f_{\text{surf}}$ is the fraction of particles that can undergo surface reactions. Note, that the effects of ice opacity to FUV radiation and the fact that photo-desorption only occurs from the top few monolayers of the ice is implicitly included in the photo-desorption yields [Cuppen et al. 2017].

Table D.4: Chemical desorption reactions.

| reaction | $\Delta H_f$ (eV) | BR | $E_a$ (K) |
|----------|-----------------|----|----------|
| J(O$_3$H) + J(H) $\rightarrow$ OH + OH | 1.47 | 0 | 0 |
| J(O$_3$H) + J(H) $\rightarrow$ J(OH) + OH | 1.47 | 0 | 0 |
| J(O$_3$H) + J(H) $\rightarrow$ J(OH) + J(OH) | 1.47 | 0 | 0 |
| J(O$_3$H) + J(H) $\rightarrow$ J(H$_2$O) | 3.69 | 0 | 0 |
| J(O$_3$H) + J(H) $\rightarrow$ J(H$_2$O) | 3.69 | 0 | 0 |
| J(HCO) + J(H) $\rightarrow$ HCO | 3.91 | 0 | 0 |
| J(HCO) + J(H) $\rightarrow$ J(HCO) | 3.91 | 0 | 0 |
| J(HCO) + J(H) $\rightarrow$ CO + H$_2$ | 3.85 | 0.43 | 130 |
| J(HCO) + J(H) $\rightarrow$ CO + H$_2$ | 3.85 | 0.35 | 130 |
| J(HCO) + J(H) $\rightarrow$ J(OH) + J(H) | 3.85 | 0.12 | 130 |
| J(HCO) + J(H) $\rightarrow$ J(OH) + J(H) | 3.85 | 0.10 | 130 |
| J(HCO) + J(H) $\rightarrow$ CH$_2$O | 0.66 | 0 | 0 |
| J(HCO) + J(H) $\rightarrow$ J(CH$_2$O) | 0.66 | 0 | 0 |
| J(HCO) + J(H) $\rightarrow$ J(CH$_2$O) | 0.66 | 0 | 0 |
| J(HCO) + J(H) $\rightarrow$ J(CH$_2$O) | 0.66 | 0 | 0 |
| J(HCO) + J(H) $\rightarrow$ J(CH$_2$O) | 0.66 | 0 | 0 |
| J(HCO) + J(H) $\rightarrow$ J(CH$_2$O) | 0.66 | 0 | 0 |
| J(HCO) + J(H) $\rightarrow$ J(CH$_2$O) | 0.66 | 0 | 0 |
| J(HCO) + J(H) $\rightarrow$ J(CH$_2$O) | 0.66 | 0 | 0 |
| J(HCO) + J(H) $\rightarrow$ J(CH$_2$O) | 0.66 | 0 | 0 |
| J(HCO) + J(H) $\rightarrow$ J(CH$_2$O) | 0.66 | 0 | 0 |
| J(HCO) + J(H) $\rightarrow$ J(CH$_2$O) | 0.66 | 0 | 0 |

Notation: We denote surface reaction rate coefficients with a capital $K_i$ and gas phase reaction rate coefficients with a lower-case $k_i$.

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Cosmic ray heating

The interaction of energetic cosmic ray protons with H and H₂ produces hot electrons that transfer their energy to the ISM in the following collisions. A detailed treatment as been presented by Glassgold et al. (2012). Generally, the heating rate of cosmic rays can be written as:

\[ \Gamma_\text{CR} = \frac{4}{3} \pi n_e q_s \beta^2 \ \text{erg s}^{-1} \text{cm}^{-3} \]  

(E.7)

where \( \Gamma_\text{CR} \) is the CR ionization rate per H nucleus in \( \text{s}^{-1} \) and \( Q \) is the average energy deposited as heat per ionization. Glassgold et al. (2012) provide values of \( Q \) for different interstellar environments as function of total density (their Table 6). \( Q \) can then be approximated by the following expression:

\[ Q(x) = 1.60218 \times 10^{-12} \times (4.37 \times 0.238 + 0.4624 \times e^{0.425x}) \ \text{erg} \]  

(E.8)

with \( x = \log_{10}(n/\text{cm}^{-3}) \). The pre-factor converts from eV to erg.

Grain photo-electric heating

The heating by hot electrons released during photo-electric (PE) absorption of FUV photons by dust particles is the most important PDR heating process under most circumstances. The photo-electrons can also recombine with the grains and cool the gas with a rate \( \Lambda_\text{PE} \), therefore \( \Gamma_\text{PE} = \Gamma_\text{GR} - \Lambda_\text{PE} \). KOSMA-\( \tau \) offers a choice of how to treat PE heating \( \Gamma_\text{PE} \). The user can decide which approximation of the PE heating (and electron recombination) to use. We implemented the description given by Barnes & Tielens (1994) (their Eqs. (41),(43),(44)) and by Weingartner & Draine (2001c) (their Eqs. (44),(45) and Table 2 and 3). They mainly differ in the applied dust size distributions and the estimates for photoelectric thresholds, yields, and electron capture rates. See Röllig et al. (2015) for more details.

Gas-grain collisions

Collision between gas particles and dust grains can transfer energy between the two. If the gas is hotter than the grains the collisions cool the gas. If the gas is cooler the collisions act as gas heating (Burke & Hollenbach, 1983) give the rate as

\[ \Lambda_\text{GR} = n_d \sigma_T \frac{8K^2}{m_d} \left( \frac{1}{r_{\text{ff}}} \right)^{1/2} \bar{\alpha}_T \Delta g \left( T_g - T_d \right) \ \text{erg s}^{-1} \text{cm}^{-3} \]  

(E.9)

We apply an approximate accommodation factor \( \bar{\alpha}_T = 0.3 \) when using the PE heating description by Barnes & Tielens (1994). In case of the PE heating described by Weingartner & Draine (2001c) we employ a modified accommodation factor given by Groenewegen (1994):

\[ \bar{\alpha}_T = 0.35 \exp \left( - \frac{T_d - T_x}{500K} \right) + 0.1 \]  

(E.10)

Carbon ionization

The ionization of atomic carbon releases hot electrons with an energy of about 1 eV = 1.602 \times 10^{7} \text{erg}. We approximate the heating rate by

\[ \Lambda_{\text{C}} = 2.2 \times 10^{22} \text{erg s}^{-1} n(C)_{\text{FUV}} \]  

(E.11)

Line cooling

Details on the computation of atomic and molecular line cooling can also be found elsewhere (e.g. Tielens & Hollenbach, 1985; Sternberg & Dalgarno, 1989; Röllig et al. 2006; Woitek et al. 2009; Papadopoulos et al. 2011). Following Sternberg (1980) the general expression for the cooling rate due to a transition from level \( i \) to level \( j \) of species \( s \) is:

\[ \Lambda_{ij}s = n_i A_{ij}s \beta(\tau_{ij}) - B_{ij}s \beta(\tau_{ij}) n_j \ \text{erg s}^{-1} \text{cm}^{-3} \]  

(E.12)

where \( A_{ij}s \) and \( B_{ij}s \) are the Einstein coefficients, \( n_i \) is the level population of level \( i \), \( n_j \) is the external radiation at the transition frequency \( v_{ij} \) and \( \beta(\tau_{ij}) \) is the escape probability at the optical depth \( \tau \). For all cooling lines we compute \( \tau \) from the perpendicular column density of the respective species. We use the expression for a spherical cloud given by Stutzki & Winnewisser (1985):

\[ \beta(\tau) = \frac{1}{\sqrt{\pi}} \int_0^{\infty} e^{-\xi^2} d\xi \]  

Line cooling

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\[ \Lambda_{ij}s = n_i A_{ij}s \beta(\tau_{ij}) - B_{ij}s \beta(\tau_{ij}) n_j \ \text{erg s}^{-1} \text{cm}^{-3} \]  

(E.12)

where \( A_{ij}s \) and \( B_{ij}s \) are the Einstein coefficients, \( n_i \) is the level population of level \( i \), \( n_j \) is the external radiation at the transition frequency \( v_{ij} \) and \( \beta(\tau_{ij}) \) is the escape probability at the optical depth \( \tau \). For all cooling lines we compute \( \tau \) from the perpendicular column density of the respective species. We use the expression for a spherical cloud given by Stutzki & Winnewisser (1985):

\[ \beta(\tau) = \frac{1}{\sqrt{\pi}} \int_0^{\infty} e^{-\xi^2} d\xi \]  

(E.13)

Details on the computation of atomic and molecular line cooling can also be found elsewhere (e.g. Tielens & Hollenbach, 1985; Sternberg & Dalgarno, 1980; Röllig et al. 2006; Woitek et al. 2009; Papadopoulos et al. 2011). Following Sternberg (1980) the general expression for the cooling rate due to a transition from level \( i \) to level \( j \) of species \( s \) is:

\[ \Lambda_{ij}s = n_i A_{ij}s \beta(\tau_{ij}) - B_{ij}s \beta(\tau_{ij}) n_j \ \text{erg s}^{-1} \text{cm}^{-3} \]  

(E.12)

where \( A_{ij}s \) and \( B_{ij}s \) are the Einstein coefficients, \( n_i \) is the level population of level \( i \), \( n_j \) is the external radiation at the transition frequency \( v_{ij} \) and \( \beta(\tau_{ij}) \) is the escape probability at the optical depth \( \tau \). For all cooling lines we compute \( \tau \) from the perpendicular column density of the respective species. We use the expression for a spherical cloud given by Stutzki & Winnewisser (1985):

\[ \beta(\tau) = \frac{1}{\sqrt{\pi}} \int_0^{\infty} e^{-\xi^2} d\xi \]  

(E.13)
Table E.1: Fine-structure and rotational line cooling data

| species | \( i \) | \( j \) | \( \Delta_{ij} \) (\( \mu \)m) | \( \Delta_{ij} \) (s\(^{-1}\)) | collision | \( \alpha \) | \( \beta \) | Ref |
|---------|-------|------|----------------|----------------|----------|-----|-----|-----|
| C\(^{3}\) | \( ^{2}P_{3/2} \) | \( ^{2}P_{1/2} \) | 157.7 | 2.29(6) | C\(^{\ast} \) + H | 3.71(10) | 0.15 | (1) |
| C\(^{3}\) | \( ^{3}P \) | \( ^{3}P \) | 609.1 | 7.93(8) | C\(^{\ast} \) + H | 1.01(10) | 0.117 | (4) |
| C\(^{3}\) | \( ^{3}P \) | \( ^{3}P \) | 230.3 | 1.71(14) | C\(^{\ast} \) + p-H\(_{2}\) | 8.00(11) | 0 | (5) |
| C\(^{3}\) | \( ^{3}P \) | \( ^{3}P \) | 370.4 | 2.65(7) | C\(^{\ast} \) + o-H\(_{2}\) | 7.50(11) | 0 | (5) |
| C\(^{3}\) | \( ^{3}P \) | \( ^{3}P \) | 370.4 | 2.65(7) | C\(^{\ast} \) + p-H\(_{2}\) | 4.49(11) | 0.194 | (4) |
| C\(^{3}\) | \( ^{3}P \) | \( ^{3}P \) | 370.4 | 2.65(7) | C\(^{\ast} \) + o-H\(_{2}\) | 3.54(11) | 0.167 | (5) |
| O\(^{3}\) | \( ^{3}P \) | \( ^{3}P \) | 63.2 | 8.91(5) | C\(^{\ast} \) + H | 1.87(11) | 0.539 | (6), (7) |
| O\(^{3}\) | \( ^{3}P \) | \( ^{3}P \) | 44.1 | 1.34(10) | C\(^{\ast} \) + p-H\(_{2}\) | 3.46(11) | 0.316 | (5) |
| O\(^{3}\) | \( ^{3}P \) | \( ^{3}P \) | 145.5 | 1.75(5) | C\(^{\ast} \) + o-H\(_{2}\) | 2.10(12) | 0.841 | (6), (7) |
| O\(^{3}\) | \( ^{3}P \) | \( ^{3}P \) | 145.5 | 1.75(5) | O + H \(_{2}\) | 7.07(11) | 0.268 | (5) |
| O\(^{3}\) | \( ^{3}P \) | \( ^{3}P \) | 145.5 | 1.75(5) | O + p-H\(_{2}\) | 5.49(11) | 0.317 | (5) |
| O\(^{3}\) | \( ^{3}P \) | \( ^{3}P \) | 145.5 | 1.75(5) | O + o-H\(_{2}\) | 2.52(10) | 0.169 | (6), (7) |
| O\(^{3}\) | \( ^{3}P \) | \( ^{3}P \) | 145.5 | 1.75(5) | O + p-H\(_{2}\) | 1.44(11) | 1.109 | (5) |
| O\(^{3}\) | \( ^{3}P \) | \( ^{3}P \) | 145.5 | 1.75(5) | O + o-H\(_{2}\) | 4.64(11) | 0.976 | (5) |
| Si\(^{3}\) | \( ^{2}P_{3/2} \) | \( ^{2}P_{1/2} \) | 34.8 | 2.20(4) | Si\(^{\ast} \) + H | 6.50(10) | 0 | (8) |
| CO, CO\(^{3}\) | J + 1 | J | tabulated | CO + p-H\(_{2}\) | tabulated | (9), (10) |
| OH | J, \( \Omega \), \( \rho \) | \( J', \Omega', \rho' \) | tabulated | OH + H\(_{2}\) | tabulated | (11), (12) |
is implemented in KOSMA-$\tau$ and visualization capabilities of Mathematica.

To make use of the advanced analysis, numerics to seamlessly integrate the toy PDR model into our research infrastructure and to make use of the advanced analysis, numerics (Wolfram Research Inc. 2020) to seamlessly integrate the toy PDR model into the internals of PDR codes. We ported PyPDR to Mathematica by Wolfram Research is used as an educational tool to learn about the basic physics and some numerical internals of PDR codes. We ported PyPDR to Mathematica by Wolfram Research (Wolfram Research Inc. 2020) to seamlessly integrate the toy PDR model into our research infrastructure and to make use of the advanced analysis, numerics and visualization capabilities of Mathematica.

The features of WL-PDR are:

- Plane-parallel, semi-infinite plane-parallel PDR model geometry
- One-side, uni-directional, perpendicular FUV illumination
- Non-LTE excitation of [O I], [C II], [C I], CO, $^{13}$CO, CH, CH$^+$, and HCO$^+$ using an escape probability approach. The molecular data is stored in the format of the LAMDA database (Schoier et al. 2005).
- Time dependent chemistry: The chemical abundances are solved by evolving the chemical rate equations up to a certain chemical age.
- AccuracyGoal→$\log_{10}(n \times 10^{-10})$, i.e. atol=1e-10*n
- PrecisionGoal→10, i.e. rtol=1e-10
- MaxSteps→$10^3$
- The thermal balance is solved self-consistently with the chemistry iteratively.
- Self-shielding factors for CO are from Visser et al. (2009)
- Heating and cooling rates are implemented for:
  - $H_2$ processes (Röllig et al. 2006), line cooling (Röllig et al. 2006), formation- and dissociation processes (Sternberg & Dalgarno 1989, Jonkheid et al. 2004)
  - Gas-grain heating/cooling (Tielens 2005)
  - Photoelectric heating and recombination cooling (Bakes & Tielens 1994)
  - Ly-$\alpha$ cooling (Sternberg & Dalgarno 1989)
  - Optical Oxygen-6300 A cooling (Sternberg & Dalgarno 1989)
  - Heating by C-ionization and cosmic rays (Jonkheid et al. 2004)
  - Line cooling by [O I], [C II], [C I] (fine structure), CO, $^{13}$CO, CH, CH$^+$, and HCO$^+$ (rotational) assuming a thermalized $H_2$ ortho/para ratio

The model output is:
- $A_V$ grid
- Abundances (cm$^{-3}$)
- Column densities to the edge of the PDR (cm$^{-2}$)

| $M_i$ ($M_{\odot}$) | $N_i$ | $m_{ij}$ (cm$^{-3}$) | $R_i$ (pc) | $N_i \times$ area (pc$^2$) | $V_i$ (cm$^{-3}$) | $N_i \times V_i$ (cm$^{-3}$) | $N_i \times M_i$ ($M_{\odot}$) |
|-------------------|------|-----------------|------------|---------------------|--------------|---------------------|---------------------|
| 0.001             | 24250.4 | 0.842 | 3.7 $\times$ 10$^3$ | 0.0300 | 0.67 (0.084) | 3.2 $\times$ 10$^{48}$ | 7.75 $\times$ 10$^{52}$ | 24.3 (0.024) |
| 0.01              | 3843.44 | 0.133 | 1.9 $\times$ 10$^5$ | 0.0081 | 0.78 (0.099) | 6.44 $\times$ 10$^{49}$ | 2.48 $\times$ 10$^{53}$ | 38.4 (0.038) |
| 0.1               | 609.144 | 0.021 | 9.2 $\times$ 10$^4$ | 0.0219 | 0.92 (0.116) | 1.30 $\times$ 10$^{51}$ | 7.91 $\times$ 10$^{55}$ | 60.9 (0.061) |
| 1                 | 96.5428 | 0.003 | 4.6 $\times$ 10$^4$ | 0.0597 | 1.08 (0.136) | 2.62 $\times$ 10$^{52}$ | 2.53 $\times$ 10$^{54}$ | 96.5 (0.097) |
| 10                | 15.301  | 10$^{-1}$ | 2.3 $\times$ 10$^3$ | 0.162 | 1.27 (0.159) | 5.27 $\times$ 10$^{52}$ | 8.07 $\times$ 10$^{56}$ | 153.0 (0.153) |
| 100               | 2.42504 | 10$^{-4}$ | 1.1 $\times$ 10$^3$ | 0.442 | 1.49 (0.187) | 1.06 $\times$ 10$^{55}$ | 2.58 $\times$ 10$^{58}$ | 242.5 (0.243) |
| 1000              | 0.384344 | 10$^{-5}$ | 5.6 $\times$ 10$^1$ | 1.2 | 1.75 (0.22) | 2.14 $\times$ 10$^{56}$ | 8.23 $\times$ 10$^{59}$ | 384.3 (0.384) |

| total | 28817.7 | 7.96 | 1.2 $\times$ 10$^{50}$ | 1000.0 |

Notes. We use the following ensemble parameters: $M_{\text{ens}} = 1000 M_{\odot}$, $r_{\text{ens}} = 10^6$ cm$^{-3}$, $\alpha = 1.8$, and $\gamma = 2.3$. Numbers in parenthesis indicate the fraction in the column total.

The integral is taken over all masses in the range [m$_i$, m$_j$]. Full radiative transfer is implemented in KOSMA-$\tau$-3D (Andree-Labsch et al. 2017).

Appendix G: WL-PDR - A sandbox PDR model code written in Wolfram Mathematica

It is useful to reduce the numerical complexity of a model to in order to better study numerical or physical aspects of the model. For some numerical tests in this paper we use the simple 1-D, semi-infinite plane-parallel PDR model code WL-PDR. The code is ported to Mathematica from PyPDR (Bruderer 2019). PyPDR is used as an educational tool to learn about the basic physics and some numerical internals of PDR codes. We ported PyPDR to Mathematica by Wolfram Research to seamlessly integrate the toy PDR model into our research infrastructure and to make use of the advanced analysis, numerics and visualization capabilities of Mathematica.

The code can be downloaded at <https://github.com/markusroellig/WL-PDR>.