Diagnostics of irradiated gas in galaxy nuclei

I. A far-ultraviolet and X-ray dominated region code

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Abstract. We present a far-ultraviolet (PDR) and an X-ray dominated region (XDR) code. We include and discuss thermal and chemical processes that pertain to irradiated gas. An elaborate chemical network is used and a careful treatment of PAHs and H\textsubscript{2} formation, destruction and excitation is included. For both codes we calculate four depth-dependent models for different densities and radiation fields, relevant to conditions in starburst galaxies and active galactic nuclei. A detailed comparison between PDR and XDR physics is made for total gas column densities between \(\sim 10^{21}\) and \(\sim 10^{25}\) cm\textsuperscript{-2}. We show cumulative line intensities for a number of fine-structure lines (e.g., [CII], [OI], [CI], [SiII], [FeII]), as well as cumulative column densities and column density ratios for a number of species (e.g., CO/H\textsubscript{2}, CO/C, HCO\textsuperscript{+}/HCN, HNC/HCN). The comparison between the results for the PDR and XDRs shows that column density ratios are almost constant up to \(N_{\text{H}} \approx 10^{22}\) cm\textsuperscript{-2} for XDRs, unlike those in PDRs. For example, CO/C in PDRs changes over four orders of magnitude from the edge to \(N_{\text{H}} = 10^{22}\) cm\textsuperscript{-2}. The CO/C and CO/H\textsubscript{2} ratios are lower in XDRs at low column densities and rise at \(N_{\text{H}} > 10^{23}\) cm\textsuperscript{-2}. At most column densities \(N_{\text{H}} > 10^{23}\) cm\textsuperscript{-2}, HNC/HCN ratios are lower in XDRs too, but they show a more moderate increase at higher \(N_{\text{H}}\).

Key words. astrochemistry – galaxies: starburst – galaxies: active

1. Introduction

Gas clouds in the inner kpc of many galaxies are exposed to intense radiation, which can originate from an active galactic nucleus (AGN), starburst regions or both. O and B stars dominate the radiation from starbursts, which is mostly in the far-ultraviolet (6.0 < \(E < 13.6\) eV), turning cloud surfaces into Photon Dominated Regions (PDRs, Tielens & Hollenbach 1985). Hard X-rays (\(E > 1\) keV) from black hole environments (AGN) penetrate deep into cloud volumes creating X-ray Dominated Regions (XDRs, Maloney et al. 1996). For each X-ray energy there is a characteristic depth where photon absorption occurs. So for different spectral shapes, one has different thermal and chemical structures through the cloud. Although one source can dominate energetically over the other (e.g., an AGN in NGC 1068 or a starburst in NGC 253), the very different physics (surface vs. volume) requires that both should be considered simultaneously in each galaxy.

In PDRs and XDRs, the chemical structure and thermal balance are completely determined by the radiation field. Therefore, PDRs and XDRs are direct manifestations of the energy balance of interstellar gas and their study allows one to determine how the ISM survives the presence of stars and AGN (Tielens & Hollenbach 1985; Boland & de Jong 1982; van Dishoeck & Black 1988; Le Bourlot et al. 1993; Wolfire et al. 1993; Spaans et al. 1994; Sternberg & Dalgarno 1995; Storzer et al. 1998; Spaans 1996; Bertoldi & Draine 1996; Maloney et al. 1996; Lee et al. 1996; Kaufman et al. 1999; Le Petit et al. 2002, and references therein).

PDRs and XDRs have become increasingly important as diagnostic tools of astrophysical environments with the advent of infrared and (sub-)millimetre telescopes. PDRs emit fine-structure lines of [CI] 609, [CII] 158 and [OI] 63 \(\mu\)m; rotational lines of CO; ro-vibrational and pure rotational lines of H\textsubscript{2}; many H\textsubscript{2}O lines as well as many broad mid-IR features associated with Polycyclic Aromatic Hydrocarbons (PAHs). In PDRs, the bulk of H\textsubscript{2} is converted into atomic hydrogen at the edge and CO to neutral carbon into ionised carbon. XDRs emit brightly in the [OI] 63, [CII] 158, [SiIII] 35, and the [FeII] 1.26, 1.64 \(\mu\)m lines as well as the 2 \(\mu\)m ro-vibrational H\textsubscript{2} transitions. The abundance of neutral carbon in XDRs is elevated compared to that in PDRs and the chemical transitions from H to H\textsubscript{2} and C\textsuperscript{+} to C to CO are smoother (Maloney et al. 1996).

In this paper, we compare a far-ultraviolet and X-ray dominated region code. For the PDR and XDR, we discuss the cooling, heating and chemical processes. Then we show four
models with different radiation fields and densities, for a semi-
infinite slab geometry and irradiation from one side without geo-
metrical dilution. We conclude with a comparison between the
column densities, integrated line fluxes and abundance ratios.
We will apply this tool to the centres of nearby active galaxies
in subsequent papers. These codes can be used over a broad
range of physical situations and scales, e.g., young stellar ob-
jects, planetary nebulae or gas outflow in galaxy clusters.

2. The photon dominated region model

The global properties of PDRs are determined by a number of
physical processes:

i. Heating through photo-electric emission by dust grains and
PAHs (cf. Bakes & Tielens 1994; Weingartner & Draine
2001).

ii. Heating by FUV pumping of H₂, followed by collisional


and 63 μm (cf. Tielens & Hollenbach 1985; Spaans et al.
1994).

v. Molecular line cooling by warm molecular gas containing
CO, H₂, H₂O, OH and CH (cf. Neufeld et al. 1995; Spaans
& Silk 2000).

vi. Ion-molecule reactions driven by the ionisation degree
of \( \sim 10^{-4} \) maintained by the ionisation of carbon in the FUV

vii. The ionisation balance of atomic gas under the influence
of photo-ionisation reactions driven by FUV photons and
counteracting recombination and charge transfer reactions with
metals and particularly PAHs (cf. Lepp & Dalgarno
1988; Bakes & Tielens 1994).

As one moves into a PDR the extinction along the line of
sight increases and the impinging radiation field is attenuated.
Consequently, there are two zones over which the chemi-
cal composition of the PDR changes in a fundamental way.
The first fundamental change occurs at the edge of the PDR
as atomic hydrogen is converted into H₂ because the Lyman
and Werner electronic bands that lead to dissociation of the
H₂ molecule in the FUV become optically thick (so-called self-
shielding). Deeper into the PDR, at about 3 mag of extinction,
ionised carbon is quickly converted into neutral form as the
FUV flux decreases due to dust absorption. C is subsequently
transformed into CO, since the FUV field is reduced by grain
opacity, H₂ shielding and some CO self-shielding.

The first few magnitudes of extinction of the PDR are usu-
ally referred to as the radical region since many carbon hy-
drides and their ions, e.g., CH, CH⁺, CN, HCN, HCO⁺ (and
also CO⁺), reach their peak abundance there, caused by the
presence of both C⁺ and H₂ and the high (\( \sim 10^{3} \) to \( 10^{5} \) K)
temperatures. Ion-molecule reactions take place that lead to the for-
mation of a large number of different molecular species. Many
of the atoms and molecules in the radical region of a PDR
are collisionally excited at the ambient densities and tempera-
tures, and emit brightly in the mid-IR, FIR, millimetre and
sub-millimetre.

<table>
<thead>
<tr>
<th>Table 1. Adopted model parameters.</th>
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<tr>
<td>Model</td>
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<tr>
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<td>3</td>
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<tr>
<td>4</td>
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</table>

The global characteristics of any PDR are defined by a few
key parameters:

i. The strength of the impinging radiation field, \( G_0 \) or \( I_{\text{FUV}} \), in
units of the Habing (1969) or Draine (1978) radiation field,
respectively, determines the total available radiative flux at
the edge of the PDR.

ii. The temperature and the ambient hydrogen density, \( n_H = \sqrt{m(H)+2m(H_2)} \), sets to a large extent the pace of the chemical
reactions and the excitation rates of the coolants.

iii. The metallicity \( Z \), in units of the solar value \( Z_{\odot} \), constrains
the total abundances possible for carbon- and oxygen-
bearing species and hence influences the chemical and ther-
mal structure.

iv. The spectral shape of the impinging radiation field, param-
eterised by the colour temperature \( T_{\text{eff}} \) for black bodies or
the frequency slope for power laws, fixes the distribution of
photon flux over energy.

The details about the thermal and chemical processes we use
in the code are discussed in the appendices. In the rest of the
paper we use \( G_0 \), the Habing flux, as the normalisation in which
we express the incident FUV radiation field, where \( G_0 = 1 \)
corresponds to a flux of \( 1.6 \times 10^{-3} \text{ erg cm}^{-2} \text{ s}^{-1} \).

3. PDR test models

In this section, we discuss the results for four PDR models in
which we have varied the radiation field \( G_0 \) and the density \( n_H \).
The models are for a semi-infinite slab geometry, but the code
also allows for two-sided slab geometries. The adopted model
parameters are listed in Table 1. Models 2 and 4 will be shown
in a paper by Röllig et al. (in prep.), where they are used to
compare 12 different PDR codes that are commonly used. The
parameters are listed in Table 1. These values are typical for
the high density, strong radiation field conditions we want to
investigate in, e.g., a starburst.

The fixed gas-phase and total abundances we use are given
in Table 2. The total abundances are the average values of
Asplund et al. (2004) and Jenkins (2004). To calculate the gas-
phase abundances, we use the depletion factors calculated by
Table 2. Abundances.

<table>
<thead>
<tr>
<th>Species</th>
<th>( \mathcal{A} ) (gas)</th>
<th>( \delta_i )</th>
<th>( \mathcal{A} ) (total)</th>
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<td>( 8.5 \times 10^{-2} )</td>
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<tr>
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<td>( 2.5 \times 10^{-4} )</td>
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<td>( 7.2 \times 10^{-6} )</td>
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<tr>
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<td>0.7</td>
<td>( 4.7 \times 10^{-6} )</td>
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<tr>
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<td>( 3.4 \times 10^{-6} )</td>
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<tr>
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<tr>
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<tr>
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<tr>
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</tr>
<tr>
<td>Ca</td>
<td>( 2.0 \times 10^{-6} )</td>
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<tr>
<td>Cr</td>
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</tr>
<tr>
<td>Ni</td>
<td>( 1.7 \times 10^{-6} )</td>
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<td></td>
</tr>
</tbody>
</table>

Notes:
\begin{itemize}
  \item \( a \) Present in both PDR and XDR chemical network.
  \item \( b \) Present in PDR chemical network.
  \item \( c \) Used to calculate \( \sigma_{\text{ff}} \) for XDR.
\end{itemize}

3.1. Heating and cooling

For both radiation fields and densities, the dominant source heating to a column density \( N_\text{H} \approx 10^{22} \text{ cm}^{-2} \) is photo-electric emission from grains. In the moderately low density, low radiation-field Model 1, viscous heating is about equally important in this range. For Model 2 where the radiation field is increased, it contributes somewhat more than 10 percent. For the low radiation-field, high density Model 3, carbon ionisation is the second most important heating source. In Model 4, where the radiation field is increased compared to Model 3, \( \text{H}_2 \) pumping is the second most important. At high column densities (\( N_\text{H} > 22.5 \text{ cm}^{-2} \)), [OI] 63 \( \mu \text{m} \) absorption and gas-grain heating are important. For the low density PDRs Model 1 and 2, only [OI] 63 \( \mu \text{m} \) dominates. When the density is increased in Models 3 and 4, gas-grain heating is equally important if not dominant. Other heating processes contribute less than 10 percent, but are sometimes important in determining the thermal balance.

In all models [OI] 63 \( \mu \text{m} \) cooling dominates to \( N_\text{H} = 10^{21.5} \text{ cm}^{-2} \). In the low density PDRs, [CII] 158 \( \mu \text{m} \) cooling contributes more than ten percent of the cooling in this range, whereas at high densities, gas-grain cooling is the second most important coolant. In the high density, high radiation-field Model 4, this contribution can be almost forty percent. Deeper in the cloud, [CI] 610 \( \mu \text{m} \) and CO line cooling become important. \( \text{H}_2 \) line cooling can contribute up to 10 percent of the total cooling rate at some point, but is always a minor coolant.

3.2. Chemical and thermal structure

The \( H \rightarrow \text{H}_2 \) and \( C^+ \rightarrow C \rightarrow \text{CO} \) transitions are quite sharp. Their actual location varies greatly, since this is strongly dependent on density and radiation field. Exposed to stronger radiation fields, the transitions occur deeper in the cloud, since the photo-dissociation rates are larger. At higher densities, the transitions occur closer to the surface of the cloud, since the recombinations rates scale as \( n^2 \). For the same reason, the \( H^+ \) and \( O^+ \) fractional abundances are systematically higher in the low density models. SiO and CS are more abundant and formed closer to the surface in the high density models, which is also the case for HCO\(^+\), HCN, HNC and \( C_2\text{H} \).

The edge temperatures (see Fig. 6) are affected most by the strength of the radiation field when the density is largest. At a density of \( N_\text{H} \approx 10^{23} \text{ cm}^{-3} \), the difference is a factor of thirty for an increase from \( G_0 = 10^3 \) to \( G_0 = 10^5 \). In the low density case this is only a factor of two. Because of optical depth effects, CO cooling is less effective at high column densities. For this reason, temperatures rise again at \( N_\text{H} \approx 10^{22} \text{ cm}^{-2} \) in the low density models.

4. The X-ray dominated region model

Unlike PDRs, XDRs are mostly heated by direct photo-ionisation of the gas, which produces fast electrons that lose energy through collisions with other electrons, as well as \( H \) and \( \text{H}_2 \). These fast electrons collisionally excite \( H \) and \( \text{H}_2 \), which subsequently emit Lyman \( \alpha \) and Lyman-Werner band photons, respectively. These photons in turn are capable of ionising atoms such as C and Si or ionise and dissociate molecules such as \( \text{H}_2 \) and CO.

Compared to PDRs, the following processes play a role in XDRs (cf. Maloney et al. 1996), in part because of the production of UV photons as described above:

- Photo-ionisation heating (i.e., Coulomb heating with thermal electrons) dominates by a large factor over the heating through photo-electric emission by dust grains and PAHs (cf. Maloney et al. 1996; Bakes & Tielens 1994).
- Emission from meta-stable lines of [CII] 9823, 9850 \( \AA \) and [OI] 6300 \( \AA \); fine-structure line cooling of [CII] 158 and [OI] 63 and 146 \( \mu \text{m} \) as well as Lyman \( \alpha \) emission (cf. Maloney et al. 1996; Tielens & Hollenbach 1985; Spaans et al. 1994). Molecular line cooling by warm molecular gas containing CO, \( \text{H}_2 \), H\(_2\)O and OH as well as gas-grain cooling where warm gas is cooled at the surfaces of lower temperature dust grains (cf. Neufeld et al. 1995; Spaans & Silk 2000).
- Ion-molecule reactions driven by the ionisation degree of \( \sim 10^{-4} \) maintained by the ionisation of carbon in the FUV (cf. Black & Dalgarno 1977; van Dishoeck & Black 1986).

The ionisation balance of atomic gas under the influence of photo-ionisation reactions driven by X-ray photons
and charge transfer. Recombination of ions on grain surfaces is a major ionic loss route at electron fractions less than $10^{-3}$ (cf. Lepp & Dalgarno 1988; Bakes & Tielens 1994; Maloney et al. 1996).

The global structure of any XDR is defined by a few key parameters: the density $n_H$ and the energy deposition rate $H_X$ (see Appendix E) per hydrogen atom. Because the heating in XDRs is driven by photo-ionisation, the heating efficiency is close to unity as opposed to that in PDRs where the photo-electric heating efficiency is of the order of $0.3-1.0\%$ (Maloney et al. 1996; Bakes & Tielens 1994). Unlike PDRs, XDRs are exposed to X-rays as well as FUV photons.

As one moves into the XDR, X-ray photons are attenuated due to atomic electronic absorptions. The lowest energy photons are attenuated most strongly, which leads to a dependence of the X-ray heating and ionisation rates at a given point on the slope of the X-ray spectrum. We assume, for energies between 0.1 and 10 keV, that the primary ionisation rate of hydrogen is negligible compared to the secondary ionisation rate and that Auger electrons contribute an energy that is equal to the photo-ionisation threshold energy (Voit 1991).

The treatment is described in the Appendices and follows, in part, the unpublished and little-known work by Yan (1997). Also, we extend the work of Maloney et al. (1996) in terms of depth dependence, $H_2$ excitation and extent of the chemical network.

5. XDR test models

In this section, we consider four models with the same energy inputs and densities as the PDRs in Table 1. The spectral energy distribution is of the form $\exp(-E/1\text{keV})$. The energy is emitted between 1 and 10 keV and $F_{\text{FUV}}$ should be replaced by $F_X$ in Table 1. This spectral shape and spectral range can be changed depending on the application. We take the parameters for the 1 keV electron to determine the electron energy deposition, since these parameters do not change for higher energies. When the spectral energy distribution is shifted towards higher energies, the X-rays will dominate a larger volume, since the absorption cross sections are smaller for higher energies.

$H_X/n$ is the most important parameter for the chemical and thermal balance, where $H_X$ is the energy deposition rate per hydrogen nucleus. The abundances used are given in Table 2. The elements H, He, C, N, O, Si, S, Cl and Fe are included in the chemical network. The other elements listed are only used to calculate the photoelectric absorption cross section, $\sigma_{\text{pa}}$.

5.1. Heating and cooling

In Fig. 1, the different heating sources are shown as a function of the total hydrogen column density, $N_H$. All heating is done by X-rays, but the way it is transferred to the gas depends on the ionisation fraction. When the gas is highly ionised, $x_e \sim 0.1$, most (~70\%) of the kinetic energy of the non-thermal electrons goes into Coulomb heating, which is the case in Models 1, 2 and 4 where $H_X/n$ is high to $N_H > 10^{23} \text{cm}^{-2}$. For smaller ionisation fractions, $x_e \sim 10^{-5}$, ionisation heating as discussed in Sect. B.2 is important or even dominant. In Model 3, ionisation heating and Coulomb heating are equally important at $N_H < 10^{21.8} \text{cm}^{-2}$. In all models ionisation heating dominates especially at high column densities. When the excitation of $H_2$ is dominated by non-thermal processes, collisional quenching of $H_2$ can heat the gas. Naively, one would expect this...
dominance to occur where most of the X-rays are absorbed, but for high energy deposition rates $H_X/n$, the temperature is high and thermal collisions dominate the population of the vibrational levels. Non-thermal excitation is dominant at low temperature, i.e., low $H_X/n$.

In Fig. 2, the important cooling processes are shown as a function of total hydrogen column density, $N_H$. At high temperatures (see Fig. 3), cooling by [CI] 9823, 9850 Å and [OI] 6300 Å metastable lines dominates, as is the case in the models with high radiation fields, Models 2 and 4. At lower temperatures, most of the cooling is provided by the fine-structure line [OI] 63 μm (90%), e.g., at the edge in the low-radiation field Models 1 and 3. In each model, gas-grain cooling dominates for low $H_X/n$. In addition, specific cooling processes can be important in special cases. $H_2$ vibrational cooling dominates at large depths in Model 2, but in Models 1, 3 and 4 it contributes no more than 10%. $H_2$ vibrational cooling is split into a radiative and a collisional part. When the excitation of $H_2$ is dominated by non-thermal electrons, the gas is heated by collisional de-excitation of $H_2$.

### 5.2. Thermal and chemical structure

In Fig. 3, we show the temperature as a function of total hydrogen column density, $N_H$. Variations in radiation field strength most strongly affect the high-density models. The temperature at the edge differs a factor of 30 in the high-density case. Since X-rays penetrate much deeper into a cloud than FUV photons, high temperatures are maintained to much greater depths into the clouds. $H_X/n$ is very important in determining the thermal balance. When $H_X/n$ is larger, this results in a higher temperature. Therefore, Model 2 has the largest temperature throughout the cloud. Density turns out to be important as well. Note that models 1 and 4 have similar incident $H_X/n$ and therefore have about the same temperature throughout the cloud.

In Figs. 3 and 4, we show the fractional abundances of selected species. $H_X/n$ is not only important in the thermal balance, but also in the chemistry. Therefore Models 1 and 4 with about the same incident $H_X/n$, show similar abundances. The most striking difference with the PDR models is that there is no longer a well-defined transition layer $C^+ \rightarrow C \rightarrow CO$ present. On the contrary, both $C$ and $C^+$ are present throughout most of the cloud having fractional abundances of $\sim 10^{-5} - 10^{-4}$. Only at very low $H_X/n$, which results in a low temperature, is there a partial transition to CO. The transition from atomic to molecular hydrogen is much more gradual than in the PDR models. A considerable amount of OH is present in all models at all column densities. The temperature determined by $H_X/n$ is important. In Model 3, OH has the greatest abundance ($>10^{-6}$) at all column densities. In other models such large fractions are seen only at very high depths into the cloud. The formation of CO and H$_2$O is most efficient at high densities and low $H_X/n$. Therefore, these species have large abundances throughout the high-density, low-radiation field Model 3. In Model 4, where the radiation field is somewhat higher, CO and H$_2$O reach high abundances only at high $N_H$. At low densities, they are only formed at large depths into the cloud (Models 1 and 2). Secondary ionisations are most important for the production of $H^+$. Recombination is slower at lower densities. Therefore, the $H^+$ fractional abundance is highest in Model 4. HCN, HCO$^+$, HNC, C$_2$H, CS and SiO have much larger abundances at high temperatures than in the PDR models.
6. Conclusion

We now perform a direct comparison between the PDR and XDR models. To emphasise that XDRs penetrate much deeper into cloud volumes than PDRs, we use the same scale for all models. Thus, it is also possible to distinguish between gradients in abundance, cumulative intensity, column density and column density ratios. XDR Model 3 is only plotted to $N_{\text{H}} \approx 10^{23.5}$ cm$^{-2}$, since $H_X/n$ becomes too small and no reliable results are obtained at higher column densities.

In Fig. 5, we show for Model 4 the abundances of selected species. At the edge, both neutral and ionised species are more abundant in the XDR models, and the relative abundances also differ with respect to one another. In the XDR for example, the neutral species CH and CH$_2$ are more abundant than CH$^+$ and CH$^+$$^2$, respectively. In the PDR, this is the other way around.
CN and CN$^+$ are almost equally abundant at the edge in the PDR, while CN exceeds CN$^+$ by three orders of magnitude in the XDR. Although the amounts of CS$^+$ and HCS$^+$ are larger than those for CS and HCS, respectively, at the edge of the cloud in the XDR, the abundance difference is less than in the PDR. The abundance of He$^+$ is five orders of magnitude larger in the XDR, due to secondary ionisations. H$^-$ is enhanced by three orders of magnitude, due to the higher ionisation degree.

It is also easily seen that in PDRs the fractional abundances vary over many orders of magnitude, while the abundances in XDR Model 4 stay almost constant to a column density of $N_H \approx 10^{22}$ cm$^{-2}$, where the transition from H to H$_2$ starts.

In Figs. 6 and 7, we show cumulative line intensities for fine-structure lines at all column densities, i.e., the emergent...
Fig. 6. Cumulative line intensities of [CII] 158σm (solid), [SiII] 34.8σm (dotted), [CI] 609σm (dashed) and 369σm (dashed), for PDR (left) and XDR (right) models.

Intensity arising from the edge of the cloud to column density $N_H = n_H z$:

$$I(z) = \frac{1}{2\pi} \int_0^z N(z') dz'.$$

(1)

Although the total [CII] 158σm line intensity is higher in the XDR, the flux originating from the edge to $N_H \approx 10^{22}$ cm$^{-2}$ is higher in the PDR except when the XDR is characterised by very high $H_K/n$ values which is the case in Model 2. In all PDR models, all carbon is in C$^+$ at the edge, while a large part of the carbon is neutral in XDR Models 1, 3 and 4. In all models, oxygen is mostly in atomic form. The [OI] 63σm line intensity to $N_H \approx 10^{22}$ cm$^{-2}$ is larger in the low-density XDR models, which is possible due to higher electron abundances. The intensity is lower in the low radiation, high density XDR Model 3, since the temperature is higher in the PDR. For Model 4 they are about the same, since the density where the line becomes thermalised is almost reached. In the XDR, all line intensities increase approximately steadily with...
increasing column density. PDRs, however, primarily affect cloud surfaces causing more sudden changes. The line intensities of [CI] 609 μm and 369 μm arise from a more or less well defined part part of the cloud and start to increase at column densities \( N_H \geq 10^{21.5} \) cm\(^{-2}\). The line intensities of [CII] 158 μm are higher than those of [SiII] 35 μm in the PDRs except in Model 4. This is in contrast to the XDR models, where the [SiII] 35 μm line intensity is always stronger. The fact that [SiII] 35 μm lines are quite strong in XDRs was already noted by Maloney et al. (1996). The line intensities for [FeII] 26 μm and 35 μm are higher for the XDR models except again for Model 3.

In Figs. 8 and 9, we show cumulative column densities for selected species. They illustrate again that XDRs affect
whole cloud volumes and PDRs create layered structures. In PDRs, the increase in column densities is very sudden for all species. For example, C and CO show this due to the very distinct $\text{C}^+$/C/CO transition. In the XDRs, however, the increases in column density are much more gradual. The only sudden change in XDRs is where the $\text{H}/\text{H}_2$ transition occurs.

In Fig. 10, the cumulative column density ratios for $\text{CO}/\text{H}_2$, $\text{CO}/\text{C}$, $\text{HNC}/\text{HCN}$ and $\text{HCO}^+$/HCN are shown as a function of total hydrogen column density. The ratios for the XDRs are almost constant up to $N_\text{H} \approx 10^{22}$ cm$^{-2}$, unlike those in PDR models. In PDRs, CO/C ratios increase by approximately four orders of magnitude from the edge ($\leq 10^{-4}$).
to \(N_H = 10^{22.3} \text{ cm}^{-2}\) (\(\geq 1\)). In XDRs, this ratio is constant to \(N_H \approx 10^{22} \text{ cm}^{-2}\) and then increases slowly. For each cloud size, while keeping the energy input the same, CO/C ratios increase at higher densities. The ratios go down for higher radiation fields. For the same density and energy input, CO/C is lower when the cloud is irradiated by X-ray photons, with the exception of Model 3 where this is only valid at \(N_H > 10^{21.7} \text{ cm}^{-2}\). CO/H\(_2\) is somewhat more complex. When only the energy input is increased in PDRs, this ratio is higher when \(N_H < 10^{21} \text{ cm}^{-2}\). For \(N_H = 10^{22.3} \text{ cm}^{-2}\), the ratios are about the same. There is also a minimum where the H/H\(_2\) transition occurs. This minimum is more prominent for higher radiation.
In XDRs, the CO/H$_2$ ratio is lower when the radiation field is higher. In PDRs and XDRs, the CO/H$_2$ ratios are higher when the density is increased. When the cloud is irradiated by X-ray photons, CO/H$_2$ ratios are lower, again with the exception of Model 3 at $N_{\text{H}} < 10^{21.5}$ cm$^{-2}$. In PDR Models 1, 2, and 3, significant column densities for HCN, HNC and HCO$^+$ are reached between $N_{\text{H}} = 10^{21.5}$ and $10^{22}$ cm$^{-2}$. Therefore, the HNC/HCN and HCO$^+$/HCN ratios discussed are for column densities $N_{\text{H}} > 10^{22}$ cm$^{-2}$. In PDRs, HNC/HCN is lower when the density is higher. No significant changes are seen for different radiation fields in these columns. HNC/HCN is generally lower for high $H_X/n$ in XDRs. At high column densities, where $H_X/n$ is low, HCN/HCN ratios are equal or somewhat higher than those for the PDR. HCO$^+$/HCN
and HNC/HCN are of the same order of magnitude in PDRs, but in XDRs HCO\(^+\)/HCN is higher in most cases.

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Appendix A: Heating processes in PDRs

A.1. Photo-electric emission

In PDRs the photo-electric emission from (small) dust grains and PAHs is the dominant heating source. We use the analytical expression given by Bakes & Tielens (1994) which is given by

\[ \Gamma_{\text{grain}} = 10^{-24} \epsilon G'_{0,\text{dust}} n_H \text{ erg cm}^{-3} \text{s}^{-1}, \quad (A.1) \]

where \( G'_{0,\text{dust}} \) is the radiation field attenuated by dust absorption (Black & Dalgarno 1977) and the heating efficiency \( \epsilon \) is given by

\[ \epsilon = \frac{4.87 \times 10^{-2}}{1 + 4 \times 10^{-3} (G_0 T_k^{1/2} / n_e)^{0.73}}, \quad \frac{3.65 \times 10^{-2} T_k / 10^{4.7}}{1 + 2 \times 10^{-4} (G_0 T_k^{1/2} / n_e)} \quad (A.2) \]

Note that the efficiency depends on the ratio \( G_0 T_k^{1/2} / n_e \), which is the ratio of the ionisation and recombination rates. \( A_V \) is the visual extinction at optical wavelengths caused by interstellar dust. Bohlin et al. (1978) relate the total column density of hydrogen, \( N_H = N(H) + 2N(H_2) \) to colour excess, \( E(B - V) \):

\[ \frac{N_H}{E(B - V)} = 5.8 \times 10^{31} \text{ cm}^{-2} \text{ mag}^{-1}. \quad (A.3) \]

The visual extinction then follows consequently:

\[ A_V = 3.1 \times (B - V) \quad \text{and} \quad A_V = 5.34 \times 10^{-22} N_H. \]

Note that the results of Savage et al. (1977) are often used, but in this paper only \( H_2 \) (and not \( H_1 \)) is taken into account.

A.2. Carbon ionisation heating

At the edge of the cloud, most of the carbon is singly ionised. The photo-electron energy released in an ionisation is \( \Delta E_C = 1.06 \text{ eV} \). The ionisation rate, at a certain point in the cloud, is given by \( \kappa_{\text{ion}} = 1.76 G'_{0,\text{carbon}} \text{ s}^{-1} \). The heating rate due to the ionisation of carbon is then given by

\[ \Gamma_C = \kappa_{\text{ion}} n(C) \Delta E_C. \quad (A.4) \]

After substitution of numerical values we get the following heating rate for the local radiation field \( G'_{0,\text{carbon}} \):

\[ \Gamma_C = 2.79 \times 10^{-22} n(C) G'_{0,\text{carbon}} \text{ erg cm}^{-3} \text{s}^{-1}, \quad (A.5) \]

where this time \( G'_{0,\text{carbon}} \) is the radiation field attenuated by dust absorption (Black & Dalgarno 1977), carbon self-absorption (Werner 1970) and \( H_2 \) (de Jong et al. 1980).

A.3. \( H_2 \) photo-dissociation heating

Absorption of Lyman-Werner band photons leads to the dissociation of \( H_2 \). About 10% of the excitations leads to decay into the continuum of the ground electronic state (Field et al. 1966; Stecher & Williams 1967). The heating rate related to this dissociation is given by

\[ \Gamma = 0.1 \kappa_{\text{exc}} \langle E_{\text{diss}} \rangle, \quad (A.6) \]

where \( \langle E_{\text{diss}} \rangle \) is the mean kinetic energy of the \( H \) atoms and is set to 0.4 eV (Spaans 1996). The excitation rate of \( H_2 \) is given by \( \kappa_{\text{exc}} = 3.4 \times 10^{-10} G'_{0,H_2} \), where \( G'_{0,H_2} \) is the local radiation field given by

\[ G'_{0,H_2} = \beta(\tau) G_0 \exp(-2.5 A_V). \quad (A.7) \]

Self-shielding is explicitly taken into account for the excitation of \( H_2 \), by the introduction of the shielding factor \( \beta(\tau) \) (see Sect. D.2.3). After substitution of numerical values we get a heating rate of

\[ \Gamma_{H_2} = 2.2 \times 10^{-23} \beta(\tau) G_0 \exp(-2.5 A_V) \text{ erg cm}^{-3} \text{s}^{-1}. \quad (A.8) \]

A.4. \( H_2 \) collisional de-excitation heating

FUV excitation is followed by decay to ro-vibrational levels in the ground state. Collisional de-excitation leads to gas heating. This cascade process is very complicated, but we simplify this process by using a two-level approximation (see Sect. D.2.2). The resulting heating rate is given by

\[ \Gamma_{H_2} = [n(H) g_{10}^H + n(H_2) g_{10}^{H_2}] n(H_2 V) E, \text{ erg cm}^{-3} \text{s}^{-1}, \quad (A.9) \]

where the coefficients are given by Hollenbach & McKee (1979)

\[ g_{10}^H = 10^{-12} T_k^{0.5} \exp(-1000/T_k) \quad (A.10) \]

\[ g_{10}^{H_2} = 1.4 \times 10^{-12} T_k^{0.5} \exp(-18100/(T_k + 1200)). \quad (A.11) \]

Both of the above expressions are in units of \( \text{cm}^{-3} \text{s}^{-1} \).

A.5. Gas-grain collisional heating

When gas and grains differ in temperature they can transfer heat through collisions. The heating rate of the gas is given by (Hollenbach & McKee 1979, 1989)

\[ \Gamma_{\text{coll}} = 1.2 \times 10^{-39} n^2 \left( \frac{T_k}{1000} \right)^{1/2} \left( \frac{100 \text{ Å}}{a_{\text{min}}} \right)^{1/2} \times [1 - 0.8 \exp(-75/T_k)] (T_d - T_k). \quad (A.12) \]

The minimum grain size is set at \( a_{\text{min}} = 10 \text{ Å} \) and the dust temperature \( T_d \) is given by

\[ T_d = \left( 8.9 \times 10^{-11} \nu_0 G_0 \exp(-1.8 A_V) + 2.75 + 3.4 \times 10^{-2} [0.42 - \ln(3.5 \times 10^{-2} T_0 T_0)] \times \tau_{1000} T_k^{0.2} \right), \quad (A.13) \]

based on the results of Hollenbach et al. (1991).

A.6. Gas-grain viscous heating

Radiation pressure accelerates grains relative to the gas and the resulting drag contributes viscous heating to the gas. Grain acceleration time scales are short compared to other time scales, and therefore the grains may be considered moving at their local drift velocity, \( \epsilon_d \). All the momentum is transferred to...
the gas, predominantly by Coulomb forces. For drift velocities \( v_d < 10^2 \) cm s\(^{-1}\) (Spitzer 1978), no significant gas-grain separation takes place. In the following we take \( v_d = 10^2 \) cm s\(^{-1}\). The heating rate is given by

\[
\Gamma_{\text{visc}} = 8 \pi e n_d \langle Z(kT_e)^{-1} \rangle \ln \Lambda \nu_d
\]

where \( \Lambda \) is the grain volume density, \( Z_d \) is the grain charge, \( n(C^+) \) and \( n_e \) are the respective \( C^+ \) and electron volume densities and the functions \( \Lambda \) and \( G(y) \) are given by

\[
\Lambda = 1.5 Z_d^{-1} e^{-3}(kT_e)^{1.5}(\pi n_e)^{-0.5}
\]

\[
G(y) = \frac{1}{2y} \left( \text{erf}(y) - \frac{2}{\sqrt{\pi}} y e^{-y^2} \right),
\]

where \( y = \nu_d/n_{th} \) and \( \nu_d \) the thermal velocity of \( C^+ \) ions and electrons. The error function \( \text{erf}(y) \) is given by

\[
\text{erf}(y) = \int_0^y e^{-t^2} \, dt.
\]

A.7. Cosmic-ray heating

At large column densities, cosmic ray heating can become important. Glassgold & Langer (1973) and Cravens & Dalgarno (1978) calculated that the amount of heat deposited in a molecular gas is about 8 keV per primary ionisation. Then, Tieltens & Hollenbach (1985) find for the total heating rate, including helium ionisation

\[
\Gamma_{\text{CR}} = 1.5 \times 10^{-11} \xi n(H_2) \text{ erg cm}^{-3} \text{ s}^{-1},
\]

where \( \xi \) is the cosmic ray ionisation rate per \( H_2 \) molecule.

Appendix B: Heating processes in XDRs

B.1. Heating due to Coulomb interactions

When X-rays are absorbed, fast electrons are produced. These fast electrons lose part of their energy through Coulomb interactions with electrons, so the X-ray heating is given by

\[
\Gamma_X = \eta n H_X,
\]

where \( \eta \) is the heating efficiency, depending on the \( H_2/\text{H} \) ratio and the electron abundance \( x \). We use the results of Dalgarno et al. (1999). Their calculated heating efficiency \( \eta \) in an ionised gas mixture is given by

\[
\eta = \frac{10 \eta_{H_2He} + \eta_{HeH}}{10 + r},
\]

where \( r = n(H_2)/n(\text{H}) \) and \( \eta_{H_2He} \) and \( \eta_{HeH} \) are the heating efficiencies for the ionised pure \( \text{He} \) and \( H_2 \) mixture and the \( \text{He} \) and \( \text{H} \) mixture, respectively. Both are parametrised through

\[
\eta' = 1 + (\eta_0 - 1)/(1 + cx^\alpha).
\]

The values of \( \eta_0, c \) and \( \alpha \) are given in Table 7 of Dalgarno et al. (1999), and \( x \) is the electron fractional abundance. It has to be modified when the \( H_2-\text{He} \) mixture is considered:

\[
x' = \frac{1.83x}{1 + 0.83x}.
\]

B.2. Heating due to \( H_2 \) ionisation

\( H_2 \) ionisation can lead to gas heating (Glassgold & Langer 1973). When \( H_2 \) is ionised by a fast electron and subsequently recombines dissociatively, about 10.9 eV (1.75 \( \times \) 10\(^{-11} \) erg) of the ionisation energy can go into kinetic energy. \( H_2^+ \) can also charge transfer with \( H \). This is an exothermic reaction, with an energy yield of 1.88 eV, of which we assume half, 0.94 eV (1.51 \( \times \) 10\(^{-12} \) erg), to go into heating. \( H_2^+ \) can also react to \( H_3^+ \), and subsequently recombine dissociatively or react with other species. Glassgold & Langer (1973) argued that for every \( H_3^+ \) ion formed 8.6 eV (1.37 \( \times \) 10\(^{-11} \) erg) goes into gas heating. The \( H_2 \) ionisation rate cooling is then given by

\[
\Gamma_{H_2 \text{ ion}} = \frac{17.5(k_e x_e + k_{H, x_H} + 13.7 k_{H, x_H})}{k_e x_e + k_{H, x_H} + k_{H, x_H}} \times 10^{-12} \xi \eta n_{\text{erg cm}^{-3} \text{s}^{-1}},
\]

where \( k_e, k_{H, x_H} \) and \( k_{H, x_H} \) are the rates of dissociative recombination, charge transfer with hydrogen and the reaction to \( H_3^+ \), respectively.

B.3. Gas-grain collisional heating

We use the results of Sect. A.5. The dust temperature was found by Yan (1997):

\[
T_d = 1.5 \times 10^4 (H_X/x_d)^{0.2} \, \text{K},
\]

where \( x_d = 1.6 \times 10^{-8} \) is the grain abundance and \( H_X \) in erg s\(^{-1}\).

B.4. \( H_2 \) vibrational heating/cooling

When the vibrational levels of \( H_2 \) are populated by non-thermal processes, thermal collisional quenching and excitation can result in a net heating despite downward radiations. When non-thermal reactions are not important, \( H_2 \) can be an important coolant. The resulting collisional vibrational heating or cooling is given by

\[
\Gamma_{H_2 \text{ vib}, \text{col}} = \Sigma \nu \nu_{ej} \times \Sigma \nu \nu \nu \times (E_{ej} - E_{\nu \nu}) \, \text{erg cm}^{-3} \text{s}^{-1}.
\]

Where \( C(\nu j \rightarrow \nu' j') \) is the total collision rate from level \( \nu j \) to \( \nu' j' \) in units of \( s^{-1} \). Radiative cooling due to downward decay of the vibrational levels is given by

\[
\Lambda_{H_2 \text{ vib}, \text{rad}} = \Sigma \nu A(\nu j \rightarrow \nu' j') \nu_{ej} \, \text{erg cm}^{-3} \text{s}^{-1}.
\]

The population of the vibrational levels is discussed in Sect. D.3.4.

Appendix C: Cooling processes

C.1. Fine-structure line cooling

Since most of the gas is atomic in the radical region, the dominant coolants are the atomic fine-structure lines. The most prominent cooling lines are the [CII] 158 \( \mu \text{m} \) and [OI] 63 \( \mu \text{m} \) and 146 \( \mu \text{m} \) lines. For the calculation of the thermal balance
we also take into account Si++, C, Si, S, Fe and Fe++. We use a compilation for the collisional data from Sternberg & Dalgarno (1995), Hollenbach & McKee (1989), Sampson et al. (1994), Duf ton & Kingston (1994), Johnson et al. (1987), Roueff & Le Bourlot (1990), Schröder et al. (1991), Mendoza (1983), Chambaud et al. (1980) and Jaquet et al. (1992). We take into account collisions with electrons, H+, H and H2 (ortho and para) for the excitation of the species to different levels. In the PDRs, collisions with H+ are not the dominant excitation source but in XDRs the ionised fraction of hydrogen can be as large as ten percent and become important for the excitation of some levels.

C.2. Metastable-line cooling

We included the metastable cooling lines of C, C++, Si, Si++, O, O++, S, S++, Fe and Fe++. All the data is taken from Hollenbach & McKee (1989) except for Si++ (Duf ton & Kingston 1994), C++ (Sampson et al. 1994) and O++ (McLaughlin & Bell 1993).

C.3. Recombination cooling

At temperatures higher than ~5000 K, cooling due to recombination of electrons with grains (PAHs) is important. The cooling depends on the recombination rate which is proportional to the product n_e n_H. The cooling rate increases when G_H0 T_0^4/n_e goes up, due to an increase in charge and hence Coulomb interaction. Bakes & Tielens (1994) calculated numerically the recombination cooling for a variety of physical conditions. An analytical fit to the data is given by

\[ \Lambda = 3.49 \times 10^{-30} T_k^4 (G_H0 T_0^{1/2} / n_e)^6 \]  

where \( \Lambda = 0.944 \) and \( \beta = 0.735/T_k^{0.008} \).

C.4. Molecular cooling by H2, CO and H2O

For the rotational and vibrational cooling of H2, CO and H2O, we use the fitted rate coefficients of Neufeld & Kaufman (1993) and Neufeld et al. (1995). They present a cooling rate for species \( i \) through:

\[ \Lambda = L n(x_i) n(H_2) \text{ erg cm}^{-3} \text{s}^{-1} \]  

where \( n(H_2) \) and \( n(x_i) \) are the densities of H2 and species \( x_i \), respectively. \( L \) is given by

\[ L = \frac{1}{L_0} + \frac{n(H_2)}{L_{LTE}} + \left( \frac{n(H_2)}{n_{1/2}} \right)^{\beta} \left( 1 - \frac{n_{1/2}}{L_{LTE}} \right). \]  

We interpolate in the tables given by Neufeld & Kaufman (1993) and Neufeld et al. (1995), to find the values \( L_0 \), \( n_{1/2} \) and \( L_{LTE} \) and \( \alpha \). \( L_0 \) is the cooling rate coefficient in the low density limit and \( n_{1/2} \) is the H2 density where \( L \) has fallen by a factor of two below \( L_0 \). \( \alpha \) is chosen to minimize the maximal fractional error in the fit at other densities. \( L_0 \) is a function of temperature, and \( L_{LTE} \), \( n_{1/2} \), and \( \alpha \) are functions of temperature and the optical depth parameter \( N(x_i) \).

For rotational and vibrational cooling, \( \Lambda_{rot} \) and \( \Lambda_{vib} \) are given by

\[ \Lambda_{rot} = n_{vis}(H_2) = n(H_2) + 7n(H) + 16n(e). \]  

For rotational cooling by CO, \( \Lambda_{rot} \) is given by

\[ \Lambda_{rot}(CO) = n(H_2) + 1.414n(H)\sigma_{H}/\sigma_{H} + 1.3 \times 10^{-3} \text{cm}^{-2} \cdot \text{s}^{-1}, \]  

where \( \sigma_{H} = 2.3 \times 10^{-15} \text{ cm}^{-2} \), \( \sigma_{H} = 3.3 \times 10^{-16}(T_k/10^3)^{-1/4} \text{ cm}^{-2} \), and \( v = 1.03 \times 10^{9} T_k^{0.5} \text{ cm s}^{-1} \). For H2O rotational cooling, \( \Lambda_{rot} \) is given by

\[ \Lambda_{rot}(H_2O) = n(H_2) + 10n(H) \]  

where \( k_{dd} \) is the rotational constant in cm−1, \( d \) the dipole moment in Debye, \( \beta = 11.600/T_k \), \( \Delta E = 2.48 \times 10^{-4} b(i + 1) \) and \( C \) is given by

\[ C = \frac{9.08 \times 10^3}{b(i + 1)} \]  

\[ C = \frac{1.93 \times 10^4}{d^2(i + 1)} \exp(-1.18/d^2) \]  

For CO vibrational cooling, \( \Lambda_{vib} \) is given by

\[ \Lambda_{vib}(CO) = n(H_2) + 50n(H) + n(e)L_{CO,e}/L_{CO,0} \]  

where

\[ L_{CO,e} = 1.03 \times 10^{-10}(T_k/300)^{0.938} \exp(-3080/T_k) \]  

\[ L_{CO,0} = 1.14 \times 10^{-14} \exp(-680/T_k^{1/3}) \exp(-3080/T_k) \]  

For H2O vibrational cooling, \( \Lambda_{vib} \) is given by

\[ \Lambda_{vib}(H_2O) = n(H_2) + 10n(H) + n(e)L_{H_2O,e}/L_{H_2O,0} \]  

where

\[ L_{H_2O,e} = 2.6 \times 10^{-6} T_k^{0.5} \exp(-2325/T_k) \]  

\[ L_{H_2O,0} = 0.64 \times 10^{-14} \exp(-475/T_k^{1/3}) \exp(-2325/T_k) \]  

In the XDR models, H2 vibrational cooling is treated differently, since non-thermal processes play an important role, which is discussed in Sect. B.4.
C.5. Cooling by electron impact with H

The cooling due to the excitation of hydrogen is important at temperatures $T > 5000$ K. The cooling rate is given by Spitzer (1978):

$$\Lambda_{\text{e-H}} = 7.3 \times 10^{-19} n_e n(H) \times \exp(-118 400/T_k) \text{erg cm}^{-3} \text{s}^{-1}. \quad (C.13)$$

Appendix D: Chemistry

For most of the chemical reaction rates, we make use of the UMIST database for astrochemistry by Le Teuff et al. (2000).

In the PDR model we use a network containing all the species with a size up to 6 atoms. For the XDR model we use all species with sizes up to 3 atoms and some of 4 atoms. These species are taken from Yan (1997). Below we discuss the additional reactions.

D.1. H$_2$ formation on dust grains

The formation of H$_2$ is very efficient over a wide range of temperatures. It was already shown by Gould & Salpeter (1963) that H$_2$ is not formed efficiently in the gas phase. Most of the formation, which is still not very well understood, takes place on grain surfaces (Hollenbach & Salpeter 1971). Recently, Cazaux & Tielens (2002, 2004) developed a model for the formation of hydrogen under astrophysically relevant conditions. They compared their results with the laboratory experiments by Pirronello et al. (1999) and Katz et al. (1999). They find a recombination rate of

$$R_{\text{H}_2} = 0.5 n_H v_H n_d \sigma_d \epsilon_{\text{H}_2} S_{\text{H}_2}(T_k) \approx 6 \times 10^{-17} (T_k/300)^{0.6} n_e \epsilon_{\text{H}_2} S_{\text{H}_2}(T_k) \text{cm}^{-3} \text{s}^{-1}, \quad (D.1)$$

where $n_d$ and $\sigma_d$ are the volume density and cross section of dust grains and $n_H$, $v_H$ and $S_{\text{H}_2}(T_k)$ are the volume density, thermal velocity and thermally averaged sticking coefficient of hydrogen atoms. We use the sticking coefficient given by Hollenbach & McKee (1979)

$$S_{\text{H}_2}(T_k) = \left[1 + 0.4(T_k + T_d)^{0.5} + 2 \times 10^{-3} T_k^{-1}\right] + 8 \times 10^{-6} T_k^{2.5} \text{cm}^{-2} \text{cm}^{-3} \text{s}^{-1}, \quad (D.2)$$

where $T_d$ is the dust temperature. Equation (D.2) is the same as Eq. (4) in Tielens & Hollenbach (1985), except for the term $\epsilon_{\text{H}_2}$, the recombination efficiency, which is given by

$$\epsilon_{\text{H}_2} = \left(\frac{\mu F}{2 \beta_{\text{H}_2}} + 1 + \frac{\beta_{\text{H}_2}}{\sigma_{\text{H}_2}}\right)^{-1}, \quad (D.3)$$

where $\mu$ is the H$_2$ fraction that stays on the surface after formation, $\beta_{\text{H}_2}$ and $\beta_{\text{H}_2}$ are the desorption rates of molecular hydrogen and physisorbed hydrogen atoms, respectively, $F$ is the flux of hydrogen atoms and $\sigma_{\text{H}_2}$ is the evaporation rate from physisorbed to chemisorbed sites. These three terms dominate in different temperature regimes. See Cazaux & Tielens (2002, 2004) for a more detailed discussion.

D.2. Additional reactions in PDR models

D.2.1. Recombination on PAHs

Collisions of electrons and ions with grains can become an important recombination process in dense clouds of low ionisation. We include reactions with PAHs following Sect. 5 of Wolfire et al. (2003) in the PDR models. The C$^+$/C transition occurs at larger column densities when PAHs are included. Deep into the cloud, the electron abundance is reduced by several orders of magnitude.

D.2.2. Vibrational excitation of H$_2$

In PDRs, molecular hydrogen can be excited by absorption of FUV photons in the Lyman-Werner bands. Fluorescence leads to dissociation in about 10% in of the cases (see Field et al. 1966; Stecher & Williams 1967), and in the remaining 90% of the cases to a vibrationally excited state of the ground electronic state (Black & Dalgarno 1976). To simplify matters, we treat the electronic ground state as having a vibrational ground state and a single excited vibrational state. London (1978) found that the effective quantum number for this pseudo-level is $\nu = 6$, and the effective energy is $E_{\nu}/k = 2.6 \text{eV/k} = 30163$ K. We treat excited molecular hydrogen, H$_2$V, as a separate species in our chemistry. H$_2$V can be destroyed by direct FUV dissociation, radiative decay or collisional de-excitation, and chemical reactions with other species. Since vibrational decay is a forbidden process, a large abundance of H$_2$V can be maintained. H$_2$V can react with other species with no activation barrier or a reduced one. In the UMIST database, the rates for a reaction between two species are parameterised as

$$R = \alpha (T_k/300)^\beta \exp(-\gamma/T_k) \text{cm}^3 \text{s}^{-1}. \quad (D.4)$$

For reactions with H$_2$V, $\gamma$ is replaced by $\gamma' = \max(0, \gamma - 30163)$. When reactions have an activation barrier lower than 2.6 eV, the barrier is set to zero. When the barrier is larger than 2.6 eV, the barrier is reduced by 2.6 eV. Tielens & Hollenbach (1985) state that for important reactions such as

$$H_2V + C^+ \rightarrow CH^+ + H$$

and

$$H_2V + O \rightarrow OH + H,$$

this is a good approximation since the activation barrier of $\sim 0.5 \text{eV}$ is a lot smaller than the vibrational excitation energy of 2.6 eV. For reactions with barriers of the same order or larger one can overestimate the reaction rates.

D.2.3. Shielding of H$_2$ and CO

In PDRs, the photo-dissociation rate of both H$_2$ and CO is influenced by line as well as continuum absorption. The dissociation rate of H$_2$ is decreased by self-shielding. For an H$_2$ line optical depth $\tau \leq 10$, we adopt the self-shielding factor given by (Shull 1978). When the line absorption is dominated by the Doppler cores or the Lorentz wings (i.e., $\tau > 10$), we use the self-shielding factor as given by de Jong et al. (1980).
The CO photo-dissociation rate is decreased by both CO self-shielding and H$_2$ mutual shielding. We use Table 5 of van Dishoeck & Black (1988), to determine the shielding factor as a function of column densities $N$(H$_2$) and $N$(CO).

**D.3. Additional reactions in XDRs**

**D.3.1. Primary ionisations**

In the XDRs we do not use the photo-ionisation rates from UMIST. X-rays are absorbed in K-shell levels releasing an electron. An electron from a higher level may fill the empty spot and with the energy surplus another so called Auger electron is ejected. This process leads to multiply ionised species. Due to charge transfer with H, H$_2$ and He, they are quickly converted into the cloud is given by

$$
\zeta_{i,\text{sec}} = \int_{E_{\text{min}}}^{E_{\text{max}}} \sigma_{\text{pm}}(E) F(E, z) \frac{E}{W_{X_i}} dE \text{ s}^{-1} \text{ per H nucleus.} \quad (D.10)
$$

We rewrite this to a rate dependent on the fractional abundance of the species $x_i$:

$$
\zeta_{i,\text{sec}} = \int_{E_{\text{min}}}^{E_{\text{max}}} \sigma_{\text{pm}}(E) F(E, z) \frac{E}{W_{X_i}} dE \text{ s}^{-1} \text{ per species i,} \quad (D.11)
$$

where $x_i$ is the fraction of species $i$. Since we integrate over the range 1–10 keV and $W$ goes to a limiting value, we use the parameters applicable to the 1 keV electron. The ionisation rate then simplifies to:

$$
\zeta_{i,\text{sec}} = \frac{1 \text{ keV}}{W(1 \text{ keV})} \int_{E_{\text{min}}}^{E_{\text{max}}} \sigma_{\text{pm}}(E) F(E, z) dE \quad (D.12)
$$

$$
= \frac{1 \text{ keV}}{W(1 \text{ keV})} H_N \text{ s}^{-1} \text{ per species i.}
$$

We also include secondary ionisations for C, N, O, Si, S, Cl, Fe, C$^+$, N$^+$, O$^+$, S$^+$ and Fe$^+$. We scale the ionisation rate of these species to that of atomic hydrogen by

$$
\zeta_{i} = \frac{\zeta_{H}}{\zeta_{H}} \text{ s}^{-1}. \quad (D.13)
$$

We integrate over the range 0.1–1.0 keV to get an average value of the electron impact ionisation cross section $\sigma_{ei}$. Using the experimental data fits of Lennon et al. (1988). The scaling factors $\sigma_{ei}/\sigma_{eiH}$ for C, N, O, Si, S, Cl, Fe, C$^+$, N$^+$, O$^+$, S$^+$, and Fe$^+$ are 3.92, 3.22, 2.97, 6.67, 6.11, 6.51, 4.18, 1.06, 1.24, 1.32, 1.97, and 2.38, respectively.

**D.3.2. Secondary ionisations**

Part of the kinetic energy of fast photoelectrons is lost by ionisations. These secondary ionisations are far more important for H, H$_2$ and He than direct ionisation. Dalgarno et al. (1999) calculate the number of ions $N_{i,\text{ion}}$ produced for a given species $i$. For a given electron energy $E$, $N_{i,\text{ion}}$ is given by

$$
N_{i,\text{ion}} = W/E, \quad (D.6)
$$

where $W$ is the mean energy per ion pair. Dalgarno et al. (1999) calculated $W$ for pure ionised H-He and H$_2$-He mixtures and parameterised $W$ as:

$$
W = W_0(1 + c \alpha), \quad (D.7)
$$

where $W_0$, $c$ and $\alpha$ are given in Table 4 of their paper. The corrected mean energies for ionisation in the H–H$_2$–He mixture are given by

$$
W(H^+) = W_{H2,He}(H^+) \left[1 + 1.89 \frac{n(H_2)}{n(H)} \right], \quad (D.8)
$$

$$
W(H^+)_2 = W_{H2,He}(H^+) \left[1 + 0.53 \frac{n(H)}{n(H_2)} \right]. \quad (D.9)
$$

The ionisation rate at depth $z$ into the cloud for species $i$ is then given by

$$
\zeta_{i,\text{sec}} = \int_{E_{\text{min}}}^{E_{\text{max}}} \sigma_{\text{pm}}(E) F(E, z) \frac{E}{W} dE \text{ s}^{-1} \text{ per H nucleus.} \quad (D.10)
$$

The values of $p_m$ are taken from Table 4.7 of Yan (1997) and values of $p_m$ are the rates for cosmic-ray induced reactions from Le Teuff et al. (2000). There is an exception for CO, however, where we take the rate, corrected for self-shielding, given by Maloney et al. (1996):

$$
R_{CO} = 2.7 \chi_{CO}^{-1/2}(T_k/1000)^{0.5} \zeta_{H2,H2} \text{ s}^{-1}. \quad (D.15)
$$

**D.3.3. FUV photons from secondary electrons**

When energetic electrons created in X-ray ionisations collide with atomic and molecular hydrogen, H$_2$ Lyman-Werner and H Lyman $\alpha$ photons are produced, which can significantly affect the chemistry. The photoreaction rate $R_i$ per atom or molecule of species $i$ is given by

$$
R_i = \frac{x_{H2} \zeta_{H2} \rho_m + x_{H} \zeta_{H} \rho_m}{1 - \omega}, \quad (D.14)
$$

where $\omega$ is the average 1 per species.

The vibrational energy release $\chi$ is parameterised as:

$$
\chi_{v'v''} = \chi_{v'v''}(v'_H - v''_H), \quad (D.16)
$$

where $v'_H$ and $v''_H$ are the vibrational quantum numbers.

**D.3.4. Vibrationally excited H$_2$**

Vibrationally excited H$_2$ can enhance reactions with an activation barrier and also be an important heating or cooling source. To calculate the populations of the vibrational levels of H$_2$, we take into account:

- Collisions with fast electron produced by X-ray photoionisation.
- Collisions with thermal electrons, H, H$_2$ and He.
- Chemical destruction and production in chemical reactions.
- Radiative decay.
We use the results of Dalgarno et al. (1999) to calculate the X-ray induced excitation to the vibrational levels \( v = 1 \) and \( v = 2 \). The ratio of the yields \( Y(v = 2)/Y(v = 1) \) is about 0.070. Excitation to higher levels is not taken into account, since the yield to higher levels decreases very rapidly. First we calculate the mean energy for excitation, \( W \), in the \( \mathrm{H}_2\)-He mixture. The parameters are listed in Table 5 of Dalgarno et al. (1999). The function \( W \) has the same form as Eq. (D.7). The mean energy for excitation also depends on the abundances of \( \mathrm{H} \) and \( \mathrm{H}_2 \). The yield has to be corrected with a factor \( C(H, \mathrm{H}_2) \), which is given by

\[
C(H, \mathrm{H}_2) = \frac{2n(\mathrm{H}_2)}{n(\mathrm{H}) + 2n(\mathrm{H}_2)}, \quad x \geq 10^{-4} \tag{D.16}
\]

\[
C(H, \mathrm{H}_2) = \frac{n(\mathrm{H}_2)/n(\mathrm{H})}{n(\mathrm{H}_2)/n(\mathrm{H}) + a(x)} 10^{-7} < x < 10^{-4}
\]

where \( a(x) = 0.5(x/10^{-3})^{0.15} \). The rates for excitation by thermal electrons are taken from Yan (1997), who finds that the transitions rates for \( \mathrm{H}_2 (v = 0) \) to \( \mathrm{H}_2 (v = 1, 2) \) are given by

\[
R(0 \rightarrow 1) = 9.7 \times 10^{-11}(T_k/300)^{0.87} \exp(-6140/T_k) \tag{D.17}
\]

\[
R(0 \rightarrow 2) = 7.5 \times 10^{-12}(T_k/300)^{0.91} \exp(-11 900/T_k) \tag{D.18}
\]

The excitation rate for the transition \( v \rightarrow v + 1 \) is taken to be \( v \) times the \( 0 \rightarrow 1 \) rate. Excitations with \( \Delta v > 1 \) are not taken into account. The quenching rates are calculated through detailed balance. The quenching rates from \( v \rightarrow v' \) by atomic hydrogen are given in Table 4.2 of Yan (1997) and are of the form:

\[
R(v \rightarrow v') = \alpha(T_k/300)^{p} \exp(-\gamma/T_k) \text{ cm}^3 \text{ s}^{-1} \tag{D.19}
\]

The excitation rates are obtained by detailed balance. For the molecular excitation and quenching rates we use the results of Tine et al. (1997). Collisions where either before or after one of the \( \mathrm{H}_2 \) molecules is in the \( v = 0 \) state are considered. The rate coefficients are of the form:

\[
\log_{10} R(v_1, v'_1 ; v_2, v'_2) = A + B/T_k + C \log_{10} T_k \tag{D.20}
\]

and are given in Table 1 of Tine et al. (1997), who also considered collisions with \( \mathrm{He} \). They give a rate coefficient for the \( v = 1 \rightarrow 0 \) transition:

\[
\log_{10} R(1 \rightarrow 0) = -8.8T_k^{-1/3} - 16.5 \tag{D.21}
\]

\[
= -18.9T_k^{-1/3} - 14.2 \quad 90 < T_k \leq 230 \text{ K}
\]

\[
= -47.4T_k^{-1/3} - 9.4 \quad T_k > 230 \text{ K}
\]

For the other transitions with \( \Delta v = 1 \), the same rates are used. The upward transitions can be obtained by detailed balance. Yan (1997) also calculated the dissociation and ionisation rates by thermal electrons and since the ionisation threshold is much higher than the vibrational energies one rate is used for all vibrational energies:

\[
R_{diss} = 7.03 \times 10^{-3}(T_k/300)^{0.41} \exp(-118 600/T_k) \tag{D.22}
\]

\[
R_{e,ion} = 8.9 \times 10^{-10}(T_k/300)^{0.57} \exp(-179 400/T_k) \tag{D.23}
\]

The dissociation rates by atomic hydrogen are given in Table 4.3 of Yan (1997), which are of the same form as Eq. (D.19). For the dissociation rates by \( \mathrm{H}_2 \) we use the results of Lepp & Shull (1983), which are given by

\[
R_{\mathrm{H}_2,diss} = 6.29 \times 10^{-15} \times A \exp(1.44v - 0.037v^2)f(T_k)/f(4500 \text{ K}), \tag{D.24}
\]

where \( A = 1.38, f(T_k) = T_k^{0.5} \exp(-\alpha), \alpha = [1 + (E_{\rm th} + 1)/kT_k] \) and \( E_{\rm th} = 4.48 \text{ eV} - E(v) \). For the dissociative attachment reaction:

\[
\mathrm{H}_2 + e \rightarrow \mathrm{H} + \mathrm{H}^+, \tag{D.25}
\]

we use the results of Wadhera & Bardsley (1978) and the reaction rates have the same form as Eq. (D.19). Vibrationally excited \( \mathrm{H}_2 \) can be destroyed in chemical reactions. Endothermic reactions with vibrationally excited \( \mathrm{H}_2 \) can lower the activation barrier, by using the energy of the vibrational level. The barrier is reduced, but cannot become negative: \( E' = \min(0, E - E(v)) \). When \( \mathrm{H}_2 \) is formed in chemical reactions which are exothermic, part of the formation energy goes into the excitation of the vibrational levels. Formation of \( \mathrm{H}_2 \) on grains can play a very significant role. \( \mathrm{H}_2 \) has a binding energy of 4.48 eV. Following Sternberg & Dalgarno (1989), we assume one third of this energy to be distributed statistically over all the vibrational levels:

\[
x(\mathrm{H}_2(v)) = \frac{\exp(-E(v)/1.493)}{\sum \exp(-E(v)/1.493)} \tag{D.25}
\]

where \( x(\mathrm{H}_2(v)) \) is the fraction of \( \mathrm{H}_2 \) formed in vibrational state \( v \). When \( \mathrm{H}_2 \) formation reactions are endothermic, all the \( \mathrm{H}_2 \) is in the ground vibrational state. When they are exothermic part of the energy is distributed statistically following Eq. (D.25). The Einstein A coefficients for radiative decay are taken from Turner et al. (1977). We take a weighted average over the rotational levels of each vibrational level, which we assume to be thermalised, to get an Einstein A coefficient for the decay from \( v \rightarrow v' \).

**Appendix E: Energy deposition rate per hydrogen nucleus**

The photon energy absorbed per hydrogen nucleus, \( H_X \), is given by

\[
H_X = \int_{E_{\min}}^{E_{\max}} \sigma_{\mathrm{ps}}(E)F(E, \xi)dE. \tag{E.1}
\]

The interval \([E_{\min}, E_{\max}]\) is the spectral range where the energy is emitted. The photoelectric absorption cross section per hydrogen nucleus, \( \sigma_{\mathrm{ps}} \), is given by

\[
\sigma_{\mathrm{ps}}(E) = \sum_i A_i(\text{total}) \sigma_i(E). \tag{E.2}
\]

Morrison & McCammon (1983) state that the X-ray opacity is independent of the degree of depletion onto grains. Therefore, we take the total (gas and dust) elemental abundances, \( A_i(\text{total}) \), as given in Table 2 to calculate \( \sigma_{\mathrm{ps}} \).

The X-ray absorption cross sections, \( \sigma_i \), are taken from...
Verner & Yakovlev (1995). The flux $F(E, z)$ at depth $z$ into the cloud is given by

$$F(E, z) = F(E, z = 0) \exp(-\sigma_{pa}(E) N_{H}),$$  \hspace{1cm} (E.3)

where $N_{H}$ is the total column of hydrogen nuclei and $F(E, z = 0)$ the flux at the surface of the cloud.