Surface chemistry in the interstellar medium

I - H₂ formation by Langmuir-Hinshelwood and Eley-Rideal mechanisms

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Abstract

Context. H₂ formation remains a major issue for the understanding of interstellar physics
Aims. We want to include as much experimental and theoretical information as possible to describe H₂ formation in astrophysical environments.
Methods. We have modified the Meudon PDR code to include detailed treatment of H₂ formation mechanisms: i) Langmuir-Hinshelwood mechanism taking into account the contribution of the different sizes of dust grains in the diffusion processes and ii) the Eley-Rideal mechanism.
Results. We are able in this way to form H₂ even in regions where dust temperature is larger than 25 K. We also show that formation by Eley-Rideal mechanism can be a significant source of heating of the gas. We derive line intensities for various astrophysical conditions.
Conclusions. Such an approach results in an enhanced H₂ formation rate compared to the “standard” 3×10⁻¹⁷ n_H n(H) cm⁻³ s⁻¹ expression.

Key words. astrochemistry - ISM: general - ISM: clouds - ISM: molecules

1. Introduction

Despite the general agreement that H₂ formation occurs on grain surfaces, the actual formation mechanisms at work in interstellar conditions are still under debate. We present in this paper a new chemical model of H₂ formation which encompasses recent laboratory experimental and theoretical results on this topic and show some consequences on model results. A follow up paper will extend these results to other molecules on grains. We recall in Sect. 2 the previous assumptions concerning H₂ formation, in relation with observational issues. Sect. 3 describes two new implementations concerning i) the contribution of different dust grain sizes to the formation process within the Langmuir-Hinshelwood mechanism (labelled LH in the following), ii) the introduction of the Eley-Rideal mechanism (labelled ER) for H₂ formation. We display and compare the results obtained for different pressures and radiation fields in Sect. 3 pertaining both to diffuse gas and dense Photon Dominated Regions (PDRs) conditions. Particular focus is given on the values of the H₂ formation rates themselves and on observational tests such as the emissivities of fine structure transitions of the abundant atoms and ions and infrared H₂ transitions. We present our conclusions in Sect. 5.

2. Historical status

2.1. H₂ formation efficiency

Hollenbach & Salpeter (1971) have estimated the binding energies of H and H₂ on various surfaces as well as the corresponding sticking efficiencies and have subsequently developed the first theory of the formation mechanism of H₂ on dust grain surfaces in interstellar conditions due to H atoms diffusion at the surface of the grains. The formation rate has subsequently been derived thanks to Copernicus VUV observations of H₂ in absorption in diffuse interstellar clouds (Jura 1974). This mean formation rate, confirmed by FUSE observations (Gry et al. (2002)), is 3×10⁻¹⁷ n_H n(H) cm⁻³ s⁻¹. The launch of ISO and the development of infrared astronomy on ground based telescopes has allowed detections of warm excited H₂ via its electric quadrupolar transitions in the infrared in Photon Dominated Regions (PDRs). At long wavelengths (~ 7 – 28 μm) pure rotational transitions are taking place and are detected thanks to spatial instruments whereas rovibational transitions at shorter wavelengths can be observed from the ground in the I, J, H and K photometric bands. Le Bourlot et al. (1995b) have shown that this reaction rate coefficient can be readily expressed in terms of the dust grain properties, i.e. density ρgr, dust to gas mass ratio G, and the minimum (a_min) and maximum (a_max) values of the grain radii, for which the size distribution is a power law d n_gr = A_gr a⁻³₅ da (Mathis et al. 1977), subsequently quoted as the MRN distribution. Le Bourlot et al. (1995b) have derived the normalization factor A_gr = 1 1.44 G n_H 3 4ρgr amin a_max × × (√ a_max − √ a_min) n_H and the formation rate of H₂:

R(H₂) = 1 2 s 3×1.4 m_H G 4ρgr a_min a_max × √ 8k T n(H) n_H

This expression involves a sticking coefficient s for impinging hydrogen atoms, the mass of atomic hydrogen m_H, the Boltzmann constant k, the gas temperature T. For typical dust properties (Table 1), this expression becomes 1.4×10⁻¹⁷ s √ T n(H) n_H. Assuming that the sticking factor is 1 up to 10 K and then decreases with temperature as 1/√T, the formation rate becomes equal to 4.4×10⁻¹⁷ n_H n(H) cm⁻³ s⁻¹. Note that...
if we take a single radius of grains with a value of 0.1 \( \mu m \), the formation rate is now \( 1.3 \times 10^{-17} \rho_{gr}\nu_{H}(H) cm^3 s^{-1} \). The present prescription also allows to derive the mean cross section per H atom:

\[
\frac{<n_{d}G>_{ff}}{4} \geq \frac{3}{4} \frac{1.4 \rho_{gr} G}{\nu_{H}^{\pi}} \cdot \frac{1}{\sqrt{\min \Delta t_{\max}}} \cdot \rho_{H}
\]

For the standard parameters, the corresponding value is \( 1.95 \times 10^{-21} \rho_{H} \).

Whereas such a simple physical picture reflects the coherence between the observations and the basic properties of dust, a new step arose when the quantitative values of the desorption experiments reported by Katz et al. (1999); Biham et al. (2001); Biham & Lipshtat (2002); Lipshat & Biham (2003); Lipshat et al. (2004) with various types of surfaces. The corresponding values are reported in Table 1 and compared to older values from Hasegawa et al. (1992). These values have been included in theoretical models of H\(_2\) formation by Biham & Lipshtat (2002) also discuss the relevance of using the rate equations formalism within the LH diffusion mechanism. In the case of small grains, Biham & Lipshtat (2002) argue that only a few hydrogen atoms can stick on the surface so that master equations describing the various probabilities of having N adsorbed H atoms are required. This formalism leads to a large number of coupled equations. Biham & Lipshtat (2002) further introduced the use of moment equations, reducing the number of equations and leading, in the case of H\(_2\) formation, to only two coupled equations. Such a procedure compares very satisfactorily to the master equation solution (Biham et al. 2005). During the diffusion process, physisorbed H atoms explore the available adsorption sites with a sweeping rate \( A = v_{0} \frac{\exp(-T_{d}/T_{gr})}{4\pi a_{r}^{2}n_{s}} \)

with \( v_{0} \) a typical vibration frequency and \( T_{d} = E_{d}/k \) the diffusion energy threshold in Kelvin. The number of available sites, \( 4\pi a_{r}^{2}n_{s} \), depends on the radius of the grain. The sweeping rate probability has subsequently been revisited by Lohmar & Krug (2006) and Lohmar et al. (2009) for various surface geometries. The desorption probability is assumed to follow a similar exponential decrease \( W = v_{0} \exp(-T_{kr}/T_{gr}) \) with the same \( v_{0} \) frequency but involves the binding energy in Kelvin \( T_{kr} = E_{kr}/k \).

The frequency \( v_{0} \) is often assumed to be equal to \( 10^{12} \) s\(^{-1}\) (Biham et al. 2001). Hasegawa et al. (1992) have introduced the vibrational frequency corresponding to an harmonic oscillator within the binding well potential in the form \( v_{0} = \frac{\sqrt{\pi}}{\pi} \frac{E_{b}}{\rho_{H}} \). The usual expression is \( v_{0} = \frac{1}{2\pi} \frac{\sqrt{E_{b}}}{\rho_{H}} \) where the force constant \( k = \frac{\partial U(r)}{\partial r} \approx \frac{E_{b}}{d_{0}} \) at the minimum of the interaction potential \( U(r) \), which defines a typical size of the bottom of the well \( d_{0} \) by identification with Hasegawa et al. (1992) expression. Kim et al. (2011) and Sakong & Kratzer (2010) show that the stretching vibration wavenumber of H on graphene is about 2600 cm\(^{-1}\), and the bending about 1200 cm\(^{-1}\). This translates to vibration frequencies of a few \( 10^{13} \) s\(^{-1}\), rather higher than usual estimates. We deduce a typical size \( d_{0} \sim 1 \AA \). The corresponding values of \( v_{0} = \frac{1}{2\pi} \frac{2E_{b}}{d_{0}^{2}\rho_{H}} \) are given in Table 1 for various dust compositions. We have verified that model results are almost insensitive to the value of \( v_{0} \).

Le Petit et al. (2009) have included the possibility of rejection of the impinging hydrogens, when they land on an already occupied site and have introduced these mechanisms in the Meudon PDR code together with the size distribution of grains, but assuming a uniform dust temperature for all grain sizes.

The net result, for H\(_2\) formation, is that the reaction is efficient only in a narrow window of dust temperatures, ranging typically from 11 K to 19K, depending on the values of desorption and diffusion barriers, as also pointed out by Chang et al. (2006). Such a restricted range of grain temperatures is difficult to reconcile with H\(_2\) observations towards dense PDRs (Habart et al. 2004, 2005; Cazaux & Tielens 2004, 2010; Habart et al. 2011) where the dust temperatures reach values close to and even larger than 30 K. As a result, new scenario have been suggested such as the reaction between a physisorbed and a chemisorbed atom (Habart et al. 2004) or reactions between two chemisorbed atoms (Cazaux & Tielens 2004, 2010).

Other attempts to improve the physics of the actual process involve morphological aspects of the dust grain surfaces such as roughness effects probed through continuous time random walk Monte Carlo simulation studies, resulting in effective formation rate coefficients depending on the surface temperature and impinging atomic flux (Chang et al. 2006). In summary, despite the amount of laboratory and theoretical studies done on this subject, a detailed description of H\(_2\) formation is still missing. As a consequence, several authors (Hollenbach et al. 2009; Islam et al. 2010; Kaufman et al. 2006; Sheffer et al. 2011) prefer to use some ad hoc “standard” value of \( 3 \times 10^{-17} \rho_{H}\rho(H) cm^{-3} s^{-1} \), determined by Copernicus and FUSE observations for diffuse clouds, and/or introduce an additional multiplication factor of 2 for dense and bright PDRs.

2.2. H\(_2\) excitation in the formation process

The excitation state of H\(_2\) in the formation process is another concern. Recent experimental studies (Hornekar et al. 2003; Islam et al. 2007; Latimer et al. 2008; Lemaire et al. 2010) have shown that H\(_2\) can be rovibrationally excited in the formation process, where the experiments have been conducted with two beams of H and D and various types of surfaces. These experiments are performed on cold surfaces, indicating that the formation mechanism involves mainly physisorbed atoms, so a LH mechanism. Alternatively, Farebrother et al. (2000); Bachelier et al. (2009); Sizun et al. (2010) have performed theoretical calculations for the ER formation mechanism of H\(_2\) on graphenic surfaces and have derived the rovibrational excitation of the nascent H\(_2\) molecule for different energies of the impinging hydrogen atoms. The latest study (Sizun et al. 2010) includes explicitly the role of the zero point energy, which leads to a slight increase of the rotational excitation within \( v = 5 \) and 6. In the astrophysical community, Duley & Williams (1993) have proposed that infrared fluorescence of H\(_2\) could be detected towards dark clouds, as a signature of its formation process. Le Bourlot et al. (1995a) showed that the excitation due to the secondary electrons generated by cosmic rays was in fact much more efficient, even for the standard value of the cosmic ionization rate. Similar conclusions have recently been derived by Islam et al. (2010) in a detailed modeling study where the most recent experimental information on the excitation of H\(_2\) has been included, assuming however the “standard” formation rate of \( 3 \times 10^{-17} \rho_{H}\rho(H) cm^{-3} s^{-1} \). Congiu et al. (2009) also find that internal excitation is quenched before desorption from experiments involving amorphous water ice. However, formation pumping signatures can also be searched for in PDRs and were reported as such by Burton et al. (2002) in the Messier 17 PDR through the mapping of the 6-4 O(3) infrared transition of H\(_2\).
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Table 1. Dust properties. We assume that adsorption sites are regularly dispatched on the grain surface so that the mean distance between them, \( d \), is the inverse of the square root of their surface number density \( n_s \). See references in text.

| Properties | “standard” | Hasegawa et al. (1992) | amorphous carbon | Olivine |
|------------|------------|------------------------|------------------|---------|
| \( s \) sticking factor (1 – 10K) | 1 | | | |
| \( a_{\text{min}} \) (\( \mu m \)) | 0.03 | | | |
| \( a_{\text{max}} \) (\( \mu m \)) | 0.3 | | | |
| dust to gas mass ratio, \( G \) | 0.01 | | | |
| density, \( \rho_{\text{gr}} \) (g cm\(^{-3}\)) | 3 | 2.16 | 3 | |
| H binding energy, \( E_b \) (meV) | - | 30.16 | 56.7 | 32.1 |
| H diffusion barrier, \( E_D \) (meV) | - | 8.62 | 44 | 24.7 |
| surface density of adsorption sites, \( n_s \) (cm\(^{-2}\)) | 1.510\(^{15}\) | 510\(^{13}\) | 2.10\(^{14}\) | |
| mean distance between adsorption sites, \( d_s \) (Å) | 2.6 | 2.6 | 14.14 | 7.07 |
| hoping rate, \( v_0 \) (s\(^{-1}\)) with \( d_0 = 1 \) Å | 10\(^{12}\) | 7.610\(^{12}\) | 10.510\(^{12}\) | 7.910\(^{12}\) |

at 1.733\( \mu m \). We investigate the possible consequences in the present study.

3. Model calculations

Le Petit et al. (2009) have studied the efficiency of H\(_2\) formation for different dust temperatures when H\(_2\) formation takes place on amorphous carbon, assuming that the grains have the same temperature, whatever their size. Such an hypothesis is inadequate as discussed by different authors (Cuppen et al. 2006; Compiègne et al. 2011) explicitly compute the dust temperatures resulting from the balance between photoelectric effects and radiative infrared emission for the different grain sizes. The results are very close to the analytic expressions given by Hollenbach et al. (1991) and used in the Meudon PDR code (Le Petit et al. 2006). We describe now two major extensions, i.e. inclusion of the different dust grain temperatures for surface reactions involving physisorbed hydrogen atoms and the introduction of the ER mechanism for H\(_2\) formation. Other recent updates of the PDR code are described in Appendix A.

3.1. Langmuir-Hinshelwood mechanism

In a pure diffusion process (LH mechanism), physisorbed hydrogen atoms, labelled as “\( ^{1}\)H”, can either diffuse on the surface, encounter another physisorbed hydrogen atom to form H\(_2\) or leave the surface through thermal desorption or another desorption process such as photodesorption. We derive the detailed rate equations in App B, taking into account size dependent dust temperatures and rejection effects. The formation rate of H\(_2\) is no longer analytic and involves a numerical integration over the dust grain sizes. In this paper, we assume a MRN distribution law, but the expressions are given for any distribution. The number of particles X physisorbed on the surface of a grain of size \( a \) is \( N_X(a) \) and is one of the unknowns we have to compute.

Considering only the balance between H and H\(_2\) (without deuterium here), we find from App B, Eqs (B.2) and (B.4):

\[
\frac{d[H]}{dt} = -k_{\text{ref}} \frac{S_{gr}}{d_s^2} [H] + k_{\text{ref}} [H] \int_{a_{\text{min}}}^{a_{\text{max}}} (N_{H_2}(a) + N_{H_2}^+(a)) dN_g + k_{ev}(a) N_{H}(a) dN_g + (k_{ph} + k_{CR}) \int_{a_{\text{min}}}^{a_{\text{max}}} N_{H}(a) dN_g
\]

In this expression, \( k_{\text{ref}}, k_{ev}, k_{ph}, \) and \( k_{CR} \) are the chemical reaction rate constants holding respectively for reaction, thermal evaporation, photo-desorption and cosmic rays induced desorption. \( k_{\text{ref}} \) is proportional to the thermal velocity of the impinging hydrogen atoms and to the sticking coefficient which is also a function of the gas temperature. \( S_{gr} \), the total grain surface per cubic centimeter, is equal to \( 3 \cdot \frac{4 \pi m_H G}{\sqrt{\pi} m_{\text{H}} a_{\text{min}} a_{\text{max}}} m_{\text{H}} \), with the MRN distribution law, and \( d_s \) is the mean distance between adsorption sites. Among the ejection processes, only thermal evaporation \( (k_{ev}(a)) \) depends on the grain size. Formation of gas phase H\(_2\) is assumed to occur directly after the encounter of adsorbed hydrogen atoms. The corresponding rate is given by Eq (B.6):

\[
\frac{d[H_2]}{dt} = \frac{d_s^2}{4 \pi} \int_{a_{\text{min}}}^{a_{\text{max}}} \left( \frac{1}{t_H(a)} a^2 \right) N_{H_2}^+(a) dN_g
\]

The hoping time \( t_H \) is dependent both on diffusion and possible tunneling. The diffusion time, \( t_D \), equal to \( v_0^{-1}\exp\left( T_\text{dis}/T_g(a)\right) \), depends now on the size of the grain. The tunneling time is derived for a rectangular barrier of height \( E_b \) and width \( d_s \),\(^1\):

\[
\tau_T = v_0^{-1} \times \left( 1 + \frac{E_b^2 \sinh^2(d_s/\lambda_D)}{4 T_g(a) E_b - T_g(a) \cdot \lambda_D} \cdot \lambda_D \right),
\]

\( \lambda_D \) is the de Broglie length, given by \( \lambda_D = h/\sqrt{2 m_{\text{H}}(E_b - k T_g(a))} \). The total hoping frequency is \( \tau_T^{-1} = \tau_D^{-1} + \tau_T^{-1} \), is a function of the grain size.

To include these equations in the chemical scheme, the mean number of H or H\(_2\) physisorbed on a grain of size \( a \), namely \( N_{H}(a) \) and \( N_{H_2}(a) \), have to be computed. We obtain from Eq (B.1), (B.3) and (B.5):

\[
\frac{dN_{H}(a)}{dt} = k_{ad}(a) [H] - k_{\text{ev}}(a) N_{H}(a) - \frac{1}{t_H(a)} \cdot \frac{d^2}{4 \pi a^2} N_{H}^+(a)
\]

\[
\frac{dN_{H_2}(a)}{dt} = k_{ad}(a) [H_2] - k_{\text{ev}}(a) N_{H_2}(a) - \frac{1}{t_H(a)} \cdot \frac{d^2}{4 \pi a^2} N_{H_2}^+(a)
\]

where \( k_{ad} \) is the chemical rate constant for adsorption. After discretization of the grain size distribution, the equations can be solved as ordinary rate equations and are thus easy to incorporate within the other chemical rate equations. However, the number of variables grows significantly.

\(^1\) Hasegawa & Herbst (1993) assume a 1 Å width between the two physisorbed sites, much smaller than the mean distance computed from the density of sites displayed in Table 1.
3.2. Eley-Rideal mechanism

We explicitly introduce in the PDR model adsorption of H atoms into chemisorbed sites, noted as H\textsubscript{2}:, as well as the subsequent reactions with impinging gas phase atomic hydrogen leading to H\textsubscript{2} formation. This process has been studied theoretically by different authors, who derive the interaction potential with the surface and the reaction probabilities. The static properties, potential well, possible barrier height, are significantly dependent on the nature of the surface, which allows some liberty on the choice of the actual value to be used in the modeling.

There is a significant difference with the adsorption process described previously, as trapping a gas phase hydrogen into a chemisorption site implies the crossing of a barrier where the exponential term involves now the gas temperature. Given the variety of grain types and surfaces properties found in the ISM, it is probable that this barrier is not unique. Those properties are poorly known and trying to derive a detailed model would, arbitrarily, increase the number of free parameters. Therefore we limit ourselves to a simple approximation that takes into account the major aspects of this process.

With the assumption that H is removed from a chemisorption site only by the formation of a molecule and using results from App C, Eq. (C.2), H\textsubscript{2} formation rate becomes:

\[ \frac{d[H_2]}{dt} = V_\text{th} <n\sigma_{gr}> \frac{\alpha(T) \exp(-T_1/T)}{1 + \alpha(T) \exp(-4/T)} [H] = k_{ER} [H] n_H (1) \]

\( \alpha(T) \) is an efficiency factor that depends on the gas temperature \( T \) and \( <n\sigma_{gr}> \) is the total surface of grains available per cubic centimeter (see the appendix for discussion on the parameters). If a more complicated set of species and reactions is used (e.g., formation of HD), then the equations given allow the computations of all necessary abundances, but the rate is no longer analytic.

The corresponding rate, \( k_{ER} = 2.8 \times 10^{-17} \times \sqrt{T} \times \frac{\alpha(T) \exp(-T_1/T)}{1 + \alpha(T) \exp(-4/T)} \), with the standard values displayed in Table 1. We notice that the numerical factor is twice the value reported in Sect. 2.1 as H\textsubscript{2} is now produced from the collision between two different partners, a gas phase H atom and a chemisorbed H\textsubscript{2}: The order of magnitude of this chemical rate constant is again within the “standard” value derived by Jura (1974). The actual value of \( k_{ER} \) depends on the chemisorption barrier \( T_1 \), and on the sticking efficiency \( \alpha(T) \) but not on the distance between adsorption sites. The influence of \( T_1 \) and \( \alpha(T) \) on the formation efficiency and line intensities is discussed in App C.

We will see below that this reaction has a major effect on thermal balance at the edge of the cloud as each H\textsubscript{2} formation as well as each destruction contributes to the gas heating. This is thus a very efficient way to couple the strong ultraviolet radiation field to the gas.

3.3. Excitation during formation

H\textsubscript{2} formation releases about 4.5 eV. Most current prescriptions assume an equipartition of this energy between translational energy, H\textsubscript{2} internal energy and heating of the grain. In this way, about 17000 K is spread in H\textsubscript{2} rovibrational states. Other scenarios have been proposed by Black & Van Dishoeck (1987). Recent experimental results obtained on cold graphitic surfaces (Islam et al. 2010) or on silicates (Lemaire et al. 2010) show that high vibrational levels are preferentially populated in the formation process.

The Meudon PDR code permits to choose between several scenarios. In this paper, for the LH mechanism, we adopt the default option in which 1/3 of the formation enthalpy is spread in internal energy with a Boltzmann distribution among rovibrational levels (see the description in Le Petit et al. 2006). Note that this is physically relevant only if enough levels of H\textsubscript{2} are included in the computations, even if their steady-state populations are negligible.

For the ER process, we follow the energy distribution obtained by Sizun et al. (2010) (their Table 1) and consider that the uncertainties are larger than the differences that they computed at incident energies of 15 and 50 meV for the impinging H atom. The energy available after formation of a H\textsubscript{2} molecule is thus split into:

- 0.3 eV (\( \sim 3500 \) K): Depth of chemical bound potential well.
- 2.7 eV (\( \sim 31300 \) K): Internal energy, spread following a Boltzmann distribution (mean level: \( \nu \sim 5, J \sim 6 \)).
- 0.6 eV (\( \sim 7000 \) K): Translational kinetic energy (heating term for the gas).
- 1 eV (\( \sim 11600 \) K): Heating of the grain.

Note that this last term is not yet included in the thermal balance of the grains.

3.4. Heating

This enhanced formation rate at the edge of PDRs provides a new contribution to the gas heating. At the edge of clouds, since the H\textsubscript{2} photodissociation rate is important and the ER mechanism is efficient, the formation-destruction cycle of H\textsubscript{2} has a short time scale. Each destruction by a UV photon leads to about 0.6 eV of kinetic energy, but each subsequent formation also provides a way to tap the formation enthalpy reservoir. As seen above (Sect. 3.3), most of this energy is in high lying rovibrational levels. So, one H\textsubscript{2} formation is usually followed by emission of an IR photon, which may be detected. However, for high enough densities, collisional deexcitation with atomic H comes in competition with spontaneous radiative decay. Above a critical density the collisional process dominates\(^2\) and the released kinetic energy provides an efficient heating mechanism. This may lead to gas temperatures in the range of a few thousands, which increases further the formation rate (which is proportional to \( v_{th} \), see Eq (1)), decreases the cycling time scales and enhances still further the heating rate.

This positive loop is quenched by the fact that our sticking coefficient goes to zero with increasing temperature, which allows for an equilibrium temperature to be reached.

For a high density and a high radiation field, this process is by far the dominant one at the edge of the cloud. Fig. 1 shows the fraction of heating provided by ER H\textsubscript{2} formation vs. photoelectric effect in a cloud where the temperature profile is fixed. Close to the edge, the high gas temperature allows for the ER process to be fast and most of the heating comes from collisional de-excitation. Once the temperature drops, that process is quenched and photo-electric heating dominates as long as the optical depth is not too high.

The transition region is chemically very active (H and H\textsubscript{2} being both abundant, and the temperature still quite high).
Formation rates of molecules such as OH or CH may be enhanced in particular if H internal energy can contribute to overcome the energy thresholds of the chemical reaction. Heat released by exothermic reactions also provides most of the heating missing from the two processes of Fig. 1.

4. Model results

In this section, we study the effect of different prescriptions for molecular hydrogen formation on grains. We model isobaric clouds since this is the simplest equation of state for dilute gas at steady-state embedded in a stationary environment where gravitation is negligible: large pressure variations (such as found in a constant density cloud with large temperature variations) would lead to some kind of relaxation. Smaller entities (clumps, filaments, etc...) may be better described as isochoric clouds within these large structures. A grid of such isochoric models, with the same physics as the isobaric models presented below has also been produced. They are not discussed in this paper but can be found in the PDR Data Base (http://pdr.obspm.fr).

Models labelled “A” correspond to a fixed formation rate of molecular hydrogen of $3 \times 10^{-17} \text{cm}^3 \text{s}^{-1}$, following prescriptions by Hollenbach et al. (2009); Islam et al. (2010); in models “B”, H$_2$ is formed only by LH mechanism, in models “C” LH and ER mechanisms are both activated to form H$_2$. The model geometry is a plane parallel infinite slab with an isotropic radiation field impinging on both sides.

We explore a large domain of gas pressure and intensity of the incident UV radiation field. The gas pressure is given by $P = n \times T = [n(H) + n(H_2) + n(\text{He})] \times T$. The radiation field is scaled versus the ISRF evaluated by Mathis et al. (1983) in the UV and visible part of the spectra. Longward of ~6000Å the ISRF is corrected using infrared observations from Hauser et al. (1998, F. Boulanger and M. Gonzalez, private communication). The scaling factor $\chi$ is applied only in the VUV range, from 13.6 to 5.17eV (corresponding to the wavelength range 912 to 2400Å) to mimic the presence of nearby bright OB stars. It represents the scaling factor of the UV part of the radiation field at a point that receives the radiation field from 4$\pi$ steradians.

Dust properties, elemental abundances ($\{X\}$ stands for the total abundance of the X element) and other parameters are given in Tables 1 and 2. The adopted dust extinction curve corresponds to the parameters of Fitzpatrick & Massa (1990) for the Galaxy. Photodissociation probabilities of H$_2$ and CO, are explicitly computed from the different discrete photodissociating transitions. We include a turbulent component to the thermal line width and take a common value of 3 km s$^{-1}$ for all transitions. We choose to display results of isobaric models with values relevant both to diffuse and dense gas.

4.1. Diffuse gas

The chemical network includes only gas phase processes, except for H and H$_2$ as well as neutralization of atomic ions on grain surfaces. It involves 131 chemical species and about 2650 chemical reactions. The analysis of UV absorption of neutral carbon lines towards a sample of translucent and diffuse line of sights (Jenkins & Shaya 1979; Jenkins & Tripp 2001, 2007) allows to derive the range of thermal pressures relevant for the galactic interstellar gas. Table 3 displays results for two isobaric chemical models corresponding to a total visual magnitude $A_V^{tot} = 1$ and $\chi = 1$ on both sides of the cloud. The impinging flux at the edge is about 0.56 times the Mathis field as some photons are coming from the opposite side of the cloud or are back-scattered by dust. The corresponding radiation pressure at the edge is $u/3$, where $u$ is the energy density per unit volume, i.e. 1.710$^{-14}$ dyne cm$^{-2}$, always smaller than the considered thermal pressures (respectively 4.14$10^{-13}$ and 1.38$10^{-12}$ dyne cm$^{-2}$). The size in pc is noted $l$ (see conversion in App D). The grains temperatures depend only on the radiation field intensity. Their common values at the edge of the clouds span a range between 10.7 and 12.5 K.

We note that the results are typical of cold neutral medium (CNM) properties, following Wolfire et al. (1995). We also find that the dependence of the displayed quantities are marginally dependent on the assumed formation scenario of molecular hydrogen. This results directly from the range of gas and dust temperatures and the assumed dust size distribution. Thus, in diffuse clouds, the role of the ER mechanism is negligible except at the edge of the low pressure models ($P = 3 \times 10^5$ cm$^{-3}$ K) = 4.14$10^{-13}$ dyne cm$^{-2}$). We also report $T_0$, the excitation temperature derived from the computed column densities of H$_2$, J = 0 and J = 1 levels: $T_0 = 170.5/\log(9N_0/N_1)$. The values are in agreement with the observations ($T \approx 67$ K from FUSE observations, Burgh et al. (2007), Rachford et al. 2009, Sheffer et al. (2008)), especially for models with $P = 3 \times 10^5$ cm$^{-3}$ K.

![Figure 1](http://pdr.obspm.fr)
the low pressure models, we note that H$_2$ formation is enhanced in models B and C compared to model A leading to a significantly higher value of the molecular fraction. The FUSE survey of diffuse clouds (Rachford et al. 2009) has not detected clouds with molecular fraction over 0.6. This is one of the difficulties in reconciling models of diffuse clouds and observations. First, molecular fractions determined by observations also include the atomic hydrogen content over the full line of sight. Second, the molecular fraction depends strongly on the size of the clouds and on the UV illumination. The detailed study is beyond the scope of this paper.

4.2. Dense PDRs

Dense and bright PDRs offer the opportunity to detect infrared transitions of molecular hydrogen and fine structure transitions of neutral and ionized atoms (O, C, C$^+$ etc.) which are then used to derive the relevant physical conditions by the observers. We again consider isobaric models irradiated on the observer side by 3 different radiation fields, respectively $10^2$, $10^3$ and $10^4$ times the standard interstellar radiation field of Mathis et al. (1983). The back side is illuminated by standard radiation field ($\chi = 1$). A total visual magnitude of 10 is assumed.

4.2.1. H$_2$ formation

We first check the role of the formation process in the atomic to molecular transition properties. Tables 4, 5, 6 and 7 display results for 4 different pressures and 3 radiation field enhancement factors.

The range of dust temperatures at the edge of the clouds has a dramatic effect on the formation rate of H$_2$, when only diffusion mechanisms are involved (B models), as expected. In this latter case, there is even no range of visual magnitudes where the local density of H$_2$ exceeds that of atomic H, when the pressure is $10^6$ cm$^{-3}$ K or smaller (shown as an ellipsis in the corresponding cells in Tables 4 and 5). The different trends can be understood from analytic developments obtained in a single grain size approximation, as given in Apps. B and C. The effect of pressure is best seen with the $\chi = 10^3$ results:

- Grains are warm (26 to 44 K), so that thermal evaporation of physisorbed hydrogen is efficient. Therefore the ER process dominates over the LH one.
- All things equal, increasing pressure in case B (where only LH is active) gives results in accordance with Eq (B.8). Temperature at the edge does not vary much, so that $[\text{H}] \propto P$ and $R_{\text{H}_2}$ is indeed proportional to $[\text{H}]$ as expected.
- Including the ER process, $R_{\text{H}_2}$ first rise with increasing $P$ due to a (at first) slow rise of temperature. Then for the highest pressure, the heating mechanism described in Sect. 3.4 is fully at play, and $R_{\text{H}_2}$ decreases as the temperature stabilizes on the right side of formation rate curve of Fig. C.1.

Increasing $\chi$ leads to similar results, with still higher grain temperatures. However complex UV pumping processes have an increasing role and Eq (B.8) is less accurate. For a lower radiation field, the range of H densities spanned by increasing pressure is within the critical densities defined in B and the full Eq (B.7) applies. In both cases, the ER rate follows closely the temperature behavior with a positive feedback being most efficient at high pressure.

We see that allowing for the possibility of chemisorption compensates, in a natural way, the deficiencies of the LH mechanism when dust grains become too warm. The values of the formation rate of molecular hydrogen attained in such bright PDR conditions become then very comparable to the values deduced from the observations (Habart et al. 2004) with an increase by a factor 2 to 5 of the standard $310^{-17} n(H) \text{cm}^{-3} \text{s}^{-1}$ value depending on impinging incident radiation field. Even if the chemisorption properties are somewhat empirical (the de-
dependence is discussed in App. C), we feel that such a mechanism allows to solve a major difficulty in the theory of H$_2$ formation.

### 4.2.2. Emission lines

We now investigate the implications of the new formation scenario on the various emissivities. We display in Tables 8 and 9 the emissivities derived from the previous models. We focus on transitions emitted in the PDR region where photo-chemical and physical effects are taking place. In line with the results already displayed, we find that the fine structure emission lines are not very dependent on the formation model of H$_2$ except in a few cases, where temperatures become of the order of thousands K, due to the enhanced heating mechanisms described in Sect. 3.4. Much more sensitive are the molecular hydrogen emission transitions. We display the emissivities of the pure rotational lines detected routinely by Spitzer as well as the 1-0 S(1) transition at 2.12 μm detected from the ground. Ratios to other vibrational lines detected in the K band are given to compare with past (Burton et al. 2002) and future observations. We have also run 190 type C models with different pressures (10$^9 - 10^6$ cm$^{-3}$K) and intensity scaling factors of the incident radiation field (1 to 10$^6$ Mathis ISRF) on the observer side to display the correspond-

#### Table 4. Model results for $P = 10^5$ cm$^{-3}$K and 3 different radiation field enhancements. Models A, B and C are identical as previously and defined in the text. $I$ is the total width of the cloud expressed in pc, corresponding to a total visual magnitude of 10. $N(X)$ stands for the resulting total column density of species X. Exponent “obs” means values at the edge of the cloud on the observer side. Numbers in parenthesis give the powers of ten.

| $\chi_{\text{obs}}$ | $T_{\text{obs}}^a$ (min) (K) | $T_{\text{obs}}^a$ (max) (K) |
|-------------------|------------------------------|----------------------------|
| $\chi_{\text{obs}}$ | $10^2$ | $10^3$ | $10^4$ |
| $T_{\text{obs}}^a$ (min) (K) | 16.7 | 26.2 | 41 |
| $T_{\text{obs}}^a$ (max) (K) | 27.7 | 44.1 | 70 |

#### Table 5. Same as Table 4 for $P = 10^6$ cm$^{-3}$K.

| $\chi_{\text{obs}}$ | $T_{\text{obs}}^a$ (min) (K) | $T_{\text{obs}}^a$ (max) (K) |
|-------------------|------------------------------|----------------------------|
| $\chi_{\text{obs}}$ | $10^2$ | $10^3$ | $10^4$ |
| $T_{\text{obs}}^a$ (min) (K) | 16.7 | 26.2 | 41 |
| $T_{\text{obs}}^a$ (max) (K) | 27.7 | 44.1 | 70 |

#### Table 6. Same as Table 4 for $P = 10^7$ cm$^{-3}$K.

| $\chi_{\text{obs}}$ | $T_{\text{obs}}^a$ (min) (K) | $T_{\text{obs}}^a$ (max) (K) |
|-------------------|------------------------------|----------------------------|
| $\chi_{\text{obs}}$ | $10^2$ | $10^3$ | $10^4$ |
| $T_{\text{obs}}^a$ (min) (K) | 16.7 | 26.2 | 41 |
| $T_{\text{obs}}^a$ (max) (K) | 27.7 | 44.1 | 70 |
ing contours in different Figures. The back side radiation field is set to $\chi = 1$ and the total visual magnitude, $A_V^{tot} = 100$ in order to neglect radiative effects from the back side. The other model parameters are given in Table 2 and the dust properties correspond to the standard values displayed in Table 1. We display results when both LH and ER mechanisms are activated for the formation of $H_2$ (C type). Figs. 2 to 6 display $H_2$, $C^+$ and $O$ line intensities contours in erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$ for a face-on geometry.

Intensity maps for other line intensities and other observation angles can be found on our VO-Theory database, PDR Database (PDRDB), under the project “H2 formation LH+ER - 2011” (http://pdr.obspm.fr). Complete outputs of the models (giving access to abundances profiles, temperature profile, formation and destruction rates, ...), input parameters and source code used to produce these models are also available through PDRDB.

Figs. 2, 3 and 4 show that intensities (excepted for the 0-0 S(0) line) are mostly dependent on $P$ for high values of $\chi/P$ and on $\chi$ for low values of $\chi/P$. Habart et al. (2004) explain this behavior in the case of isochoric models. At the $H/H_2$ transition, for high $\chi/n_H$ photons are mostly absorbed by grains whereas for low $\chi/n_H$, they are absorbed in $H_2$ lines (self-shielding). It can be shown that in the first case, $H_2$ line intensities are proportional to the $H_2$ formation rate and so to $n_H$ whereas, in the second case, they are proportional to the intensity of the incident radiation field. In the case of isobaric models, an analytical derivation is less obvious, but, as we can see on intensity maps, this trend is valid over three orders of magnitudes of $P$. In this $P$ range, $T$ varies only by a factor lower than 10 (Tables 4 to 7). So, the variation of $P$ is essentially dominated by the variation of $n_H$, and the same argument applies.

The orders of magnitude of $H_2$ line intensities are in good agreement with observations by Spitzer as presented in Habart et al. (2011). For example, our comparison of our intensity maps to observations towards the Horsehead for $H_2$ lines (Habart et al. 2011) and O at 63$\mu$m (Goicoechea et al. 2009) gives $\chi$ of a few hundreds in Mathis units which is consistent with previous models. Gas pressure is more difficult to constrain this way since, for moderate $\chi$, intensities of those lines are poorly dependent on $P$. Of all $H_2$ lines 0-0 S(3) is the more difficult to reproduce. We also notice that the intensity of the 1-0 S(1) line as well as the ratios of vibrational transitions displayed in table 9 as potential tests of formation pumping are within values reported for R1 and R2 towards M17 by Burton et al. (2002) for a pressure of $10^4$ cm$^{-3}$ K and radiation field enhancement factor of $10^4$. However the corresponding modeled R3 ratio is significantly smaller. Models in this paper have been done using typical properties of the interstellar medium (as grains properties) that may not be applicable for a detailed interpretation of the observations towards specific line of sights. As an example, the star illuminating the Horsehead is a O9.5 type star with an effective temperature of 33000 K. Scaling a Mathis ISRF as done here does not spread the UV energy in the same way than a stellar spectrum. This can affect level excitation. Note that most of the PDRs observations presented in Habart et al. (2011) are seen edge on whereas our plane parallel model we provide in this paper line intensities for PDRs seen face on and in PDRDBs up to 60 degrees. Applications to specific lines of sight will be performed subsequently by including all possible constraints derived from the observations.

5. Conclusions

In this paper, we presented implementations of Langmuir-Hinshelwood and Eley-Rideal mechanisms to describe $H_2$ formation on grain surfaces within the Meudon PDR code. This is the first of a series intended to discuss the formation of other molecules on grains in the light of recent experimental and theoretical progresses. Eley-Rideal mechanism involving chemisorbed sites is an efficient process to form $H_2$ in regions where the gas is hot and dust grains are warm. In previous versions of the code, the sole Langmuir-Hinshelwood mechanism allows to recover the value of the mean formation rate of $H_2$ derived from VUV observations of diffuse and translucent clouds. However, it led to strongly reduced values of $H_2$ formation rates in denser and strongly illuminated clouds due to the increasing importance of H evaporation compared to diffusion at the surface of the dust grains. Observations of these high excitation PDRs by, e.g., Habart et al. (2011) and references therein suggest mean formation rates typically a factor of 2 to 5 higher (with large uncertainties). This is now recovered by our treatment of the Eley-Rideal process whose efficiency rises with increasing gas temperature (up to a threshold). Thus, considering that observed rates are mean values along the line of sight and across a large variety of physical conditions wether our theoretical rates are local values computed from micro-physics considerations alone, the agreement between model and observations is now quite satisfactory in high excitation regions too.

The Eley-Rideal mechanism also provides an efficient process to heat the gas. Following Sizun et al. (2010) prescription to spread the energy released by the formation of a $H_2$ molecule in kinetic energy and internal energy, we showed that this formation process can be the major heating mechanism under some specific conditions. In particular, in regions where $H_2$

### Table 7. Same as Table 4 for $P = 10^4$ cm$^{-3}$ K.

| $\chi^{obs}$ | $10^3$ | $10^4$ | $10^5$ |
|--------------|--------|--------|--------|
| $T^{obs}_{\rho}$ (min) (K) | 16.7 | 26.2 | 41 |
| $T^{obs}_{\rho}$ (max) (K) | 27.7 | 44.1 | 70 |
| Model | A | B | C | A | B | C | A | B | C |
| $\rho_{H_2}$ (cm$^{-3}$) | 6.8(-4) | 6.1(-4) | 6.1(-4) | 1.2(-3) | 1.2(-3) | 1.3(-3) | 4.0(-3) | 3.7(-3) | 5.2(-3) |
| $T^{obs}_{\rho}$ (K) | 375 | 123 | 1386 | 502 | 179 | 1647 | 990 | 773 | 1565 |
| $R^{obs}_{H_2}$ (cm$^{-3}$ s$^{-1}$) | 3.0(-17) | 3.5(-18) | 1.3(-16) | 3.0(-17) | 2.4(-24) | 1.5(-16) | 3(-17) | 1.0(-28) | 1.5(-16) |
| $A_V(H = H_2)$ | 7(-3) | 2.0(-3) | 4.9(-4) | 4.0(-2) | 0.50 | 1.7(-2) | 0.48 | 2.1 | 0.40 |
| $m_H(H = H_2)$ (cm$^{-3}$) | 4.4(5) | 1.4(6) | 2.4(5) | 4.4(5) | 1.75(6) | 2.1(5) | 3.2(5) | 2.6(6) | 2.1(5) |
| $T(H = H_2)$ (K) | 296 | 91 | 534 | 298 | 74 | 601 | 411 | 48 | 618 |
| $N(H)$ (cm$^{-2}$) | 3.1(19) | 1.5(19) | 8.7(18) | 1.0(20) | 9.0(20) | 9.3(19) | 8.4(20) | 4.8(21) | 7.2(20) |
| $N(H_2)$ (cm$^{-2}$) | 9.3(21) | 9.3(21) | 9.4(21) | 9.3(21) | 8.9(21) | 9.3(21) | 8.9(21) | 6.9(21) | 9.0(21) |
Figure 2. Intensity of H$_2$ lines in erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$ seen in a face on geometry, for model C, a) 0-0 S(0), b) 0-0 S(1), c) 0-0 S(2), d) 0-0 S(3).

Table 8. Emissivities in erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$. Numbers in parenthesis refer to powers of ten.

| $p$ (cm$^{-3}$ K) | $\chi_{obs}$ | Model | $10^4$ | $10^5$ | $10^6$ |
|----------------|-------------|-------|--------|--------|--------|
|                |             | A     | B      | C      | A      | B      | C      | A      | B      |
| $10^5$         |              |       |        |        |        |        |        |        |        |
| CI 138 $\mu$m  | 9.1(-5)     | 9.6(-5)| 8.6(-5)| 1.7(-4)| 1.9(-4)| 1.6(-4)| 2.3(-4)| 2.9(-4)| 2.4(-4)|
| CI 610 $\mu$m  | 2.4(-6)     | 2.4(-6)| 2.4(-6)| 2.9(-6)| 3.1(-6)| 3.1(-6)| 3.5(-6)| 4.7(-6)| 4.8(-6)|
| CI 370 $\mu$m  | 3.4(-6)     | 3.4(-6)| 3.4(-6)| 4.7(-6)| 4.9(-6)| 4.9(-6)| 6.4(-6)| 7.0(-6)| 7.5(-6)|
| OI 145 $\mu$m  | 2.2(-6)     | 2.0(-6)| 2.2(-6)| 6.3(-6)| 5.7(-6)| 6.3(-6)| 1.0(-5)| 9.3(-5)| 1.0(-4)|
| OI 63 $\mu$m   | 6.4(-5)     | 6.4(-5)| 6.1(-5)| 1.8(-4)| 1.8(-4)| 1.7(-4)| 2.9(-4)| 3.2(-4)| 2.9(-4)|
| $10^6$         |              |       |        |        |        |        |        |        |        |
| CI 138 $\mu$m  | 1.3(-4)     | 1.3(-4)| 1.3(-4)| 3.2(-4)| 3.2(-4)| 3.1(-4)| 5.2(-4)| 5.4(-4)| 5.1(-4)|
| CI 610 $\mu$m  | 2.7(-6)     | 2.7(-6)| 2.7(-6)| 3.1(-6)| 3.4(-6)| 3.4(-6)| 3.7(-6)| 4.3(-6)| 4.4(-6)|
| CI 370 $\mu$m  | 5.7(-6)     | 5.6(-6)| 5.6(-6)| 7.6(-6)| 8.3(-6)| 8.3(-6)| 1.0(-5)| 1.1(-5)| 1.2(-5)|
| OI 145 $\mu$m  | 5.7(-6)     | 4.1(-6)| 5.8(-6)| 3.8(-5)| 3.2(-5)| 3.9(-5)| 8.4(-5)| 7.2(-5)| 8.7(-5)|
| OI 63 $\mu$m   | 1.9(-4)     | 1.9(-4)| 1.8(-4)| 1.1(-3)| 1.1(-3)| 9.8(-4)| 2.3(-3)| 2.4(-3)| 2.2(-3)|
| $10^7$         |              |       |        |        |        |        |        |        |        |
| CI 138 $\mu$m  | 5.8(-5)     | 5.7(-5)| 5.7(-5)| 2.4(-4)| 2.3(-4)| 2.4(-4)| 2.4(-4)| 4.9(-4)| 5.1(-4)|
| CI 610 $\mu$m  | 2.8(-6)     | 2.8(-6)| 2.8(-6)| 3.3(-6)| 3.5(-6)| 3.5(-6)| 3.3(-6)| 3.8(-6)| 4.2(-6)|
| CI 370 $\mu$m  | 6.7(-6)     | 6.7(-6)| 6.7(-6)| 9.6(-6)| 1.0(-5)| 1.0(-5)| 1.0(-5)| 9.6(-6)| 1.3(-5)| 1.5(-5)|
| OI 145 $\mu$m  | 4.9(-6)     | 3.8(-6)| 4.3(-6)| 9.0(-5)| 5.7(-5)| 9.9(-5)| 9.0(-5)| 2.7(-4)| 3.6(-4)|
| OI 63 $\mu$m   | 3.6(-4)     | 3.5(-4)| 3.5(-4)| 3.4(-3)| 3.3(-3)| 3.3(-3)| 3.4(-3)| 1.1(-2)| 1.0(-2)|
| $10^8$         |              |       |        |        |        |        |        |        |        |
| CI 138 $\mu$m  | 6.5(-6)     | 1.0(-5)| 9.8(-6)| 1.1(-4)| 1.2(-4)| 1.1(-4)| 3.5(-4)| 3.8(-4)| 3.3(-4)|
| CI 610 $\mu$m  | 2.2(-6)     | 2.3(-6)| 2.3(-6)| 3.0(-6)| 3.3(-6)| 3.3(-6)| 3.4(-6)| 3.6(-6)| 4.2(-6)|
| CI 370 $\mu$m  | 5.8(-6)     | 5.7(-6)| 5.7(-6)| 1.0(-5)| 1.1(-5)| 1.2(-5)| 1.4(-5)| 1.5(-5)| 1.8(-5)|
| OI 145 $\mu$m  | 3.5(-5)     | 2.4(-6)| 3.0(-6)| 9.9(-5)| 7.3(-5)| 1.1(-4)| 5.7(-4)| 4.4(-4)| 6.1(-4)|
| OI 63 $\mu$m   | 1.7(-3)     | 3.7(-4)| 3.9(-4)| 5.7(-3)| 4.9(-3)| 5.9(-3)| 2.3(-2)| 2.1(-2)| 2.3(-2)|

self-shielding is not yet fully efficient and with densities above the critical density of collisions with H, a significant amount of energy can be transferred into kinetic energy of the gas. Signatures of formation pumping are not straightforward at the light of present knowledge on the internal state of newly formed H$_2$.

The efficiency of the Langmuir-Hinshelwood process depends on the temperature of the grains. As shown by many authors this formation mechanism can only take place in a small window of grain temperatures (Biham & Lipshtat 2002; Biham et al. 2005; Le Petit et al. 2009), 10-20 K for amorphous carbons. As a consequence, LH mechanism becomes the major H$_2$
formation process at moderate visual extinctions. The strong dependence on $T_{gr}$ implies that a proper computing of grains temperature has to be done in numerical models, including temperature fluctuation of the smallest grains.

We compared results of PDR models in which H$_2$ formation is treated by these detailed mechanisms to models using a constant formation rate with $R_{H_2} = 3 \times 10^{-17}$ cm$^3$ s$^{-1}$. For diffuse clouds parameters, the main effect is to shift the H/H$_2$ transition and to increase the molecular fraction. For stronger PDRs, we showed that at high radiation field, line intensities depend strongly on gas pressure. The difference between detailed treatment of H$_2$ formation and a constant formation rate can lead to differences up to a factor 3 in the most commonly observed H$_2$ line intensities. We provide maps of such line intensities for a set of 190 models for different pressures and intensities of the incident radiation field$^3$.

Acknowledgements. This work was partially funded by grant ANR-09-BLAN-0231-01 from the French Agence Nationale de la Recherche as part of the SCHISM project and by the French CNRS national program PCMI. The authors acknowledge support for computing resources and services from France Grilles and the EGI e-infrastructure as well as MESOPSL, the computing center for Paris Sciences et Lettres. Some kinetic data have been downloaded from the online KIDA (Kinetic Database for Astrochemistry, http://kida.obs.u-bordeaux1.fr) database. We thank our colleagues from the “Laboratoire des Collisions Atomiques et Moléculaires” in Orsay, V. Sidis, N. Rougeaud and D. Bachellerie for fruitful discussions on the ER process. We thank David Languignon, Nicolas Moreau, Benjamin Ooghe and Emeric Bron for their help in running some of the models and setting them up on the on-line database.

Appendix A: Other recent updates to the PDR code

Different progresses have been achieved in computing fine structure and rotational excitation due to collisions with H and/or H$_2$ as reported in the BASECOL (Dubernet et al. 2006) and LAMDA (Schöier et al. 2005) databases. We have updated and/or implemented collisional excitation rates which play an active role in the cooling processes and compute explicitly their emission spectrum by solving the statistical equilibrium equations, including radiative pumping by the cosmic background radiation field and dust infrared emission (Gonzalez Garcia et al. 2008). Let us point out that the new fine structure excitation collision rates of atomic oxygen computed by Abrahamsson et al. (2007) have a significant impact on the temperature at the edge of PDRs. As an example, for a typical proton density of $10^5$ cm$^{-3}$ and a radiation scaling factor of 10, the temperature at the edge is 90K with the old Launay & Roueff (1977) atomic oxygen collision rates and only 67K with the recent values displayed in Abrahamsson et al. (2007). In the present stage, emission spectra of millimeter and submillimeter transitions of HCN, OH, CH$^+$, O$_2$ are readily computed and implementation of other molecules is straightforward and depends only on the availability of collision rates by the relevant perturbers. Another significant issue is the inclusion of the thermal and charge balance of the grains in the overall ionization fraction. The thermal balance is obtained through a coupling with the DustEM program Compiègne et al. (2011) which can be switched on through the F_Dustem parameter ($F_{Dustem}=1$). If not ($F_{Dustem}=0$), the temperature of the various grain bin sizes is obtained from the formula (5) of Hollenbach et al. (1991), where the actual value of the radi-

$^3$ Full results are found at http://pdr.obspm.fr
Figure 4. Intensity of H$_2$ lines in erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$ seen in a face on geometry, for model C, a) 2-1 S(1), b) 2-1 S(2), c) 2-1 S(3).

Figure 5. Intensity of O at 63 and 145 $\mu$m in erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$ seen in a face on geometry, for model C.

The determination of the grain charge is obtained from the balance between photoelectric effect and recombination on dust particles, expanding on the treatment of Draine & Sutin (1987) and Bakes & Tielens (1994).

We also compute photodissociation rates from the integration of the photodissociation cross-sections, when available, with the interstellar radiation field. The attenuation by dust particles is then directly obtained from the dust properties considered in the model, i.e. their absorption and extinction coefficients which depend on the size and the nature of the dust particles. Different options are proposed depending on the treatment of the grain temperatures. If $F_{\text{Dustem}}=1$, we use the absorption and scattering coefficients computed by the DustEM code (Compiègne et al. 2011). If $F_{\text{Dustem}}=0$, we derive the albedo and dust properties from the extinction curve given by the Fitzpatrick and Massa analytic expansion (Fitzpatrick & Massa 2007), extended towards longer wavelengths by the data from Weingartner & Draine (2001). It is remarkable that we recover the dust free photodissociation rates displayed in van Dishoeck (1988) for the Mathis or Draine incident radiation field. The $A_V$ available from http://www.astro.princeton.edu/~draine/dust/dustmix.html
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Figure 6. Intensity of C$^+$ at 157.63$\mu$m in erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$ seen in a face on geometry, for model C.

Table 9. Emissivities of H$_2$ transitions in erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$. Number in parenthesis refer to powers of ten. $R_1 : 1 - 0S(1)/2 - 1S(1)$, $R_2 : 1 - 0S(1)/1 - 0S(7)$, $R_3 : 1 - 0S(1)/6 - 4O(3)$.

| $p$ (cm$^{-3}$ K) | $\chi_{obs}$ | $10^5$ | $10^6$ | $10^7$ | $10^8$ |
|------------------|--------------|--------|--------|--------|--------|
|                  | Model        | A      | B      | C      | A      | B      | C      | A      | B      | C      |
| 0-0 S(0)         | 1.9(-6)      | 3.3(-7)| 2.5(-6)| 1.2(-5)| 3.2(-7)| 1.8(-5)| 2.2(-5)| 1.3(-9)| 2.9(-5)|        |
| 0-0 S(1)         | 6.2(-7)      | 6.4(-7)| 9.7(-7)| 1.4(-5)| 3.2(-8)| 4.4(-5)| 4.7(-5)| 1.2(-9)| 1.1(-4)|        |
| 0-0 S(2)         | 3.8(-7)      | 1.9(-7)| 4.5(-7)| 3.1(-5)| 9.4(-8)| 1.3(-5)| 1.1(-5)| 4.7(-9)| 2.8(-5)|        |
| 0-0 S(3)         | 4.7(-7)      | 2.5(-7)| 5.3(-7)| 1.4(-6)| 1.1(-7)| 3.4(-6)| 2.1(-6)| 2.9(-9)| 5.6(-6)|        |
| 0-1 S(1)         | 4.0(-7)      | 1.6(-7)| 6.2(-7)| 8.1(-7)| 5.9(-8)| 1.6(-6)| 1.1(-6)| 1.2(-9)| 2.1(-6)|        |
| $R_1$            | 2.0          | 2.0    | 2.0    | 1.9    | 2.0    | 1.9    | 1.9    | 1.9    | 1.9    |        |
| $R_2$            | 7.5          | 7.1    | 5.4    | 7.7    | 8.1    | 4.9    | 7.4    | 93     | 4.8    |        |
| $R_3$            | 3.6          | 3.6    | 3.5    | 3.5    | 4.0    | 3.9    | 4.0    | 4.2    | 4.0    |        |
| 1-0 S(1)         | 4.0(-7)      | 1.6(-7)| 6.2(-7)| 8.1(-7)| 5.9(-8)| 1.6(-6)| 1.1(-6)| 1.2(-9)| 2.1(-6)|        |
| $R_1$            | 2.0          | 2.0    | 2.0    | 1.9    | 2.0    | 1.9    | 1.9    | 1.9    | 1.9    |        |
| $R_2$            | 7.5          | 7.1    | 5.4    | 7.7    | 8.1    | 4.9    | 7.4    | 93     | 4.8    |        |
| $R_3$            | 3.6          | 3.6    | 3.5    | 3.5    | 4.0    | 3.9    | 4.0    | 4.2    | 4.0    |        |

dependence of the photodissociation rates reflects then directly the appropriate dust environment.

Appendix B: Langmuir-Hinshelwood mechanism

Upon landing on a grain most heavy species may build an ice mantle. In that case, it is possible to account for the total number of physisorbed molecules by integrating on the grain size distribution. This is the subject of a forthcoming paper on surface chemistry (Le Petit et al., to be submitted). However this is probably not the case for the lightest species (H, H$_2$, D, HD, ...). We assume here that they only build a single monolayer above either the grain surface or the ice mantle.

In that case, two effects must be taken into account:

- Upon landing on a site already occupied by a light species, the impinging species is rejected to the gas phase.
Table B.1. Abscissae and weights for the Gaussian integration of a MRN size distribution with \( n_{pg} = 12 \), \( \alpha = 3.5 \), \( a_{min} = 3 \times 10^{-7} \) cm and \( a_{max} = 3 \times 10^{-3} \) cm. The weights do not include the normalization factor \( A_{gr} \) nor the gas phase density \( n_{H} \). In the text, \( w_i = A_{gr} n_{H} w_i' \).

| \( a_i \) (\( \times 10^{-7} \)) | \( w_i' \) |
|-----------------|--------|
| 3.57699063968688527E-007 | 5792151389936155.0 |
| 6.98799352447769293E-007 | 205685967306352.5 |
| 1.66467328055428966E-006 | 235554962470170.16 |
| 3.55645670102603961E-006 | 2807187236201.828 |
| 6.3897792931362064E-005 | 4932081459260.9521 |
| 9.9762390393405377E-005 | 1234971510565.4812 |
| 1.4034374717140631E-005 | 403598849340.4542 |
| 1.82200037492632748E-005 | 1606151293420764 |
| 2.21882637436107715E-005 | 7267983247191898 |
| 2.5581883794095445E-005 | 3568978431959213 |
| 2.81455972293716657E-005 | 1738274116685666 |
| 2.96417164382822754E-005 | 64574542663027544 |

B.1. Adsorption

If the outer layer of the grain is populated by light species (H, \( H_2 \)) then any of them may lead to reaction of an impinging atom. Let us consider \( n_j \) such species. Then, the number of accretion of a species \( X \) per unit time interval on a single grain of size \( a \) is:

\[
s(X)[X] \pi a^2 \left(1 - \frac{d_i^2}{4\pi a^2} \sum_{j} n_{Y_j}(a)\right)
\]

where \( s(X) \) is the sticking coefficient of species \( X \), \( d_i \) the mean distance between adsorption sites (supposed identical for all grains) and the term in parentheses takes into account rejection by any species \( Y_j \) that is already on the grain. \( \frac{d_i^2}{4\pi} \) is the total number of adsorption sites on a grain of size \( a \). Formally, this equation may be split into a first order formation reaction with rate \( k_{ad}(a) = s(X) \pi a^2 \), and \( n_j \) different second order destruction reactions with rate \( k_{rej} = s(X) \pi a^2 \). The relevant creation and destruction equations are thus:

\[
\frac{dN_X(a)}{dt} = k_{ad}(a)[X] - \sum_{j} k_{rej} N_{Y_j}(a) \tag{B.1}
\]

\[
- \frac{d[X]}{dt} = \left( \int_{a_{min}}^{a_{max}} k_{ad} dn_g \right) [X] - \sum_{j} \int_{a_{min}}^{a_{max}} k_{rej} N_{Y_j}(a) dn_g [X]
\]

or:

\[
- \frac{d[X]}{dt} = k_{rej} S_{gr} [X] - k_{rej} \sum_{j} \sum_{i} w_i N_{Y_j}(a_i) [X] \tag{B.2}
\]

Here, \( S_{gr} \) is the total surface of grains per unit volume. One can see that, although the form of the reaction terms is preserved (first or second order polynomial in the variables) the total number of individual contributions becomes large (one accretion leads to \( n_j \times n_{pg} + 1 \) reactions).\(^6\)

B.2. Desorption processes

Ejection can occur spontaneously (thermal evaporation) or by photo-desorption or cosmic rays ejection. All processes are similar in the sense that they only involve a single variable \( N_X(a) \) on a grain of size \( a \).

If the vibration frequency of the adsorbed particle is \( \nu_0 \), the temperature of the grain is \( T_g(a) \) and the binding energy is \( T_b(X) \), then the number of evaporation per unit time is:

\[
\nu_0 \exp\left( \frac{T_b(X)}{T_g(a)} \right) N_X(a)
\]

If the flux of photons (resp. cosmic rays) is \( F_{ph} \) (resp. \( F_{cr} \)) and the number of particles desorbed by impact is \( \nu_{ph} \) (resp. \( \nu_{cr} \)), then the number of desorption is (for a photon):

\[
F_{ph} \pi a^2 \eta_{ph} \frac{d_i^2}{4\pi a^2} N_X(a) = F_{ph} \eta_{ph} \frac{d_i^2}{4} N_X(a)
\]

\(^5\) They are computed automatically during the initialization phase of the code.

\(^6\) In the Meudon PDR code, we use a specific Gaussian scheme to integrate over the MRN distribution. This keeps \( n_{pg} \) to a reasonably low value (typically 12).
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Writing \( k_{ev}(a) = v_0 \exp\left(-\frac{T_d \gamma(a)}{T_g a^2}\right) \), \( k_{ph} = F_{ph} \eta_{ph} \frac{d^2}{T_g} \) and \( k_{CR} = F_{CR} \eta_{CR} \frac{d^2}{T_g} \), we have:

\[
- \frac{dN_X(a)}{dt} = \left(k_{ev}(a) + k_{ph} + k_{CR}\right) N_X(a)
\]

\[
\frac{d[X]}{dt} = \sum_i n_{pg} k_{ev}(a_i) w_i N_X(a_i) + \left(k_{ph} + k_{CR}\right) \sum_i w_i N_X(a_i)
\]

**B.3. Surface reactions**

We seek to compute the number of encounters per grain and per unit time. Let us look at things from the point of view of \( X \). On a single grain of size \( a \) the number of encounters per \( s \) is proportional to \( 1/\gamma \) the inverse hoping time of \( X \); the probability to find a \( Y \) upon landing and the number of \( X \):

\[
N_X(a) \frac{1}{\gamma \times 4\pi a^2} N_Y(a)
\]

During the same time, from the point of view of \( Y \), the number of encounter made is

\[
N_Y(a) \frac{1}{\gamma \times 4\pi a^2} N_X(a)
\]

So the total number of encounters is:

\[
\frac{1}{2} \left(\frac{1}{\gamma_X} + \frac{1}{\gamma_Y} \right) \frac{d^2}{8\pi a^2} N_X(a) N_Y(a)
\]

where the factor of \( \frac{1}{2} \) takes care of the fact that each encounter has been counted twice. Thus, for two surface species, we can write \( k_{for} = \frac{1}{\gamma_X(a) + \gamma_Y} \frac{d^2}{8\pi a^2} \) and:

\[
- \frac{dN_X(a)}{dt} = - \frac{dN_Y(a)}{dt} = k_{for} N_X(a) N_Y(a)
\]

The production rate of \( Z \) in the gas phase, occurring directly after the encounter of two adsorbed atoms, is obtained after integration on the grain size distribution:

\[
\frac{d[Z]}{dt} = \frac{d^2}{8\pi} \sum_i n_{pg} \left(\frac{1}{\gamma_X(a_i)} + \frac{1}{\gamma_Y(a_i)}\right) w_i N_X(a_i) N_Y(a_i)
\]

**B.4. Approximate \( H_2 \) formation rate**

For a single grain size, and negligible photodesorption and cosmic rays desorption, we can derive an analytic approximation to the \( H_2 \) formation rate in the spirit of the discussion of Biham & Lipshiat (2002). If \( H \) is the only atom sticking to a grain of size \( a \) with a sticking probability of 1, then:

\[
\frac{dN_H}{dt} = k_{ad}[H] - k_{rej}[H] N_H - k_{ev} N_H - 2 k_{for} N_H^2
\]

At steady state, this leads to:

\[
N_H = \frac{[H]}{[H]_b} \left(1 + \frac{[H]_b}{[H]}\right) \left[-1 + \sqrt{1 + 2 N_{max}^H \frac{[H]_b}{[H]} \frac{1}{1 + [H]_b/[H]}\right]
\]

with \( N_{max}^H = \frac{4 \pi a^2}{T_g} \) the maximum number of \( H \) on the grain, and the two critical densities \( [H]_a \) and \( [H]_b \) defined as:

\[
[H]_a = \frac{k_{ev}}{k_{rej}} = \frac{4 v_0}{T_g a^2} \exp\left(-\frac{T_b}{T_g}\right)
\]

Table B.2 gives the values of the critical densities for different grain temperatures:

The \( H_2 \) formation rate per grain is then (with \( n_g \) the number of grains per cubic centimeter of gas and \( 3 \cdot 1.4 \cdot m_H G \)):

\[
\frac{1}{n_g} \frac{d[H_2]}{dt} = k_{for} N_H^2
\]

and can be given analytically from the previous formulae. \([H]_a\) and \([H]_b\) vary slowly with the gas temperature, but very strongly with the grain temperature. Thus, we can define two limiting regimes for the gas phase atomic hydrogen density:

- \([H]_a \gg [H]_b > [H]_b\). Then:
  \[
  N_H = N_{max}^H \frac{1}{n_g} \frac{d[H_2]}{dt} \frac{1}{l_{LH}} = \frac{4 \pi a^2}{T_g} \exp\left(-\frac{T_b}{T_g}\right)
  \]

This is possible only for cold grains (typically below 15K). So, it requires both a high density (or pressure) and low radiation field.

- \([H]_a \ll [H]_b < [H]_a\). Then:
  \[
  N_H = \frac{N_{max}^H}{[H]_a} \frac{[H]}{\gamma_0} \exp\left(-\frac{T_b}{T_g}\right)
  \]

This is the case for all grain sizes as soon as \( T_g \) is above about 25K. So it applies to all high radiation field models. Here the formation rate grows as the square of the density of \( H \).

The usual expression for the formation rate \( R_{H_2} \) in \( cm^3 s^{-1} \) follows from:

\[
\frac{d[H_2]}{dt} \bigg|_{LH} = R_{H_2} n_H [H]
\]

Since \( n_g \) is proportional to \( n_H \) we see that in the first case \( R_{H_2} \propto 1/[H] \), whereas in the second \( R_{H_2} \propto [H] \). These relations apply only with the approximations made here.

**Appendix C: Eley-Rideal mechanism**

**C.1. Formalism**

Let us consider the impact of a fast atom (hot gas) with a grain. Since a full detailed description (taking into account all possible kinds of surfaces) is much beyond the capacity of our model, we look for an approximate mechanism that takes into account the following constraints:

- It is efficient in “hot” gas and on “hot” grains. Therefore the impinging H atom must eventually reach a chemisorbed site on the grain.
– It leads to H₂ formation rates consistent with observational constraints.
– The number of free parameters is kept to the lowest possible number.

Since this process takes place at the edge of the cloud, we assume that the grains are essentially bare (without ice coating) and that the process does not depend on the grain temperature. This approximation is justified since, at the edge of PDRs, grain temperatures (at most 100 K) are much lower than the gas temperature or chemical binding energies on grain surfaces.

On impact, the gas phase H can find either a free chemisorption site or an already chemisorbed H. In the second case, since the formation of H₂ releases 4.5 eV, an energy far higher than the chemisorbed well, we assume that a newly formed H₂ is immediately released in the gas phase. So:

\[ \frac{d[H_2]}{dt|_{ER}} = - \frac{d[H ::]}{dt|_{dest}} = v_{th} < n \sigma_{gr} > [H] \frac{[H ::]}{[H ::]_{max}} \]

where \([H ::]_{max}\) is the maximum number of chemisorbed H atoms (saturated grains) and \([H ::]\) the corresponding abundance. \(v_{th}\) is the thermal velocity of the gas phase H and we consider the geometrical cross-section to compute the total amount of grain surface per unit volume \(< n \sigma_{gr} >\). If the mean distance between chemisorption sites is \(d_s\) and is the same on all types of grains, one can see (from purely geometric considerations) that:

\[ \frac{< n \sigma_{gr} >}{[H ::]_{max}} = \frac{d_s^2}{4} \]

This is true for any grain size distribution. If the gas phase atom impacts a free chemisorption site, we have to estimate the probability that it sticks to the grain. The simplest hypotheses requires that it be proportional to the number of collisions of H with grains per unit of time \((v_{th} < n \sigma_{gr} >)\), possibly with a barrier to cross \(\exp(-\frac{A}{kT})\) (where \(T\) is the gas temperature and \(T_1\) the threshold), with a temperature dependent sticking coefficient \(\alpha(T)\) and proportional to the “free room” \((1 - \frac{[H ::]}{[H ::]_{max}})\). So we write:

\[ \frac{d[H ::]}{dt|_{form}} = \alpha(T) v_{th} < n \sigma_{gr} > [H] \exp\left(\frac{-T_1}{T}\right) \left(1 - \frac{[H ::]}{[H ::]_{max}}\right) \]

This equation is split in the code in two: a direct formation reaction and a “pseudo” rejection reaction. The corresponding rates are:

\[ \frac{d[H ::]}{dt|_{form,d}} = \alpha(T) v_{th} < n \sigma_{gr} > \exp\left(\frac{-T_1}{T}\right) [H] \]

\[ \frac{d[H ::]}{dt|_{form,r}} = -\alpha(T) v_{th} \frac{d_s^2}{4} \exp\left(\frac{-T_1}{T}\right) [H][H ::] \]

### C.2. Sticking coefficient and choice of \(T_1\)

There is not much information on how to define the sticking function \(\alpha(T)\), but we expect that it goes to 0 for very high temperatures (the atom just bounces on the grain without time to evacuate the excess kinetic energy). We introduce the empirical form:

\[ \alpha(T) = \frac{1}{1 + \left(\frac{T}{T_1}\right)^\beta} \]  

(C.1)

In this expression, the index \(\beta\) controls the steepness of the decrease of \(\alpha(T)\) and \(T_2\) defines the temperature such that \(\alpha(T_2) = \frac{1}{2}\).

We may constrain the value of \(\beta\) by the following considerations:

- An estimate of the velocity \(v_2\) above which the atom bounces back to the gas is given by:
  \[ v_2 \sim d_s v_0 \]

- The sticking coefficient is approximated as the fraction of gas phase atom with velocity lower than \(v_2\). Using a Maxwell distribution at temperature \(T\) we have:

  \[ \alpha(T) \approx \sqrt{\frac{2}{\pi}} \left(\frac{m}{kT}\right)^{3/2} \int_0^{v_2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv \]

  \[ = \operatorname{erf}\left(\sqrt{\frac{m v_2^2}{2kT}}\right) - \frac{2}{\sqrt{\pi}} \sqrt{\frac{m v_2^2}{2kT}} \exp\left(-\frac{mv_2^2}{2kT}\right) \]

At low temperatures, this expression tends to 1 as expected. At high temperatures, we may expand this expression as a function of \(mv_2^2/2kT\). Defining \(T_2\) by \(v_2 = \sqrt{\frac{8 kT_2}{\pi m}}\), we get:

\[ \alpha(T) \approx \frac{4}{3 \sqrt{\pi}} \left(\frac{m}{2kT}\right)^{3/2} v_2^3 = \frac{32}{3\pi^2} \left(\frac{T_2}{T}\right)^{3/2} \]

This shows that \(\beta = \frac{3}{2}\) in Eq (C.1) is exact. The prefactor is 1.08, which we can take as 1 given the approximations involved; thus Eq (C.1) is a good approximation over the whole temperature range. The estimate of \(v_2\) gives \(T_2\) in the range \(400–500\) K.

Given \(\alpha(T)\), we may investigate which barrier \(T_1\) gives a “standard” formation rate of \(3 \times 10^{-11} \text{cm}^3 \text{s}^{-1}\) at a given temperature \(T\). We find:

\[ T_1 = T \log\left(\alpha(T) \left(\frac{2.8}{3} \sqrt{T} - 1\right)\right) \]

Postulating that where grains are warm, the gas is warm too, we may require that this standard rate is reached for a temperature in the range \([150 : 450]\) K. This translate into a range

\(^7\) The value \(T_2 = 464\) K was selected to match a previous “guesstimate” proportional to \(10^{-4} T^\beta\).
[100 : 800] K for $T_1$. Our choice of $T_1 = 300 \text{ K}$ favors an efficient formation, and reflects the idea that chemisorption is easy (but not instantaneous) on grains with lots of surface defects. This leads to a higher formation rate at high gas temperature as found observationally by Habart et al. (2004).

**C.3. Analytical approximation**

If hydrogen is the only chemisorbed species, the abundance of $\text{H} ::$ can be analytically derived at steady state:

$$[\text{H ::}] = \frac{\alpha(T) \exp\left(-\frac{1}{T}\right)}{1 + \alpha(T) \exp\left(-\frac{1}{T}\right)} [\text{H ::}]_{\text{max}}$$

This leads to an $\text{H}_2$ formation rate of:

$$d[H_2]|_{\text{ER}} = v_{th} < n\sigma_{gr} > \kappa(T) [\text{H}] = k_{\text{ER}} [\text{H}] n_H$$

with:

$$\kappa(T) = \frac{\alpha(T) \exp\left(-\frac{1}{T}\right)}{1 + \alpha(T) \exp\left(-\frac{1}{T}\right)}$$

In this expression, $v_{th} < n\sigma_{gr} > [\text{H}]$ refers to a purely geometric collisional process. Fig. C.1 displays the variation of the chemisorption rate as a function of gas temperature (relative to the one at $100\text{ K}$). The rate is negligible at low temperature (due to the exponential barrier). It grows as the square root of $T$ once the barrier is negligible, then is quenched by the sticking cut-off. The chemisorption efficiency, $\kappa(T)$, is displayed on Fig. C.1 (right axis). It peaks at a few hundred Kelvin and keeps significant values up to a few thousands.

This behavior is qualitatively similar to results found by Cuppen et al. (2010) (their Fig. 2) from Monte Carlo simulations of $\text{H}_2$ formation including both physisorption and chemisorption. They find also that formation efficiency increases for gas temperatures around a thousand K.

In Sect. 4.2.2 we present several line intensities computed from models in which $\text{H}_2$ is formed by ER and LH mechanisms. In these models, we adopt $\beta = 1.5$, $T_1 = 300 \text{ K}$ and $T_2 = 464 \text{ K}$. Fig. C.2 presents the effect of variations of $T_1$ and $T_2$ on the intensity of one line of $\text{H}_2$. We note that $T_1$ is the most important parameter and that the line intensity can be reduced by a factor $\approx 5$ if this parameter is increased from $300 \text{ K}$ to $1000 \text{ K}$. For other lines, as $0-0 \text{ S}(0)$ this decrease can reach a factor of 10. As mentioned above, for real interstellar grains, we can expect to have a large range of $T_1$ depending on the nature and structure of the grains surfaces. Even if most of chemisorbed sites have high thresholds, it only requires a few low thresholds sites for the ER mechanism to be efficient.

**Appendix D: $A_V$ to size conversion**

For constant dust properties along the line of sight, it is possible to convert optical depth in the visible to a distance (in pc) analytically. Let $C_d$ be the total proton column density to color index ratio, and $R_V$ the usual extinction to color index ratio:

$$C_d = \frac{N_H}{E_{B-V}}; \quad R_V = \frac{A_V}{E_{B-V}}$$

Then, using $A_V = 2.5 \log_{10}(e) \tau_V$, we have:

$$N_H = \int_0^l n_H ds = C_d \frac{E_{B-V}}{A_V} 2.5 \log_{10}(e) \int_0^{\tau_V^{\text{max}}} d\tau_V$$

so, with $C_v = \frac{C_d}{R_V} 2.5 \log_{10}(e)$, we have:

$$l = \int ds = C_v \int_0^{\tau_V^{\text{max}}} \frac{1}{n_H} d\tau_V$$

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![Figure C.1. Left axis: Variation of $k_{\text{ER}}$ with gas temperature $T$ (relative to the one at 100 K). Right axis: chemisorption efficiency $\kappa$ (see text).](image1)

![Figure C.2. Effect of the variation of $T_1$ and $T_2$ on the intensity of H$_2$ 1-0 S(1) line for the model $P = 10^7$ cm$^{-3}$ K and $x = 1000$. Values plotted in the plane $T_1, T_2$ are $I(T_1, T_2)/I(300, 464)$.](image2)
