A new and simple approach to determine the abundance of hydrogen molecules on interstellar ice mantles

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ABSTRACT

Context. Water is usually the main component of ice mantles, which cover the cores of dust grains in cold portions of dense interstellar clouds. When molecular hydrogen is adsorbed onto an icy mantle through physisorption, a common assumption in gas-grain rate-equation models is to use an adsorption energy for molecular hydrogen on a pure water substrate. However, at high density and low temperature, when H\textsubscript{2} is efficiently adsorbed onto the mantle, its surface abundance can be strongly overestimated if this assumption is still used. Unfortunately, the more detailed microscopic Monte Carlo treatment cannot be used to study the abundance of H\textsubscript{2} in ice mantles if a full gas-grain network is utilized.

Aims. We present a numerical method adapted for rate-equation models that takes into account the possibility that an H\textsubscript{2} molecule can, while diffusing on the surface, find itself bound to another hydrogen molecule, with a far weaker bond than the H\textsubscript{2}-water bond, which can lead to more efficient desorption. We label the ensuing desorption “encounter desorption”.

Methods. The method is implemented first in a simple system consisting only of hydrogen molecules at steady state between gas and dust using the rate-equation approach and comparing the results with the results of a microscopic Monte Carlo calculation. We then discuss the use of the rate-equation approach with encounter desorption embedded in a complete gas-grain chemical network.

Results. For the simple system, the rate-equation model with encounter desorption reproduces the H\textsubscript{2} granular coverage computed by the microscopic Monte Carlo model at 10 K for a gas density from $10^4$ to $10^{12}$ cm\textsuperscript{-3}, and yields up to a factor 4 difference above $10^{12}$ cm\textsuperscript{-3}. The H\textsubscript{2} granular coverage is also reproduced by a complete gas-grain network. We use the rate-equation approach to study the gas-grain chemistry of cold dense regions with and without the encounter desorption mechanism. We find that the grain surface and gas phase species can be sensitive to the H\textsubscript{2} coverage, up to several orders of magnitude, depending on the species, the density, and the time considered.

Conclusions. The method is especially useful for dense and cold environments, and for time-dependent physical conditions, such as occur in the collapse of dense cores and the formation of protoplanetary disks. It is not significantly CPU time consuming, so can be used for example with complex 3D chemical-hydrodynamical simulations.

Key words. astrochemistry – molecular processes – methods: numerical – ISM: molecules – ISM: abundances

1. Introduction

Gas-grain chemical models, which are useful tools for studying the chemistry in the interstellar medium, often include the rate-equation approach to calculate the evolution of species in the gas phase and on the grain surface (e.g., Herbst & Klemperer 1973; Hasegawa et al. 1992). Regarding the chemistry on dust grains and their ice mantles, the rate-equation approach can be used in the basic two-phase approach, in which no distinction is made between the surface of the ice and layers underneath it, the three-phase model, in which chemistry only takes place on the surface, or even a multi-layer approach (e.g., Hasegawa et al. 1992; Hasegawa & Herbst 1993b; Taquet et al. 2012). Even the two-phase approach can describe the chemistry reasonably accurately (Garrod et al. 2008), and rate-equation methods are efficient for large chemical networks where thousands of reactions are taken into account. Some limitation exists when the average number of species per dust grain is below unity, and stochastic methods are more accurate (Tielens & Charnley 1997; Caselli et al. 1998; Herbst & Shematovich 2003; Lipscat & Bihm 2003; Stantcheva & Herbst 2004). Contrary to microscopic kinetic Monte Carlo models, and other detailed stochastic treatments, (Chang et al. 2005, 2007; Cuppen & Herbst 2005; Cuppen et al. 2009; Cazaux et al. 2010; Chang & Herbst 2012, 2014; Iqbal et al. 2012), rate-equation models do not take into account each individual process that occurs on and beneath the ice surface. For example, when a molecule is adsorbed on the grain surface, the desorption energy should depend on the substrate and other grain surface parameters, which are functions of the location on the grain surface, itself continuously in evolution as a function of time. For rate-equation treatments, however, a single binding energy per adsorbate is commonly used depending upon physical conditions and type of source. Since water ice is often the main component of dust grain mantles in cold dense interstellar clouds (Tielens & Hagen 1982; Whittet et al. 1998), the adsorption energies used in models of these sources are usually the ones of a given adsorbate on a water substrate. A list of desorption energies for a selection
of physisorbed adsorbates on water and other substrates can be found in Table 3 of Cuppen & Herbst (2007). In this paper we will be concerned with the binding of H2 on a water substrate and on itself, and will be using 440 K and 23 K on H2 for the two values, respectively (Cuppen & Herbst 2007).

Determination of the amount of H2 on a dust grain in a cold cloud is a difficult task for several reasons. First, it is difficult if not impossible to include the adsorption and desorption of hydrogen molecules in a complete treatment of the surface chemistry via the kinetic Monte Carlo approach given the speed with which these processes can happen. The situation gets worse if complex simulations of star formation, such as three-dimensional hydrodynamical simulations (Furuya et al. 2012; Hincelin et al. 2013), or even warm-up models (e.g. Viti et al. 2004; Garrod & Herbst 2006), are undertaken, because the kinetic Monte Carlo models are very time-consuming computationally. Secondly, the large difference between the binding energy of H2 to a water ice substrate and to itself means that a rate-equation model with only one binding energy for H2, the one with water, can lead to an overestimate of the H2 granular abundance, especially at low temperature and high density (>10 K and >10^10 cm^-3), and on the contrary, considering a single binding energy of 23 K prevents adsorption of H2 onto grain surfaces, which is not real except at high temperatures. Thus, a simple and efficient numerical approach to deal with H2 coverage as a function of temperature, density, and time, and applicable to rate-equation chemical models, is desirable. The goal of this paper is to present one such approach and to use it in treatments of cold and dense regions. This new approach differs from earlier approaches of Wolff et al. (2010), Cuppen & Garrod (2011), and Garrod & Pauly (2011).

The remainder of the paper is structured as follows. We present our treatment in terms of a rate equation in Sect. 2. In Sect. 3, we then consider a simple steady-state model in which we only include a fixed amount of H2 and calculate the surface abundance of H2 as a function of density for a cloud at 10 K. We compare the results of this simple model with those of a detailed kinetic Monte Carlo approach. The two approaches lead to very similar results for the H2 surface abundance. In Sect. 4, we introduce a large gas-grain network and code with encounter desorption, based on the Nautilus model (Hersant et al. 2009), and use it to obtain the H2 surface abundance as a function of density. The good agreement with the simple treatments suggests that we can use a large gas-grain rate-equation treatment with encounter desorption to determine the overall chemistry that occurs as a function of H2 surface abundance. The chemistry is discussed in Sect. 5, and a conclusion follows.

2. The “encounter desorption” mechanism

Water is the main component of the ice mantle, therefore the desorption energy of a species on a water substrate is usually used. However, at very high density, H2 can become quite abundant on the grain surface, since it is the most abundant species in the gas phase. In an extreme case, we would need to use the binding energy of adsorbates to H2 and not to water (Morata & Hasegawa 2013). To take this problem into account, Garrod & Pauly (2011) calculated effective binding energies and diffusion barriers according to the fractional coverage of the surface with H2. This method produces a maximum H2-ice fraction of around 10% under cold molecular cloud conditions. Unfortunately, desorption energies and diffusion barriers of every species become time dependent using this technique. Then the differential equation system become stiffer than usual and as a consequence more difficult to solve, which could be a handicap for complex hydrodynamical simulations (Furuya et al. 2012; Hincelin et al. 2013), where computing time is a critical limitation.

Our approach, which we label “encounter” desorption, is a different one. Figure 1 shows an interstellar grain consisting of a silicate or carbonaceous core, and an ice mantle assumed mainly to be of water ice, with water molecules in the top layer illustrated in dark blue, and hydrogen molecules in white. Individual hydrogen molecules diffuse for the most part over water molecules until they reach another hydrogen molecule beneath them, at which time the binding energy of the diffusing species is sharply reduced from 440 K to 23 K, raising the likelihood of desorption. The desorption of an H2 molecule due to the lower desorption energy, when the molecule ends up on an H2 substrate, is modeled by considering the encounter of two H2 molecules on the same surface site. The grain surface “reaction” H2(grain) + H2(grain) → H2(gas) is added to the reaction network with a specific reaction rate R_{H2,H2} to take into account this process.

The rate is given by

$$R_{H2,H2} = \frac{1}{2} k_{H2,H2} n(H2) n(H2) \kappa(H2),$$

in units of cm^-3 s^-1, where $k_{H2,H2}$ is the rate coefficient (cm^-3 s^-1) at which two hydrogen molecules diffuse into the same lattice site (Hasegawa et al. 1992; Caselli et al. 1998), the hydrogen concentration on grain surfaces is written as $n(H2)$ (cm^-3) and $\kappa(H2)$ is the probability of desorption rather than diffusion. This probability is given by the equation

$$\kappa(H2) = \sum_x \frac{k_{X,H2}(H2)}{R_{diff}(H2) + \sum_x k_{X,H2}(H2)}$$

where the sum over X is a sum over the thermal desorption rate coefficient and assorted non-thermal desorption rate coefficients (s^-1) due to photons and cosmic rays. In the general case, we take into account thermal desorption, cosmic ray induced desorption, and photodesorption from direct interstellar UV photons and secondary photons generated by cosmic rays (see Hasegawa et al. 1992; Hasegawa & Herbst 1993a; Leger et al. 1985; Öberg et al. 2007, 2009a,b,c; Hassel et al. 2008, 2010) while $R_{diff}$ is the diffusion rate (s^-1) of one H2 molecule on an H2 substrate (Hasegawa et al. 1992; Caselli et al. 1998).
3. A comparison between different methods
for a simple system

Before we apply our encounter desorption mechanism to a realistic gas-grain simulation, the validity of the mechanism has to be tested. Since the microscopic Monte Carlo approach is the most rigorous simulation method, ideally we should compare the results of the rate equation approach including encounter desorption with analogous results with the microscopic Monte Carlo simulation results using a full reaction network. However, since the gas phase H$_2$ abundance is too large to be treated by the Monte Carlo method, we choose a system that is as simple as possible. In this section, we report the results of a comparative study of such a simple system, in which we consider only H$_2$ and a mantle of effectively water ice. We then compute the steady-state fraction of molecular hydrogen on the dust grains at 10 K as a function of total H$_2$ density. We take a typical grain with radius 0.1 $\mu$m and $10^5$ binding sites, and a gas-to-dust number density of $10^{-12}$. H$_2$ from the gas can accrete onto a grain surface and then diffuse or desorb from the surface. Thermal desorption is treated in the standard manner, while the rate coefficient for encounter desorption is treated as in Eq. (1), but without non-thermal desorption mechanisms.

The simple rate equation approach is based on setting the time derivative of the concentration of H$_2$ on grains to zero:

$$\frac{dn_{\text{H}_2}(i)}{dt} = k_{\text{ads}}(i)n_g(i) - R_{\text{H}_2} - k_{\text{des}}(i)n_s(i) = 0 \quad (3)$$

and solving for the H$_2$ grain concentration. In the equation, $n_g(i)$ is the gas-phase H$_2$ abundance, $k_{\text{ads}}$ is the adsorption rate coefficient for H$_2$, $k_{\text{des}}$ is its thermal desorption rate coefficient (Hasegawa et al. 1992), and the rate for encounter desorption is to be found in Eq. (1).

The microscopic Monte Carlo simulation method has been explained in detailed in Chang et al. (2005), so will only be discussed briefly here. A grain surface with N binding sites is represented as an $L \times L$ square lattice, where $L$ is the number of sites on grain surface in one dimension. We keep track of the position and movement of H$_2$ species on the lattice. The movements, which include hopping, desorption, and adsorption, are modeled as Poisson processes, so that the time interval between two successive movement operations, $\Delta t$, is given by

$$\Delta t = \frac{\ln(x)}{k}, \quad (4)$$

where $x$ is a random number uniformly distributed within 0 and 1, and $k$ (in $s^{-1}$) is the hopping rate coefficient $k_{\text{hop}}$, the thermal desorption rate coefficient $k_{\text{des}}$, or the adsorption rate coefficient $k_{\text{ads}}$, depending on the specific movement operation. Moreover, hopping will compete with desorption for an H$_2$ species that resides in a binding site. We combine hopping and desorption as a joint Poisson process and then use a competition mechanism to decide whether the species will hop or desorb (Chang et al. 2005).

Figure 2 shows the steady-state molecular hydrogen abundance on a grain surface, calculated as a function of H$_2$ total density (gas and grain surface) for three models, two of which contain no encounter desorption using a desorption energy for H$_2$ of either 440 K, the H$_2$-water value, or 23 K, the H$_2$-H$_2$ value. For these models, only the rate-equation result is shown. The third model contains the encounter desorption rate process as well as thermal desorption using the 440 K desorption energy, which is a very slow process at 10 K. For this case, we also plot the result of the kinetic Monte Carlo approach, which should reproduce the H$_2$ granular abundance of the encounter desorption rate-equation model if the latter is accurate. Note that the kinetic Monte Carlo model assumes a constant gas phase H$_2$ abundance, which is not the case using the rate-equation approach. The grain surface abundance of H$_2$ is, however, very small compared with the gas phase H$_2$ using the Monte Carlo model, so this assumption does not change our results presented in the figure.

Both models without encounter desorption show a linear dependence of the H$_2$ surface abundance on total proton density $n_H$ for at least a portion of the H$_2$ densities considered. With the higher desorption energy, H$_2$ is slowly desorbed, so that as the H$_2$ density approaches $10^{14}$ cm$^{-3}$, virtually all molecular hydrogen is located on grains, reaching a fractional abundance of 0.5 with respect to the total proton density. With the lower desorption energy, the average number of H$_2$ molecules per grain is less than unity even at the highest density utilized (abundance $\approx 10^{-14} - 10^{-15}$). With encounter desorption, the results lie in-between, with the H$_2$ granular fractional abundance at a standard dense cloud gas density of $10^4$ cm$^{-3}$ approximately $10^{-9}$, which corresponds to about 40 molecules per grain, and, at the highest density studied, $4 \times 10^6$ molecules per grain, which corresponds to about 4 monolayers. The surface fractional abundance calculated with the rate equation model including encounter desorption is slightly larger than the value obtained with the microscopic Monte Carlo model at densities larger than $10^{12}$ cm$^{-3}$, because in the rate-equation model, the H$_2$ grain surface concentration is approximately linearly dependent on the density of the medium, whereas the Monte Carlo model involves one monolayer of H$_2$ as a limit. However, even at the highest density in our simulation, $10^{14}$ cm$^{-3}$, the encounter desorption model result for the grain H$_2$ abundance is only about a factor of 4 larger than the microscopic Monte Carlo model value.

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1. In this third model, 440 K is used in the rate coefficient $k_{\text{des}}$, in Eq. (1), while 23 K is used in the different terms of the probability $x(H_2)$ shown in Eq. (2).
Table 1. Model designations for full gas-grain simulation.

| Model     | H₂ desorption energy | Encounter desorption |
|-----------|-----------------------|----------------------|
| 440-noED  | 440 K                 | disabled             |
| 23-noED   | 23 K                  | disabled             |
| 440-ED    | 440 K                 | enabled              |

4. Results with encounter desorption and a large gas-grain reaction network

Given the degree of agreement between the kinetic Monte Carlo method and the encounter desorption rate-equation method for a simple system, we have chosen to extend the encounter desorption approach to a full gas-grain model, using the Nautilus code (Hersant et al. 2009). The two-phase rate-equation approach is used, in which no distinction is made between the inner and surface layers of the mantle. Details on the processes included in the code are presented by Semenov et al. (2010) and Hersant (2012). The potential energy barrier against diffusion, $E_b$, is linked to the desorption energy $E_D$ by the equation $E_b = a E_D$. We set $a$ equal to 0.5 as in Garrod & Herbst (2006), although other estimates exist, typically ranging from 0.3 to 0.77 (Watson 1976; Tieless & Allamandola 1987; Hasegawa et al. 1992; Ruffle & Herbst 2000). We used the chemical network of Hinkel et al. (2013), which includes the latest recommendations from the KIDA experts on gas-phase processes until October 2011 $^3$. Photodesorption has been included following Öberg et al. (2007, 2009a,b,c) and Hassel et al. (2008, 2010) and a limiting factor is added to restrict the mechanism to two monolayers. Two sources of incident UV radiation are considered: direct interstellar UV photons, and secondary photons generated by cosmic rays. We used the elemental abundances following Hinkel et al. (2011) $^3$ with an oxygen elemental abundance relative to hydrogen of $3.3 \times 10^{-4}$. The species are assumed to be initially in an atomic form as in diffuse clouds except for hydrogen, which is initially in H₂ form. Elements with an ionization potential below 13.6 eV – C, S, Si, Fe, Na, Mg, Cl, and P – are initially singly ionized. From the initial state, the chemistry evolves under cold and dense conditions. The gas and grain temperature are equal to 10 K, the cosmic-ray ionization rate is $1.3 \times 10^{-17}$ s⁻¹, and the visual extinction is set to 30. The density is once again varied in the range $10^4$ cm⁻³ to $10^{14}$ cm⁻³. We have run three different models, summarized in Table 1, which are analogous to those used for the simple models. In models 440-noED and 23-noED, the desorption energy of H₂ is fixed to 440 K and 23 K, respectively, and the encounter desorption mechanism is disabled. In model 440-ED, the desorption energy of H₂ is fixed to 440 K and the encounter desorption mechanism is enabled with a desorption energy equal to 23 K.

Figure 3 shows the abundance of H₂ at steady state in the gas phase and on a grain surface for all three models, as a function of total gaseous plus surface hydrogen density. Steady state for H₂ is reached before 10 yr since its high abundance in the gas phase causes a high adsorption rate, and because we start with all hydrogen in its molecular form. The steady-state results in Fig. 3 are quite similar to those in Fig. 2. Thus, the addition of a “complete” gas-grain reaction network does not change significantly the abundance of surface H₂ as a function of density. We note specifically the results for a standard cold dense cloud with the inclusion of encounter desorption (model 440-ED): the H₂ fractional surface abundance lies between $10^{-11}$ and $10^{-10}$ for a standard cold dense cloud, which represent respectively ~10 and ~100 molecules on the surface of a dust grain.

The use of encounter desorption, as seen in Figs. 2 and 3, clearly reduces the amount of surface H₂ at all densities chosen. These lowered abundances, however, are still significantly higher than what can be obtained if we assume that H₂ cannot stick to grains at all, and that all of the molecular hydrogen on grains comes directly from its formation from two H atoms that have accreted onto the surface. Thus the implementation of encounter desorption does not lead to the same situation as the assumption of no sticking of H₂, at least at the densities studied.

The amount of surface hydrogen is likely to affect the chemistry and abundance of other species, both gaseous and solid-state, especially at densities significantly higher than those pertaining to cold dense clouds. Some of the effect derives from radical-H₂ surface reactions that can occur even at low temperatures on the surface via tunneling (Hasegawa & Herbst 1993a). In the following section, we discuss the impact of H₂ grain coverage on the abundances of other species for sources at 10 K and a range of densities.

5. Discussion

We computed the time-dependent chemical evolution under the same range of physical conditions as used previously and with the models listed in Table 1. Although the higher density models are not relevant to dense cores, they can be relevant to the dense midplane of protoplanetary disks and to centers of prestellar isothermally collapsing cores. Moreover, hydrodynamic calculations can lead to temporary high densities and low temperatures.

We start with a comparison of the gas-phase abundances measured for the cold cores TMC-1CP and L134N and the gas-phase results of the three models using a comparison parameter $D$ between modeling results and observational constraints, given by the equation

$$ D(t) = \frac{1}{N} \sum_{j} \left[ \log \left( \frac{X_{\text{mod}}(t)}{X_{\text{obs}}(t)} \right) \right] . $$

\(^2\) An electronic version of this network is available at http://kida.obs.u-bordeaux1.fr/models.

\(^3\) Values used in this study come from Graedel et al. (1982), Wakelam & Herbst (2008), and Jenkins (2009).
Here, $X^{\text{obs}}_j(t)$ is the observed abundance of species $j$ at time $t$, and $N$ is the number of observed species in the cloud. The smaller the value of $D$, the closer the agreement. We used the observed abundances listed in Agúndez & Wakelam (2013). There is little difference in the results for $D(t)$ using the three models at densities of $2 \times 10^4$ and $2 \times 10^5$ cm$^{-3}$, as shown in Fig. 4.

For individual species, however, the three models can yield different results, even in the gas-phase. For example, let us consider the major species water, CO, and methane, and the atomic carbon. Panels A and B of Fig. 5 show the abundances of water, carbon monoxide, and methane both on the grain surface and in the gas phase, as a function of total H$_2$ density, for the three models at 10$^7$ yr, a time relevant for protoplanetary disks and older cold cores. Grain surface abundances of these three species are sensitive to the model used, but in the gas phase, only water is strongly affected by the choice of model. However, while the grain surface abundances of these species vary by a maximum factor of three, the gas phase water abundance is decreased by three orders of magnitude at 10$^3$ cm$^{-3}$ going from model 440-ED to 440-noED, which corresponds to an increase in sH$_2$, where the "s" stands for "grain surface". The depletion in gaseous H$_2$ leads to a depletion of precursors to gaseous water and to an increase of sH$_2$, which consumes sOH so that the production of gas phase water through reactive desorption with sH is lessened. The abundance of solid atomic carbon, seen in Panel C, also depends strongly on the sH$_2$ abundance. In model 440-noED, where sH$_2$ is highest, the abundance of sC is lowest due to its destruction via reaction with sH$_2$.

Depending on the density and the time considered, a general behavior can be seen for the majority of grain surface species,
methane which is essentially formed on the grain surface; the abundance of water is decreased by a factor of two at most while the factor can be as high as ten for methane. The abundance of sCO is modified by less than a factor two. This small effect stems from two opposing processes: the adsorption rate of CO is lower when $S$ is reduced to 0.5, but the surface reaction rates involving sCO are also lower.

While the abundance for a given molecule can be different when the sticking probability is reduced from 1.0 to 0.5, the relative results of the three models 440-ED, 440-noED, and 23-noED exhibit the same pattern whatever the value of the coefficient is. For example, the abundance of sC is still much lower in the case of the 440-noED model than the other two models, while the gas phase abundances of CO, CH$_4$, and H$_2$O are still not dependent on the model, except for water at densities higher than $10^2$ cm$^{-3}$ for the 440-noED model as shown in panel B of Fig. 5. As a consequence, we conclude that the value of the sticking coefficient does not impact the relative efficiency of encounter desorption significantly.

5.2. Initial abundances

We typically start with all hydrogen in its molecular form. To test the sensitivity of encounter desorption to this assumption, we also performed some simulations with all hydrogen initially in its pure atomic form. The results for the three models 440-ED, 440-noED, and 23-noED are presented in Fig. 7, at the same time ($10^6$ yr) and for the same species as in Fig. 5 to allow for an easy comparison. The abundance profiles of surface atomic carbon and gas phase water, carbon monoxide, and methane are similar to our previous simulation. Due to the high density, adsorption of atomic hydrogen is efficient, and H$_2$ is formed quickly on the grain surface. Grain surface H$_2$ needs about 1 yr or less depending on the density to reach steady state, and gas phase H$_2$ needs about $10^6$ and $10^3$ yr to reach steady state at a total proton density of $2\times10^4$ and $2\times10^8$ cm$^{-3}$ respectively. The case of the main ices is however slightly different. They are formed faster, since hydrogenation by $s$-H is more efficient. Besides, surface atomic carbon is primarily converted into methane rather than carbon monoxide. For these ices, the abundance of sH$_2$ seems less critical than for our previous simulations and as a consequence differences between the results of models 440-ED, 440-noED, and 23-noED are reduced. In conclusion, our results are still sensitive to encounter desorption at $10^6$ yr using atomic hydrogen as an initial condition, depending on the considered species.

5.3. Motion through quantum tunneling

We typically assume thermal diffusion. We also studied the sensitivity of our three models 440-ED, 440-noED, and 23-noED to the motion of H$_2$ through quantum tunneling. The abundances of H$_2$ in the gas phase and on the grain surface are not changed for the two models 440-noED and 23-noED using this new assumption, at all times and densities. For the third model, abundance of s-H$_2$ is however reduced by about three orders of magnitude compared to the same model without tunneling, at all times and densities. Since motion through quantum tunneling is faster than thermal diffusion at 10 K, encounter desorption happens more frequently and reduces the surface abundance of H$_2$. As a consequence for the molecules studied in this paper, the results of 440-ED model are closer to those of the 23-noED model. Depending on the density and the time however, results of these two models can still be quite different.

6. Conclusion

We have developed a new approach to prevent a huge accumulation of H$_2$ on interstellar grain surfaces at low temperatures and high densities, which should not occur because the desorption energy of H$_2$ on an H$_2$ substrate is much lower than on a water...
substrate. This method, which is to be used in gas-grain rate-equation simulations, is based on the facile desorption of molecular hydrogen when it encounters a molecule of an H₂ substrate. We have named this process “encounter desorption”.

In order to test our approach, we first used a very simple system including the encounter desorption process to calculate the surface abundance of H₂ molecules as a function of density at a temperature of 10 K. We then compared our result with an analogous but more exact result obtained using a microscopic Monte Carlo stochastic method. A comparison between the steady-state results of the rate-equation model with encounter desorption and the Monte-Carlo approach gives very good agreement for gas densities from $10^4$ to $10^{12}$ cm$^{-3}$. Above $10^{12}$ cm$^{-3}$, the rate-equation model slightly overestimates the H₂ grain surface abundance, by a factor of up to 4. We then used a complete gas-grain network with the Nautilus model to which encounter desorption was added and repeated the steady-state rate-equation calculation of the surface abundance of H₂ vs. density, obtaining very similar results to both the simple rate-equation and Monte Carlo treatments. We thus conclude that the approach is a reasonable one, although the mathematics do not distinguish between the surface layer of an ice mantle and the inner layers.

We also studied the impact of different H₂ surface abundances on the abundance of other species, using two models with a fixed desorption energy of H₂ (23 K and 440 K) and one model with the encounter desorption mechanism. The sensitivity of the results of these models is relatively complex, and depends on the considered chemical species, the density of the medium, and the time. Nevertheless, the calculated abundances can often be divided into three regions depending upon whether the H₂ surface coverage is low, intermediate, or high. Reducing the sticking coefficient for adsorption from unity to 0.5 does not change these results.

We tested the sensitivity of our models to a different initial condition – hydrogen initially in atomic form instead of molecular – and to the motion of H₂ via quantum tunneling instead of only thermal diffusion. These assumptions may change the abundances of some species depending on the density and the time, but our simulations are generally still sensitive to the encounter desorption mechanism, and the results mentioned in the previous paragraph often still hold.

Our results highlight the need to incorporate in rate-equation models a way to more correctly model H₂ coverage at low temperature and high density. This need becomes even more pressing when physical conditions present huge variations, such as during the collapse of a prestellar core to form a protostar surrounded by a disk. In this scenario, matter transits through variations of both density and temperature, which lead to potentially large variations of H₂ coverage, some quite unphysical such as the limit in which all H₂ lies on interstellar grain mantles. The encounter desorption method keeps the amount of H₂ at physically reasonable values by using both the desorption energy of H₂ on a water ice mantle and on a mantle with some H₂ on its surface. The approach computes the rate of encounter desorption “on the fly”, i.e., as a function of time and H₂ coverage, and therefore is well designed for a scenario in which the physical conditions are rapidly changing. In addition, it is relatively easy to implement, and is not significantly CPU time consuming. Although H₂ is the most abundant molecule in the interstellar medium, a possible extension to this work would be to consider encounter desorption for other weakly bound atoms and molecules.

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