Dust as interstellar catalyst

I. Quantifying the chemical desorption process

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ABSTRACT

Context. The presence of dust in the interstellar medium has profound consequences on the chemical composition of regions where stars are forming. Recent observations show that many species formed onto dust are populating the gas phase, especially in cold environments where UV- and cosmic-ray-induced photons do not account for such processes.

Aims. The aim of this paper is to understand and quantify the process that releases solid species into the gas phase, the so-called chemical desorption process, so that an explicit formula can be derived that can be included in astrochemical models.

Methods. We present a collection of experimental results of more than ten reactive systems. For each reaction, different substrates such as oxidized graphite and compact amorphous water ice were used. We derived a formula for reproducing the efficiencies of the chemical desorption process that considers the equipartition of the energy of newly formed products, followed by classical bounce on the surface. In part II of this study we extend these results to astrophysical conditions.

Results. The equipartition of energy correctly describes the chemical desorption process on bare surfaces. On icy surfaces, the chemical desorption process is much less efficient, and a better description of the interaction with the surface is still needed.

Conclusions. We show that the mechanism that directly transforms solid species into gas phase species is efficient for many reactions.

Key words. astrochemistry – solid state: refractory – solid state: volatile – ISM: abundances – ISM: molecules – molecular processes

1. Introduction

The chemical composition of regions where stars are forming influences the thermal balance and the evolution of interstellar clouds on their way to form stars (Hocuk et al. 2014). Recent observations of cold environments (i.e., pre-stellar cores) have shown unexpected amounts of some molecules in the gas phase (Bacmann et al. 2012), while these species were expected to be depleted from the gas phase and adsorbed onto cold dust grains ($T < 20$ K) in physisorbed states (Collings et al. 2004).

To understand these observations, the transition between solid and gas phases has been studied in laboratory under physical-chemical conditions present in the interstellar medium (ISM). In particular, many studies have been focused on thermal desorption (Bisschop et al. 2006; Noble et al. 2015) and nonthermal processes, such as photo-desorption (DeSimone et al. 2013; Bertin et al. 2013), sputtering (Johnson et al. 2013; Cassidy et al. 2013), cosmic ray (CR) desorption (Leger et al. 1985; Hasegawa & Herbst 1993; Ivlev et al. 2015), and chemical desorption (Cazaux et al. 2010; Dulieu et al. 2013; Minissale et al. 2014).

Differently from the other processes, chemical desorption links the solid and gas phases without the intervention of any external agents such as photons, electrons, or other energetic particles. In other words, it could be efficient in UV-shielded and low-CR environments where photodesorption, CR (thermal) desorption, or sputtering cannot be efficient. The chemical desorption process starts from the energy excess of some

radical-radical reactions. As described in Minissale & Dulieu (2014), its efficiency essentially depends on four parameters: enthalpy of formation, degrees of freedom, binding energy, and mass of newly formed molecules.

The aim of this article is to quantify the chemical desorption mechanism (part I) and its impact on the chemical composition of interstellar gas (part II). The paper is organized as follows: in Sect. 2 we present the experimental protocol and results. In Sect. 3 we derive a law to quantify the chemical desorption mechanism. In Sect. 4 we discuss the main results of this work.

2. Experiments

The experiments were performed using the FORMOLISM setup (Amiaud et al. 2006; Congiu et al. 2012). In an ultra-high vacuum chamber a gold mirror covered with amorphous silicates, oxidized graphite, or compact amorphous water substrate was held at very low temperatures (~ 10 K). All the experiments were performed in the submonolayer regime to ensure that the interaction occurred on bare surfaces and was not perturbed by any other layer properties. The surface coverage is known from the specific desorption properties of the second layer (Noble et al. 2012b). A typical experiment proceeded as follows: one layer (or less) of non-self-reactive molecules was deposited at low temperature. Just after its deposition, another beam was aimed at the solid sample, and the desorption flux was monitored simultaneously with a movable quadrupole mass spectrometer (QMS),

placed 3 mm away from the surface. These experiments are referred to as during exposure desorption (DED).

For radical-radical systems we sometimes used two simultaneous beams (i.e., [O+H] system) because each separate beam will lead to a complete recombination (i.e., $H+H \rightarrow H_2$) and so a sequential deposition is meaningless. The DED technique collects species in the gas phase during the reactive phase (beam exposure). As a result of poor angular collection, signals are weak but are unambiguously due to the reactive systems. For example, if mass 20 is measured during the irradiation of an O_2 layer (O_2 with mass of 32 a.m.u.) by D atoms (mass 2), this is direct evidence that D_2O is produced and undergoes chemical desorption. Such a signal is presented in Fig. 6 of Chaabouni et al. (2012). Mass confusions with cracking patterns of the QMS are still possible, but can be estimated by careful calibration. DED measurements allow determining the coarse efficiency of the chemical desorption process for many considered reactions. Even though it is a direct measurement, most of the reactive systems are actually composed of many reactions. In the former example, it is clear that the $O_2 + D$ reaction cannot directly produce D_2O , even though this signal appears as soon as the D exposure begins. For the case of water formation, more than ten reactions are taking place simultaneously (see Fig. 7 of Chaabouni et al. 2012 for a graphical description). DED is a direct measurement of products, but the link between one product and one reaction is not necessary direct.

The DED technique can be completed by indirect measurements of the chemical desorption. In a second phase of the experiment, the surface temperature is increased after the exposure, and the desorption flux is monitored. This second phase, called temperature-programmed desorption (TPD) experiments, allows us to determine the amount of formed products that did not desorb upon formation. A TPD experiment is therefore an indirect process for measuring the loss of surface species that is due to chemical desorption.

2.1. Determining the chemical desorption efficiency: the test case of the O+O system

In recent experiments (Minissale et al. 2014; Congiu et al. 2014) we studied the formation of ozone and O_2 on different surfaces obtained by deposition of a unique beam composed of 85% of O and 15% of O_2 . We chose this example because in contrast to most of the other reactive systems, there are here only two efficient reactions, $O+O \rightarrow O_2$ and $O+O_2 \rightarrow O_3$. This means that there is no ambiguity or multiple possible assignments in the chemical reaction network. Each product corresponds to one reaction. At the end of the exposure, the temperature of the surface has increased and the amount of O_2 and O_3 (TPD) that were present on the surface could be measured. Figure 1 reports the results for experiments performed on water ice (squares), silicates (triangles), and graphitic (circles) surfaces. Keeping the same total exposure beam, the experiments can be repeated with various substrate temperature (so-called vs. T_s experiments), or keeping the same surface temperature (usually 10 K), the exposure time can be varied so that the effect of the deposited dose can be studied (so-called vs. dose). In all the experiments, all the atoms were consumed during the exposure phase, and we collected the O_2 and O_3 signals. The numbers reported in the X and Y axes are the fractions of O_2 and O_3 measured in the TPD. Point A in Fig. 1 (coordinate 0, 1) represents an experiment in which almost all the deposited O/ O_2 was transformed into ozone. This occurs in high surface temperature conditions where the mobility of O atoms is high and thus any atom can

Fig. 1. Normalized fraction of O_2 and O_3 for the [O+O] reactive system obtained after TPD. The filled symbols represent the surface temperature variation (between 6.5 K and 25 K), while the empty symbols represent the dose variation (between 0.05 ML and 1.0 ML). The black dots represent the data of Minissale & Dulieu (2014), who reported the method in detail. Other points are adopted from Minissale et al. (2013), Minissale et al. (2014), and Congiu et al. (2014) or are original data. The solid black line represents the zone of the plot in which no chemical desorption is measured.

react with an O_2 molecule. Point B (0.8, 0.2) corresponds to the case where 80% of the products desorbed in the form of O_2 . This is the case for very low temperatures and coverage. In these conditions, the $O+O$ reaction dominates the O_2+O reaction. If the total fraction of O_2 and O_3 is equal to 1 (the sum of coordinates), then all the oxygen species sent on the surface are desorbing from the substrate during the TPD. This case is represented by the thick line that crosses both O_2 and O_3 fraction origin axes at coordinate 1. In contrast, point C (0.25, 0.25) in the figure represents a case for which the amount of species desorbing from the surface after the deposition is about equal to half of the total amount of species that were deposited. Some oxygen species are missing from the TPD experiments because of the chemical desorption process that occur during the exposure phase. The general conclusion drawn from Fig. 1 is that the chemical desorption process can be efficient in some specific conditions.

We note that the experiments made on water substrates (blue points) are all located around the thick line representing the absence of chemical desorption. The reactions occurring on water ice surfaces lead to products remaining on the surface, and the chemical desorption process is almost negligible or within the error bars. Experiments made on silicates and graphite surfaces, however, show a high deficit in oxygen species. The experimental results show that almost 50% of the oxygen is missing from the surface for reactions occurring on graphite surfaces, while this fraction is 30% for reaction on silicates and is negligible on water ices. For graphite and silicates surfaces, the amount of missing oxygen can vary with the coverage of the species on the surface (open triangles for silicates and open circles for graphite), which indicates that the chemical desorption process strongly depends on the surface coverage (Minissale & Dulieu 2014). The presence of a neighbor of similar mass on the surface strongly increases the probability of energy transfer. The energy detained by the molecule upon its formation is quenched very efficiently. In this case, the chemical desorption process is minimized.

That oxygen species are missing from the TPD experiments is attributed to the chemical desorption process. To confirm that

Fig. 2. *Left panel:* raw DED measurements of mass 32 (O₂) during O/O₂ deposition (between 1.5 and 4.5 min) on graphite (green) and water ice (red) held at 10 K. *Right panel:* mean DED measurements over the 3 min exposure with associated error bars.

the chemical desorption process is at the origin of the loss observed in the TPD, DED measurements were performed. This technique consists of directly measuring the increase of the partial pressure of the gas during the exposure of the reactants. For this type of measurements, the QMS head is close to the surface, but still allows the deposition of species on the surface. This also implies that the position of the QMS is not optimized to detect the desorbing species. Furthermore, molecules that formed directly may have a high kinetic energy, which reduces their interaction time while passing through the QMS head. This mostly explains why the DED signals are low. In the left panel of Fig. 2 we show the raw data measured during the exposure of O atoms on silicates and water ice surfaces. Before exposure (for time ≤ 1.5 min), and after exposure (for time ≥ 4.5 min), the signal at mass 32 (a.m.u.) is very low. The signal during exposure, located between 1.5 and 4.5 min, is stronger for O₂ desorbing from a graphite surface than from a water ice surface. This is exactly the opposite situation to what we found in the TPD. This shows that the missing oxygen from our TPD is released into the gas during exposure, through the chemical desorption process, and that this process strongly depends on the surface on which reactions occur. The chemical desorption is found to be less efficient on water substrate than on oxidized graphite through direct measurement (DED) or indirect measurement (TPD). We note that for the specific case of DED of a beam of O, a part of the O₂ beam is not dissociated and is detected in the QMS and therefore does not come from the formation and desorption of O₂ on the surface. The DED technique provides good qualitative information, but is not suitable for quantitative analyses. It is possible for us, however, to sort qualitatively desorbing species. The species that we easily detect by DED should have an efficiency of few tens of %, whereas those close to our detection limit should be in the 5–15% range, depending on the level of background noise.

By combining TPD and DED experiments for O₂ on several surfaces, we were able to obtain an accurate measurement of the chemical desorption efficiency for the [O+O] system. This was possible because of the limited number of reactions occurring in this system. We studied many other systems. Some are quite simple, for example, [N+N] (or [H+H]), where it is reasonable to assume only one reaction $N+N \rightarrow N_2$. But most other systems are more complex.

2.2. Determining the chemical desorption efficiency: more complex systems

Table 1 lists the different experiments we performed and the main reactions involved in each experiment. For the [O+H] experiment, there are two main reactions occurring in the experiment, $O+H \rightarrow OH$ and $OH+H \rightarrow H_2O$, that we can measure

with TPD and DED. To derive the chemical desorption efficiency for the reaction $OH+H \rightarrow H_2O$, we assumed that the fraction of H₂O detected is due to the OH molecules that stayed on the surface upon formation. The amount of chemically desorbed H₂O observed in this experiment indirectly gives information on the amount of OH that remains on the surface or is desorbed upon formation. We detected OH for the [O+H] system, but not for the [O₂+H] or [O₃+H] systems. From the possible reaction network of water, we can attribute the high chemical desorption efficiency of OH to the O+H reaction. This is not trivial because other routes can produce OH, for instance, $H_2O_2+H \rightarrow H_2O+OH$ or $O_2H+H \rightarrow 2 OH$.

To summarize, by combining TPD and DED experiments, the “missing species” can be identified by using a small reaction network. This allowed us to derive some estimates of the chemical desorption efficiency for the formation of different species on surfaces. Here we present several experiments, which are listed in Table 1. For each experiment, as mentioned previously, more than one reaction can occur, leading to different products with distinct chemical desorption efficiencies. These reactions, as well as the enthalpy of reaction, the chemical desorption efficiency on water ice, amorphous silicates, and oxidized graphite are reported in Table 1.

3. Theoretical estimate of the desorption efficiency

We propose to use a simple assumption of equipartition of energy to reproduce the chemical desorption observed experimentally. We assumed that the total energy budget ΔH_R (see Table 1) is shared among all the degrees of freedom $N = 3 \times n_{\text{atoms}}$. We used the generic third degree of freedom per atom. For a diatomic molecule, it would be decomposed into three degrees for translation, one degree for vibration, and two for rotation axis. Of course, the symmetry can slightly affect this number, but this would be a small correction. Among these degrees of freedom, only the kinetic energy perpendicular to the surface will allow the newly formed species to desorb, with the condition that this kinetic energy is more important than the binding energy (E_{binding}). The binding energies of the species considered in our network are reported in Table 2. Initially, the translational momentum is negligible because in most of our experiments the species admitted on the surface probably thermalize rapidly and the diffusion mechanism is the dominant process. To desorb from the surface, the newly formed products have to bounce against the surface to gain velocity in the direction perpendicular to the surface. The simplest way to treat this process is to assume an elastic collision,

$$\epsilon = \frac{(M - m)^2}{(M + m)^2}. \quad (1)$$

Here ϵ is the fraction of kinetic energy retained by the product m colliding with the surface, which has an effective mass M . For the specific case of hyperthermal scattering of O₂ on graphite surface, Hayes et al. (2012) have proposed an equivalent mass of 130 a.m.u. The effective mass is much higher than one single C atom or even a carbon ring because the rigidity of the surface induces a collective behavior of the atom and a higher effective mass.

The chemical energy is certainly split in many different rovibronic states, not at all in thermal equilibrium. We assumed that an equal share of energy is spread throughout all the degrees of freedom, so that the total chemical energy available for the kinetic energy perpendicular to the surface is $\epsilon \Delta H_R / N$. We

Table 1. Experimental chemical desorption efficiencies for different reactions on three different surfaces (np-ASW, amorphous silicate, and oxidized graphite).

Experiments	Surface temperature	Coverage range	Method		Reaction	Desorbing product	ΔH_R	Experimental CD efficiency			Theoretical CD efficiency
			DED	TPD				np-ASW	Amorphous silicate	Oxidized HOPG	
	(K)	(ML)					eV	%	%	%	%
[O+H]	10	<1	✓	✓	O+H	OH	4.44	25 ± 15*	–	50 ± 25*	39
					OH+H	H ₂ O	5.17	30 ± 15*	–	50 ± 25*	27
					OH+H	H ₂ O	5.17	<40 ± 20 ^a	<70 ± 20 ^a	<80 ± 20 ^b	27
					O ₂ +H	O ₂ H	2.24	<8*	10 ± 10 ^b	–	1.4
[O ₂ +H]	10	0.5-1	✓	✓	O ₂ H+H	H ₂ O ₂	3.69	<8*	<5 ^b	–	0.5
					O ₂ H+H	2 OH	1.47	<8*	<5 ^b	–	0.3
					H ₂ O ₂ +H	H ₂ O+OH	2.95	<5*	<5 ^b	–	2.1
					O ₃ +H	O ₂ +OH	3.33	–	<10 ^b	<8*	8
[O ₃ +H]	10 and 45	0.5-1	✓	✓	OH+H	H ₂ O	5.17	–	80 ± 20 ^b	–	27
					O+O	O ₂	5.16	<5 ^c	40 ± 10 ^{#,d}	80 ± 10 ^{#,e}	68
[O+O]	8 to 25	<1	✓	✓	O ₂ +O	O ₃	1.1	<5 ^c	<5 ^d	<5 ^e	0
					[N+N]	N ₂	9.79	>50 ^{&,*}	>70 ^{&,*}	>70 ^{&,*}	89
[CO+H]	10	0.8–2.5	✓	✓	CO+H	HCO	0.66	–	–	10 ± 8*	0.7
					HCO+H	CO+H ₂	3.85	–	–	40 ± 20*	47
					HCO+H	H ₂ CO	3.91	–	–	<8*	7
					H ₂ CO+H	CH ₃ O	0.88	–	–	<8*	0
[H ₂ CO+H]	10 and 55	0.8–2	✓	✓	H ₂ CO+H	HCO+H ₂	0.61	–	–	10 ± 5*	0
					HCO+H	CO+H ₂	3.85	–	–	40 ± 20*	47
					HCO+H	H ₂ CO	3.91	–	–	10 ± 5*	7
					CH ₃ O+H	CH ₃ OH	4.56	<8*	–	<8*	2.3
[Ar+H]	10	1	✓	✓	Ar+H	Ar		–	<5*	–	
[NO+H/O/N]	10	0.5–5	X	✓	many	many		<8*	<8*	<8*	
[CO+O]	10	0.5–4	✓	✓	CO+O	CO ₂	5.51	<5*	–	<5*	22
[H ₂ CO+O]	10 and 55	0.8–2	X	✓	H ₂ CO+O	CO ₂ +H ₂	5.45	<10*	–	<10*	8
[CH ₃ OH+H]	10	0.5–2	✓	✓	CH ₃ OH+H	CH ₃ OH		<8*	–	<8*	
[CH ₃ OH+O]	10	0.5–2	✓	✓	CH ₃ OH+O	CH ₃ OH		<8*	–	<8*	

Notes. For the cases in which we were unable to quantitatively measure the CD efficiency, we provide upper or lower limits. We list theoretical CD efficiencies calculated for an oxidized graphite. *Surface temperature* indicates deposition temperature of both reactants. *Coverage range* indicates the coverage of molecular ice growth before atom irradiation; in the case of experiments performed only with atomic species, *coverage range* indicates the total amount of species placed on the surface. ✓ and X are used to indicate whether the experimental procedure (DED or TPD) was used or not; ^(#) CD decreases as a function of coverage; ^(&) experiments performed with excited particles (see Minissale 2014); ^(a) Chaabouni et al. (2012); ^(b) Dulieu et al. (2013); ^(c) Minissale et al. (2013); ^(d) Minissale et al. (2014); ^(e) Minissale & Dulieu (2014); ^(*) this work.

assumed that the only velocity perpendicular to the surface corresponds to a distribution of speed and temperature. In this sense, $kT = \epsilon \Delta H_R / N$. The probability for the product to have an energy (or liberation velocity) higher than the binding energy becomes

$$CD = e^{-\frac{E_{\text{binding}}}{\epsilon \Delta H_R / N}}. \quad (2)$$

In Fig. 3 we compare the results obtained experimentally (blue triangles) to our predictions. We first used a constant ϵ of 0.4, which implies that we assumed that 40% of the total energy is retained by the product (red hexagons). In this case, our predictions do not reproduce the experimental results well. In a second step, we considered a fraction ϵ that depends on the mass of the products, as described in Eq. (1). These predictions are represented as green squares and do match the chemical desorption efficiencies observed experimentally very well. This clearly indicates that the chemical desorption process is sensitive to the binding energy, the energy distributed in the products (depending on their mass), and the degrees of freedom. For some of the reactions such as OH+H, O+H, our predictions slightly underestimate the experimental results.

The formula (Eq. (2)) can be translated to the case of silicates surfaces. The efficiency is slightly lower, and thus reducing the

effective mass from 130 to 110 matches the most constrained reaction (O+O) very well. Taking the degree of inaccuracy of our experimental determination of CD into account, adopting a common value of 120 a.m.u. is appropriate to treat the trend of CD for bare grains.

The case of water substrate (np-ASW), which is even more important from the perspective of explaining the return of complex organic molecules (COMs) in the gas phase, appears to be more complex. We have two contradictory results. The chemical desorption of O+O is at least eight times lower, but the OH+H reaction seems to be still efficient, even if weaker by a factor of ~2. The mass argument does no longer stand. In part II of our work, we assume that the chemical desorption efficiency on ices is our CD coefficient divided by 10 for the reactions that have not been constrained ($CD_{\text{ice}} = CD_{\text{bare}}/10$, while $CD_{\text{ice}}(\text{OH}+\text{H}) = 25\%$, $CD_{\text{ice}}(\text{O}+\text{H}) = 30\%$, and $CD_{\text{ice}}(\text{N}+\text{N}) = 50\%$).

4. Discussion

Garrod et al. (2007) have previously proposed a formula in their models that can be used to describe the chemical desorption (or reactive desorption). They derived the probability of

Table 2. Binding energies on bare and icy surfaces.

Species	E_{bare}	E_{ice}
H	550 ^{a,b}	650 ^c
H ₂	300 ^{a,d}	500 ^e
O	1500 ^b	1400 ^f
OH	4600 ^g	4600 ^g
H ₂ O	4800 ^g	4800 ^h
O ₂	1250 ⁱ	1200 ⁱ
O ₃	2100 ^j	2100 ^j
HO ₂	4000 ^g	4000 ^g
H ₂ O ₂	6000 ^g	6000 ^g
CO	1100 ⁱ	1300 ^{i,k}
CO ₂	2300 ⁱ	2300 ^{i,k}
HCO	1600 ^l	1600 ^l
H ₂ CO	3700 ^m	3200 ^m
CH ₃ O	3700 ^l	3700 ^l
CH ₃ OH	3700 ⁿ	3700 ⁿ
N	720 ^f	720 ^f
N ₂	790 ^o	1140 ^p

Notes. For HCO, CH₃O, and CH₃OH we assume $E_{\text{ice}} = E_{\text{bare}}$.
^(a) Cazaux & Tielens (2004); ^(b) Bergeron et al. (2008); ^(c) Al-Halabi & van Dishoeck (2007); ^(d) Amiaud et al. (2007); ^(e) Pirronello et al. (1997);
^(f) Amiaud et al. (2006) for low coverage; ^(g) Minissale et al. (2015);
^(h) Dulieu et al. (2013); ⁽ⁱ⁾ Speedy et al. (1996); ^(j) Fraser et al. (2001)
energy derived of 5800 K with pre-factor of 10^{15} s^{-1} here corrected to have a pre-factor of 10^{12} s^{-1} ; ^(k) Noble et al. (2012a); ^(l) Borget et al. (2001);
Minissale (2014); ^(m) Karssemeijer & Cuppen (2014); ⁽ⁿ⁾ Garrod & Herbst (2006);
^(o) Fuchs et al. (2006); ^(p) Minissale et al. (2012b); ^(q) Collings et al. (2004);
^(r) Fuchs et al. (2006); ^(s) extrapolated from Kimmel et al. (2001).

Fig. 3. Measured CD efficiencies plotted in blue with error bars. In green we show the result of the formulae (Eq. (2)) that include division between the degree of freedom and the fraction of kinetic energy after bounce (ϵ is mass dependent). In red we show the equal share of energy and the constant value of ϵ .

undergoing desorption in two steps. The first step is based upon Rice-Ramsperger-Kassel-Marcus (RRKM) estimation and takes into account energetic aspects (degree of freedom, enthalpy of reaction, and binding energy). In most of the cases this coefficient is found to be high. The second step, interaction with the surface, is parametrized with an analytic formula. We unsuccessfully tried to use this approach. The main problem, as already mentioned by the authors, is that the first step (energetic aspects) does not really distinguish in case of exothermic reactions, whereas the second step, which is unknown, is the most important. The net result is that when this formula is used, the reactions

Fig. 4. Illustration of the chemical desorption process. After an initial meeting (1), the molecule is highly excited; (2) and converts a fraction of its energy into vertical motion through interaction with the surface (3).

are not separable. However, we clearly demonstrated that O+O has a high probability to desorb and O₂+O has not, while both of these reactions are exothermic. This a strong argument to reject the former approach.

Our simple hypothesis of equipartition of energy, coupled with elastic collision with the surface, reproduces the observations well. Although it is an empirical approach, it allows sorting among the products that should undergo the chemical desorption. The basic idea underlying our proposition is inspired by dynamic calculations in specific systems such as H+H on graphite (Morisset et al. 2004; Bachellerie et al. 2007) or O+H on graphite (Bergeron et al. 2008). We have illustrated the mechanism of this scenario in Fig. 4. The first step consists of a collinear approach parallel to the surface. When the molecule is formed, the trajectories of both atoms adopt a more disordered motion symptomatic of the high internal energy in vibration and rotation of the newly formed molecules, up to a point where the molecule interacts with the surface and that a part of the motion is transferred perpendicularly to the surface that causes the desorption.

We point out that the chemical desorption process seems to favor small molecules with low binding energies. Therefore, this process may be part of the reason COMS are present in dark clouds. We note that our prediction of about one percent of chemical desorption for methanol would be sufficient to sustain the observed value, as modeled by Vasyunin & Herbst (2013). The second part of our paper will examine the effect of the deriving our formulae in an astrophysical context.

That the chemical desorption efficiency on water ice substrates is reduced is somehow to be expected. A similar behavior has been observed in photodesorption of CO. Pure CO ices exhibit an efficient wavelength-dependent photodesorption of up to one percent per incident photon (Bertin et al. 2013) or possibly lower by a factor 3–11 (van Hemert et al. 2015). Some authors have estimated the CO photodesorption on water substrate to be about 10^{-3} (Öberg et al. 2009) or one order of magnitude lower (DeSimone et al. 2013). However, even if the CO photodesorption process is poorly constrained, the water substrate clearly prevents or dramatically reduces its efficiency. This probably is due to the very fast transportation of energy in the water network and to the reduction of the indirect photodesorption.

For chemical desorption on water substrate, the weakness of our coarse model probably lies in the assumption of elastic collisions, which are not adapted to the case of water. Many more experimental investigations and detailed computations would help to solve this problem. Finally, we note that even if water ice substrate seems to be a good trapping environment and can

dramatically reduce the chemical desorption efficiency, CO layers in the central part of dark clouds are expected to cover an inner water layer around the solid seeds of dust. Therefore, another set of experiments needs to be performed using a CO ice substrate.

5. Conclusions

We presented a collection of experiments conducted to quantify which fraction of species forming on surfaces is ejected into the gas phase upon formation. This process, called chemical desorption, has been observed experimentally (Dulieu et al. 2013). With this work we derived an analytical expression to quantify the chemical desorption process on different substrates such as oxidized graphite and amorphous silicate. This formula, which depends on the equipartition of the energy of newly formed products and the binding energy of the products, reproduces the experimental results on bare surfaces well. However, on icy surfaces the chemical desorption process is strongly reduced and cannot be well quantified by our experimental results.

In part II of our study, we address the importance of the chemical desorption process on the composition of interstellar gas by combining gas-phase chemistry and surface and bulk chemistry, and by using our analytical formula to account for the chemical desorption process.

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References

- Al-Halabi, A., & van Dishoeck, E. F. 2007, *MNRAS*, **382**, 1648
- Amiaud, L., Dulieu, F., Baouche, S., et al. 2006, in *Astrochemistry – From Laboratory Studies to Astronomical Observations*, eds. R. I. Kaiser, P. Bernath, Y. Osamura, S. Petrie, & A. M. Mebel, *AIP Conf. Ser.*, **855**, 55
- Amiaud, L., Dulieu, F., Fillion, J.-H., Momeni, A., & Lemaire, J. L. 2007, *J. Chem. Phys.*, **127**, 144709
- Bachellerie, D., Sizun, M., Teillet-Billy, D., Rougeau, N., & Sidis, V. 2007, *Chem. Phys. Lett.*, **448**, 223
- Bacmann, A., Taquet, V., Faure, A., Kahane, C., & Ceccarelli, C. 2012, *A&A*, **541**, L12
- Bergeron, H., Rougeau, N., Sidis, V., et al. 2008, *J. Phys. Chem. A*, **112**, 11921
- Bertin, M., Fayolle, E. C., Romanzin, C., et al. 2013, *ApJ*, **779**, 120
- Bisschop, S. E., Fraser, H. J., Öberg, K. I., van Dishoeck, E. F., & Schlemmer, S. 2006, *A&A*, **449**, 1297
- Borget, F., Chiavassa, T., Allouche, A., & Aycard, J. P. 2001, *J. Phys. Chem. B*, **105**, 449
- Cassidy, T. A., Paranicas, C. P., Shirley, J. H., et al. 2013, *Planet. Space Sci.*, **77**, 64
- Cazaux, S., & Tielens, A. G. G. M. 2004, *ApJ*, **604**, 222
- Cazaux, S., Cobut, V., Marseille, M., Spaans, M., & Caselli, P. 2010, *A&A*, **522**, A74
- Chaabouni, H., Minissale, M., Manicò, G., et al. 2012, *J. Chem. Phys.*, **137**, 234706
- Collings, M. P., Anderson, M. A., Chen, R., et al. 2004, *MNRAS*, **354**, 1133
- Congiu, E., Fedoseev, G., Ioppolo, S., et al. 2012, *ApJ*, **750**, L12
- Congiu, E., Minissale, M., Baouche, S., et al. 2014, *Faraday Discuss.*, **168**, 151
- DeSimone, A. J., Crowell, V. D., Sherrill, C. D., & Orlando, T. M. 2013, *J. Chem. Phys.*, **139**, 164702
- Dulieu, F., Congiu, E., Noble, J., et al. 2013, *Nature Sci. Rep.*, **3**, 1338
- Fraser, H. J., Collings, M. P., McCoustra, M. R. S., & Williams, D. A. 2001, *MNRAS*, **327**, 1165
- Fuchs, G. W., Acharyya, K., Bisschop, S. E., et al. 2006, *Faraday Discuss.*, **133**, 331
- Garrod, R. T., & Herbst, E. 2006, *A&A*, **457**, 927
- Garrod, R. T., Wakelam, V., & Herbst, E. 2007, *A&A*, **467**, 1103
- Hasegawa, T. I., & Herbst, E. 1993, *MNRAS*, **263**, 589
- Hayes, W. W., Oh, J., Kondo, T., et al. 2012, *J. Phys. Cond. Matt.*, **24**, 104010
- Hocuk, S., Cazaux, S., & Spaans, M. 2014, *MNRAS*, **438**, L56
- Ivlev, A., Padovani, M., Galli, D., & Caselli, P. 2015, *ApJ*, **812**, 135
- Johnson, R. E., Carlson, R. W., Cassidy, T. A., & Fama, M. 2013, in *The Science of Solar System Ices*, 551
- Karssemeijer, L. J., & Cuppen, H. M. 2014, *A&A*, **569**, A107
- Kimmel, G. A., Stevenson, K. P., Dohnálek, Z., Smith, R. S., & Kay, B. D. 2001, *J. Chem. Phys.*, **114**, 5284
- Leger, A., Jura, M., & Omont, A. 1985, *A&A*, **144**, 147
- Minissale, M. 2014, Ph.D. Thesis, University of Cergy-Pontoise
- Minissale, M., & Dulieu, F. 2014, *J. Chem. Phys.*, **141**, 014304
- Minissale, M., Congiu, E., Baouche, S., et al. 2013, *Phys. Rev. Lett.*, **111**, 053201
- Minissale, M., Congiu, E., & Dulieu, F. 2014, *J. Chem. Phys.*, **140**, 074705
- Minissale, M., Congiu, E., & Dulieu, F. 2015, *A&A*, in press, DOI: 10.1051/0004-6361/201526702
- Morisset, S., Aguillon, F., Sizun, M., & Sidis, V. 2004, *J. Chem. Phys.*, **121**, 6493
- Noble, J. A., Congiu, E., Dulieu, F., & Fraser, H. J. 2012a, *MNRAS*, **421**, 768
- Noble, J. A., Theule, P., Mispelaer, F., et al. 2012b, *A&A*, **543**, A5
- Noble, J. A., Theule, P., Congiu, E., et al. 2015, *A&A*, **576**, A91
- Öberg, K. I., Garrod, R. T., van Dishoeck, E. F., & Linnartz, H. 2009, *A&A*, **504**, 891
- Pirronello, V., Liu, C., Shen, L., & Vidali, G. 1997, *ApJ*, **475**, L69
- Speedy, R. J., Debenedetti, P. G., Smith, R. S., Huang, C., & Kay, B. D. 1996, *J. Chem. Phys.*, **105**, 240
- van Hemert, M. C., Takahashi, J., & van Dishoeck, E. F. 2015, *J. Phys. Chem. A*, **119**, 6354
- Vasyunin, A. I., & Herbst, E. 2013, *ApJ*, **769**, 34