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Binding energies: New values and impact on the efficiency of chemical desorption

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ABSTRACT

Recent laboratory measurements have confirmed that chemical desorption (desorption of products due to exothermic surface reactions) can be an efficient process. The impact of including this process into gas-grain chemical models entirely depends on the formalism used and the associated parameters. Among these parameters, binding energies are probably the most uncertain ones for the moment. We propose a new model to compute binding energy of species to water ice surfaces. We have also compared the model results using either the new chemical desorption model proposed by Minissale et al. (2016) or the one of Garrod et al. (2007). The new binding energies have a strong impact on the formation of complex organic molecules. In addition, the new chemical desorption model from Minissale produces a much smaller desorption of these species and also of methanol. Combining the two effects, the abundances of CH_3OH and COMs observed in cold cores cannot be reproduced by astrochemical models anymore.

1. Introduction

It is now well established that the surface of interstellar dust plays a crucial role for the formation of many chemical species starting with H_2. With the revision of some rate coefficients for gas-phase reactions (Luca et al., 2002; Geppert et al., 2006), it appeared impossible to form methanol (CH_3OH) in the gas-phase only whereas it was quite easy to form large quantities of this molecule through Langmuir-Hinshelwood reactions on the dust surfaces even at low temperature (Garrod et al., 2006). In order to reproduce the $\sim10^{-9}$ abundance observed in cold cores (Pratap et al., 1997), an efficient non-thermal desorption mechanism is needed to bring it back to the gas-phase. The observation of complex organic molecules in cold and dense environments of the interstellar medium has increased the interest of the community onto such processes (Bacmann et al., 2012; Cernicharo et al., 2012; Vastel et al., 2014).

Several non-thermal desorption mechanisms have been considered. The partial or entire heating of grains due to cosmic-ray particle collisions has been investigating by many authors (Leger et al., 1985; Hasegawa and Herbst, 1993; Willacy and Millar, 1998; Shen et al., 2004). Photo-evaporation due to direct UV photons or photons induced by cosmic-rays has also been proposed and intensively studied experimentally. For the recent measurements, it seems that the photo-evaporation is an indirect process for some molecules and that the efficiency depends on the specie, the nature of the surface, and the wavelength of the impacting UV photons (Muñoz Caro et al., 2010; Fayolle et al., 2011; Bertin et al., 2012, 2013; Fayolle et al., 2013). Another non-thermal desorption that has been proposed is associated with the energy released by the formation of H_2 on the surface (Roberts et al., 2007). The formation of H_2 at the surface of the grain would be so exothermic that it would result in the partial desorption of the mantles. The fraction of the mantle evaporating remains an unconstrained parameter in the models. Generalizing this idea, the process of chemical desorption has been proposed by Garrod et al. (2007). For any exothermic reaction occurring at the surface of the grains, the released energy could be transferred to the products and induce their evaporation. Although the mechanism has been included in astrochemical models (for instance Garrod et al., 2007; Vasyunin and Herbst, 2013; Wakelam et al., 2014), its efficiency has been a free parameter. Minissale et al. (2016) recently conducted experiments of this process and found that the efficiency decreases with the ice coverage of the surface. Although they could do some measurements only on a small number of systems, they also proposed a new formalism to include this mechanism into gas-grain astrochemical models. Both formalisms from Garrod et al. (2007) and Minissale et al. (2016) depend on the binding energy of the species to the surface. In this paper, we propose a new model to compute the binding energies for species

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on water ice surfaces and investigate the new chemical desorption model proposed by Minissale et al. (2016).

The paper is organized as follows. Section 2 contains a general description of our gas-grain chemical model, the methods to compute the branching ratios of chemical desorption from Garrod et al. (2007) and Minissale et al. (2016), and the new model to compute binding energies. The list of new binding energies is available in the appendix. In Section 3, we compare our model results for cold cores conditions obtained with the two chemical desorption models, with and without the updated binding energies. We then conclude in the next section.

2. Chemical modeling

2.1. Model description

The chemical composition of the gas and the dust icy mantles is computed with the gas-grain code Nautilus described in Ruaud et al. (2016). The reactions considered for the gas-phase chemistry are listed in the public chemical network kida.uva.2014 (Wakelam et al., 2015). The surface network is based on the one of Garrod and Herbst, (2006). The chemical model includes physisorption of gas-phase species on grain surfaces, diffusion of species at the surface of the grains resulting in chemical reactions and several desorption mechanisms. The species on the surface can be desorbed due to the temperature (thermal desorption), cosmic-ray heating (cosmic-ray induced desorption, Hasegawa and Herbst, 1993), UV photon impact (photodesorption) and chemical desorption (see Section 2.2). The surface chemistry is solved using the rate equation approximation and assuming a different chemical behavior between the surface of the mantle and the bulk (three-phase model), the surface and the bulk being both chemically active. All details and equations (except for the chemical desorption which is the subject of this paper) are given in Ruaud et al. (2016).

2.2. Computation of chemical desorption branching ratios

The chemical desorption mechanism is based on the idea that the energy released by exothermic reactions at the surface of the grains is partly transferred to the produced species. This energy is then distributed over the degrees of freedom of the molecule. The part of the energy that goes to the direction perpendicular to the surface will allow for the molecule to bounce on the surface with a probability to result in the desorption of the species. The efficiency of this process depends on the amount of energy that stays in the product and is not lost in the grain. This last parameter depends on the surface and is quite uncertain. In all cases, we assume that if the reaction results in more than one product, the chemical desorption is not efficient since the energy would then be distributed in the two products (see Garrod et al., 2007).

Two formalisms have been proposed in the literature to include this process in chemical models. Garrod et al. (2007) have used the theory of Rice–Ramsperger–Kessel (Rice and Ramsperger, 1927; Kassel, 1928), in which the probability of desorption is expressed as

$$P = \left(1 - \frac{E_D}{E_{\rm reac}}\right)^{s-1}$$

with $E_{\rm D}$ the binding energy of the product, $E_{\rm reac}$ the energy released by the reaction (enthalpy of reaction), and s the number of vibrational modes in the molecule/surface-bound system. This last parameter is equal to 2 is the product of the reaction is a diatomic species while it is $3n - 5$ (with n the number of atoms in the specie) for other species. From P, we compute the fraction of products that would desorb at the end of the reaction by:

$$f = \frac{aP}{1 + aP}$$

with $a = \nu/\nu_{\rm S}$, and ν is the surface-molecule bond-frequency and $\nu_{\rm S}$ the frequency at which the energy is lost to the grain surface. The value of a is unknown and most studies consider values between 0.01 and 0.1, identical for all species, which leads to values of f approximately equal to that of a, i.e. between 1 and 10%. We will call this formalism RRK in the rest of the paper.

Table 1
Percentage of products chemically desorbed during surface reactions computed with the two formalisms. The values for RRK have been computed with $a = 0.01$.

Reaction	RRK	MDCH
$O + H \rightarrow OH$	0.9	30
$O + OH \rightarrow H_2O$	0.7	0.25
$N + H \rightarrow NH$	0.9	5.5
$NH + H \rightarrow NH_2$	0.7	2.6
$NH_2 + H \rightarrow NH_3$	0.5	1.1
$HCO + H \rightarrow H_2CO$	0.7	2
$CH_3O + H \rightarrow CH_3OH$	0.25	3×10^{-2}
$O + CO \rightarrow CO_2$	0.9	1.7
$HS + H \rightarrow H_2S$	0.8	1.7
$C_3H_3 + H \rightarrow CH_3CCH$	0.2	2×10^{-3}

More recently, Minissale et al. (2016) have proposed a new formalism, in which the fraction of evaporation depends on the mass of the product based on experimental results of a few surface reactions such as hydrogenation of O and CO, O+O and N+N reactions. In their formalism, the fraction of products evaporated is

$$f = e^{-\frac{E_D}{\epsilon E_{reac}/N}}$$

with N the number of degree of freedom's of the produced molecule ($N = 3n$) and $\epsilon = \frac{(M-m)^2}{(M+m)^2}$ is the fraction of the energy kept by the product with a mass m. M is the effective mass of the surface, which depends on the nature of the surface and is not well constrained. Minissale et al. (2016) have shown that chemical desorption on water ices was much less efficient than on bare silicate or graphite grains. In fact, for most studied systems, the efficiency was below the detection level of the experiment. We have thus used the recommendation by these authors: 1) we have computed f assuming the surface effective mass for bare grains of 120 amu and divided the obtained values by 10 and, 2) for the three systems where the chemical desorption could be measured, we used the measured values ($f_{\rm O+H} = 30\%$, $f_{\rm OH+H} = 25\%$ and $f_{\rm N+N} = 50\%$). We will call this formalism MDCH (for the names of the authors) in the rest of the paper. Except for the measured systems, this formalism produces evaporation fractions smaller than 10% and negligible fractions for most systems as f decreases very rapidly with the binding energy of the product. Using the equations of Garrod et al. (2007), f still decreases with $E_{\rm D}$ but much less rapidly so that all surface reactions lead to the partial evaporation of the products. The percentage of product evaporation, for a selection of surface reactions, is given in Table 1 using the two formalisms. For both formalisms, the chemical desorption is only active for the surface layer.

2.3. Update of binding energies

Whatever the formalism chosen for the chemical desorption, its efficiency depends on the binding energy of the product. The binding energies on Amorphous Solid Water (ASW) are not well known, particularly for radicals. An estimation of these binding energies is usually derived from temperature-programmed desorption (TPD) experiments. This technique has been widely used to determine the binding energies of stable molecules and has been reviewed by Burke and Brown (2010) and Hama and Watanabe (2013). We partly complete these reviews in Table 2 including recent measurements for some atoms (H, O and N) for which the uncertain-