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Modeling the chemistry in the icy mantles of interstellar grains

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Abstract. The diffusion and photoprocessing of molecules within interstellar ices has been verified experimentally but often not fully included in astrochemical models. With models that consider photodissociation, binary reactions, and diffusion for molecules on the surface and in bulk ice, we explored the chemistry of interstellar and circumstellar ices in gravitationally contracting low-mass starless and prestellar cores, and a protostellar envelope.

Results. Photoprocessing gradually converts mixed H_2O and CO ices into CO_2 and allows for a late synthesis of icy organic species. Different layers within a single icy mantle favor the synthesis different species. Deuterium-rich molecules are concentrated on the outer surface of ice. Formation of organic molecules in bulk ice lowers their average deuterium content. The abundances of major icy species can be changed by about 25-50 % because of ice photoprocessing. Inter-layer diffusion of icy species allows sequential evaporation in protostellar envelopes, which occurs over a prolonged period.

Keywords. astrochemistry, molecular processes, methods: numerical, stars: formation, ISM: clouds, molecules

1. Introduction

Ices in star-forming regions are a likely environment for the production of various chemical species, such as water, ammonia, carbon dioxide, complex organic molecules, hydrogen sulfide. The relevant synthesis pathways and efficiency are affected by external factors, such as irradiation, and factors specifically characteristic to ices, such as diffusion of molecules. The aim of this paper (poster) is to present the effects on ice composition caused by photoprocessing by ultraviolet photons and molecule diffusion between ice layers.

We review our recent modeling work on chemistry within the icy mantles of interstellar grains. Three recent articles are discussed: Kalvāns (2015b, hereafter Paper I), Kalvāns (2015c, Paper II), and Kalvāns *et al.* (2017, Paper III). We also show new results concerning ice photoprocessing. One of the novelties of this research is that processes in the whole volume of the icy mantles are explicitly considered, not just the surface.

The objects in consideration are gravitationally contracting cloud cores (Paper I). As the core becomes denser and darker, ice starts to accumulate onto the dust grains. Depending on their parameters, such cores can develop into starless or star-forming cores. In the former, modeled in Paper II, ices are slowly processed by ultraviolet photons within the core. In the envelopes of star-forming cores (Paper III), any ices are heated until they eventually evaporate. In this paper we focus on the aspects concerning major ice components that define the properties and possible chemical transformations of any other molecules in the icy mantles.

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2. Physical models

We employed the astrochemical model Alchemic-Venta, which is based on the ALCHEMIC code (Semenov *et al.* 2010). The center part of a collapsing cloud core was considered. The increase in gas density was calculated following Nejad *et al.* (1990). The adopted initial density is $\approx 3 \times 10^3\,\mathrm{cm}^{-3}$. This rises to $10^7\,\mathrm{cm}^{-3}$ for assumed prestellar cores (Papers I and III) and up to $4 \times 10^5\,\mathrm{cm}^{-3}$ in the case of starless cores (Paper II). Additionally, in Paper III we explored the chemical evolution in envelope that is heated by the protostar according to the temperature profile T2 of Garrod & Herbst (2006). Papers II and III considered a Plummer-like density profile, which is more adequate than the flat density profile in our previous works.

A standard hydrogen ionization rate by cosmic rays of $1.3\times10^{-17}\,\mathrm{s}^{-1}$ was assumed. The flux of cosmic-ray induced secondary photons was taken to be $4875\,\mathrm{s}^{-1}\mathrm{cm}^{-2}$ (Roberts *et al.* 2007).

3. Chemical model

The numerical codes of Papers I and II employed updated versions of the gas-grain chemical network by Garrod *et al.* (2008) with many organic compounds. Paper III used another derivation of the OSU chemical database, one that considers the chemistry of deuterium (Albertsson *et al.* 2013). Surface and bulk-ice chemical reactions were described with the modified rate-equations method with rates adjusted for reaction-diffusion competition according to Garrod & Pauly (2011).

For molecules in the outer layer, the whole grain surface is available for diffusion until they encounter a reaction partner (Hasegawa *et al.* 1992). However, bulk-ice molecules were assumed to be locked in cells with only a small number of possible reactants available at a given instant (Paper I). This approach evolved from a model that considered reactions on the surface of pores within ice (Kalvāns & Shmeld 2010).

Neutral gas-phase species were allowed to stick on grain surfaces. In the model, icy mantles are accumulated on grains with a radius of $0.1\,\mu$m and can reach thickness up to 180 monolayers (MLs). Adsorbed molecules can be released to the gas by several mechanisms:

- thermal evaporation;
- photodesorption by interstellar and secondary UV radiation;
- desorption by cosmic-ray induced whole-grain heating with iron cosmic-ray flux taken to be $2.06 \times 10^{-3}\,\mathrm{s}^{-1}\mathrm{cm}^{-2}$ (Roberts *et al.* 2007);
- reactive desorption with the method outlined by Garrod *et al.* (2007);
- indirect reactive desorption, as described in Paper I.

Observations and laboratory studies have shown that interstellar ices have a polar component with water as dominating species and a non-polar component, dominated by solid CO (Sandford *et al.* 1988, Tielens *et al.* 1991. Thus, to describe properly the basic processes occurring in bulk-ice layers, these two components must be accounted for. We describe the icy mantles as consisting of a total of four layers – the surface (typical thickness 1-2 MLs) and three subsurface bulk-ice layers ('sublayers', up to 60 MLs). The separate MLs within these four layers are assumed to be completely mixed. This description allows to include polar, non-polar and mixed ice components, in addition to the reactive surface. A similar approach – the '(2+n)-phase model' – has been used by Furuya *et al.* (2017).

In the following sections we focus on the diffusion of icy species between the ice mantle layers and photoprocessing of bulk-ice molecules. This includes discussing the employed

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Table 1. Calculated relative abundances of solid water and carbon oxides in ices. The ordinate shows integration time t prior to the supposed starbirth in the modelled cloud core.

Ice species	**Abundance** $\times 10^{-5}$ **with** $\epsilon_{\rm pd} = 0.0$	**Abundance** $\times 10^{-5}$ **with** $\epsilon_{\rm pd} = 1.0$
H_2O	11.9	8.89
CO	8.29	5.62
CO_2	5.67	8.35

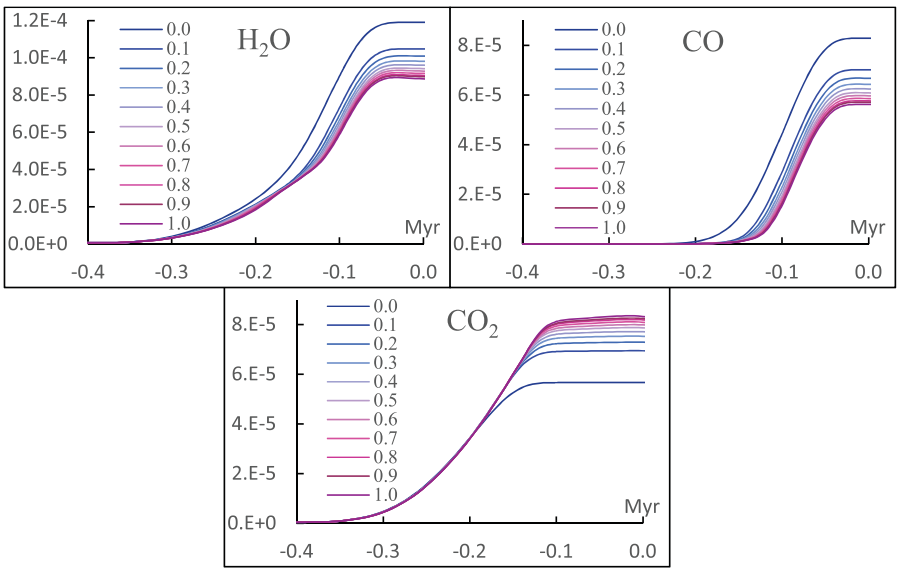

Figure 1. Calculated relative abundances of major icy species for models with various values for $\epsilon_{\rm pd}$ (ratio of photodissociation rates for icy species versus gas-phase species), as indicated in the plots.

methods and the resulting implications on the composition of interstellar and circumstellar ices.

4. Ice photoprocessing

Photoprocessing of icy molecules involves two main steps: the dissociation of a molecule and the subsequent reactions by the fragments, which often are active chemical radicals. The efficiency of photoprocessing is affected by the rate of dissociation. For adsorbed species, photodissociation was first used in astrochemical numerical simulations by Ruffle & Herbst (2001). They assumed that the photodissociation coefficient $k_{\rm pd,i}$ of icy species on grain surface is similar to the coefficient for these species in the gas phase $k_{\rm pd,g}$.

For the aims of this paper, the photodissociation rate of icy molecules can be loosely described with the help of an efficiency parameter $\epsilon_{\rm pd}$:

$$\epsilon_{\rm pd} = k_{\rm pd,g}/k_{\rm pd,i}. \tag{4.1}$$

The expected values for $\epsilon_{\rm pd}$ are in the range of 0...1, i.e., photodissociation rate of icy molecules is likely to be similar or lower than that in the gas phase. This is because the photodissociation fragments may immediately recombine to form the parent molecule.

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Additionally, dissociation yield can be lower thanks to stabilizing bonds to a neighbor molecules in a solid. Current astrochemical models that explicitly consider bulk-ice typically assume either $\epsilon_{\rm pd} = 0$ (e.g., Furuya *et al.* 2017, Ruaud *et al.* 2016, and Taquet *et al.* 2014) or $\epsilon_{\rm pd} = 1$ (Chang & Herbst 2016, Furuya *et al.* 2017, Garrod *et al.* 2017, Vasyunin *et al.* 2017, and Papers I-III). Perhaps the only models that considered ice molecule photodissociation at a lower rate were those of Kalvāns & Shmeld (2010, 2013).

Photoprocessing most intensively affects ice composition during the period when a cloud core slowly contracts, darkens, and cools. Water ice appears at an extinction $A_{\rm V}$ along the line of sight of ≈ 3.2 mag (Whittet *et al.* 2001), CO_2 ice at ≈ 4.3 mag (Bergin *et al.* 2005), and CO ice at ≈ 6.8 mag (Whittet *et al.* 2007). These values correspond to translucent cloud cores. Ice accumulation in translucent cores is reproduced by the above-mentioned numerical simulations.

The above means that a part of the ice is formed under irradiation by interstellar photons. This affects the overall composition of ice because molecules can be dissociated and re-formed on the surface. The observed approximate proportions of solid H_2O:CO:CO_2 of 100:31:38 (Öberg *et al.* 2011) in cold cores are the result of molecule accretion onto grains, ice photoprocessing, and desorption. Paper I considered active bulk-ice chemistry with $\epsilon_{pd} = 1$. It was found that selective desorption of surface species is required to explain the observed proportions of H_2O, CO, and CO_2.

Photoprocessing continues to affect ice composition in dark, dense cores even when the interstellar photons are attenuated. In this case, cosmic-ray induced photons are the main dissociation agents (Prasad & Tarafdar 1983). Kalvāns & Shmeld (2010) found that photoprocessing in dark cores slowly converts CO and H_2O icy mixtures into CO_2, while the excess hydrogen diffuses out and is lost to the gas phase. This result was confirmed by the more detailed starless core model of Paper II.

The CO_2:H_2O ice abundance ratio can be used to estimate the age of a quiescent cloud core. This ratio likely does not exceed 50 % in the interstellar medium (Boogert *et al.* 2011). In Paper II we estimated the maximum age of quiescent cores to be 1 Myr. This time can be higher if ϵ_{pd} is taken to be lower than unity. A second interesting conclusion was that photoprocessing promotes the synthesis of different organic an inorganic compounds in different layers of ice. The production and destruction of a particular minor species depend on the abundances of the major ice components H_2O, CO, CO_2, NH_3, and N_2 in the considered layer. For example, formaldehyde formation is most effective in CO-rich ice, while methanol largely is formed in the water-rich layers.

In addition to UV photons, interstellar ices are chemically processed also by cosmic-ray particles. Kalvāns (2015a) estimated that such processing may change the abundances of the above-mentioned major ice components by no more than a few per cent. For minor species, e.g., carbon-chain compounds, the abundances can change much more significantly, by up to two orders of magnitude.

Photoprocessing has implications on the deuterium chemistry in the icy mantles. Deuterated species are concentrated on ice surface (Kalvans & Shmeld 2013, Taquet *et al.* 2013). For complex organic molecules (COMs) and many other minor species deuterium content decreases over time. This is because new molecules, synthesized primarily in the bulk-ice, are deuterium-poor (Paper III). However, the total deuterium proportion in ice mantles (i.e., D content in solid H_2O and NH_3) increases for time-scales of 100 kyr and longer (for both, starless cores and circumstellar envelopes). This is because the light hydrogen isotope diffuses out of the mantle more easily and its amount in photoprocessed ice decreases faster (Kalvāns 2014).

In addition to the findings of previous papers, described above, we present a small theoretical study of ice photoprocessing in a low-mass collapsing core. This is a

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preliminary study for a subsequent more detailed investigation. Our aim was to quantify the influence of photodissociation rate on the calculated composition of interstellar ices. For this aim, we calculated the abundances of major icy species (water and carbon oxides) in a collapsing prestellar core, i.e., during the ice formation epoch. The dissociation rate was modified by assuming different values of ϵ_{pd}.

Eleven simulations were performed with adopted $\epsilon_{\rm pd}$ values in the range of 0...1.0. We employed the exact model of Paper III with a single change: removed indirect reactive desorption. This mechanism has unknown efficiency, which has been adjusted in order to obtain a better agreement of calculated ice composition and observations of interstellar ices (see Paper I). Because ice composition *is the subject* of our limited study, this desorption mechanism was dropped. Here we considered only the prestellar phase of the model described in Paper III, i.e., up to integration time $t = 0\,$Myr.

Figure 1 shows that photoprocessing has the effect of increasing the abundance of CO_2 ice at the expense of CO and H_2O. Table 1 presents a quantitative comparison – the relative abundances of H_2O, CO, and CO_2 ices at the densest stage of the prestellar core at $t = 0.0\,$Myr. Comparing cases with no ice photodissociation versus full photoprocessing, the relative abundances of CO and H_2O have decreased by 2.7×10^{-5} and 3.0×10^{-5}, respectively. At the same time, the relative abundance of CO_2 ice has increased by 2.7×10^{-5} due to photoprocessing. These numbers represent abundance changes in the range of 25-50 %. Thus, while ice photoprocessing is not a decisive process in ice accumulation, its influence is significant, and probably can be quantified with the help the available observational data (e.g., Whittet *et al.* 2007).

5. Inter-layer diffusion of molecules in icy mantles

The inter-layer mobility of icy molecules was probably first considered by Cuppen & Herbst (2007). The rate of diffusion for each molecule on ice surface is governed by its binding, or diffusion, energy, $E_{\rm b}$. The latter is often obtained from the desorption energy $E_{\rm D}$ by assuming a fixed $E_{\rm b}/E_{\rm D}$ ratio. In Papers I-III this ratio was taken to be in the range 0.35-0.50 (Garrod & Herbst 2006, Garrod & Pauly 2011). Species in the bulk are surrounded by ice molecules and thus are more strongly bound in the ice lattice. We assumed that their *absorption energy* $E_{\rm B}$ is three times higher than the desorption energy of surface species (Paper I), $E_{\rm B}/E_{\rm D} \approx 3$. The binding energy for mantle species was modified proportionally.

It was assumed that radial diffusion of molecules in bulk ice between the four layers occurs thanks to irregularities and cracks in the amorphous ice. The diffusion rate of a molecule depends on its own binding energy. This is different from, e.g., Garrod (2013), who assumed that diffusion occurs via swapping of water molecules. The latter approach is not suited, for example, a case of CO-dominated ice.

The above means that each molecule diffuses through ice at its own rate. This is approximately consistent with temperature-programmed desorption experiments (e.g., Fayolle *et al.* 2011). In circumstellar envelopes, where the icy mantles are heated up, chemical radicals with increasing binding energies become mobile, activating various reaction chains that affect the abundances of minor species (see, e.g., the discussion by Kalvāns 2015a). The major ice components evaporate in three steps: first, CO and N_2, then CO_2, and then H_2O and NH_3 (Paper III). With the evaporation of CO, the production of new COMs in bulk-ice becomes insignificant. It is completely shut down when CH_4, H_2CO, and CO_2 disappear from the icy mantles.

The evaporation of icy species with our model is a prolonged process taking at least several kyrs. First, molecules on the outer surface evaporate. This produces an initial

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spike for the gas-phase abundance for some species (see figures 4, 5, A1, and A2 of Paper III). Because $E_{\rm b}$ for a molecule in bulk ice layers is higher than $E_{\rm D}$ for a molecule on the surface, radial diffusion occurs at higher temperatures than evaporation. This produces a close second peak in species' gas-phase abundance. The second peak often is broader because molecule diffusion from the inner ice layers takes time. These two evaporation stages must be temporally and spatially close, and are unlikely to be discerned by observations.

6. Summary

We have reviewed our recent astrochemical models of interstellar cloud cores and circumstellar envelopes. Results on photodissociation of icy species and diffusion between molecule layers in icy mantles were discussed. A modeling study showed that photodissociation can alter the abundances of major icy species, an effect that can be studied by numerical simulations calibrated by observational results.

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References

Albertsson, T., Semenov, D. A., Vasyunin, A. I., Henning, T., & Herbst, E. 2013, *ApJS*, 207, 27
Andersson, S. & van Dishoeck, E. F. 2008, *A&A*, 491, 907
Bergin, E. A., Melnick, G. J., Gerakines, P. A., Neufeld, D. A., & Whittet, D. C. B. 2005, *ApJL*, 627, L33
Boogert, A. C. A., Huard, T. L., Cook, A. M., Chiar, J. E., Knez, C., Decin, L., Blake, G. A., Tielens, A. G. G. M., & van Dishoeck, E. F. 2011, *ApJ*, 729, 92
Chang, Q. & Herbst, E. 2016, *ApJ*, 819, 145
Cuppen, H. & Herbst, E. 2007, *ApJ*, 668, 294
Fayolle, E. C., Öberg, K. I., Cuppen, H. M., Visser, R., & Linnartz, H. 2011, *A&A*, 529, A74
Furuya, K., Drozdovskaya, M. N., Visser, R., van Dishoeck, E. F., Walsh, C., Harsono, D., Hincelin, U., & Taquet, V. 2017, *A&A*, 599, A40
Garrod, R. T. 2013, *ApJ*, 765, 60
Garrod, R. T., Belloche, A., Mller, H. S. P., & Menten, K. M. 2017, *A&A*, 601, A48
Garrod, R. T. & Herbst, E. 2006, *A&A*, 457, 927
Garrod, R. T. & Pauly, T. 2011, *ApJ*, 735, 15
Garrod, R. T., Wakelam, V., & Herbst, E. 2007, *A&A*, 467, 1103
Garrod, R. T., Weaver, S. L. W., & Herbst, E. 2008, *ApJ*, 682, 283
Hasegawa, T. I., Herbst, E., & Leung, C. M. 1992, *ApJS*, 82, 167
Hincelin, U., Chang, Q., & Herbst, E. 2015, *A&A*, 574, A24
Kalvāns, J. & Shmeld, I. 2010, *A&A*, 521, A37
Kalvāns, J. & Shmeld, I. 2013, *A&A*, 554, A111
Kalvāns, J. 2014, *PASP*, 126, 811
Kalvāns, J. 2015a, *A&A*, 573, A38
Kalvāns, J. 2015b, *ApJ*, 803, 52 (Paper I)
Kalvāns, J. 2015c, *ApJ*, 806, 196 (Paper II)
Kalvāns, J., Shmeld, I., Kalnin, J. R., & Hocuk, S. 2017, *MNRAS*, 467, 1763 (Paper III)
Nejad, L. A., Williams, D. A., & Charnley, S. B. 1990, *MNRAS*, 246, 183

https://doi.org/10.1017/S1743921317006706 Published online by Cambridge University Press

Öberg, K. I., Boogert, A. C. A., Pontoppidan, K. M., van den Broek, S., van Dishoeck, E. F., Bottinelli, S., Blake, G. A., & Evans, N. J. II 2011 *ApJ*, 740, 109

Prasad, S. S. & Tarafdar, S. P. 1983, *ApJ*, 267, 603

Roberts, J. F., Rawlings, J. M. C., Viti, S., & Williams, D. A. 2007, *MNRAS*, 382, 733

Ruaud, M., Wakelam, V., & Hersant, F. 2016, *MNRAS*, 459, 3756

Ruffle, D. P. & Herbst, E. 2001, *MNRAS*, 322, 770

Sandford, S. A., Allamandola, L. J., Tielens, A. G. G. M., & Valero, G. J. 1988, *ApJ*, 329, 498

Semenov, D., Hersant, F., Wakelam, V., Dutrey, A., Chapillon, E., Guilloteau, St., Henning, Th., Launhardt, R., Pietu, V., & Schreyer, K. 2010, *A&A*, 467, 1763

Taquet, V., Charnley, S. B., & Sipilä, O. 2014, *ApJ*, 791, 1

Taquet, V., Peters, P. S., Kahane, C., Ceccarelli, C., López-Sepulcre, A., Toubin, C., Duflot, D., & Wiesenfeld, L. 2013, *A&A*, 550, A127

Tielens, A. G. G. M., Tokunaga, A. T., Geballe, T. R., & Baas, F. 1991, *ApJ*, 381, 181

Vasyunin, A. I., Caselli, P., Dulieu, F., & Jimnez-Serra, I. 2017, *ApJ*, 842, 33

Whittet, D. C. B., Gerakines, P. A., Hough, J. H., & Shenoy, S. S. 2001, *ApJ*, 547, 872

Whittet, D. C. B., Shenoy, S. S., Bergin, E. A., Chiar, J. E., Gerakines, P. A., Gibb, E. L., Melnick, G. J., & Neufeld, D. A. 2007, *ApJ*, 655, 332

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