Astronomy in Focus, Volume 1, Focus Meeting 12
XXIXth IAU General Assembly, August 2015
Piero Benvenuti, ed.

doi:10.1017/S1743921316003136

Laboratory constraints on ice formation, restructuring and desorption

Karin I. Öberg

Harvard-Smithsonian Center for Astrophysics
60 Garden St, Cambridge, MA 02138
email: `koberg@cfa.harvard.edu`

Abstract. Ices form on the surfaces of interstellar and circumstellar dust grains though freeze-out of molecules and atoms from the gas-phase followed by chemical reactions. The composition, chemistry, structure and desorption properties of these ices regulate two important aspects of planet formation: the locations of major condensation fronts in protoplanetary disks (i.e. snow lines) and the formation efficiencies of complex organic molecules in astrophysical environments. The latter regulates the availability of prebiotic material on nascent planets. With ALMA it is possible to directly observe both (CO) snowlines and complex organics in protoplanetary disks. The interpretation of these observations requires a detailed understanding of the fundamental ice processes that regulate the build-up, evolution and desorption of icy grain mantles. This proceeding reviews how experiments on thermal CO and N_2 ice desorption, UV photodesorption of CO ice, and CO diffusion in H_2O ice have been used to guide and interpret astrochemical observations of snowlines and complex molecules.

Keywords. astrochemistry, astrobiology, molecular processes, methods: laboratory, ISM: molecules

1. Introduction

In the cold and dark phases of star and planet formation the surfaces of interstellar dust grains become coated with icy mantles. These ices are built up in molecular clouds through a combination of direct freeze-out of gas-phase molecules (e.g. $CO \rightarrow CO_{gr}$) and freeze-out followed by atom addition reactions (e.g. $O_{gr} + H_{gr} \rightarrow OH_{gr} \rightarrow H_2O_{gr}$). The resulting ice mantle is typically dominated by H_2O followed by CO and CO_2 (20–30% with respect to H_2O) and smaller amounts of CH_3OH, CH_4 and NH_3 (Öberg *et al.* 2011a, Boogert *et al.* 2015). When a cloud core collapses to form a star, some of the icy grains become incorporated into the circumstellar disk that is the formation site of planets. The volatile composition of forming planets depend intimately on the ice and gas composition in the disk (Öberg *et al.* 2011b), which is set by the desorption energies of the main ice constituents (together with initial conditions and disk chemistry). Major condensation fronts, of e.g. H_2O, CO_2, CO and N_2, may locally enhance planet formation.

Icy grain mantles are also important from a prebiotic perspective. Ice chemistry is the proposed main cause of the chemical complexity observed toward protostars (Garrod *et al.* 2008, Herbst & van Dishoeck 2009). The complex organics that become incorporated into protoplanetary disks and further into planets may seed the origins of life. The abundance and composition of this organic material depend on the efficiency at which simple ice mantles are converted into different kinds of complex organic ices.

Our ability to model both the organic content and the bulk volatile composition of nascent planets then depends fundamentally on our understanding of a small number of ice processes: accretion from the gas-phase, diffusion of atoms, radicals and molecules on top of and inside of ice, reactions when different species encounter one another in the

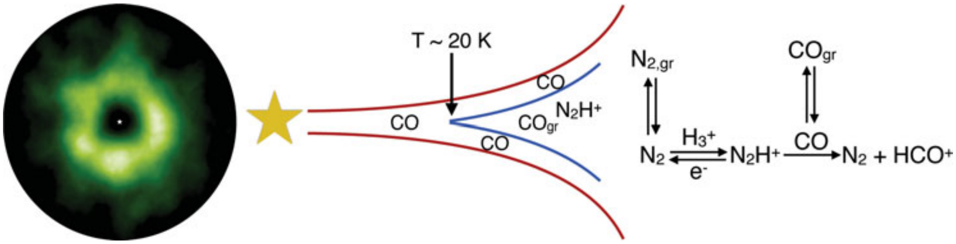

Figure 1. N_2H^+ observation toward the disk around TW Hya (left, after Qi *et al.* 2013), and cartoon and reaction diagram summarizing the relation between CO freeze-out ($CO \rightarrow CO_{gr}$) and the appearance of N_2H^+ in disks. In essence the inner rim of the green N_2H^+ ring traces the onset of CO freeze-out in the disk midplane, i.e. the CO snowline.

ice, and thermal and non-thermal desorption. Quantifying these processes, including their energy barrier heights, requires experiments. This proceeding presents three observations related to disk snowlines and organic chemistry – a N_2H^+ ring in the disk around young star TW Hya, a double DCO^+ ring in the disk around young star IM Lup and the presence of complex organics in cold cloud cores – and three ice experiments that aid in interpreting these observations. The focus is on CO, both because it is an excellent model system, and because of its importance for ice organic chemistry and the volatile structure in disks during planet formation.

2. CO and N_2 ice desorption and observations of CO snowlines

Snowlines influence several aspects of planet formation, including the efficiency of the initial grain coagulation step and the bulk compositions of forming planets. Observational constraints on snowline locations in disks are therefore important. Based on laboratory experiments on CO desorption energy barriers (Collings *et al.* 2003), CO snowlines are expected at disk midplane temperatures of ~20 K, which corresponds to disk radii of ~30 AU in disks around young Solar type stars. This is readily resolvable by modern interferometers like the Atacama Large Millimeter and submillimeter Array (ALMA). Direct imaging of snowlines is challenging, however, due to the presence of vertical temperature gradients in disks, which maintains large quantities of CO in the gas-phase in the disk atmosphere at all disk radii, which can hide loss of CO emission from the CO freeze-out zone in the disk midplane (Fig. 1).

A potential solution is to identify a tracer that robustly anti-correlates with CO gas and therefore traces CO freeze-out regions. N_2H^+ is such a tracer as long as N_2 freeze-out occurs at (slightly) lower temperatures compared to CO. N_2H^+ forms through gas-phase reactions between N_2 and H_3^+ and is rapidly destroyed by proton transfer to CO, if there is any CO gas present. If CO is frozen out and N_2 is not, N_2H^+ can become quite abundant and N_2H^+ emission should trace the CO freeze-out zone, i.e. the inner radii of N_2H^+ emission should coincide with the CO snowline. Laboratory experiments have shown that there is a small difference in desorption energy barriers for CO and N_2 in pure ices (Öberg *et al.* 2005, Bisschop *et al.* 2006). More recent experiments have demonstrated that this difference persists for water-rich ices (Fayolle *et al.* in prep.). The utility of N_2H^+ as a CO snowline tracer was recently demonstrated observationally by the presence of a N_2H^+ ring in the disk around the young star TW Hya (Fig. 1), with an inner rim at 30 AU, the expected radius of the CO snowline in this disk (Qi *et al.* 2013). Snowline locations are thus accessible to observations through interferometric chemical imaging.

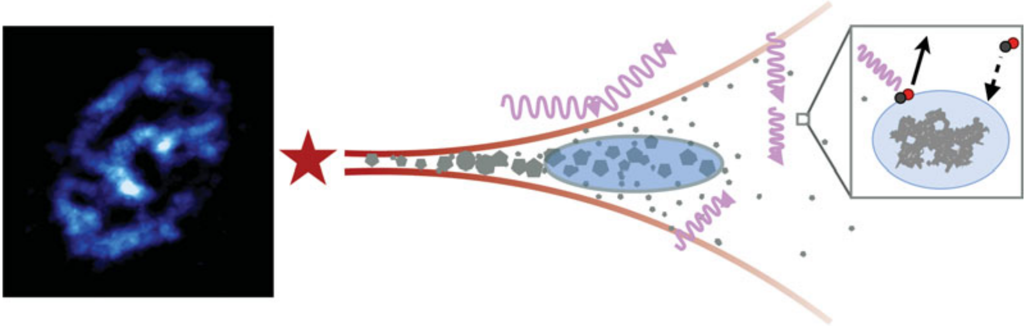

Figure 2. Observation of DCO$^+$ in the disk around young star IM Lup (left) and a cartoon illustrating the complete freeze-out zone of CO in a disk (light blue oval), limited by thermal desorption of CO inwards, and non-thermal desorption in the outer disk. DCO$^+$ is expected to be the most abundant just interior to the inner CO snowline and in the non-thermal desorption region, where the two ingredients of efficient DCO$^+$ formation – low temperatures and CO gas – are both present.

3. CO ice photodesorption and a DCO$^+$ double ring in a disk

In addition to the thermal desorption described in the previous section, ices can desorb non-thermally through interactions with UV, electrons, and cosmic rays, and through the release of chemical energy. In the dense, inner regions of protoplanetary disks, the disk mid planes are efficiently shielded from all external radiation. The division of molecules between ice and gas is therefore mainly set by gas adsorption onto grains and thermal desorption of ice, regulating e.g. the location of the CO snowline (Fig. 1). In the absence of non-thermal desorption, almost no CO is expected in the midplane exterior to the CO snowline. Further out yet in the disk some the gas can be partially repopulated by CO through a combination of low adsorption rate (caused by the low densities found in the outer regions of disks) and the activation of non-thermal desorption pathways, such as UV photodesorption of ice. The latter can occur if 1) the dust column becomes to small to efficiently shield the disk midplane from external radiation, and 2) UV photodesorption is an efficient process.

UV photodesorption of ices have been explored extensively through laboratory experiments (Öberg *et al.* 2009a, Munoz Caro *et al.* 2010, Fayolle *et al.* 2011), and the efficiencies are high, at least 10^{-3} per incident UV photon. These high desorption efficiencies imply that in the outer tenuous disk, UV photodesorption could partially repopulate the disk midplane with CO gas . The effects of ice photodesorption (or a related non-thermal desorption process) are manifest in the disk of IM Lup. The disk presents a set of concentric DCO$^+$ rings (Öberg *et al.* 2015), where the outer disk can be attributed to DCO$^+$ formation following desorption of (some) CO back into the gas-phase at large disk radii. Based on our understanding of isotopic fractionation chemistry and CO desorption we can interpret the two concentric DCO$^+$ rings as marking 4 distinct disk regions: an inner disk region where CO is in the gas-phase, but where it is too warm for efficient deuterium chemistry (inner hole), a region close to the CO snowline where CO is still in the gas phase and temperatures are sufficiently low for DCO$^+$ to be enhanced (the inner DCO$^+$ ring), a CO freeze-out region where both thermal and non-thermal desorption are very slow and all CO based chemistry is turned off, and an outer disk region where CO photodesorption becomes efficient and DCO$^+$ therefore reappears (the second ring).

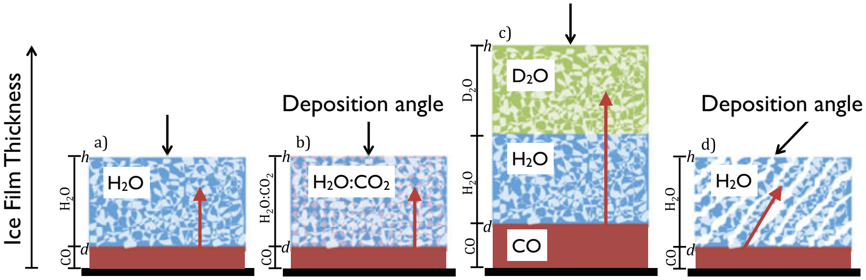

Figure 3. Cartoon illustrating CO diffusion experiments by Lauck *et al.* (2015), where CO diffusion into water ice was measured spectroscopically employing initially layered CO and H_2O ices of different ice thicknesses, porosities and isotopic compositions.

4. CO ice diffusion and a cold complex organic ice chemistry in space

A puzzle in astrochemistry is the presence of complex organic molecules in cold molecular cloud cores (Öberg *et al.* 2010, Bacmann *et al.* 2012, Cernicharo *et al.* 2012). In these regions the commonly invoked interstellar pathway for forming complex organics – photodissociation of CH_3OH and other ice molecules into radicals followed by radical diffusion and reactions – seem to fail. With the currently used prescriptions for diffusion in ices, the icy grain mantles in these cores are simply too cold for radical diffusion (e.g. Garrod *et al.* 2008). There are very few measurements of diffusion of radicals and molecules in ices, however, and it is therefore unclear whether existing assumptions on diffusion barriers are realistic. A number of recent studies have attempted to measure CO diffusion in H_2O ice to test these assumptions (e.g. Karssemeijer *et al.* 2014, Lauck *et al.* 2015). Our experimental approach is summarized in Fig. 3. The studies find consistently lower diffusion barriers than expected for CO in H_2O ice; we find a diffusion to desorption energy ratio that is $\sim$0.15, which can be compared to commonly assumed ratios of 0.3–0.7 (Lauck *et al.* 2015). This suggests that molecules and radicals can be mobile in ices at lower temperatures than previously assumed, perhaps explaining the existence of complex organics molecules in cold interstellar environments.

References

Bacmann, A, Taquet, V, Faure, A, *et al.* 2012, *A&A*, 541, 12
Bisschop, S. E. and Fraser, H. J., Öberg, K. I. *et al.* 2006, *A&A*, 449, 1297
Cernicharo, J, Marcelino, N, & Roueff, E, 2012, *A&A*, 759, L43
Collings, M. P., Dever, J. W., & Fraser, H. J. 2003, *ApJ*, 583, 1058
Fayolle, E. C., Bertin, M., & Romanzin, C. 2011, *ApJL*, 739, L36
Garrod R. T., Weaver S. L. W., & Herbst E. 2008, *ApJ*, 682, 283
Herbst, E., & van Dishoeck, E. F. 2009, *ARA&A*, 47, 427
Karssemeijer, L. J, Ioppolo, S, & van Hemert, M. C, 2014, *A&A*, 781, 16
Lauck, T., Karssemeijer, L., Shulenberger, K. *et al.* 2015, *ApJ*, 801, 118
Munoz Caro, G. M, Jimenez-Escobar, A, & Martin-Gago, J. A, 2010, *A&A*, 522, 108
Öberg, K. I., van Broekhuizen, F., Fraser, H. J. *et al.* 2005 *ApJL*, 621, L33
Öberg, K. I., van Dishoeck, E. F., & Linnartz, H. 2009 *A&A*, 496, 281
Öberg K. I., Boogert A. C. A., Pontoppidan K. M. *et al.* 2011 *ApJ*, 740, 109
Öberg, K. I., Murray-Clay, R., & Bergin, E. A. 2011 *ApJL*, 743, L16
Öberg, K. I., Furuya, K., & Loomis, R. 2015 *ApJ*, 810, 112
Qi, C., Öberg, K. I., Wilner, D. J. *et al.* 2013, *Science*, 341, 630