Monte Carlo Modeling of Astrophysically-Relevant Temperature-Programmed Desorption Experiments

Aspen R. Clements,[1] **Ilsa Cooke,**[1] **and Robin T. Garrod**[1,2]

[1]Department of Chemistry, University of Virginia,
P.O. Box 400319, Charlottesville, VA 22904-4319
email: `ac8hq@virginia.edu`

[2]Department of Astronomy, University of Virginia,
P.O. Box 400325 Charlottesville, VA 22904-4325

Abstract. The formation of molecules in the interstellar medium is significantly driven by grain chemistry, ranging from simple (e.g. H_2) to relatively complex (e.g. CH_3OH) products. The movement of atoms and molecules on amorphous ice surfaces is not well constrained, and this is a quintessential component of surface chemistry. We show that ice structure created by utilizing an off-lattice Monte Carlo kinetics model is highly dependent on deposition parameters (i.e. angle, rate, and temperature). The model, thus far, successfully predicts the densities of deposition rate- and temperature-dependent laboratory experiments. The simulations indicate, when angle and deposition rate increase, the density decreases. On the other hand, temperature has the opposite effect and will increase the density. We can make ices with desired densities and monitor how molecules, like CO, percolate through H_2O ice pores. The strength of this model lies in the ability to replicate TPD-like experiments by monitoring molecules diffusing on and desorbing from user-defined surfaces.

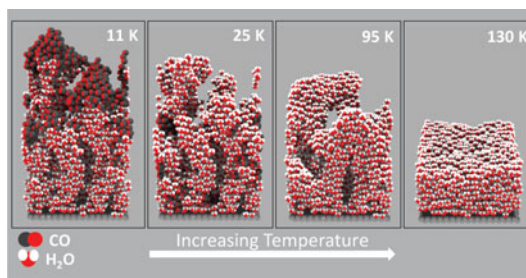**Keywords.** Keyword1, keyword2, keyword3, etc.

1. Introduction

Amorphous solid water (ASW) is a major component of astronomically-important structures, including mantles on interstellar grains, protoplanetary disks, planetary rings, satellites, and comets (e.g. Gibb *et al.* 2004 Oberg *et al.* 2011). Water ice in the ISM is found to be primarily amorphous, or in a disordered state, and can contain large, empty pockets called pores, which may trap species such as CO. The entrapment of CO enhances the production of molecules such as CH_3OH, a molecule potentially important for the formation of prebiotic molecules (Hidaka *et al.* 2008). The ability for molecules to incorporate into the ice is highly dependent on structure. For instance, porous ASW can absorb 20 to 50 times more gas than a compact, non-porous ASW (Ayotte *et al.* 2001). The formation of such an ice structure is dependent on many parameters, including the formation timescale, grain and gas temperatures, deposition angle, and deposition rate. Laboratory ice experiments are used by astrochemists to understand the behavior and formation of ices in the ISM; however, the deposition parameters often differ between the two, leading to cases in which the laboratory ice may not be truly representative of an ice in the ISM.

These ice experiments are essential for the understanding of astrochemistry because they provide insight into the identity of gas- and solid-phase species, the viability of proposed surface and gas reactions, and reaction rates and barriers. Given the utility of these experiments, ensuring they can be extrapolated to ISM ices is essential. For solid-phase chemistry, desorption energies set the temperature in which gas-phase species accrete and stick onto the grains. The method used to find the desorption, or binding, energies is called temperature-programmed desorption (TPD), in which molecules are thermally desorbed from an ice. In these experiments, an ice is deposited onto a surface at a specified temperature, determined by the desired structure (see below); the ice is then heated at a linear rate via an electrical current, and the desorption of molecules is monitored using a mass spectrometer. The TPD profiles, showing desorption rate as a function of temperature, will have unique profiles depending on the ice composition and structure, aiding in the identification of ice components (Collings *et al.* 2004). The interpretations of these results can be overly simplistic, not taking into account the ice structure or porosity and may not reflect processes in the ISM because of the discrepancies in conditions. Given the utility of laboratory experiments, ensuring their extrapolation to ISM ices and processes is a top priority. We attempt to control for various deposition parameters and mimic laboratory experiments with a kinetic Monte Carlo model.

2. Model

The model used in this study is the Model for Interstellar Monte-Carlo Ice Chemical Kinetics, or MIMICK. The predecessor of this model is discussed in more detail in Garrod (2013) . The code has been updated to use lateral periodic conditions to mimic a larger ice. All chemical species are treated as isotropic spheres with radii of 1.6 $\mathring{A}$, for simplicity. MIMICK is an off-lattice model, allowing for amorphous surface structures with micro- and macro-pores, as opposed to the always-ordered structures of on-lattice models with pre-determined binding sites (Cuppen *et al.* 2005). Within the model,

Figure 1. The CO diffuses into pores of H_2O until it begins to desorb around 25 K. By 130 K, H_2O has lost large pores and compacted. Experimental conditions from Fayolle *et al.* 2016.

there are a large number of parameters that can be changed (e.g. deposition angle, rate, and temperature).

3. Results

Full results and comparisons of models run with varying deposition parameters will be published shortly Clements *et al.* in prep). Preliminary research aimed to to replicate a TPD experiment from Fayolle *et al.* (2016a). The experiment involves depositing H_2O and, subsequently, CO; the chamber is slowly heated and desorbing molecules are monitored. The underlying H_2O ice structure will impact when and how CO molecules diffuse and, eventually, desorb into the gas phase. The laboratory deposition conditions are used in MIMICK to grow ices, with the aim of creating similar ice structures. Growing ices at 90 K and 11 K produces compact and porous ASW, respectively. The layered ices are then heated with a linear ramp rate around 1 K/min. Analogous to the purpose of

a mass spectrometer, MIMICK monitors every molecule in the model, including when that leaves the ice surface. TPD profiles are generated and compared to the experimental data; figure 1 depicts the warm-up process within the model, following deposition. The model qualitatively demonstrates the expected changes in ice structure, during a warm-up process, and the diffusion and desorption of CO.

Generated TPD profiles of the described system can be seen in color in Figure 2. Figure 2(a) shows the compact H_2O and topped with CO ice. There is a two-peak structure, implying multiple CO binding energies. The first peak likely denotes CO-CO interactions because CO-CO interactions are expected to be weaker than CO-H_2O interactions.

Then, the second peak must correspond to the CO-H_2O interaction, likely showing the CO desorbing from within the ASW pores. Figure 2(b) (right) is the porous ice grown (11 K) and only has a one-peak structure, most likely the CO-H_2O interaction A compact ice grown at 90 K should have a significantly lower surface area, eliminating area for CO-H_2O interactions, and forcing more CO-CO interactions. When surface area is increased, like in the porous ice, CO-H_2O interactions should dominate, depending on the thickness of CO ice. The number of peaks in each panel matches the laboratory data, overlaid in black in the figure, and shows that MIMICK is already able to qualitatively replicate some experimental work.
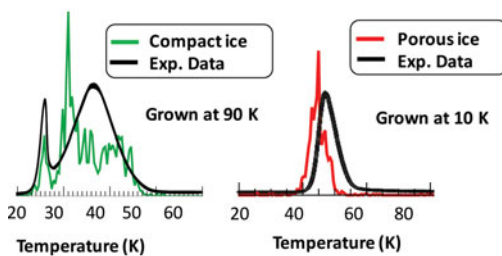
Figure 2. The TPD profiles from the model shown in color with the Fayolle data in black. The green shows the compact water ice and red the porous ice grown at 100 and 11 K, respectively.

4. Future Work

We have briefly shown, in these proceedings, the power of MIMICK and early results from initial experiments. The capabilities of MIMICK go far beyond TPD experiments, and results will be published shortly, as mentioned earlier, on experiments investigating the growth of ices under different deposition conditions (e.g. angle, temperature) and with incorporating a relaxation process. Clements *et al.* (in prep) The aforementioned TPD experiments will be optimized for use in quantitatively constraining the pair-wise interactions, rather than only qualitatively, as expressed here. As well, these experiments will be used to quantitatively characterize the diffusion of CO into and from H_2O. Furthermore, long-term goals include incorporating water ice formation reactions on the surface via depositing hydrogen and oxygen atoms, rather than direct deposition of water molecules, and running models with astronomical, rather than laboratory, deposition conditions to explore the formation of ices in the ISM. The strength of MIMICK lies in its vast number of utilities and applications, and we aim to make use of as many of them as possible.

5. Summary

We have introduced MIMICK as a tool to extend our understanding of surface processes within laboratory ice experiments. With the ability to control deposition parameters and resulting ice densities, observations and descriptions of how molecules percolate through ASW pores is possible, as shown in the case of CO in these proceedings. Noting the results

that MIMICK produces, e.g. ASW porosity decreases during a warm-up process; pair-wise interaction energies are porosity dependent; and controlling for deposition parameters alters the resulting ice density, we have shown the model is able to successfully simulate laboratory ice experiments and can be used as a tool to study ice experiments. We then discussed the vast utility of MIMICK in a variety of applications.

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