Surface Astrochemistry

Paving the way to biomolecule formation

In this exercise we will be making use of the concepts introduced during the lecture to understand which molecules can be formed on the surfaces of icy dust grains.

In the very early stages of dense molecular clouds, not only H and H_2 adsorb, but also atoms such as C, N, and O freeze-out on the surface of cold dust grains. That leads to an icy mantle surrounding the dust grain composed of, mainly, H_2O mixed with, e.g., CH_4 (methane) and NH_3 (ammonia), see panel 1 in Fig. 1. As the density increases, eventually heavier species will also adsorb, and carbon monoxide (CO) does so during a 'catastrophic freeze-out', leading to the formation of a CO-rich, or apolar, layer on the icy mantle, see panel 2 in Fig. 1.

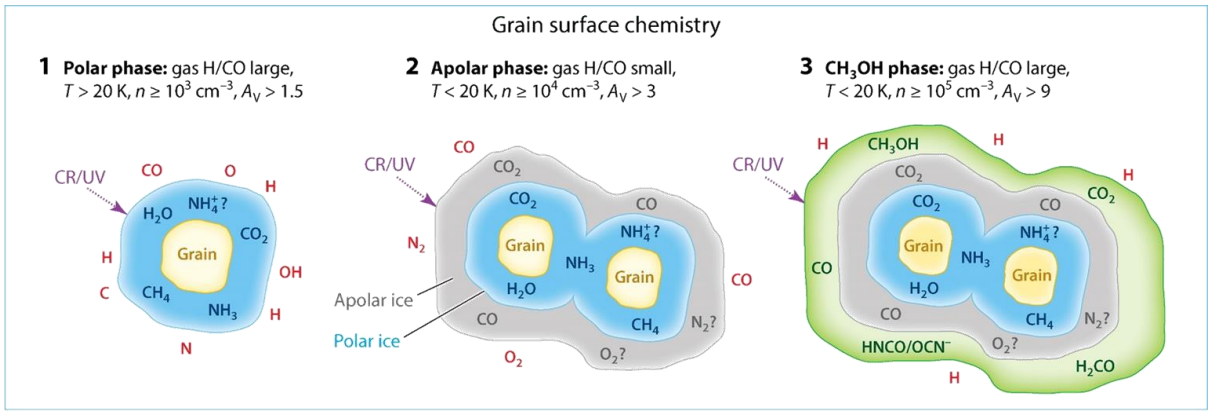

Figure 1. Boogert et al. Ann. Rev. Astron. Astrophys. 53 (2015)

Consider the formula describing the adsorption process:

$$f_{acc,X} = S_X v_X n_{grain} \pi r^2 n_g(X) \quad \text{with} \quad v_X = \sqrt{\frac{8 k_B T_{gas}}{\pi m_X}}$$

A. For the sticking coefficient S_X, what difference do you expect when you compare H and CO? Which kind of computational chemical tools can be used to calculate the sticking coefficient of a given atom X on an ice surface Y?

B. Explain why v_X and $n_g(X)$ together determine when this catastrophic CO freeze-out takes place.

The process opposing adsorption is desorption, where a species originally adsorbed on the surface is returned to the gas phase. The desorption rate essentially determines the residence time of a species on the surface. The simplest expression for the desorption rate constant is:

$k_{des,X} = \nu_{trial} \exp\left(-\frac{E_{bind,X}}{T}\right)$ and $\nu_{trial} = \sqrt{\frac{2N_S E_{bind,X}}{\pi^2 m_X}}$ in s^{-1}.

C. With a binding energy of 600 K for CO and 200 K for H atoms. The site density can be taken as 1E15 cm^{-2}. What is the residence timescale for both species at 10 K? And what about 20 K?

As indicated in the lecture, we will try to understand how the simplest sugar, glycoaldehyde can be formed via surface hydrogenation of CO, which itself has a triple bond between the C and O atoms.

D. The first hydrogenation step, i.e., the reaction H· + CO, leads to the HCO radical. Draw the Lewis structure of the radical. Where do you think the unpaired electron is centred?

E. When another hydrogen atom approaches this HCO radical, which kind of reaction do you expect (radical-radical or radical-neutral) and which molecule is formed?

Interstellar complex organic molecules (COM) are defined as species with 6 atoms or more, composed ideally of multiple heavy atoms.

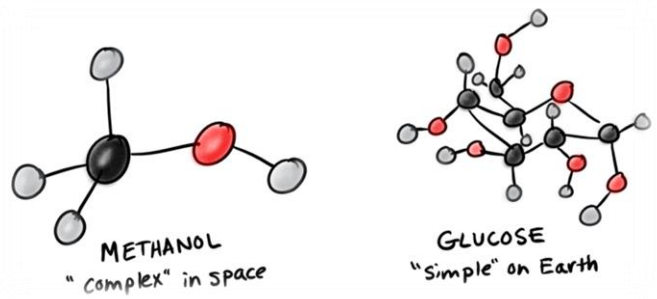

Figure 2. Courtesy of Olivia Wilkins

F. If two HCO radicals meet, a reaction is possible that leads to the formation of a COM. (i) Which reaction is that, (ii) is it barrierless or not, (iii) which molecule is formed, (iv) google it's name.

G. How could one perform a computational simulation to treat this reaction?

H. Now, instead of having two HCO radicals that can freely rotate, let's assume that these species are bound to a water ice, see Fig. 3.

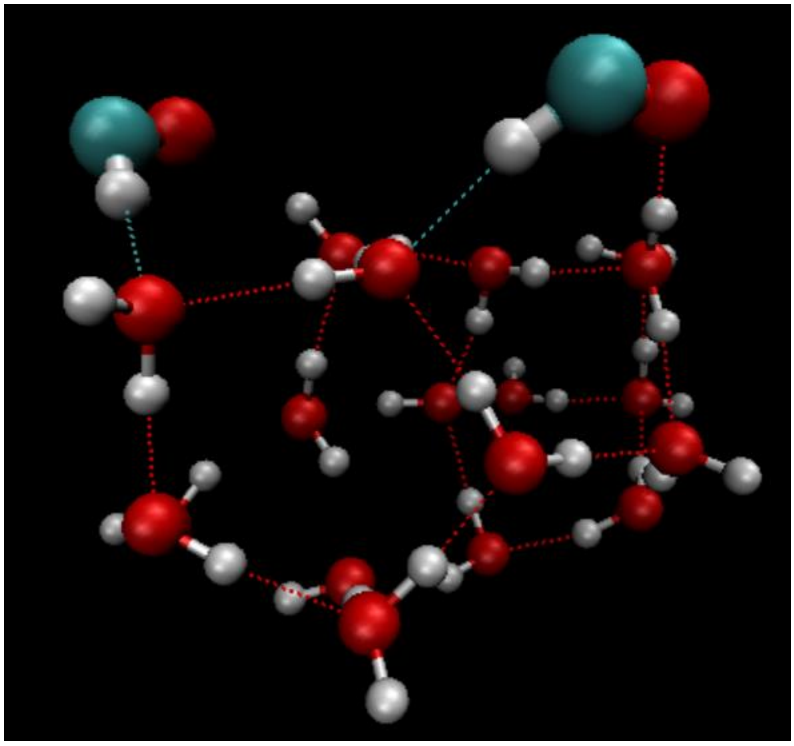

Figure 3. HCO radicals adsorbed on a water ice.

How do you expect this influences the possibility for the two radicals to react and do you think the energetics of the reaction would change?

I. The molecule you have just 'created' is a COM, but it is not a sugar (yet). Which atoms need to be added in order to create glycoaldehyde? Do you expect the first step in that reaction pathway to be barrierless or an over the barrier? Check if your answer is correct in the following paper: https://doi.org/10.1093/mnras/sty1478

J. In recent literature there is an ongoing debate as to whether COMs are formed on the surface of icy mantles, in the gas phase or via combination of both. Assuming that grain-surface reactions play a role in the formation of glycoaldehyde, and taking a rough binding energy of 3500 K, which kind of desorption mechanism do you think could be at play in cold regions?

K. Assuming that excitation leads to desorption, how would one be able to computationally treat that at a microscopic level?