

Methane and ethane adsorption and nucleation on tholins

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Abstract

The nucleation properties of methane and ethane on tholins depends upon few specific key parameters which are generally poorly defined ; the wetting parameters m (equal to the cosine of the contact angle made by the embryo on the substrate) and the desorption energy of the condensing species on the substrate, ΔF_{des} . Often, wetting parameter are found in the range [0.9-1.0] to promote cloud formation. The desorption energies are taken from experimental results on substrates approximatively similar to carbon or organic material, sometimes taken from other cases (like water on mineral substrates applied to condensation of hydrocarbons on photochemical aerosols) when not simply ignored. In this work, we used the results of an experiment dedicated to characterize the adsorption isotherm prior to nucleation and the nucleation/condensation saturation threshold of methane and ethane on tholins, an analogous of Titan aerosols.

1. Principle of the work

We used the experimental results of Curtis et al., (2008). For this experiment, the size distribution of the tholin grains and the total volume is fully characterized. Then, the experiment consists in increasing the saturation level from $S=0$ to the critical saturation S_c of methane or ethane beyond which nucleation and condensation starts. The results that we are going to use are the adsorption isotherms of methane (at 45 K) and ethane (75 K) prior to nucleation and the saturation threshold that trigger nucleation.

We used the Langmuir isotherm to reproduce methane adsorption and the Brunauer-Emmett-Teller (BET) isotherm for the ethane adsorption. The choice of the isotherm model is primarily defined by the type of the adsorption isotherm, following the IUPAC (Thommes et al., 2005) classification. For each isotherm, the main free parameter is the desorption energy ΔF_{des} of the

adsorbing molecules on the solid substrate. We also have to define other parameters like for instance the molecule jump frequency or the density of adsorption, which are better constrained.

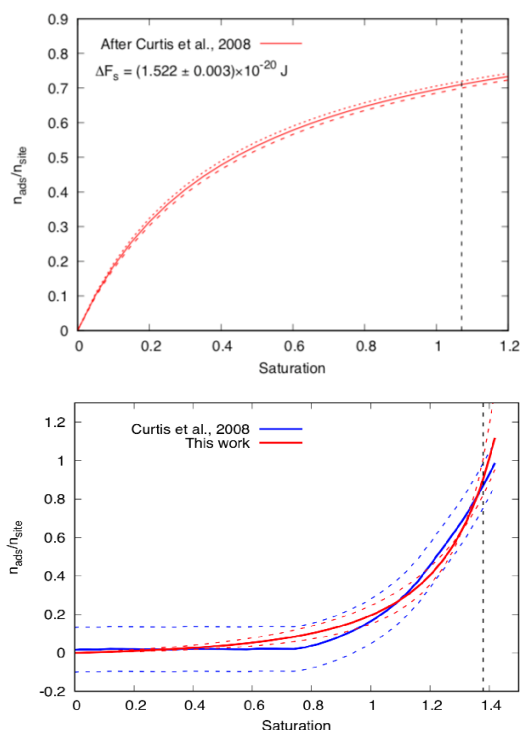


Figure 1: Langmuir isotherm (IUPAC type I) and BET isotherm (IUPAC type III) fitting the methane (top) and ethane (bottom) adsorption as a function of the saturation ratio

Once the desorption isotherm is understood and the corresponding parameters are defined for each molecules, we can study the condensation threshold. We used a microphysical model based on the classical equations of nucleation (Pruppacher and Klett, 1997). However, we used the relevant adsorption isotherm to calculate the nucleation rate, instead of the simpler rule used in the classical laws. We simulate as closely as possible the Curtis et al.,

(2008). We reproduce, with a time resolved model, the increase of the saturation and we compute at each time step the nucleation rate and condensation growing rate. Our model predicts the size of the condensation droplets which appear, then we can also compute the opacity of the methane layer that forms due to condensation and we are able to define an optical threshold for the transmission.

We use this model over the complete range of possible values for m (that is between -1 and +1) and for each values of m , we simulate the nucleation and the adsorption up to trigger the condensation. This allows to define, for each gas, the range of value for m which is consistent with the observed critical saturation.

2. Main results

We find that methane adsorption follows very well the Langmuir adsorption isotherm, as already noted by Curtis et al. (2008). We find that the desorption energy is $\Delta F_{des} = 1.5220 \pm 0.0715 \times 10^{-20}$ J if we include all the uncertainties and the wetting factor $m = 0.994 \pm 0.001$. Ethane adsorption, fitted with a BET isotherm, only allows to retrieve $\Delta F_{sub} - \Delta F_{des} = 2.723 \times 10^{-21}$ J where ΔF_{sub} is the ethane latent heat of sublimation. The interpretation of the ethane adsorption will be discussed because it is not straightforward, and it could be understood in at least two different ways. However, the value of m can be retrieved regardless the way to interpret the isotherm, and we find the value $m = 0.966 \pm 0.007$

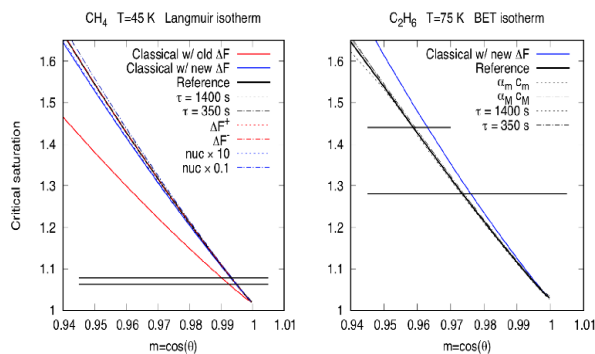


Figure 2: Critical threshold as a function of m for different parameters of the microphysical model for methane (left) and ethane (right). The horizontal layers indicate the experimental values of the actual critical observed in Curtis et al., 2008 experiment.

3. Consequences on microphysical models

The last part of this work will consist in investigating the consequences of our finding on microphysical models. First we show how and why the nucleation laws should be modified to account for a more detailed description of the adsorption isotherm. We also investigate the consequences on the actual case of Titan (and possibly on other planets with photochemical aerosols). We find that because m is close to 1, finally, the fine detail of the adsorption or nucleation have little impact provided that the desorption energy is well known. For cases with smaller values of m , (< 0.97) the type of isotherm used to calculate nucleation may matter.

We finally give suggestion of what could be done to go further. Indeed, we used experimental results done with one specific type of tholins, while we know that the composition of laboratory tholins varies with their formation condition. Their chemical composition can also evolve with time while they get older. This could have an impact on the physical parameters that govern adsorption and nucleation. Of course, such study should also be performed with other gases relevant to planetary atmospheres.

4. References

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