Distribution of CO binding energies on two types of polycrystalline water ice





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INTERNSHIP REPORT

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Understanding the reaction of molecules and their binding energies in different surfaces as well as different conditions of temperature and pressure in the Inter-Stellar medium. During the research in astrochemical environment we were able to have a better concept of astrophysics and astrochemistry regarding various chemical compounds in the Inter-Stellar Medium with the help of quantum chemistry and various computational tools such as python, and the two multi beam apparatuses called VeNUS and FORMOLISM.

1 Introduction

In an attempt to understand the main mechanisms involved in the formation of primitive molecules in the solid phase, the laboratory is developing molecules in solid phase also developing advanced devices that allow to reproduce as well as which is possible in the extreme conditions in which these molecules would be formed. The realization of such experiments can thus be done thanks to can be done thanks to two experimental devices currently: FORMOLISM (FORmation of MOLecules in the InterStellar Medium) - developed since 2001 - , and VENUS (VErs de NoUvelles Synthèses) -developed since 2011

The interest of the experiments carried out in the laboratory being to simulate the conditions of the interstellar medium, we can do physiorption with VENUS, since the cryostat allows to scan a range of cold temperatures.

With FORMOLISM, it is possible to make chemisorption, because the temperatures can go up to 600 K. However, most of the time, the machine is not heated to this point to avoid any alteration of the graphite surface.

On the first week of my internship we did the study of the multi beam apparatus: VeNUS It is a multi-beam ultra-high vacuum apparatus is presented to us on the first day of our internship which is achieved to study surface reactions and reaction diffusion processes that leads to the formation of atoms containing more than 6 molecules (COMs) via non energetic processes and under the condition of Inter Stellar Medium (ISM). By thorough understanding we see a vacuum space created in our machine which thus makes it useful for the study of the molecules interaction in a non-polluted environment.

The objective of this apparatus is to contribute in future with the James Webb Space telescope which is the largest optical telescope in space, it is equipped with high-resolution and high-sensitivity instruments, allowing it to view objects too old, distant, or faint for the Hubble Space Telescope currently conducting infrared astronomy.

2 VeNUS DESIGN AND OVERVIEW

VENUS, a device developed since 2011, works to reproduce and analyze these conditions and the physico-chemical reactions taking place. The principle behind this apparatus is that when a beam of light is passed to an atom under the surveillance of infra-red and quadrupole mass spectrometer and under certain temperature and pressure (high /low) we can measure the binding energies of atoms/molecules on selected surfaces of astrophysical interest. However in order to see the phase change state especially of solids very very low temperatures and pressures were required, taking these conditions into account adapting ultra-high vacuum technology and the use of cryogenics this set up was constructed for the study of monolayers



Fig : Schematic Diagram of the apparatus



3 Theory

Phenomena of physisorption: It refers to the adsorption of molecules or atoms onto a solid surface through weak intermolecular forces. It is a reversible process influenced by temperature, pressure, surface area, and the nature of the adsorbate and adsorbent. A surface phenomenon in which molecules or atoms adhere to the surface of a solid material through weak van der Waals forces or electrostatic interactions. It is a type of adsorption that occurs at relatively low temperatures and is reversible.

Physisorption is different from chimisorption, which involves stronger chemical bonds formed between the adsorbate (the substance being adsorbed) and the adsorbent (the surface material). In physiorption, the adsorbate interacts with the surface through weaker forces, such as dipole-dipole interactions, or hydrogen bonding.

The process of physiorption is influenced by several factors, including temperature, pressure, surface area, and the nature of the adsorbate and adsorbent. At low temperatures and high pressures, the adsorption capacity tends to increase. Additionally, materials with larger surface areas generally exhibit higher physiorption capacities because they provide more sites for adsorption.

Phenomena of chimisorption: Chemisorption is a type of adsorption that involves the formation of chemical bonds between the adsorbate (gas or liquid) and the adsorbent (solid material). Unlike physiorption, which is based on weak van der Waals forces, chemisorption leads to the creation of a new chemical species on the surface of the adsorbent. Chemisorption is a crucial phenomenon here.

We also focus mainly on the *Phenomena of desorption* which refers to the release or removal of adsorbed or absorbed substances from a solid or liquid surface. It can occur through various mechanisms and is influenced by factors such as temperature, pressure, and surface properties.

Once an atom/molecule has been adsorbed on the cold sample of VENUS by Physisorption phenomenon, it can move on the cold surface, and react in solid phase with other atoms sent from the jets. Move on the cold surface, and react in solid phase with other atoms sent from the jets, the atoms are not in reality adsorbed completely randomly on the surface. They are in fact directed towards preferential sites where their adsorption energy is important, to stay there as long as possible. If other sites offer a better adsorption energy, the atoms can move to these sites. This mechanism is called diffusion, and can be done because of the thermal agitation of the atoms, the thermal agitation of the atoms, or by "tunneling" (a quantum effect). Because of this phenomenon, the chemical reactions on the cold surface can take place different ways In view of this phenomenon, chemical reactions on the cold surface can take place in three different ways, as explained below:

- According to the Langmuir-Hinshelwood (LH) mechanism: the atoms meet and bond chemically

chemically while they diffuse at the same time on the surface (both are mobile).

- According to the Eley-Rideal (ER) mechanism: an atom sent by the jets does not bind to the surface but directly to another atom previously adsorbed.

- According to the Harris-Kasemo (HA for Hot-Atom) mechanism: an atom diffuses on the surface and binds with another adsorbed atom (only one of the two atoms is mobile).

Principal of desorption and TPD(Temperature Programmed Desorption)

When the gas phase molecules have been adsorbed on the extremely cold surface of the interstellar dust grains, we see that they react chemically in the solid state before being interstellar dust grains, We have also seen that they react chemically in the solid state before "coming out", detaching themselves from the grains, to return to the gas phase.

In the laboratory, once a deposit of molecules is finished, we provoke this rise in temperature by adjusting the cryostat (generally to go from 10 K to 200 K). The molecules are thermally agitated, their adsorption energy decreases, leading to their detachment from the surface: we say that they are they are said to be desorbed. We say desorption rate is measured in terms of TPD Temperature Programmed Desorption.

This desorption process depends on many parameters, including the temperature T which evolves linearly as a function of time t from an initial temperature T. The equation (1) shows the relation between temperature and time:

$$T = T_0 + \beta t$$
 (Equation.1)

$$\beta = \frac{d}{d}$$

, the ramp (linear heating rate) which gives us our experiences is 12 K/minute (or With 0.2 K/s).

The number of molecules desorbed as a function of temperature (and by extension of time) is quantifiable and obeys the Arrhenius law, according to the equation (2) of Polanyi-Wigner

$$r(N, E_{ads}, T) = -\frac{dN}{dt} = AN^n e^{-E_{ads}/k_B T}$$
(Equation.2)

With r, the taux of desorption in molecules.cm $^{-2}$.s $^{-1}$,

Eads, the energy of desorption in J

N, the number of total molecules or atoms absorbed on the surface

n, the order of the desorption

A, the prefacteur en s⁻¹

T, the temperature of desorption in K

 k_b , la constante de Boltzmann valant = 1,38. 10⁻²³ J. K⁻¹

4 Several graphical analysis of H2O ice TPD (n=0)

In this internship, we analyzed the two types of polycrystalline water ices with the help of experimental model that was created. The experiments were performed in an ultrahigh vacuum~UHV! Chamber with a base pressure below 10⁻¹⁰ mbar. These experiments were done in 2012, which we will explore throughout the detail in the report.

After passing the water molecules with the interaction on the surface it forms clusters, and thus with the help of Lakeshore (controls temperature) and Opus (controls infrared) programs the graphical results were obtained. However we have here used a custom made program to obtain simulations and analysis of our graphs.

In its experimental aspect, ice is stable without measurable sublimation in an ultrahigh vacuum (UHV) at temperatures below 120 K. Under this condition, ice surfaces can be prepared and maintained in a vacuum without being contaminated by environmental gases and can be examined using UHVcompatible surface spectroscopic techniques. Such investigations can reveal detailed information about the structure and chemical composition of ice surfaces. In addition, when a reaction occurs on an ice

surface, it occurs very slowly and its speed can be substantially varied by controlling the temperature of the ice. This gives us the opportunity to observe the progress of the reaction in real time, and sometimes, to even halt the reaction at an intermediate stage and identify the intermediate species using spectroscopic methods. Efforts based on modern spectroscopic techniques, which has markedly advanced our understanding of the structure, dynamics, and reactions of ice surfaces.

The most abundant form of water in the interstellar medium is ASW (obtained at 110K). Before 140K it's always amorphous it is in the DISORDERED structure and after 140 K then the water is ORDERED structure like crystalline structure. There are also two different types of Polycrystalline ice found which are only found in some places .These three major ice morphologies are used to simulate the icy mantles covering the grains of dust in dark clouds:

<u>POROUS ASW</u>: this mimics a very disordered substrate with a high effective surface area because of the presence of cracks and pores having themselves an internal surface area. To produce porous ASW, water vapor is dosed, while the surface is held at a constant temperature between 10 K and 40 K, depending on the required degree of surface disorder

<u>NON POROUS ASW</u> : this mimics the compact ASW ice, which comprises the bulk of interstellar ice. To produce non-porous ASW, water is dosed, while the surface is held at a constant temperature of 110 K.

<u>CRYSTALLINE water ice</u>: this mimics the crystalline ice seen in some star-forming regions. To form crystalline water films, the surface is held at 120 K during the deposition, then flash heated at 50 K min⁻¹ to 140 K, and finally at 10 K min⁻¹ to 142.5 K. Complete crystallization of the ice film is checked through verification of the infrared water band profile between 3400 cm⁻¹ and 3100 cm⁻¹ and thus cooled down to 130 K.

TYPES OF ICES USED

In this study we compared the surface morphology of two types of polycrystalline ice (PCI).

<u>PCI1 (previously "cubic")</u>: polycrystalline ice sample grown by depositing water vapor on the cold surface kept at 110 K (formation of amorphous ice), then annealing to 165 K was performed to crystallize the sample. This is a typical procedure used to grow crystalline ice for astrophysical purposes.

<u>PCI2 (previously "hex")</u>: polycrystalline ice sample grown by depositing water vapor on the cold surface kept at 160 K (direct formation of crystalline ice, then annealing to 180 K was performed to induce a possible change in the ice crystalline structure.

Interpretation of the analysis we did together on H2O TPDs at 12 K/min:

-we could see the phase change is induced by heating amorphous ice to a higher temperature, which causes the rearrangement of molecules as viewed in the blue curve of the graph in **Fig.1**. We see a subtle decrease in the desorption rate of water ice (ln[M18]) corresponding to the phase change around (0.00625 K⁻¹ ~ 1/160K) from amorphous solid to crystalline ice, that is, PCI1 (blue solid curve).

- During the study of this dynamic process we could conclude that the more volatile the molecules are the more the low binding energy E_{ads} is (amorphous solid water). After heating we could view that the phase change into crystalline ice (with larger E_{ads}) slows down the desorption rate and that is when the crystalline ice was being formed. The following steeper trend confirms that the crystalline sample is less volatile and desorbs with a higher binding energy.



By calculating the ln of equation 2, the resulting linear curve has a slope that corresponds to the binding energy $-E_{ads}/k_B$ (expressed in K). Fig. 1 shows the TPD curves (in terms of ln[desorption rate] vs 1/T) of the water ices used in this work and the calculated adsorption energies. The blue trace represents the annealing phase of PCI1 showing the initial desorption of amorphous ice then the transition (change in slope) to crystalline ice; the black trace shows the annealing phase of PCI2; the red curve is just a control experiment done in the end to desorb the whole sample of PCI2.

5 Analysis of the graphs of ¹³CO desorption

The desorption of ¹³CO from the two types of polycrystalline ices described above has been studied by the TPD technique in the 15–55 K temperature range. The TPD spectra from PCI1 and PCI2 water ices films were compared. In fact, CO can be hopefully used to probe the differences between these two surface morphologies, as this molecule can somehow probe the defects in the ice surface prior to forming a multilayer. The simulation of the TPD experimental profiles provides the corresponding CO binding-energy distributions, which is how differences between the two ice surfaces can be proved.

We did the observation reading on different analysis that had been already done before. The analysis was done on CO adsorbed on water ice and by the study of several desorptions. According to the program By analyzing a set of different doses of CO on the surface we could see easily evaluate the dose corresponding to the 1st full monolayer (1 ML). We then only worked with number 1 ML CO doses which filled up the surface with time.





This Energy potential diagram shows how the surface may probably like and where the molecules fill up first. The first molecule will occupy the deepest site (largest E_{ads}) whereas the other molecules are obliged to occupy to the less deep site accordingly. We also come to know that the energy profile distribution is different from surface to surface and thus we calculate them on our further slides. The two figures below shows the rate of desorption energy of ¹³CO along time. According to the formula of Polanyi Wigner the desorption rate is:

$$r(N, E_{ads}, T) = -\frac{dN}{dt} = AN^n e^{-E_{ads}/k_BT}$$

Where n=1 for CO molecule

The several analysis of ¹³CO molecules done in order to know the formation of monolayer after each does of ¹³CO provided with the change of time. The TPD's (Temperature Programmed Desorption). Observed below are done from the program Origin with the data's provided by my tutor. The ¹³CO TPD graphs helps us in the analysis of presence of first monolayer (1ML=10¹⁵ molecules/cm²), that is corresponding to the dose that marks the halt of the leftward shift in TPD



profiles.



For a polycrystalline water ice grown at 160 K and annealed to 180K (PCI2) we can see that the first monolayer was formed after deposition of 2min 30 s (orange curve).



According to the logarithmic figure 4 shown above we can see the trend is linear on the onset of the second layer of ¹³CO molecules being filled up (multilayer limit, lowest E_{ads}). The second peak shows us that the second layer of molecules have started to form.

Similarly with another set of data's for the dose of ¹³CO passed on a second sample "cubic" (PCI1) of crystalline ice obtained by annealing amorphous solid water deposited at 110K.



Fig.5 and Fig.6 show us that the first monolayer of ¹³CO crystalline ice is found at 3 min and 15 seconds (cyan curve). Similarly we have the logarithmic graph below we do not see a linear trend as for ¹³CO on PCI2, because here the 2nd layer had just started to be filled even with a 4 minute deposition.



Focusing on the 1st monolayer CO doses for PCI1 and PCI2 I did multiple simulations as seen below are the results obtained with the help of a designed program.

Simulations of ¹³CO from PCI 1

 1^{st} Simulation for desorption energies done for 13 CO dose 2 min 30 sec on crystalline ice with linear heating time (rampe de chauffage) :12K/min; delta represents the energy interval in the energy profile distribution, so the simulated profile is built by adding N simple TPDs whose unique $E_{ads,i}$ are separated by 40K.



 2^{nd} Simulation for desorption energies done for 13 CO dose 2 min 30 sec on hexagonal ice with linear heating time (rampe de chauffage) :18.1K/mn



 3^{rd} Simulation for desorption energies done for ${}^{13}CO$ dose 2 min 30 sec on hexagonal ice with linear heating time (rampe de chauffage) :6K/mn



In comparison to the graphs we can see that the heating ramp is different for the same dose of CO at this time we can say that for different heating ramps like for 18 K/mn and 6 K/mn they give us independent measurements of the binding energy distribution for 1 monolayer. In the same way the molecules desorbed away with different rates however the binding energy of adsorption sites being unchanged the energy distribution would remain the same as well as the energy distribution profile. However the Energy absorption (E_{ads}) is not unique for different sites.

Simulations of ¹³CO from PCI 2

1st Simulation for desorption energies done for ¹³CO dose 2 min 30 sec on PCI2 with linear heating time (rampe de chauffage): 12K/mn;



 2^{nd} Simulation for desorption energies done for 13 CO dose 2 min 30 sec on PCI2 with linear heating time (rampe de chauffage):18.1K/mn











In comparison between these three simulations on PCI2, we can see that the heating ramp is different for the same dose of ¹³CO at this time we can say that for different heating ramps like for 18 K/mn and 6 K/mn they give us independent measurements for 1 monolayer energy distribution. Here the molecules desorbed away more slowly or faster, however the energy distribution would remain the same and thus the energy distribution profile is the same.

6 Summarizing the energy Distribution Results

Table 1 summarizes the ¹³CO energy distributions obtained on PCI1 and PCI2. The energy range for PCI1 is between 780 K and 1620 K, while it goes from 780 K to 1700 K (1780 K for the 6 K/min TPD) on PCI2, which can be explained by 2 hypotheses :

- 1) The surface of PCI2 possesses higher energy absorption sites, or
- 2) The high temperature ice formation method induces defects in the crystal corresponding to tighter bound molecules.

In addition, we can see that the energy of the sites corresponding to the highest population of CO molecules is also different, that is 1260-1300 K for PCI1 and 1220 K for PCI2, which suggests that the two types of polycrystalline water ice have real differences at their surface.

E _{Ads}	Ramp	PCI1	PCI2
	6 K/min	820 K	780 K
Emin (multilayer limit)	12 K/min	820 K	780 K
	18 K/min	780 K	780 K
	6 K/min	1620 K	1780 K
Emax (defects)	12 K/min	1620 K	1700 K
	18 K/min	1620 K	1700 K
	6 K/min	1260 K	1220 K
Emost populated	12 K/min	1300 K	1220 K
	18 K/min	1260 K	1220 K

Table 1: Comparison between CO energy distributions obtained on PCI1 and PCI2.

7 Conclusion

Understanding the different reactions possible under the extreme conditions is a fundamental scientific aspect widely studied at LERMA-Cergy. The potential benefit from it would be to understand the formation of molecules (which is translucent clouds and mix of dust particles) in the outer space.

During the different analysis of CO binding energies on the water ice surface we could detect efficiently the formation of first monolayer and sometimes second layer as well. We could also conclude that for different water ice surfaces porous, non-porous or crystalline shows us distinguished results. Two other studies that I was able to observe from the PhD students showing us the result of binding energies of ethyl amine and ethanol on water ice surfaces. The result showed ethyl amine having very close desorption rate with water relative to quadruplet mass spectrum in the phase form of crystalline ice. However, with different molecules being passed on the water surface we could see different desorption rate.

The main role of CO for being passed here was to probe the surface in our case the water surface. Based on the experimental concepts in order to have a better understanding of formulated hypothetical concepts we could do several analysis. Thus, after the various analytical techniques I could have a better view of the occurring's in the interstellar medium.

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