Physics and chemistry at the surface of interstellar dust grains: the influence of O-atom diffusion and chemical desorption on a H-N-C-O reaction network.

A DISSERTATION PRESENTED
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“Now, under this game-scenario, how might we wish to see the drawings as functioning, here?”
He settled back down with Lenore’s help, looked at her.
“The sliding-man drawing, under this scenario, might say, hey, ho, watch how you go.
Perceive how you we-perceive Lenore’s being … ’missing’. Don’t just look at it; think about how to look at it.
Maybe it...means the opposite of what you think it does, of the way it...looks.”

“The Broom of the System”
David Foster Wallace

“[..] la connaissance du tout et de ses lois, de l’ensemble et de sa structure, ne saurait être débâtie de la connaissance séparée des parties qui le composent : cela veut dire qu’on peut regarder une pièce d’un puzzle pendant trois jours et croire tout savoir de sa configuration et de sa couleur sans avoir le moins du monde avancé : seule compte la possibilité de relier cette pièce à d’autres pièces […], considérée isolément une pièce d’un puzzle ne veut rien dire ; […] mais à peine a-t-on réussi, au terme de plusieurs minutes d’essais et d’erreurs, ou en une demi-seconde prodigieusement inspirée, à la connecter à l’une de ses voisines, que la pièce disparait, cesse d’exister en tant que pièce.”

“La vie mode d’emploi”
Georges Perec
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The baryonic matter of our Galaxy, in common with that of all other galaxies in the Universe, is in perpetual evolution. Analogous to the cycle of life on Earth, the birth and death of stars continuously cycles matter. In each new cycle, heavy elements are created in the interior of a star and, upon its death, these elements are expelled into the InterStellar Medium (ISM) (Figure 1). Spectroscopic and photometric observations show that ISM consists of gas and elongated tiny dust grains. Such a medium is not uniformly distributed in our galaxy but condenses in clouds that settle on the galactic plane. To date, plenty of molecules (> 170) are known to exist in the ISM. The presence and the abundance of most of them can be understood in terms of gas phase reactions but some key species (like molecular hydrogen, the most abundant and important species in the Universe, water and some carbon bearing molecules) are not formed efficiently enough and need the intervention of dust grains, that play the role of catalysts. In fact, although it is in warm regions that the large majority of molecules are seen, these species are not necessarily formed there, at that evolutionary
stage. The synthesis of interstellar molecules is a long and complex process that starts when
(and where) the UV photons emitted by galactic stars are shielded by H atoms, in so-called
molecular clouds; and chemical complexity increases throughout the star formation process.

The various steps involved in interstellar molecule synthesis can be summed up as follows:

1. Cold gas phase reactions: Neutral - ion chemical reactions at low temperatures (< 20
K) in the gas phase form a plethora of molecules at relatively low abundances (< 10^{-7}
with respect to H nuclei), with the exception of CO. This occurs especially in molecular
clouds. Note that the synthesised species can be observed via their rotational lines.

2. Species adsorption: H, O and C atoms not bound in CO, as well as molecules formed
in the gas phase stick onto interstellar grains and are adsorbed. The colder and denser
the region, the more efficient the process is. The density plays a role because the
probability of the atom/molecule encountering interstellar grains increases with density.
The temperature is important because, depending on the atom/molecule, it regulates
the residence time of the species, i.e. whether it sticks for a long time or just bounces
back rapidly into the gas. A key temperature is that at which CO freezes-out, around
23 K. Freeze-out occurs mostly during the, so-called, prestellar core phase, just before
the collapse of the cloud, in the very cold (≤ 10 K) and dense (> 10^5 cm^{-3}) zone. Similar
conditions are also found in a large fraction of protoplanetary disks, where planets are
eventually formed.

3. Grain surface chemistry: Once on the grain, H atoms diffuse on the surface and react
with other frozen species to eventually form new molecules. The most notable example
is H_2, which is formed on the grain surface due to the fact that gas phase H_2 formation
is extremely slow and, hence, inefficient. Additionally, other polyatomic molecules are
formed, notably H_2O, CO_2, H_2CO and CH_3OH, whose key role in astrochemistry will
be discussed later. Grain surface chemistry is particularly important in the prestellar
core and protoplanetary disk phases. Most of the species synthesised on grain surfaces
remain frozen in the, so-called, ice mantles and are only detectable via IR absorption
bands in those serendipitous cases where an IR bright source is located behind the cloud
or core. It is possible, but not yet proven, that even more complex species are formed
during warming up of the grain mantles.

4. Species desorption: When and where the temperature of the dust exceeds the subli-
mation temperature of the frozen species, the molecules in the icy grain mantles are
injected into the gas, where they once again become observable via their rotational lines.
In principle, different molecular species desorb at different temperatures; furthermore,
the desorption temperature varies in mixed ices. A key desorption temperature is that
of water, the major component of the grain mantles, at about 100 K. In the formation
route to low mass protostars, the regions where water ice sublimation occurs are called
hot corinos.

5. Hot chemistry: Once in the gas phase, the grain mantle components undergo fast
neutral-neutral reactions, increasing the chemical complexity of the gas. Molecules are
observable via their rotational lines. Regions where hot chemistry plays a dominant
role are hot corinos and the warm zones of protoplanetary disks.

Molecules can be simple diatomics or polyatomics, depending on the environment and evolu-
tion of the material. Even in the densest regions of the ISM, the gas shows an unsuspected
chemical complexity in such harsh environments characterized by extremely low densities and
temperatures. In summary, the chemical transformation of matter during the star formation
process passes through “bright” periods where gas phase molecules can be directly observed
via their rotational lines, and “dark” periods where, except for the most abundant molecules
(observable via IR absorption spectra of background stars), molecules are “hidden” in the
solid phase. Unfortunately, the birth-place of the molecular complexity is partially hidden
and locked in the solid phase. For this reason, freezing and synthesis of complex molecules
on micron-sized cold dust particles remain ambiguous. Pagani et al. (2012) have shown that
CO and N_2 species present very different depletion behaviors, in spite of their similar sticking
probability and desorption efficiency (Bisschop et al. 2006). Bacmann et al. (2012) have observed unexpected "high" gas-phase abundances of large molecules like CH$_3$OCH$_3$ in very cold environments (i.e. pre-stellar cores): such molecules should remain trapped on the solid phase. In other words the solid and gas phase equilibrium is still an open problem and a key point for observations. It could explain origins of solid condensates found in comets and meteorites.

The study of all these processes (species reactivity and diffusion, gas-solid equilibrium) is the challenge of Molecular Astrophysics. Due to its intrinsic difficulties, until fifteen years ago this field of Molecular Astrophysics (often called “Astrochemistry”, see i.e. Caselli & Ceccarelli (2012)) had been tackled only from a theoretical and observational point of view and only from the second half of the nineties laboratory simulations of the interaction gas-solid have been performed in the conditions and for the surfaces that are encountered in interstellar clouds. Surface reactions on grains constitute today the frontier of astrochemistry, being the youngest and the still less studied field.

In this thesis I will report different results of a laboratory investigation I performed with some colleagues mostly at the LERMA-lab in the University of Cergy-Pontoise. The experimental set-up housed in this laboratory is called FORMOLISM, i.e. FORMation of MOLECules in the ISM. The purpose of FORMOLISM is to investigate the formation of molecules of Astrophysics interest, as the name of instrument suggests, and to study the interaction of atoms and molecules and the chemical reactions among them on surfaces that simulate those of dust grains under interstellar conditions.

This thesis is organized as follows:

Chapter 1 This chapter presents some theoretical elements of surface physics and surface chemistry. It focus on different mechanisms of catalysis and on the phases that lead to molecules formation on surface: accretion, diffusion, reaction and ejection.

Chapter 2 A quite detailed description of the different parts that form the set-up FORMOLISM (the laboratory equipment in Cergy-Pontoise University) is given in this chapter. Furthermore this chapter describes the experimental methods used to carry out the experiments: TPD (Temperature Programmed Desorption) and DED (During-Exposure Desorption) techniques, methods of flux calibration of each experimental beam and the different methods of water ice growing.

Chapter 3 This chapter carefully presents the rate equation model used to simulate and fit our experimental results. Moreover it explains how model results are linked to physical-chemical quantities.

Chapter 4 The experiments discussed in this chapter study different physical processes occurring on different surfaces. In particular, this chapter focuses on O-atom diffusion, on binding energy of several molecules and atoms, and on chemical desorption process.

Chapter 5 This chapter deals with experiments about molecular synthesis on cold surface: from water to nitrogen dioxide, from carbon dioxide to methanol.

Conclusion This last chapter presents possible applications to astrophysics of our experimental findings. Moreover some of personal perspectives are briefly described.
Theoretical background

You have doctors for everything, even the inside of your mind. 
You don’t really mean that we got to be frightened all the time of nothing? 
Life, said Piggy expansively, is scientific, that’s what it is. 
In a year or two when the war’s over they’ll be traveling to Mars and back. 
I know there isn’t no beast – not with claws and all that. I mean – but I know there isn’t no fear, either.

“Lord of the Flies”
William Golding

We live, I regret to say, in an age of surfaces

“The Importance of Being Earnest”
Oscar Wilde

This thesis is mostly centered around two fields of interest: surface science and its application to Astrophysics, or better Astrochemistry. In this chapter we will present some theoretical elements necessary to understand the results presented in the three last chapter. The chapter is subdivided as follows:

1. Surface Physics
   1.1. From the bulk to the surface
   1.2. Adsorption (and sticking)
   1.3. Desorption
   1.4. Surface migration

2. Gas Phase Chemistry
   2.1. Chemistry in gas phase
   2.2. Exothermicity of reactions

3. Surface Chemistry
   3.1. Eley-Rideal mechanism
   3.2. Langmuir-Hinshelwood mechanism
   3.3. Hot-Atom mechanism
1.1 Surface Physics

1.1.1 Sub-monolayer and multilayer: surface and bulk

Surface physics can be defined as the study of the structure and dynamics of atoms (and their associated electron clouds) in the vicinity of an interface, usually at the boundary between a solid and a low-density gas. There are three main processes concerning solid-gas interfaces and surface physics: adsorption, leading particles from gas to solid phase; surface diffusion; and desorption, leading particles from solid to gas phase. These three processes depend on different parameters: the mass, the polarization, and the energy of the particles, as well as the physical-chemical properties of the surface, i.e. its chemical structure and its temperature. These parameters govern how the energy can be shared (or transferred) from a phase to another, and as consequence they rule the solid-phase interaction. Generally speaking, a monolayer is defined as a layer of material that is one molecule thick. The dynamics and the reactivity of atoms can be studied in two different regimes: sub-monolayer and multilayer. The regime transition is accompanied by a switch on the physics of the system (Hörnström et al. 1958; Evans et al. 2007). Actually surface atoms do not experience the same potential as bulk atoms: binding energies change (i.e. Cuppen & Herbst 2007), diffusion properties vary (i.e. Benderski&Wight 1996; Minissale et al. 2013; Lee et al. 2014), reactivity is modified (i.e. Dulieu et al. 2010; Miyachi et al. 2008). In other words, the physical-chemical description is quite different in the two regimes. The experiments described in this thesis were performed in a sub-monolayer regime. For this reason, we will describe only surface processes linked to sub-monolayer regimes.

1.1.2 Adsorption

1.1.2.1 Physisorption and chemisorption

The initial step for any surface process is the collision of gas phase species at the surface. The collision depends on the potential interaction between the approaching atom and the surface. The collision of impinging atoms with a surface can lead to two different kinds of bonding as shown in Figure 1.1

- Physisorption (physical adsorption) in which the forces involved are intermolecular forces; it is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption. The potential describing physisorption is a combination of an attractive and a repulsive part. The attractive potential is due to van der Waals forces. The energy of the induced dipole $p_{ind}$ in the electric field of the original atom is negative (attractive interaction) and proportional to $r^{-6}$. Consequently, atoms attract each other even in the absence of chemical bonding. At smaller distances, Pauli-repulsion between closed shells eventually balances the attractive van-der-Waals interaction. Pauli-repulsion is proportional to the overlap of wave functions and increases therefore exponentially with decreasing distance. For convenience, the exponential dependence is traditionally replaced by an $r^{-12}$-dependence in analytical calculations. The resulting potential is the Lennard-Jones potential

$$U(r) = D_\epsilon \left[ \sigma \left( \frac{\sigma}{r} \right)^{12} - \sigma \left( \frac{\sigma}{r} \right)^{6} \right]$$  \hspace{1cm} (1.1)

where $D_\epsilon$ defines the strength of the potential and $\sigma$ is its range. Typical binding energy of physisorption is about $10-400$ meV ($100-5000$ K/$k_B$).

- Chemisorption (chemical adsorption) in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds. New chem-
ical bonds are generated at the adsorbant surface. The potential describing chemisorption is described through a Morse potential

\[ U(r) = D_\epsilon [1 - e^{-\alpha(r-r_e)}] \] (1.2)

where \( D_\epsilon \) defines the strength of the potential, \( \sigma \) is its range, and \( r_e \) the equilibrium distance. Chemisorption usually forms bonds with energy of 1-10 eV. Chemisorption can occur only if: (1) the surface contain chemically active sites; (2) the impinging species are not saturated molecules (i.e., \( \text{H}_2 \), \( \text{O}_2 \), or \( \text{CO}_2 \)); (3) impinging species are able to overcome activation barriers for reaction. Except for some particular cases, these three conditions were not present simultaneously in our experiments, and as consequence we can neglect chemisorption in our studies.

![Diagram showing the interaction between an atom adsorbate and a surface as a function of the distance to the surface.](image)

**Figure 1.1:** The interaction between an atom adsorbate and a surface as a function of the distance to the surface. In this picture, it can be recognized weak physisorbed sites (Van der Waals interaction, \( E_{\text{phy}} \)) with well depths in the range 10-400 meV at a distance of a few angstroms and chemisorbed sites (covalent bond, \( E_{\text{chem}} \)) with a strength of \( \approx 1-10 \text{ eV} \) close to the surface. The physisorption potential has been assumed to be a Lennard-Jones potential, whereas chemisorption is described in this diagram by a Morse potential.

We remark that all the physical-chemical processes described in this thesis occur with physisorbed adparticles in non-metallic surfaces. Inversely, we stress that the most part of existing scientific work concerning surface physical-chemistry considers chemisorbed adparticles in metallic surfaces. Physisorbed and chemisorbed adparticles (on non-metallic and metallic surfaces, respectively) span two different energetic ranges. Roughly speaking, physisorption imply smaller energy for the gas and quicker energy transfer (leading from a gas-particle-surface system to a adparticle-surface system), and vice versa for chemisorption. As consequence some processes are facilitated under certain conditions rather than others.

### 1.1.2.2 Sticking

The probability that an atom remains on the grain surface upon collision with it is estimated by the sticking coefficient.
The sticking coefficient has been introduced by Langmuir at the beginning of the last century, and the theory of sticking has been developed by Kistlin in the mid-nineteenth century. Here we want to stress just a few key points concerning the sticking coefficient. The sticking coefficient could be considered a measure of how fast energy of gas phase atoms is transferred to the surface. Plenty of scientific works (experimental and theoretical) deal with parameters influencing sticking coefficients. The coefficient is a function of surface temperature, surface coverage and structural details as well as the kinetic energy and mass of the impinging particles. Wang & Gomer (1979) and Kneitz et al. (1999) (and references therein) show sticking coefficient changes as function of temperature of gas and surface; in particular the higher the temperature of gas and surface temperature, the smaller the sticking coefficient. We want to pinpoint here that the sticking coefficient shows a temperature (both of gas and of surface) dependence only in a big range of temperature (i.e., $\approx 600$ K from 30 to 650 K, Wang & Gomer 1979). This means that the sticking coefficient is constant in our experiments, since we work with a surface temperature variation of 50 K (form 10 to 60 K) and a gas temperature variation < 150 K. We can use the following simple law to evaluate the sticking coefficient

$$s \propto \frac{E_s}{E_s + E_k}$$

(1.3)

where $E_s$ is the “sticking energy” (determined by the physisorption binding energy $E_b$, see Krügel 2003) and $E_k$ is the energy of gas particles. If $E_s >> E_k \rightarrow s \approx 1$.

In our experiments, for an O$_2$ molecule, $E_s > E_b \approx 0.1$ eV and $E_k \approx 0.025$ eV so $s > 0.8$. Inversely, for an H$_2$ molecule, $E_s < 0.04$ eV and $E_k \approx 0.025$ eV so $s < 0.6$. In this evaluation we have not considered that the sticking coefficient increases as a function of mass ratio of gas-to-surface atom (it would increase $s$ for O$_2$ and decrease it for H$_2$). In summary, we realize that under our experimental conditions we have a sticking coefficient constant near to unity for all the species used (O$_2$, CO, N$_2$, H$_2$O and so on), except H$_2$ and D$_2$; this result has been already shown experimentally by Bisschop et al. (2006), Matar et al. (2008), and Chaabouni et al. (2012a).

1.1.3 Desorption

Once molecules are accommodated on the grain surface, they may remain almost indefinitely in that state. Due to thermal or non-thermal processes, the adsorbed species can acquire sufficient energy to overcome the activation barrier for desorption and return into the gas phase. Moreover we stress here that the energy acquired by adsorbed species can lead to other processes as: (1) decomposition of a molecular species to yield either gas phase products or other surface species; (2) diffusion of an adsorbate on the surface or into the bulk of the underlying solid. These two processes will be discussed in the following.

The way in which the adsorbed species acquires the energy produces essentially two types of desorption: thermal and non-thermal. The main difference between the two desorptions is the thermodynamic state. In the first case, the system is at any given time in thermal equilibrium and chemical equilibrium. More precisely the system changes linearly and continuously over the time, and it is in a metastable equilibrium. In the second case the system is in a non-equilibrium state and discontinuously undergoes a flush of matter and energy to and from other systems and/or to chemical reactions.

1.1.3.1 Thermal desorption

In the thermal desorption, we define the “residence time” as

$$\tau_{des} = \frac{1}{\nu_0} \exp\left(\frac{E_b}{k_b T_s}\right)$$

(1.4)

where $E_b$ is binding energy of the adsorbate and $T_s$ the surface temperature. It is, essentially, the characteristic time scale for a species to acquire sufficient energy, through thermal fluctuations, to desorb. $\tau_0 = 1/\nu_0$ corresponds to the period of vibration of the bond between
the adsorbed molecule and substrate. Thus $\nu_0$ is the vibrational frequency of the adsorbed species on the surface and it can be evaluated by this equation

$$\nu_0 = \sqrt{\frac{2n_s E_b}{\pi^2 m}}$$

(1.5)

where $n_s$ indicates the surface density of sites, $m$ is the mass of the adatom. For $\nu_0$, one may use the frequency of lattice vibration of the grain, typically a few times $10^{12} - 10^{13} s^{-1}$.

Thermal desorption is usually analyzed through the Polanyi-Wigner equation. The desorption rate is expressed by a rate law of $n$th order

$$r_{\text{des}} = -\frac{d\theta}{dt} = k_n \cdot \theta^n$$

(1.6)

where $n$ is the so-called “order” of the desorption and $\theta$ is the surface coverage. If the rate constant $k_n$ is described by an Arrhenius equation (see Eq. 1.17 in Sec. 1.2.1) then the rate law is usually referred to as the Polanyi-Wigner equation

$$r_{\text{des}} = -\frac{d\theta}{dt} = \nu_n \cdot \exp\left(\frac{-E_b}{k_b T}\right) \cdot \theta^n$$

(1.7)

The factor $\nu_n$ can also be considered to be the “attempt frequency” at overcoming the barrier to desorption. Thus the pre-exponential/frequency factor ($\nu_n$) may also be equated with the frequency of vibration of the bond between the molecule and substrate; this is because every time this bond is stretched during the course of a vibrational cycle can be considered an attempt to break the bond and hence an attempt to desorption (See Nix, 1997 for more details).

We postpone to subSec. 2.2.2.4 the discussion about experimental study of thermal desorption, and to Chapter 4 the evaluation of binding energies for different species.

1.1.3.2 Non-thermal desorption

Non-thermal desorption is the release in the gas phase of adsorbed species when the system is not at the thermodynamic equilibrium. Different types of non-thermal desorption can be considered. In the following we present a summary list.

1. **Photo desorption**: the absorption of a UV photon by a molecule condensed on a surface can result in its desorption (direct photo desorption) or in the kick-out of a nearby molecule (indirect photo desorption) (i.e. DeSimone et al. 2013; Bertin et al. 2013; Fillion et al. 2014; Yarnell/Yates 2013).

2. **Sputtering**: an atom is ejected from a solid target material (i.e. ice) due to bombardment of the target by energetic particles, i.e. ions or electrons (i.e. Behrisch 1981; Johnson et al. 2013; Cassidy et al. 2013). The condition to observe sputtering is that the kinetic energy of the energetic particles is much higher than conventional thermal energies ($\gg 1$ eV). Sputtering can lead to significant erosion of bombarded materials or ice.

3. **Chemical desorption**: the energy excess of an exothermic reaction is not dissipated on the surface and provokes the ejection of the newly formed species in the gas phase (Astarita&Savage 1980; Dulieu et al. 2013).

1.1.4 Surface migration: Thermal hopping and tunneling

Another important process for the description of surface physics is the migration of adsorbed atoms on the surface. Atoms and molecules physically adsorbed on a surface find themselves in a potential minimum, and they cannot travel freely along the surface. Nevertheless, depending on the surface temperature, adsorbed species could be mobile in their physically adsorbed (or even chemisorbed) precursor states. The motion of an adatom on a periodic and regular
Surface can be thought as a random site-to-site hopping process, namely a random-walk motion. The diffusing atom will have a mean square displacement in the time \( t \) given by

\[
\langle \Delta r^2 \rangle = \nu a^n t
\]

(1.8)

where \( \nu \) is the frequency of hops, \( a \) is the jump distance, and \( n \) is the number of dimensions. Clearly in the case of surface diffusion, \( n=2 \). It is possible to define the diffusion coefficient \( D \) as the ratio of the mean square displacement over time weighted on the number \( z \) of neighboring sites where the adatom can hop:

\[
D = \frac{\langle \Delta r^2 \rangle}{z t} = \nu a^n
\]

(1.9)

The adsorbed atom vibrates and thereby swaps its kinetic and potential energy with a characteristic frequency \( \nu_0 \). For two states separated by an energy difference \( E_{\text{diff}} \) (see Figure 1.2b), we can define the hopping frequency as

\[
\nu_{\text{hop}} = \nu_0 \exp\left(-\frac{E_{\text{diff}}}{k_B T}\right)
\]

(1.10)

where \( T \) is the surface temperature. Diffusion occurs when \( E_{\text{diff}} \approx k_B T \). \( E_{\text{diff}} \) is smaller than \( E_{\text{des}} \) (the desorption energy) and typically \( E_{\text{diff}}/E_{\text{des}} \) ranges between 0.05 and 0.5 (see Figure 1.2c). In general, the lower the desorption energy, the higher the mobility. Diffusion can take place under different conditions, depending on the level of adsorbate coverage at the surface.
surface or on the nature of the diffusion environment. Typically, four schemes are considered (Oum et al. 2003).

- **Tracer diffusion.** Individual adparticles motion. This condition is present at very low coverages where the interaction between adspecies is negligible. Tracer diffusion is a good approximation even for an ensemble of particle in which each adparticles can be considered to move independently of the others.

- **Chemical diffusion.** Ensemble adparticles motion. This condition is present at high coverages where interactions between adspecies become important. These interactions alter diffusion properties of individual adatoms and so surface diffusion coefficient may depend strongly on coverage (Ehrlich 1977).

- **Intrinsic diffusion.** It is the diffusion occurring on a uniform surface such as a single terrace, where no adatom traps or sources are present. Typically intrinsic diffusion can be measured in a small area compared to the inter-defect separation; in this case the activation barrier of a single terrace surface diffusion is measured (Gomer 1983).

- **Mass transfer diffusion.** It is the diffusion occurring on a irregular surface where adatom traps or sources are present. As in the case of chemical diffusion, these defects alter diffusion properties of individual adatoms. Inversely to intrinsic diffusion, mass transfer diffusion is measured over a distance that is large compared to the defect site size; in this case, the activation energy includes contributions due to transient binding to these sites.

Surface diffusion can occur through different mechanisms. These mechanisms influence different parameters as for example the temperature dependence and the kinetics of movement. Below, a list of the most important of these mechanisms.

1. **Hopping mechanism.** The adatoms reside on adsorption sites on the surface lattice (see Figure [1.3a]). Motion occurs through successive jumps to adjacent sites, the number of which depends on the nature of the surface lattice. It has been observed experimentally for many species on different surfaces, i.e. nitrogen on Fe(100) (Pedersen 2000).

2. **Tunneling mechanism.** The adatoms tunnel across diffusion barriers (see Figure [1.3a]). It can occur for low diffusing particle mass and low $E_{diff}$, and has been observed experimentally in the case of hydrogen diffusion on tungsten and copper surfaces (Laubon & Ho 2000; Manicò et al. 2001). Diffusion via tunneling mechanism presents a nearly temperature-independent behavior.

3. **Atom Exchange mechanism.** The adatom exchanges place with an adjacent atom within the surface lattice (see Figure [1.3b]). The surface atom becomes a new adatom (Oum et al. 2000; Antczak & Ehrlich 2007).

4. **Vacancy mechanism.** An atom jumps on a vacancy, so the vacancy will disappear in the place where it was, and appears in the place where the atom was. Another atom could jump on the newly formed vacancy, and another vacancy will originate, and so on the vacancy will move in random directions (see Figure [1.3c]). It is a predominant mechanism of surface diffusion at high coverage. This process is similar to the so called “sliding puzzle”. It has been observed experimentally by Ural et al. (1998) or through the Kirkendall effect (Aloke 2004).

Many experimental techniques exist to measure surface diffusion coefficients: some techniques are used to determine macroscopic mobility (distances of nm or more), others to study local diffusion (on the scale of nm). Both the different techniques used and the possibility that several surface diffusion mechanisms may be operative can influence the quantitative parameters describing the surface diffusion rate.

Here we focus our attention on two mechanisms: thermal hopping and tunneling. We can define, here, the hopping time $\tau_{hop}$ as the inverse of Eq. (1.10)

$$\tau_{hop} = \nu_0^{-1} \exp\left(\frac{E_{diff}}{k_B T_s}\right)$$

(1.11)
where $T_s$ is the surface temperature. It is evident from Eq. 1.11 that the hopping is dependent on temperature, and the higher the temperature, the smaller is $\tau_{\text{hop}}$. Naturally if the temperature becomes too high the atoms or molecules can also evaporate; in fact, when the temperature increases the ratio of $\tau_{\text{des}}$ to $\tau_{\text{hop}}$ quickly decreases to unity. In other words, the particle can hop many times at low temperature, while at high temperature the probabilities of hopping and evaporate have similar values. Similarly to Eq. 1.11, the tunneling time through a rectangular barrier with height $E_{\text{diff}}$ and width $a$, is equal to

$$
\tau_{\text{tun}} = \nu^{-1} \exp\left(\frac{2a}{\hbar (2ME_{\text{diff}})^{1/2}}\right),
$$

(1.12)

where $M$ is the mass of the adsorbate. Figure 1.4 shows a sketch of particles adsorbed with a zero point energy in a surface potential. They have to overcome (or pass through) a barrier of dimension $E_{\text{diff}}$ and $a$ to diffuse. Tunneling diffusion is a low-temperature phenomenon. It should be the dominant process below the crossover temperature $T_{\text{tn-th}}$. Above $T_{\text{tn-th}}$, surface diffusion follows thermally-activated Arrhenius behavior, namely the thermal hopping. Due to the term $(2ME_{\text{diff}})^{1/2}$ in Eq. 1.12 the larger the mass of the adsorbate, the smaller should be the probability of tunneling. This statement would suggest that, experimentally, observing H tunneling is easier with respect to the one of other molecules. In truth, the mass of the adsorbate affects the hopping diffusion too. This means that the crossover temperature $T_{\text{tn-th}}$ is placed at low temperatures, from which comes the difficulty to observe the tunneling behavior of diffusion. For the same reason a quantitative description of isotopic effect for the tunneling diffusion of atomic hydrogen is quite complicated. Some old works found diffusion slightly faster for heavy hydrogen isotopes, suggesting an anomalous inverse isotope effect (DiFoggio & Gomer 1982; Wang & Gomer 1985). More recent reports suggest that the isotope effect is negligible (Daniel & Gomer 1995; Wong et al. 1995). In any case, the theoretical issue remains unsettled, in part because of difficulties in describing phonon-adsorbate interactions (Auerbach et al. 1987; Lee et al. 1993).
1.1.4.1 An evaluation of the crossover temperature $T_{tn-th}$.

We use two different theoretical models to evaluate how the two processes (thermal hopping and tunneling) affect diffusion as a function of surface temperature. The first one has been proposed by Messiah (1961), and recently used by Cazaux&Tielens (2004) in the case of $H$ and $D$ diffusion. In this model, the transmission coefficient (TC) from site $i$ to site $j$ by tunneling is given by

$$T_{C_{tunn}} = 4 \sqrt{\frac{E - E_{diff}(ij)}{E}} \left[ 1 + \sqrt{\frac{E - E_{diff}(ij)}{E}} \right]^{2} +$$

$$+ \frac{E_{diff}(i) E_{diff}(j)}{(E_{diff}(i) - E) E} \left[ \sinh \left( a \sqrt{\frac{2m(E_{diff}(i) - E)}{\hbar^{2}}} \right) \right]^{-1}, \text{ if } E < E_{diff}(i)$$

where $E_{diff}(i)$ and $E_{diff}(j)$ are the energy of the two sites and

$$E_{diff}(i) - E_{diff}(j) = E_{diff}(ij),$$

is the energy of the barrier between two neighbour sites. Similarly the transmission coefficient from site $i$ to site $j$ by thermal diffusion is

$$T_{C_{thermal}} = 4 \sqrt{\frac{E - E_{diff}(ij)}{E}} \left[ 1 + \sqrt{\frac{E - E_{diff}(ij)}{E}} \right]^{2} +$$

$$- \frac{E_{diff}(i) E_{diff}(j)}{(E_{diff}(i) - E) E} \left[ \sin \left( a \sqrt{\frac{2m(E-E_{diff}(i))}{\hbar^{2}}} \right) \right]^{-1}, \text{ if } E < E_{diff}(i)$$

Figure 1.4: Scheme of surface potential in which two particles of different mass are trapped. Diffusion coefficients depend on the height $E_{diff}$ and width $a$ of the barrier, as well as on the mass of diffusing particles.
The transmission coefficients have to be integrated over the range of energies available to the adatom and multiplied by the frequency factor to have the diffusion coefficients. Once again, in these equations we see that there are three parameters affecting the diffusion coefficients: height $E_{diff}$ and width $a$ of the barrier, and the mass of diffusing particles. Figure 1.5 shows the influence of each parameters for the diffusion coefficients as function of surface temperature. The choice of parameters values is arbitrary for all the simulations shown in Figure 1.5, and it is not driven by any physical intuition. Each parameter has a different effect both on the absolute value of diffusion coefficients and in the crossover temperature $T_{tn-th}$. Panel $\alpha$ of Figure 1.5 shows the sum of tunneling and thermal diffusion coefficients as a function of surface temperature for three different values of mass particle (2, 10, and 20 amu). The height $E_{diff}$ is fixed at 380 K while the width is 2 Å. Here, the increase in the particle mass shifts the crossover temperature $T_{tn-th}$ to high temperature, and it has a drastic effect on the absolute value of diffusion coefficients along all the considered range of surface temperature. For example at 10 K, there is a difference of sixteen orders of magnitude between red and blue curves. Panel $\beta$ shows the sum of thermal hopping and tunneling diffusion coefficients as a function of surface temperature for four different values of $a$ (1, 2, 3, and 4 Å). The height $E_{diff}$ is fixed at 380 K while mass is 2 amu. Panel $\gamma$: sum of thermal hopping and tunneling diffusion coefficients as a function of surface temperature for three different values of mass particle (2, 10, and 20 amu). The height $E_{diff}$ is fixed at 380 K while the width is 2 Å.

**Figure 1.5:** Panel (a): sum of thermal hopping and tunneling diffusion coefficients as a function of surface temperature for three different values of $E_{diff}$ (100, 380, and 800 K). The width $a$ is fixed to 3 while mass is 2 amu. Panel (b): sum of thermal hopping and tunneling diffusion coefficients as function of surface temperature for four different values of $a$ (1, 2, 3, and 4 Å). The height $E_{diff}$ is fixed at 380 K while mass is 2 amu. Panel (c): sum of thermal hopping and tunneling diffusion coefficients as a function of surface temperature for three different values of mass particle (2, 10, and 20 amu). The height $E_{diff}$ is fixed at 380 K while the width is 2 Å.

as a function of surface temperature for three different values of $E_{diff}$ (100, 380, and 800 K). The width $a$ is fixed to 3 while the mass is 2 a.m.u. (atomic mass unit). The increase in height $E_{diff}$ shifts the crossover temperature $T_{tn-th}$ to a higher temperature, and it has a drastic effect on the absolute value of diffusion coefficients along all the considered range of surface temperature. For example at 10 K, there is a difference of sixteen orders of magnitude between red and blue curves. Panel $\beta$ shows the sum of thermal hopping and tunneling diffusion coefficients as a function of surface temperature for four different values of $a$ (1, 2, 3, and 4 Å). The height $E_{diff}$ is fixed at 380 K while the mass is 2 amu. Here, the width $a$ has a big influence only at low temperature. On the contrary, the crossover temperature $T_{tn-th}$ is shifted brutally to high temperature as the width decreases. Finally panel $\gamma$ shows the sum of thermal hopping and tunneling diffusion coefficients as a function of surface temperature for three different values of mass particle (2, 10, and 20 amu). The height $E_{diff}$ is fixed at 380 K while the width is 2 Å. Here the increase in the particle mass shifts the crossover temperature $T_{tn-th}$ to low temperature and in general it should hinder diffusion (both by hopping or by tunneling). A practical application of this model is shown in Chapter 4 where the diffusion of oxygen atoms is treated.

The evaluation of the crossover temperature $T_{tn-th}$ can be performed using another model. Mott (1969), Poljak (1972) and Mott & Davis (1979) show that the temperature dependence of tunneling can be expressed as follows

$$
\tau_{\text{tun}} = \nu_0^{-1} \exp \left( \frac{2a}{\hbar} \sqrt{2mE_{diff}} \right) \exp \left( \frac{E_1 - E_2}{3k_bT} \right)
$$

(1.16)

$^2$We express energy in K rather than eV by using the relation $eV = k_B T$ where $k_B$ is the Boltzmann constant.
where $E_1$ and $E_2$ are the energy of two different adsorption sites. By inverting Eq. 1.11 and Eq. 1.16 we can move from the diffusion time to the diffusion coefficients and compare thermal hopping and tunneling terms. We obtain results similar to the Messiah's model. Panel $\alpha$ of Figure 1.6 shows the comparison of thermal hopping and tunneling terms for the two models. For both models the height $E_{\text{diff}}$ of the barrier is 380 K, the width $a$ is to 3 Å and the particle mass is 2 amu. Thermal hopping diffusion terms present a similar behavior for both the models, while an important difference is present in relation to tunneling terms, especially at high temperature. In any case, this does not affect the total diffusion coefficients since at high temperature thermal hopping is dominant. The total diffusion coefficients of the two models differ at maximum by a factor eight (at low temperature) and the crossover temperature $T_{\text{tn-th}}$ arrives almost at the same time: 11 K for Mott model and 12 K for Messiah model. In conclusion, we can remark that tunneling should have a temperature

dependence and in particular it becomes more probable with temperature increase. The evaluation of the crossover temperature $T_{\text{tn-th}}$ and therefore of the ratio between thermal hopping and tunneling is not trivial, since it depends on three parameters ($E_{\text{diff}}$, $a$ and mass of particle) and also on the model used. Moreover a further complication comes from the percolation theory according to which only a small fraction of sites are accessible. This last concept will be treated in detail in Sec. 4.1.3

1.2 Gas Phase Chemistry

In this section we will present a smattering of chemical notions used both in gas phase chemistry and surface chemistry.

1.2.1 Chemistry in the gas phase

A chemical reaction is a process that leads to the transformation of one set of chemical substances to another. The rates of most reactions in gas phase are temperature sensitive, and an understanding of the molecular basis of this dependence is an essential goal in theoretical investigations of the kinetics. In 1889, Svante Arrhenius defined the activation energy as the minimum energy that has to be input to a chemical system with potential reactants to cause a chemical reaction. Experimentally, it has been found that the rate constant $k$ of reactions is related to the temperature according to the following

$$k = A \exp \left( -\frac{E_a}{k_b T} \right)$$

(1.17)
which is called the Arrhenius equation, where $k_b$ is the Boltzmann constant and $T$ is the system temperature. This law can be modified to make the temperature dependence of the pre-exponential factor explicit (IUPAC 2006). The modified equation is usually of the form

$$k = A \left( \frac{T}{T_0} \right)^n \exp\left( -\frac{E_a}{k_b T} \right)$$

(1.18)

where $T_0$ is a reference temperature and $n$ is a value ranging between -1 and 1. In the case of classical Arrhenius equation $n$ is 0. The equation contains two parameters:

- $A$ is called the pre-exponential factor and has the units of the rate constant. $A$ is correlated with the steric factor $\rho$ through this equation $A \propto <\sigma v> \rho$, where $<\sigma v>$ is the collision frequency ($\sigma$ is the cross section, v the velocity). The steric factor $\rho$ is semi-empirically related to the orientation of the colliding molecules and can be regarded as the ratio of the cross section for reactive collisions to the total collision cross section.

- $E_a$ is the activation energy. At an absolute temperature $T$, the fraction of molecules that have a kinetic energy greater than $E_a$ can be calculated from the Maxwell-Boltzmann distribution, and turns out to be proportional to $e^{-E_a/k_b T}$.

### 1.2.2 Exothermic and endothermic reactions: enthalpy and activation barrier

Two different types of chemical reaction can be distinguished in nature, as shown in Figure 1.7, depending on how enthalpy changes ($\Delta H$) from the initial to the final system:

1. **Endothermic reaction**, $\Delta H$ is positive. The system absorbs energy from its surroundings in the form of heat. The term derives from the union of the prefix “endon” (from the greek ενδον) meaning “within” and the root “therm” (from the greek θερµ-) meaning “hot”.

2. **Exothermic reaction**, $\Delta H$ is negative. The system releases energy to the surroundings in the form of heat (or light, sound and so on). The term derives from the union of the prefix “exo” (from the greek εχο) meaning “outside” and the root “therm” (from the greek θερµ-) meaning “hot”.

![Figure 1.7: Enthalpy of exothermic (green curve) and endothermic (red curve) reactions.](image)
Endothermic reactions are not likely to occur in our experiments due to the low energy that the surroundings (the cold surface) can provide to the system (the adsorbed molecules). Figure 1.7 shows that the initial system has to overcome an energy barrier (namely activation energy), it does not matter the type of reaction. The initial (reactants) and final (products) systems can be thought as two minima for the potential energy separated by an energy barrier. The height of this barrier ($E_a$) indicates how fast a reaction can proceed. The activation barrier is a property of a reaction (reactants-products system), but it can change due to the presence of a third inert body, namely a catalyst or an inhibitor. A catalyst (or an inhibitor) can speed up (or slow down) a chemical reaction by providing a different route, with lower (or higher) $E_a$. A surface could be a catalyst. Particularly, interstellar dust grains act as a catalyst for the chemistry of ISM. Surface reactions can occur mainly via three mechanisms: Eley-Rideal, Langmuir-Hinshelwood and Harris-Kasemo. In the following sections we present, one by one, each mechanism.

### 1.3 Surface Chemistry

Surface chemistry can be roughly defined as the study of chemical reactions at interfaces. The presence of a surface can deeply change the rate of a reaction. For example the chemistry at the surface of dust grains plays a very important role in the formation and destruction of interstellar molecules. Interstellar grains in fact provide a surface on which accreted atoms and molecules from the gas can gather and react (through surface diffusion). In short, grains behave as catalysts.

Although most of the molecules detected in the interstellar clouds appear to be formed via sequences of gas-phase reactions (Smith et al. 2004; Herbst 2001), this is not true for all species in all types of sources. The most important exception remains the formation of molecular hydrogen from precursor hydrogen atoms, a process that must be very efficient to form copious amounts of H$_2$ even in diffuse clouds (Pirronello et al. 1997; Vidali et al. 2009; Matar et al. 2008). The formation of H$_2$ is certainly not the only example of reactions that occur more efficiently on surfaces in interstellar clouds. Today the formation of several other molecules by surface reactions has been studied. Among them there are carbon dioxide, water, formaldehyde, methanol and carbonic acid (i.e. see works of: Dulieu's group of Cergy-Pontoise University, Linnartz's group of Leiden Observatory, Watanabe's group of Sapporo University, and Vidali’s group of Siracuse University).

#### 1.3.1 Eley-Rideal mechanism

In this mechanism, proposed in 1938 by D. D. Eley and E. K. Rideal, only one of the molecules is adsorbed and the other one reacts with it directly coming from the gas phase, without being adsorbed on the surface of the catalyst (see Figure 1.8):

\[
A(gas) + \text{Surface} \rightarrow A(S) 
\]

\[
A(S) + B(gas) \rightarrow \text{Products} 
\]

ER reactions are somehow similar to gas phase reactions. The impinging particles either collide and react with one adsorbate or have enough energy to hop on the surface before thermalizing and accommodating in an empty adsorption site. In other words, ER mechanism is a nonthermal surface mechanism because it leads to a reaction between a thermally adsorbed surface species and a reactant which has not yet thermally accommodated to the surface. This point is of crucial importance to evaluate the activation barrier of a reaction, as we will discuss in Sec. B.2.
1.3.2 Langmuir-Hinshelwood mechanism

This mechanism describes the formation of molecules on a surface when two reaction partners are already adsorbed on the surface $S$, if at least one of them is mobile (see Figure 1.9):

\[
\begin{align*}
A(gas) + \text{Surface} &\rightarrow A(S) \quad (1.21) \\
B(gas) + \text{Surface} &\rightarrow B(S) \quad (1.22) \\
A(S) + B(S) &\rightarrow \text{Products} \quad (1.23)
\end{align*}
\]

The LH mechanism is a thermal surface mechanism because both reactants are thermalized to the surface temperature. Two possible rate limiting steps can be envisaged: either mobility of the reaction partners or the reaction itself. These two points will be discussed in Sec. 3.2.

1.3.3 Hot atom mechanism

Generally, only the ER and LH mechanisms are considered when the formation of molecules via surface chemistry is concerned. However, a molecule arriving at the surface may not be chemisorbed (or physisorbed) upon the first impact due to the inefficient energy transfer between the impinging particle and the surface. Before the complete dissipation of its incident energy, the adsorbed particle is not in thermal equilibrium with the surface. Hence, impinging particles could be able to hop on the surface and react with already adsorbed molecules lying several Angstroms away from the impact site. In the literature, this process is called “Hot Atom” (HA) or Harris-Kasemo \( (Harris\&Kasemo\ 1981) \) mechanism (see Figure 1.10). The cross section of this mechanism is about one order of magnitude higher than that of the so-called Eley-Rideal mechanism.

To date, HA has been studied mainly from a theoretical point of view (Martinazzo et al.)
Figure 1.10: A schematic representation of the Harris-Kasemo mechanism.

2004, and Molinari/Tomellini 2002, and references therein), although some experimental studies exist (Wei & Haller 1996, and Dinger et al. 2001, and references therein). Previous works considered metallic surfaces only, and atoms with an energy greater than 0.5 eV or light atoms (H or D); under these conditions, the energy transfer between the particles and the surface is slow, so there is a high probability that the HA mechanism occurs. In our experiments, we worked under very different conditions. We performed the experiments on non-metallic surfaces (silicate, graphite, and water ice), atoms have an energy <0.01 eV and are heavier than H (i.e. O atoms, mass(O)/mass(H) = 16). These considerations lead us to assume that the HA mechanism should not be important under our experimental conditions, especially at low coverages.

Bibliography


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Experimental apparatus and methods

2

This chapter presents the experimental apparatus and methods used to perform the experiments described along this thesis. All experiments described in this thesis are performed at LERMA-Cergy (Laboratoire d’Etude du Rayonnement et de la Matière en Astrophysique et Atmosphères) laboratory in Cergy-Pontoise University (France) through the so called FORMOLISM (FORmation of MOlecules in the ISM) set-up; it is dedicated to the investigation of physico-chemical processes occurring to atoms and molecules on cold surfaces, i.e., dust grains dwelling in the interstellar medium.

2.1 Experimental apparatus

Figure 2.1 shows a schematic drawing of the FORMOLISM set-up. FORMOLISM consists of different parts:

1. an ultra high vacuum (UHV) chamber, i.e., the main chamber;
2. two triply differentially pumped atomic/molecular beamlines;
3. two microwave cavities mounted in the first stage of each beam and used for dissociating molecular gases;
4. A sample holder connected to a cryostat;
5. A quadrupole mass spectrometer (QMS);
6. An infrared spectrometer (FT-RAIRs).

Each part will be described in detail in the next sections.
2.1.1 The main chamber

The UHV main chamber consists of a stainless steel chamber, a cylinder of radius 15 cm and height 120 cm, that is evacuated by a cryopump, a titanium sublimation pump, a turbo molecular pump and an ion pump, so the residual pressure inside the chamber reaches values of $10^{-10} - 10^{-11}$ mbar corresponding to a molecular/atomic density of about $2 \times 10^6$ cm$^{-3}$. We are not able to perform experiments with pressure similar to those of interstellar medium, i.e. $10^{-13} - 10^{-14}$ mbar, for two reasons:

- from a technical point of view, ultra high vacuum systems cannot reach this pressure;
- from a practical point of view, at these pressures, each single experiment would need weeks or months to be performed.

In any case, even if the pressure in the main chamber is higher than that encountered in interstellar medium, it is low enough to keep the amount of pollutants low on the surface of the sample; in fact, with a pressure of $10^{-10}$ mbar and with a surface temperature of 10 K, the sample-holder is coated with $\approx 1$ ML of water vapour after only $\approx 5000$ minutes (see Accolla, 2010). In the main chamber there is a leak valve equipped with a microchannel doser (Figure 2.2) that is used to make water ice films on the sample surface. When it is opened, water contained in a small vial, can diffuse into the chamber via a micro capillary array. The water diffuser can be moved and placed in front of or above the sample holder, depending on the kind of water ice to be grown on the surface of the sample, as described in Sec. 2.2.1.

2.1.2 The beamlines

The two beamlines form an angle of 18° and converge on an ideal point lying onto the central axis of the main chamber. This is the same design devised by Pirronello et al. (1997). Each beamline has three differentially pumped (atomic/molecular) stages, connected with

---

$^1$The majority of the residual pressure is due to H$_2$, while H$_2$O, N$_2$, CH$_4$, and so on represent only 10% of the total residual pressure ($\approx 10^{-11}$ mbar).
Figure 2.2: Photo of the water diffuser facing the sample holder surface, during water ice growth.

The two beamlines (that can be separated by the main chamber by two manually-operated valves) are always kept under vacuum. The three stages are continually pumped by turbo-molecular pumps, backed by mechanical rotary pumps, even when the beamlines are not in use.

A removable metallic plate (called “beam flag”) is placed between the third stage and the main chamber. The flag is able to intercept the beam flux and the particles do not arrive directly to the icy sample, but they fill the main chamber: in this case, the particles will condense on the icy sample by “background” deposition with a flux 2 or 3 orders of magnitude less intense. When the flag is open the beam of particles reaches the sample surface directly. Figure 2.3 shows how the beam direction is adjusted and the gas is centered on the surface. A pointing laser, located in front of the quartz tube, passes through the diaphragms holes and arrives on the surface. The laser spots of the two beams are centered on the same area of the surface, through micro movement of the diaphragms and, also, of the whole beam stages.

2.1.3 The microwave cavities

Each beamline is equipped with a microwave cavity (a Surfatron cavity) and a microwave power supply delivering up to 300 W at 2.45 GHz. These two components are used for dissociating molecular gases such as hydrogen, deuterium, nitrogen or oxygen to produce atomic or molecular radicals. The molecular gases pass in a quartz pipe (diameter 4 mm, length 10-20 cm) traversing the microwave cavity with a pressure ranging from 0.3 to 4 mbar. Microwaves transfer energy to the gas by exciting and ionizing the species. They create a plasma in which electrons are accelerated. The dissociative electronic excitation of H\textsubscript{2}, D\textsubscript{2}, N\textsubscript{2}, or O\textsubscript{2} produce atoms in the discharge zone. At the pressures used, the large number of collisions, especially on the walls of the pipe, favors the recombination of molecules after being dissociated. To minimize the spontaneous recombination of the atomic species and to reduce the discharge temperature the cavity is cooled by a flux of compressed air around the tube and by a water circuit cooling the metallic parts. We have estimated that the temperature...
of the gas coming out from the pipe is lower than 450 K. Actually, due to multiple collisions the atoms generated in the discharge can thermalize upon impacts with the pipe internal surfaces. It is possible, however, that a gradient of temperature is present in the pipe. By considering the thickness of the pipe, the difference between the outer and the inner part should be lower than 100 K. Hence, an upper limit for the translational temperature is 450 K. SubSec. 2.3 presents the method used to know the excitation state of dissociated species. Figure 2.4 shows the discharge glows of H$_2$ (purple) and O$_2$ (off-white) gases.

2.1.4 The sample holder and the sample

The sample holder is an oxygen-free high thermal conductivity (OFHC) copper cylinder, with radius equal to 5 mm. The sample holder is placed in the center of the main chamber, at the same height of the beamlines, and an electric resistance is able to heat the sample holder up to 400 K. The sample holder is in contact with a closed-cycle He cryostat. By throttling the flow of liquid helium the sample can be cooled to 6.5 K. A buckler, made of a mixture of copper and nickel, protects and isolates the sample holder, the “400 K interface” and the second stage of the cryostat from IR radiation coming largely from the walls of the chamber (See Figure 2.5).

The sample holder is mounted on a translation plate, that allows us to move back and forth the sample holder with respect to the center of the chamber in order to allow a better positioning of the sample with respect to the QMS or the water vaporizer. The “400 K interface” is connected to a controller (Lakeshore 340), that allows the reading of the different temperatures and, by varying the power of the heater, to regulate the sample temperature.

The sample is interchangeable by opening the main chamber. Two different sample were used to perform the experiments:

1. a non-porous amorphous olivine-type silicate
2. a HOPG (Highly Ordered Pyrolytic Graphite) slab
The silicate sample was obtained by thermal evaporation of San Carlos olivine (Mg$_{1.8}$Fe$_{0.2}$SiO$_4$) onto a gold-coated substrate (1 cm in diameter), operating at temperatures between 6.5 K and 350 K. The surface density of adsorption sites is about the same of the one found on compact water ice samples. Sample preparation and surface analysis are described extensively in Djouadi et al. (2005).

The HOPG surface used in the experiments are a ZYA-grade HOPG samples, produced by MaTeck company; all HOPG samples had been previously exposed to an O-atom beam (oxidized) to avoid surface changes during the experimental sequences.

### 2.1.5 The Quadrupole Mass Spectrometer

Figure 2.6 shows a photo and a scheme of the Quadrupole Mass Spectrometer (QMS). In red the three main components, (i) an ionizer (bombardment by electrons from a hot filament), (ii) a mass filter (discrimination zone) consisting of four parallel metal rods, and (iii) the ion detector (electron multiplier). A gas (residual or desorbing from a surface) is ionized by electron impact. Free electrons are obtained by thermal emission from an electrically heated tungsten filament. Thermal electron emission can be described by Richardson-Dushman expression (Richardson 1929)

\[ J = A_G T^2 \cdot \exp\left(-\frac{\phi}{kT}\right) \]  

(2.1)

with \( J \) the current density of emitted electrons, \( T \) is the thermodynamic temperature of the metal, \( \phi \) the work function of the filament material and \( A_G \) is

\[ A_G = \lambda_R A_0 \]  

(2.2)

with

\[ A_0 = \frac{4\pi mk^2e}{\hbar^3} \]  

(2.3)

and \( \lambda_R \) is a material-specific correction factor that is typically of order 0.5. Ions are subsequently accelerated towards the quadrupole analyzer which consists of four cylindrical rods, arranged symmetrically at a distance \( r_0(x,y) \) around the optical axis \( z \) of the system. Opposite rods are electrically connected. These four metallic rods represent the
The ion mass filter able to select species according to their mass-to-charge ratio ($m/z$); in fact, a voltage combination of a direct and a radio frequency component is applied between adjacent and opposite rods. Varying the direct and the radio frequency component, the QMS is able to scan all the ions up to a chosen mass-to-charge ratio technically fixed (in our case 50 $m/z$). In the following, unless specified otherwise, $z$ is equal to one and it will be omitted.

The ion detector is a Channeltron (an electron multiplier). The output current generated in the Channeltron is converted into a digital signal. The digitized signal is then analyzed by the software provided by the QMS manufacturer HIDEN. It allows to monitor and record the acquired information, but also to adjust the electronic setting of the QMS and the dwelling time on each mass value. Moreover, it is possible to record simultaneously the sample temperature measured by a Lakeshore controller during TPD experiments.

The QMS is mounted in the upper part of the main chamber. It can be rotated by $190^\circ$ around the sample and moved vertically. This detector is used in the lower position in order to measure the intensity of the incoming beams and the products of reaction occurring on the surface of the sample. In the upper position, the QMS is used to analyze the abundances of residual gases in the main chamber.

### 2.1.6 The Infrared Spectrometer

FORMOLISM is equipped with a Bruker Tensor 27 Fourier transform infrared spectrometer (FTIR) used to monitor the adsorbed/formed species in situ. Figure 2.7 shows a scheme of the spectrometer: a mid-IR source (Globar) is used as coherent thermal light source to produce a beam containing frequencies in the $4000-8000$ cm$^{-1}$ ($2.5-10$ µm). The light passes through an aperture (typically of 2 mm) and arrives in a Michelson interferometer. The interferometer
is composed of a beamsplitter (KBr) that splits the beam light in two parts, one is sent to a fixed mirror and the other to a moving mirror. The movement of this last mirror produces beams with different optical path length (namely different combination of frequencies in the recombined beam). The beamsplitter recombines the beams coming from the two mirrors. The resulting beam passes through an exit port and it is focused on the surface through an off-axis parabolic gold-plated mirror (effective focal length $FL = 250$ mm). The mirror is mounted within a differentially pumped housing adjacent to the UHV chamber and isolated from it with a differentially pumped potassium bromide (KBr) window. The FTIR is set up in a reflection-absorption infrared spectroscopy (RAIRS) configuration (see Figure 2.7) and the spectra are recorded at a grazing incidence angle of $83 \pm 1^\circ$. The parallel and unpolarized infrared beam is focused onto the sample using a $90^\circ$ reflecting mirror (see Figure 2.7). Through a second pumped KBr window, the reflected infrared beam arrives in a second pumped housing using an off-axis ellipsoidal gold-plated mirror. This mirror has conjugate foci located at 250 mm and 40 mm, corresponding to distances to the surface sample and the MCT detector. The liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector collects the raw data that are sent to the PC. Afterwards, OPUS software assembles all these data and turn the interferogram (the raw data, light absorption for each mirror position) into the typical IR spectrum (light absorption for each wavelength) through a Fourier transform. Each spectrum is usually acquired with a resolution of 4 cm$^{-1}$ prior or subsequently to either deposition or TPD. The sample must be moved backward to allow for acquisition of a RAIR spectrum. One major problem of RAIR spectroscopy is the sensitivity. The signal is usually very weak owing to the small number of adsorbing molecules; in fact for an area of 1 cm$^2$ with less than $10^{15}$ adsorbed molecules, even for a IR active species, the signal is typically less than 0.01% of total absorption (or transmittance).

2.2 Experimental methods

In the next sections the experimental methods used are presented. We describe here how ices are grown (in particular water ice) on the sample, the techniques used to probe the products.

**Figure 2.6:** Photo and schematic view of the QMS head.
and to monitor ices (mass spectroscopy and infrared spectroscopy), and finally how the beam fluxes and surface coverages are calibrated.

### 2.2.1 Water ice deposition on the sample holder

Two different techniques of water ice growth are used in the FORMOLISM set-up: either the “spray deposition” or the “background deposition”. Both of them will be described in the following two sections.

The deposition by spraying is a direct way to grow the amorphous solid water (ASW) ice layer quickly and it is used to deposit large amount of water molecules. During the spray deposition, the microchannel array doser is placed at 2 cm in front of the sample holder surface maintained at 110 K, as shown in Figure 2.2. As it is shown in Sec 2.1.1, a small glass vial containing purified liquid water is connected with the water diffuser located into UHV chamber via a leak valve. By opening this leak valve, the local pressure in the region between the diffuser and the copper substrate reaches about $10^{-4}$ mbar, while the residual pressure into the chamber is $10^{-9}$ mbar. It has been evaluated that the mean free path of H$_2$O molecules is about 1 m while the residual pressure is $10^{-6}$ mbar. Since the distance between the diffuser and the cold surface is smaller than the mean free path, the majority of the water molecules will hit the sample holder and the cryoshield and stick on them. For this reason, water molecules sent into the chamber during the direct deposition contribute marginally to the UHV pressure.

Spray deposition allows the growth of about a hundred monolayers of ASW within 5 minutes.
Experimental methods

(i.e. 0.33 \(ML/s\)).

The background deposition method is performed by filling uniformly the entire volume of the chamber with water vapor. Now the microchannel doser is kept high above the sample holder surface.

Knowing the pressure \(P\), the temperature in the chamber \(T\) and the mass of impinging molecules \(m\), the flux \(\phi\) of molecules hitting the cold surface is

\[
\phi = \frac{\bar{v} n}{4} = \frac{P}{4KT} \sqrt{\frac{8KT}{\pi m}} \tag{2.4}
\]

where \(\bar{v}\) is the molecular mean velocity and \(n\) is the molecular number density, while \(1/4\) is a corrective factor due to the projection of a sphere on a disk.\(^2\)

The background method can be used only for the deposition of thin ice films due to the long time required. For a pressure of \(1 \times 10^{-8} \text{ mbar}\), a monolayer is grown in around 5 minutes. The recovery of the base pressure \((10^{-10} \text{ mbar})\) takes about 30 minutes.

### 2.2.2 Mass spectroscopy: the different uses of the QMS

#### 2.2.2.1 Cracking pattern

In subSec. 2.1.5 we have briefly described the QMS operation. We have claimed that gas species are detected after their ionization. This occurs in the so called ionization zone through electron impacts. Here we pinpoint that electron impacts could produce dissociation of species in addition to ionization. Actually it is necessary to pay attention to the fragment distribution of ionic species which results from dissociation and ionization of multi-atomic molecules of any given species in the ionizer, the so called cracking pattern. The probabilities of ionization and dissociation depend on molecular geometry (and intra-molecular bonds energy), angle of impact between molecules and ionizing electrons of the QMS, and the energy of ionizing electrons. For these reason, signals (and peaks) at different masses can derive from the same molecule, reflecting its partial fragmentation in the QMS head.

Figure 2.8 shows the TPD curves of \(\text{CH}_3\text{OH}\) and six major signals are presented. Table 2.1 reports the cracking pattern of some molecules: \(\text{NO}_2\), \(\text{O}_3\), \(\text{H}_2\text{CO}\), \(\text{NH}_2\text{OH}\), \(\text{HCOOH}\), and \(\text{CH}_3\text{OH}\). The signals are normalized to the highest mass signal.

Nitrogen dioxide is the simplest case listed in Table 2.1.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
<th>Peak 4</th>
<th>Peak 5</th>
<th>Peak 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NO}_2)</td>
<td>30-100</td>
<td>46-14</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\text{O}_3)</td>
<td>32-100</td>
<td>48-67</td>
<td>16-4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\text{H}_2\text{CO})</td>
<td>30-100</td>
<td>29-85</td>
<td>28-15</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\text{NH}_2\text{OH})</td>
<td>17-100</td>
<td>33-86</td>
<td>16-86</td>
<td>30-66</td>
<td>32-14</td>
<td>-</td>
</tr>
<tr>
<td>(\text{ND}_2\text{OD})</td>
<td>30-100</td>
<td>18-88</td>
<td>30-23</td>
<td>34-8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\text{HCOOH})</td>
<td>29-100</td>
<td>46-65</td>
<td>28-60</td>
<td>44-47</td>
<td>45-43</td>
<td>-</td>
</tr>
<tr>
<td>(\text{CH}_3\text{OH})</td>
<td>31-100</td>
<td>32-67</td>
<td>15-50</td>
<td>29-45</td>
<td>30-16</td>
<td>28-7</td>
</tr>
</tbody>
</table>

This molecule is detected through mass 46 (\(\text{NO}_2^+\)) and mass 30 (\(\text{NO}^+\)) and the ratio between these masses is around 10 - 20 %, as shown in Minissale et al. (2013b). As already seen in Mokrane et al. (2009) and Minissale et al. (2014), the ozone signal is simultaneously detected at mass 48, 32, and 16. This is because the dissociation of \(\text{O}_3\) is energetically more favorable than its ionisation (3.77 eV vs 12.53 eV). When \(\text{O}_3\) enters the QMS head, it can undergo different processes:

- \(\text{O}_3 (+ e^-) \rightarrow \text{O}_3^+ (\Delta H_f=12.97 \text{ eV})\)

\(^2\)In this equation the sticking coefficient of \(\text{H}_2\text{O}\) should be taken into consideration, but it is neglected because it is close to unity in the range of temperature 10 - 120 \(K\), thus every molecules hitting the surface will stick on it.
Experimental methods

Figure 2.8: TPD curves of masses 32, 31, 30, 29, 28, and 15 after deposition of 1 ML of methanol. All the peaks at different masses derive from the same molecule, reflecting its partial fragmentation in the QMS head.

- \( O_3^+ (+ e^-) \rightarrow O_2^+ + O \ (\Delta H_f = 13.17 \text{ eV}) \)
- \( O_3^+ (+ e^-) \rightarrow O^+ + O_2 \ (\Delta H_f = 14.72 \text{ eV}) \)

The third process is less probable than the first two, and in fact the peak at mass 16 is 4% of the peak at mass 32. The difference between mass 32 and 48 could be explained by further electron impact. This last is more probable for \( O_3^+ \) rather than \( O_2^+ \). Actually due to its mass, \( O_3^+ \) has a lower speed and it spends more time in the ionization zone. We can draw on similar arguments (ionization versus dissociation, double electron impacts) to explain mass spectroscopy of \( \text{H}_2\text{CO} \). In this case signals at masses 30 (\( \text{H}_2\text{CO}^+ \)), 29 (\( \text{HCO}^+ \)), and 28 (\( \text{CO}^+ \)). As evident from the table, the larger the molecule, the higher the number of the mass signals. In particular, methanol (\( \text{CH}_3\text{OH} \)) cracking is very complex as evident from Figure 2.8. In conclusion, we claim here that, if on one hand the molecule fragmentation in the QMS complicates the mass spectroscopy analysis, on the other hand it is a powerful instrument to figure out some ambiguous cases. For example, molecules of the same masses, like \( \text{CH}_3\text{OH} \) and \( \text{O}_2 \) (mass 32) or \( \text{CO} \) and \( \text{N}_2 \) (mass 28), would be undistinguishable without the help of the cracking pattern.

2.2.2.2 Residual gas analyzer: knowing beam composition

In FORMOLISM set-up, the QMS can be rotated and put in front of the beams to know their gas composition. This method allows us to know if a molecular beam is polluted with other species. In particular, dissolved gases are contained (or present) in some species, that at standard temperature and pressure are in liquid or solid phase (i.e. \( \text{CH}_3\text{OH}, \text{H}_2\text{O}, \text{or H}_2\text{CO} \)). The degasification process can be checked and followed by verifying the gas composition as a function of time. Formaldehyde gas is obtained through depolymerization of paraformaldehyde (a white crystalline solid shown in Figure 2.9), depolymerization is achieved by immersing the phial containing paraformaldehyde on water constantly held at 62 °C. The resulting gas contains \( \text{H}_2\text{CO} \), but also residual \( \text{CO} \) and \( \text{H}_2\text{O} \). By placing paraformaldehyde under vacuum, we make the residual gas less soluble and its concentration decreases. Figure 2.9 shows all the steps of the \( \text{H}_2\text{CO} \) beam preparation from the depolymerization to the injection of the gas in the beam. When all the residual gas is pumped we have, at beginning of the beam (gauge
Figure 2.9: Photos of all the steps of the \( \text{H}_2\text{CO} \) beam preparation. From the top left, anticlockwise we have: paraformaldehyde powder, heating of paraformaldehyde by immersion in hot water, injection of \( \text{H}_2\text{CO} \) in the beam, and particular of the gauge used to measure the source pressure.

shown in Figure 2.9, a pressure of 0.42 mbar, corresponding to QMS signal of 810 and 690 cps for masses 30 and 29, respectively. Table 2.2 and top panel of Figure 2.10 show the ion count per second for four mass (30, 29, 28, and 18) during \( \text{H}_2\text{CO} \) beam preparation. These masses should correspond to three species: \( \text{H}_2\text{CO} \) for masses 30, 29, and 28; CO and/or \( \text{N}_2 \) for mass 28; \( \text{H}_2\text{O} \) for mass 18. The bottom panel of Figure 2.10 shows the evolution of the abundance ratio between these species. The ratio is calculated by considering that signal at mass 28 is composed of two parts, one is the residual gas (CO+\( \text{N}_2 \)), the other is cracked \( \text{H}_2\text{CO} \):

\[
\text{Mass}28 = \text{H}_2\text{CO} + \text{Residual gas} \approx 0.15 \times \text{Mass}30 + \text{Residual gas}. \tag{2.5}
\]

At the beginning of the degasification process the ratio (CO+\( \text{N}_2 \))/\( \text{H}_2\text{CO} \) is

\[
\frac{\text{Mass}28 - \text{Mass}30 \times 0.15}{\text{Mass}30 + \text{Mass}29 + \text{Mass}30 \times 0.15} = \frac{1300 - 90}{580 + 420 + 90} = 1.11, \tag{2.6}
\]

while after 150 minutes of pumping it becomes

\[
\frac{\text{Mass}28 - \text{Mass}30 \times 0.15}{\text{Mass}30 + \text{Mass}29 + \text{Mass}30 \times 0.15} = \frac{10}{810 + 690 + 120} \approx 0. \tag{2.7}
\]

Similar trends are obtained for \( \text{H}_2\text{O}/\text{H}_2\text{CO} \), starting from 0.84 and arriving at 0.

Up to now we have described how the QMS is used to know the beam composition of a molecular species, during the degasification process or generally speaking from a gas bottle. Clearly this method can be extended to determine the composition of a plasma. As already described in Sec. 2.1.3 each beamline of FORMOLISM houses a microwave cavity for dissociating molecular gases such as hydrogen, deuterium, nitrogen, or oxygen. The fraction of gas dissociated in the beamline can be measured comparing the molecular signal (\( \text{D}_2 \), \( \text{H}_2 \), \( \text{N}_2 \), or \( \text{O}_2 \)) when the microwave discharge is switched on and off. The dissociation fraction is given by

\[
\tau_{\text{diss}} = \frac{S_{\text{off}} - S_{\text{on}}}{S_{\text{off}}} \tag{2.8}
\]

where \( S \) is the signal for a species (for a specific mass) with either dissociation on or off. We obtained with this apparatus, a dissociation fraction of about 70-90% for \( \text{D}_2 \), 60-80% for \( \text{H}_2 \),
Experimental methods

Figure 2.10: Top panel: ion count per second at mass 30, 29, 28, and 18 as a function of pumping time during H\textsubscript{2}CO beam preparation. Bottom panel: ratio of CO/H\textsubscript{2}CO and H\textsubscript{2}O/H\textsubscript{2}CO as a function of pumping time.

10-40% for N\textsubscript{2}, and 40-80% O\textsubscript{2}. Figure 2.11 shows the counts per second of mass 32 (O\textsubscript{2} molecules) and 16 (O atoms), respectively red and black curves, without and with discharge. When the discharge is off the signal at mass 32 is around 5000 cps and mass 16 is almost zero, except for a tiny signal coming from O\textsubscript{2} dissociation itself. On the contrary when the discharge is on mass 32 signal decreases to 1800 cps and mass 16 signal raises to 1200. By using Eq. 2.8 we find in this case a dissociation fraction for O\textsubscript{2} of around 65%.

2.2.2.3 Knowing electronic state of atoms and molecules

The QMS is also used to know the quantum state of the species sent on the substrate. Usually the energy of ionizing electrons is set to 30 eV to have a good ionization cross section and a reduced cracking pattern (which raises in complexity with electrons energy). Nevertheless the electrons energy can be tuned from 0 to 100 eV with a resolution of 0.2 eV. Each molecule has an ionization threshold which depends on the initial quantum state that has to be overcome to detect the species. By tuning the energy of the ionizing electrons of the QMS, we can selectively detect ground state or excited atoms and molecules, as described in Congiu et al. (2009). Here we stress that this method can only distinguish between electronic excited states, due to the 0.2 eV resolution; actually the energy difference between two vibrational (rotational) states is of 10\textsuperscript{-1}-10\textsuperscript{-2} (10\textsuperscript{-3}-10\textsuperscript{-4}) eV. Top and bottom panels of Figure 2.12 show, respectively, signals of O/O\textsubscript{2} (Mass16/Mass32) and N/N\textsubscript{2} (Mass14/Mass28) as function of electron energy when the discharge is ON (red curves) and OFF (green curves). In the O/O\textsubscript{2} case (top panels), we see that the Mass 16 signal drops off at around 13.5 eV (green curve is not present because no O atoms are present in the un-dissociated O\textsubscript{2} beam), while Mass 32 signals (red and green curves) fall to zero at 12.1 eV. We can explain these results by looking at the energy of the excited states of O and O\textsubscript{2}. Atomic orbital theory predicts that O atoms in the ground state (3\textsuperscript{P}) are ionized by 13.6 eV electrons (Moore 1993) while in the first
Table 2.2: Count per second (Cps) of Masses 30, 29, 28, and 18 are reported as a function of pumping time. These masses correspond respectively to detection of H$_2$CO (Masses 30 and 29), CO (Mass 28), and H$_2$O (Mass 18).

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Mass 30</th>
<th>Mass 29</th>
<th>Mass 28</th>
<th>Mass 18</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>580</td>
<td>420</td>
<td>1300</td>
<td>920</td>
</tr>
<tr>
<td>10</td>
<td>650</td>
<td>490</td>
<td>1110</td>
<td>520</td>
</tr>
<tr>
<td>25</td>
<td>740</td>
<td>570</td>
<td>620</td>
<td>150</td>
</tr>
<tr>
<td>50</td>
<td>810</td>
<td>680</td>
<td>120</td>
<td>10</td>
</tr>
<tr>
<td>90</td>
<td>810</td>
<td>690</td>
<td>130</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>810</td>
<td>690</td>
<td>120</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 2.11: Counts per second of O and O$_2$ as a function of the energy of ionizing electron of the QMS with and without discharge.

excited state $^1$D the minimum energy necessary for ionization is 11.7 eV (+1.9 eV). Hence, electrons less energetic than 13.6 eV can ionize excited ($^3$P ro-vibrational excited states or $^1$D electronic excited state) O atoms only. The same argument can be applied to molecular oxygen. O$_2$ molecule has two low-lying excited singlet states, O$_2$($a^1\Delta^+_g$) and O$_2$(b$^1\Sigma^+_g$), while the ground state is the triplet O$_2$(X$^3\Sigma^+_g$) state. The energy difference between the lowest energy of O$_2$ in the singlet state, and the lowest energy in the triplet state is about $T_e$(a$^1\Delta^+_g$ - X$^3\Sigma^+_g$) = 0.98 eV (Schweitzer&Schmidt 2003). The required energy to ionize an O$_2$ molecule in the ground state is 12.07 eV (Tanaka&Tanaka 1973). This means that electrons less energetic than this value cannot ionize O$_2$ in the ground state, while O$_2$(a$^1\Delta^+_g$) molecules can be ionized by electrons with energy >11.09 eV. Finally electrons with energy below 11.09 eV can ionize O$_2$(b$^1\Sigma^+_g$). By considering these arguments we can go back to the top panels of Figure 2.12 and claim that the beam did not contain O or O$_2$ in an excited state. The O beam was thus composed of at least 99% ground-state O and O$_2$. In the case of nitrogen, theory predicts that N atoms in the ground state ($^4$S) are ionized by 14.53 eV electrons (Moore 1993) while in the first excited state $^2$D the minimum energy necessary for ionization is 12.15 eV (+2.38 eV). Hence, electrons in the range 14.53-12.15 eV can ionize excited ($^4$S ro-vibrational excited states or $^2$D electronic excited state) N atoms only. The ground state of N$_2$ molecule is the singlet N$_2$(X$^1\Sigma^+_g$) state, while the first electronic excited state of N$_2$ molecule is the triplet states, N$_2$(A$^3\Sigma^+_u$) (Lofthus&Krupenie 1977). The energy difference between the two states is about $T_e$(A$^3\Sigma^+_u$ - X$^1\Sigma^+_g$) $\approx$ 6 eV

---

3 For the sake of completeness and clarity, in Appendix 6.2.2 we explain the meaning of the molecular spectroscopy symbols.
Figure 2.12: Signals at mass 16, 32 (O and O$_2$), 14, and 28 (N and N$_2$) when the discharge is ON and OFF (red and green curves respectively) as a function of the energy of ionizing electrons. The pinstriped bars indicate the required energy for ionizing the corresponding quantum state.

The required energy to ionize an N$_2$ molecule in the ground state is 15.6 eV (Loftus & Krupenie 1977). This means that electrons less energetic than this value cannot ionize N$_2$ in the ground state, but can ionize N$_2$(A$^3\Sigma^+_u$) molecules or ro-vibrational excited N$_2$(X$^1\Sigma^+_g$). Bottom panels in Figure 2.12 show that the N$_2$ beam did not contain N atoms in an excited state (green curve is not present because N atoms are not present in the un-dissociated N$_2$ beam). Similarly N$_2$ are not excited if the discharge is OFF (green curve), but excited N$_2$ are present when the discharge is ON.

2.2.2.4 TPD: Temperature Programmed Desorption

In subSec. 1.1.3 we have described the desorption process. We have claimed that two type of desorption can occur: thermal and non-thermal. In thermal desorption the adsorbed species acquires thermal energy to desorb. One of the most important methods to study thermal desorption is the Temperature Programmed Desorption (TPD). It consists in observing desorbed molecules from a surface when the surface temperature is increased. During the TPD the sample is heated linearly vs time with a rate $\beta$ from its initial value $T_0$

$$T = T_0 + \beta t$$  \hspace{1cm} (2.9)

where $T$ is the temperature at time $t$, $T_0$ is the starting temperature value and

$$\beta = \frac{dT}{dt} \text{ in the units of K/sec}$$ \hspace{1cm} (2.10)

Two examples of temperature ramps are shown in Figure 2.13. The intensity of the desorption signal, $I(T)$, is linked to the rate at which the surface concentration of adsorbed species
Figure 2.13: Sample temperature ramp as a function of elapsed time during two different TPD experiments; the red one from 10 K to 220 K with a rate of 2.4 K/min, the blue one from 10 K to 100 K with step of 10 K/min. If $\beta$ is too large, the TPD loses its linearity because the heating capability of the system is not powerful enough.

decreases. This can be expressed as

$$I(T) \propto \frac{d\theta}{dt} = \nu_n \theta^n \cdot \exp(-\frac{E_b}{k_b T})/\beta$$

(2.11)

where $\theta$ is the coverage. TPD methods can be understood with the help of the graphical representation shown in Figure 2.14. The expression of the signal intensity consists of three terms: one constant, $\nu$, and two, the surface coverage and the exponential term, dependent on $T$. At low temperatures, the exponential term (blue curve in the top panel of Figure 2.14) is small; it increases with the temperature and the increase becomes significant when the value of $k_b T$ is equal to $E_b$. On the other hand, the coverage dependent term (red curve in top panel of Figure 2.14) is initially constant and decreases rapidly as the desorption becomes important and attains the value of zero at the end of the desorption. Bottom panel of Figure 2.14 shows the desorption trace. The description given is very simplistic but it suffices to understand the origin and shape of the desorption trace. Coming back to Eq.1.7, it can be seen that for $n = 0$, the desorption is independent from coverage, as in the case where the desorption comes from several layers of adsorbate. A typical signature of 0th order desorption is the presence of a common leading edge for different coverages and a rapid drop when all the molecules have desorbed. The case of $n = 1$ is called first order desorption, and corresponds to the thermal desorption of molecules already formed on the surface; a distinguishing trait is an asymmetrical desorption peak with the same peak position as a function of coverage. The case of $n = 2$ corresponds to second order desorption, in which the reaction rate is proportional to the product of the concentrations of the reactants. It is observed when the reaction occurs between two adsorbate species that become mobile on the surface during the heating and react with each other before desorbing. In this case, a symmetrical desorption peak shifts towards lower temperatures as the coverage increases. See Figure 2.15 for a comparison among the three cases. The TPD techniques allow the determination of kinetic and thermodynamic parameters of the desorption processes and of chemical reactions, if they occur.

Recently Kimmel et al. (2001) and Amiaud et al. (2006) used a different approach to explain TPD curves: they resorted to a binding energy distribution of adatoms-surface system. Newly adsorbed molecules are mobile enough to explore the surface and find the
**Experimental methods**

**Figure 2.14**: Simplified interpretation of a TPD peak. Top panel: variation of the pre-exponential term and exponential term as a function of temperature. Bottom panel: the shared area represents the desorption peak.

strongest bonding sites prior to desorption (\(a\) panel in Figure 2.16). With the increase in the doses deposited on the surface, the TPD curves gradually broaden towards lower temperatures (\(b\) and \(c\) panel in Figure 2.16). As the surface coverage increases, the molecules are adsorbed in less tightly bound adsorption sites, namely, the desorption temperature \(T_{des} \propto\) desorption energy \(E_{des}\) (with peaks growing in height too). When the leading edge of the TPD curves (\(d\) panels in Figure 2.16) stops shifting towards lower temperatures, it means that all the adsorption sites on the surface are occupied, and any other incoming molecule is adsorbed on top of the first layer of molecules already adsorbed on the surface. This is when TPDs exhibit a 0th order desorption, the maxima of the desorption peaks increase and start shifting towards higher temperatures with increasing doses. The range of desorption temperatures is the signature of a distribution of binding energies available on the surface. The origin of such an energy distribution is linked to the disordered nature of the surface. As we have shown in this first example of TPDs, the partial pressure of atoms and molecules desorbing from the sample are measured by mass spectrometry. During TPDs, the QMS is placed in front of the sample to maximize the signal. In general, the data obtained from such experiments consist of intensity variations of each recorded mass fragment as a function of time/surface temperature. In the case of a simple reversible adsorption process it may only be necessary to record one signal - that is attributable to the molecular ion of the adsorbate concerned. A typical TPD trace for the desorption of NO from ASW ice at about 50 K is shown in Figure 2.17. To sum up, the following points are worth noting:

1. The area under a peak is proportional to the amount of molecules originally adsorbed, i.e. proportional to the surface coverage.

2. The kinetics of desorption (obtained from the peak profile and the coverage dependence of the desorption characteristics) gives information on the state of aggregation of the adsorbed species.

3. The position of the peak (the peak temperature) is related to the enthalpy of adsorption,
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Figure 2.15: Representative thermal desorption curves with varying initial coverage and with parameters $\nu_n$ and $E_{des}^{PW}$ held constant.

...i.e. to the strength of the binding to the surface.

If there is more than one binding state for a molecule on a given surface (and if these have significantly different adsorption enthalpies) then one will be able to discriminate them by the presence of multiple peaks in the TPD spectrum.

2.2.2.5 DED: During-Exposure Desorption

As described in the previous section mass spectroscopy allows us to study the thermal desorption. In this case the QMS is placed in front of the sample to maximize the signal. We can also monitor the signal during the deposition phase: in this case the QMS is rotated to allow the beam to reach the sample, and at the same time to have a rather good detection. Thus we can study the sticking or one of the non-thermal desorption processes described in Sec. 1.1.3, the chemical desorption. In analogy with acronym TPD, we called this method DED (During-Exposure Desorption). Actually, we probe desorption directly and we do not force the desorption as in the TPD’s case. In general, DED is useful when the species, arriving from the gas phase or newly formed on the surface, are unable to thermalize on the surface, and they are released into the gas phase. The top panel of Figure 2.18 shows the QMS in the DED configuration; it is placed closed to the surface, with an angle of about 35°.

The bottom panel of Figure 2.18 shows an example of measurements. We monitor the mass signal of D$_2$O (mass 20) during three distinct phases: before exposure, during exposure of D atoms on pre-adsorbed O$_2$ molecules, after exposure. We observe a direct D$_2$O signal far above the noise level in the exposure time (between 2 and 5 minutes), indicating that D$_2$O is chemically desorbed, during the D exposure.

2.2.3 Calibration of the H$_2$ and D$_2$ beams

To understand the physical-chemical processes occurring on the surface, it is mandatory to know how many molecules or atoms are aimed on the sample surface per second during exposure. Considering the so-called “fluence” (namely, the total number of particles sent per unit area), our experiments can simulate in a few minutes the chemical-physical reactions happening in thousands of years in an interstellar cloud. To put it quantitative grounds it

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$^4$Chemical desorption will be described extensively in Sec. 4.3 of Chapter (Dulieu et al. 2013).

$^5$In fact the order of magnitude of the atomic hydrogen flux in a molecular cloud is $\approx 10^7$ atoms s$^{-1}$ cm$^{-2}$ (Li&Goldsmith 2003) while the D-atoms flux in FORMOLISM set-up is $\approx 10^{13}$ atoms s$^{-1}$ cm$^{-2}$.
is very important to know as accurately as possible the flux of impinging particles during the irradiation.

In order to estimate the flux of D$_2$ molecules coming from the beam, the so-called King and Wells method has been used. This experimental method, accurately described by Amiaud et al. (2007), is generally used to evaluate the sticking coefficient of particles incident on a surface.

The experimental procedure is described hereunder. Initially, a non-porous ASW film ($\approx$ 100 ML thick) is grown at 110 K on the copper sample holder. Then, the icy sample is cooled down until 10 K, and irradiated with D$_2$. Simultaneously, the mass spectrometer detects the indirect D$_2$ signal in the vacuum chamber in real time (DED). The variation of the D$_2$ signal with time monitored by the QMS and shown in Figure 2.19 arises from the interaction between deuterium molecules and the icy surface. D$_2$ exposure begins when the beam is allowed into the main chamber at $t = 0$ s. During the first 125 s, an almost linear decrease of D$_2$ signal is observed due to the adsorption on the cold surface; then, there is a rising edge that reaches a plateau at $t = 220$ - $230$ s: the plateau lasts as long as the surface is irradiated by the beam. Indeed, this region represents the steady state regime, because the number of molecules hitting the surface is equal to the number of molecules escaping from it. The initial decrease of the D$_2$ signal ($0 < t < 125$ s) can be explained as an initial increase in the sticking coefficient of the icy sample. As a consequence of the gradual saturation of the surface after 125 s, the D$_2$ signal into the chamber begins to increase, thereby stressing that a lower number of molecules are sticking on the compact ice film.

Some laboratory experiments (e.g. Palumbo, 2006; Raut et al., 2007) seem to indicate the predominant non-porous nature of interstellar ices.
According to the estimation made by Amiaud et al. (2007), a compact ice layer begins to saturate after an exposure to 0.45 ML of D$_2$ (i.e. $0.45 \times 10^{15}$ mol/cm$^2$). Hence, the flux of the D$_2$ beam is roughly given by

$$\phi_{D_2} = \frac{0.45 \times 10^{15}}{125} \approx 3.6 \times 10^{12} \text{ mol cm}^{-2} \text{ s}^{-1}$$

(2.12)

Usually, rate of molecular dissociation is $\tau_{diss} = 60-80$ % are used, so it is possible to evaluate the atomic flux as follows:

$$4.3 \times 10^{12} \text{ mol cm}^{-2} \text{ s}^{-1} < \phi_D = 2 \times R_{diss} \times \phi_{D_2} < 5.7 \times 10^{12} \text{ mol cm}^{-2} \text{ s}^{-1}$$

(2.13)

where the factor 2 in the equation arises from the fact that the cracking of D$_2$ produces two atoms of D.

### 2.2.4 Calibration of the molecular beams

The calibration of molecular beams has been partially explained in Sec. 2.2.2.4. The technique used to determine the molecular flux was adapted from Kimmel et al. (2001). The molecular flux is calibrated by saturation of the first monolayer of molecules as shown in Figure 2.20 for the case of O$_2$. The method consists of depositing different amounts of O$_2$ (or another molecule) - under identical conditions of flux - on the surface maintained at the same temperature (typically $T_s = 10$ K). In the case of Figure 2.20, molecular oxygen is deposited on a non-porous ASW ice (in this case $T_s = 15$ K). After each deposition the sample is heated up to 55 K and the thermal desorption of O$_2$ is monitored with the QMS. Afterwards, the temperature of the sample is cooled again to 15 K, and the same procedure is repeated by depositing different amounts of O$_2$. With the increase in the doses deposited on the surface, the TPD curves gradually broaden towards lower temperatures. In fact, as the surface coverage increases, the molecules are adsorbed in less tightly bound adsorption sites, namely the desorption temperature $T_{des}$ shifts towards lower temperatures because the desorption energy $E_{des}$ decreases (with peaks growing in height too). When the leading edge of the TPD curves stops shifting towards lower temperatures, it means that all the adsorption sites on the surface are occupied, and any other incoming molecule is adsorbed on top of the first layer of molecules already adsorbed on the surface. In this case TPDs exhibit a 0$^{th}$ order desorption, the maxima of the desorption peaks increase and start shifting towards higher temperatures with increasing doses. The unit of coverage we adopt – the monolayer (ML) – is defined as a single layer of atoms or molecules adsorbed on a surface. Similarly to Figure 2.15, Figure 2.20 shows different TPD spectra obtained by increasing the coverage of O$_2$. The shape of the TPD spectra changes with the coverage and multilayer peaks start to show up when the coverage exceed 1 ML. In these experiments, the first monolayer was...
Figure 2.18: Top panel: schematic top-view and photo of DED method. Bottom panel: DED spectra during D-exposure on O$_2$.

obtained for an exposure time of about 6 minutes and therefore the O$_2$ flux is

$$\phi_{O_2} = \frac{10^{15}}{360} \approx 2.8 \times 10^{12} \text{ mol cm}^{-2} \text{ s}^{-1} \quad (2.14)$$

Here we have shown how O$_2$ monolayer and flux is determined on non-porous ASW ice; the calibration of other molecular species on other substrates follows substantially the same procedure. A particular case is represented by the O$_3$ molecule as described in the next section.

### 2.2.4.1 Determination of O$_3$ monolayer and detection efficiency

When a beam of O$_2$ is used, it is easy to calibrate the flux and understand when the saturation of one ML occurs. This is not the case for deposition of O$_3$. To calibrate one ML of O$_3$, it is necessary to study and evaluate the cracking pattern and the detection efficiency of ozone by the QMS, with respect to the well known O$_2$ detection, as described in Sec. 2.2.2.1. The left panel of Figure 2.21 displays the TPD spectra at mass 32 and 48 between 55 K and 90 K after a deposition of 5 minutes of oxygen atoms on silicate. The two traces exhibit the same shape, namely, the mass-32/mass-48 ratio remains constant (right panel of Fig. 2.21). The two curves are clearly due to the desorption of the same parent molecule (ozone) formed on the substrate. We determined that the mass-32 peak is due to ozone desorption and its fragmentation upon detection. The deposition of ozone from ex-situ synthesis confirms this fact: the amount of desorbing ozone can be monitored either via mass 32 or mass 48. By
Figure 2.19: Background signal of molecular deuterium detected in the chamber by the mass spectrometer during the D\textsubscript{2}-atoms exposure of compact water ice. The D\textsubscript{2} signal is used for the calibration of the molecular beam.

Figure 2.20: (a) Temperature programmed desorption spectra of O\textsubscript{2} from compact non porous ASW. The different O\textsubscript{2} exposures are displayed in the figure. (b) Simulated TPD spectra are over-plotted on the experimental curves.

computing the ratio between the two signals (mass32/mass48) after deposition of different doses, as shown in Figure 2.21 (right panel), a mean value of 1.5 was found. This fact led us to monitor ozone by the signal at mass 32, instead of that at mass 48, to have a better signal-to-noise ratio. We note here that this point explains the difference between conclusions of Jing et al. (2012) and Minissale et al. (2014).

Due to its important dissociative ionization, the ozone detection efficiency has to be determined for every single QMS. Actually, the results of the present work has been obtained during two periods of experiments, when two different QMSs were used. Even though the settings of the two instruments were, at any time, exactly the same, the O\textsubscript{3}/O\textsubscript{2} detection efficiencies found were different up to a factor of 30%. However, all the experimental values presented here were obtained with a constant O\textsubscript{3}/O\textsubscript{2} detection efficiency. It should also be noted that, for this specific molecule (O\textsubscript{3}), any other correction factor among those present in the literature would have been wrong in our case. To estimate the O\textsubscript{3}/O\textsubscript{2} detection efficiency at mass 32, it is necessary to compare the area under the TPD curve of one ML of O\textsubscript{2} and that of one monolayer of O\textsubscript{3}. Therefore, we also needed to determine for what O-exposure time we reached a complete monolayer of ozone. To calibrate the ozone monolayer, we adopted the same first layer-saturation method used for O\textsubscript{2}. To do so, we gradually increased the amount of ozone formed on the surface (via O+O\textsubscript{2} reaction), until the second-layer desorption peak appeared. In fact, the second-layer desorption peak is a clear signature that the first monolayer has been completed and that a new layer is being grown. In Figure 2.22 we show four TPD curves of ozone obtained by increasing the exposure time of oxygen atoms (6, 8, 10, and 12 minutes). The saturation of the first layer corresponds to the red trace (squares),
**Figure 2.21:** Adapted from Minissale et al. 2014a. *Left panel:* Ozone TPD curves at mass 32 and 48 between 55 and 90 K after deposition of 5 minutes of oxygen atoms on silicate held at 10 K. *Right panel:* Ratio of the integrated area of mass 32 and mass 48 TPD peaks (55-90 K) as a function of different doses of oxygen atoms.

**Figure 2.22:** Adapted from Minissale et al. (2014a). Panel a: ozone TPD traces (at mass 32) between 50 and 90 K after four depositions of 6, 8, 10, and 12 minutes of oxygen atoms on silicate held at 10 K (Circles, squares, pentagons, and triangles respectively). Panel b: ozone TPD traces at mass 16, 32, and 48 between 50 and 90 K after deposition of 12 minutes of oxygen atoms on silicate held at 10 K.
and the appearance of the second peak is observed in green (pentagons). The apparent inconsistency between the TPD peak intensity in Figure 2.21 (left panel) and Figure 2.22 is due to different QMS settings. Still, we cannot be certain that the adsorption site densities for ozone and molecular oxygen are the same. If this hypothesis is true, we can finally derive the total detection efficiency ($ef$), by comparing the $O_2$ and $O_3$ monolayer. By applying the derived $ef$ factor, we should find that the number of O atoms desorbed as $O_2$ and $O_3$ are equal to the number of O atoms exposed

$$O(\text{sent}) = O(TPDO_2) + ef \times O(TPDO_3).$$

In the case of efficient chemical desorption, the condition will be the following

$$O(\text{sent}) < O(TPDO_2) + ef \times O(TPDO_3).$$

This subject will be treated in Sec. 4.1.2 and 4.3.

2.2.5 Can reactions occur on gas phase?

In this section we show that all the reactions we study in our experiments are solid-state reaction and they cannot occur on the gas phase. Minissale et al. (2013b) shows that the order of deposition of the species changes the amount of reactants consumed and products formed. In this article we study the $NO_2$ formation via $NO + O_2$ reaction. Three cases are considered:

a. NO deposited on pre-adsorbed $O_2$;

b. NO and $O_2$ co-deposited;

c. $O_2$ deposited on pre-adsorbed NO;

Without going into the details of the reaction (it will be treated extensively in Chapter 5), in all the cases we see $NO_2$ formation. In particular $NO_2(a) > NO_2(b) > NO_2(c)$. We should expect that $NO_2(b) > NO_2(a) \approx NO_2(c)$ if the reactions occur in the gas-phase. Moreover the relation $NO_2(a) > NO_2(c)$ shows that the order of deposition of species and, as consequence, the surface chemistry play the main role in the consumption and formation of species.

Beyond this practical example, we know that in our experiments:

$$Flux_{mol} < 10^{13} \frac{mol}{cm^2 s}$$

and

$$v_{mol} = 5 \times 10^4 cm/s$$

so the density is

$$n_{mol} = \frac{Flux_{mol}}{v_{mol}} = 2 \times 10^8 mol/cm^3$$

The mean free path $\lambda$ will be

$$\lambda_{mol} = \frac{k_B T}{\sqrt{2 \pi d^2 n}} = \frac{1}{\sqrt{2 \pi d^2 n}} \approx 10^5 cm = 1 km$$

where $d$ is the diameter of molecules. The mean free path is 6 order of magnitude larger than the zone of beams interaction (few mm). Moreover interaction of beam molecules with residual gas of the main chambers can be neglected due to UHV conditions (pressure of $10^{-10}$ mbar). To sum up, we can exclude gas phase reactions in our experimental conditions.
Bibliography


2.22 Tanaka, K. and Tanaka, I., *Photoelectron spectra from some autoionizing state of O$_2$ near the ionization threshold*, The Journal of Chemical Physics, Volume 59, p. 5042 (1973)
This chapter presents the model used to explain and describe our experimental results. It is subdivided as follows:

1. Model
   1.1. Initial conditions
   1.2. Flux: $\phi_x$
   1.3. Reaction probability: $r$
   1.4. Diffusion coefficient: $k_{\text{diff}}$
   1.5. Desorption coefficient: $\alpha_{N_x,\text{des}}$

2. From model parameters to physical-chemical quantities
   2.1. Reactivity: reaction probability and activation barrier
   2.2. Mobility: $k_{\text{diff}}$ and surface migration
   2.3. Desorption: desorption probability and binding energy

3.1 Model

In this section, we present the model used to simulate our experiments. The goal of the model is to understand which processes (physical or chemical) occur on the surface by fitting the experimental data.

This model was inspired by the one presented in Katz et al. (1999); we used rate equations (i.e., differential equations) to describe the temporal evolution of a system. The physical chemistry on cold surfaces is modeled by using a rate equation for each state of the system, namely the atomic or molecular species deposited on the surface and the ones formed. Among the processes described in Sec. 1.1 and 1.3, we are interested mainly in diffusion and reactivity (activation barrier for reaction) of the species. Other parameters, i.e., desorption energy of
molecules, are modeled independently as shown in Amiaud et al. (2007) and Noble et al. (2011), and they are not used as a free parameter in this model.

To describe the model, we consider a very simple case, hereafter called model 1. We suppose that a species, called \( N_1 \), is deposited on a surface; \( N_1 \) can diffuse on the surface and react with another \( N_1 \) to form \( N_2 \)

\[
N_1 + N_1 \rightarrow N_2. \tag{3.1}
\]

We suppose that \( N_2 \) is formed only on the surface, that is an inert species and it cannot react either with \( N_1 \) or another \( N_2 \). To simulate this condition we will use a set of two rate equations, one for \( N_1 \)

\[
\frac{dN_1}{dt} = \phi_1 - 2 r_{ER} \phi_1 N_1 - 4 r_{LH} k_{diff} N_1^2 - \alpha_{N_1 \text{des}} N_1 \tag{3.2}
\]

and, similarly, one equation for \( N_2 \)

\[
\frac{dN_2}{dt} = \phi_2 + r_{ER} \phi_1 N_1 + 2 r_{LH} k_{diff} N_1^2 - \alpha_{N_2 \text{des}} N_2 \tag{3.3}
\]

On the left side of the equations we find the evolution over the time of the surface population of each species. Here, we stress that \( N_x \) is a dimensionless term, and it indicates the fraction of surface covered by the species \( x \). Figure 3.1 shows four different cases: two in which the surface is covered with \( N_1 \) or \( N_2 \) and another two in which both the species are on the surface in different ratios. \( N_x \) can be multiplied by the surface density of adsorption sites of the considered surface to move from a dimensionless to a dimensional quantity; in example, if a surface contains \( 10^{15} \) sites per cm\(^2\), a value for \( N_x \) of 0.5 means that \( 5 \times 10^{14} \) molecules per cm\(^2\) are present on the surface. The surface population of each species varies depending on the terms of the right side of Eq. 3.2 and 3.3 where we find positive terms, i.e., accretion from the gas phase (\( \phi_x \)) or formation of new species (\( r_{ER} \phi_1 N_1 + r_{LH} k_{diff} N_1^2 \)), and negative terms, i.e., consumption of the reactive species (\( -2 r_{ER} \phi_1 N_1 - 4 r_{LH} k_{diff} N_1^2 \)), or desorption into the gas phase (\( \alpha_{N_x \text{des}} N_x \)). Clearly, each of these terms will depend in a different way on the surface density:

1. **Accretion from the gas phase:** this term is independent, or almost independent, on surface population. It is governed by \( \phi_x \) (in s\(^{-1}\)) that represents the fraction of surface covered each second by the incoming species. It is obtained by normalizing the flux
(described in subSecs 2.2.4 and 2.2.3) with respect to the site density of the surface. $\phi_x$ is an experimental parameter because it can be tuned experimentally and it is a constant parameter in the model. $\phi_x$ fulfills the following conservation law

$$N_x(t_f) = \int_0^{t_f} \frac{dN_x}{dt} = \int_0^{t_f} \phi_x = 1$$

(3.4)

where $N_x$ is an inert species and $t_f$ is the time to cover all the surface with $N_x$.

2. **Molecular formation (and consumption)**: this term depends strongly on the surface population of reactants. A reaction should consume more than one reactant, and the stoichiometric number accounts for this number, defined as positive for the products (molecular formation) and negative for the reactants (molecular consumption). Molecular formation (and consumption) is governed by the $r_{ER}$ if the reaction occurs via ER mechanism and by $r_{LH} k_{diff}$ if the reaction occurs via the LH mechanism. $r_{ER}$ and $r_{LH}$ are the reaction probabilities ranging between 0 and 1; $k_{diff}$ (in $s^{-1}$) is the diffusion coefficient and represents the fraction of surface scanned per second by a particle. By dividing by the density of the sites we can find the diffusion coefficient in the usual units, i.e., cm$^2$s$^{-1}$.

3. **Desorption into gas phase**: this term depends on the surface population of the reactants. The desorption into the gas phase is governed by $\alpha N_{des}$ that is the rate constant for desorption. It is called additional parameter because it is obtained by using different models (see Amiaud et al 2007 and Noble et al 2011) and it is a constant in the model.

By rewriting Eq.3.2

$$\frac{dN_1}{dt} = \frac{\phi_1}{\text{experimental parameter}} - 2 \frac{r_{ER}}{\text{model parameter}} \phi_1 N_1 - 4 \frac{r_{LH} k_{diff}}{\text{model parameters}} N_1^2 - \alpha N_{des} N_1$$

(3.5)

we note that the parameters of the model are essentially three: $r_{ER}$, $r_{LH}$, and $k_{diff}$. Through a fine-tuning of these parameters, the solution of Eq.3.2 has to converge to the following final condition

$$N_1(t_f) = N_1 \text{ (amount measured in the experiments)},$$

(3.6)

starting from the initial conditions of our experiments

$$N_1(0) = \text{experimental conditions at t=0.}$$

(3.7)

This point will be discussed in Sec. 3.1.2. Below we recap the key points of the model:

- $dN_1/dt$ is the variation of the surface population of $N_1$; it depends on the terms on the right side as well as on its initial conditions (see Sec. 3.1.1).

- $\phi_x$ represents the flux of the particles accreting from the gas phase. It induces an increase of surface population (see Sec. 3.1.2).

- $r_{ER}$ and $r_{LH}$ represents the reaction probabilities of ER and LH, respectively; they are two of the free parameters. The role of the reaction probability is discussed in Sec. 3.1.3.

- $k_{diff}$ represents the diffusion coefficient. It is the third free parameter of the model and its role is discussed in Sec. 3.1.4.

- $\alpha N_{des}$ represents the desorption coefficient. It is an additional parameter and it is tuned using different models as discussed in Sec. 3.1.5.
3.1.1 Initial condition

To simulate the physical-chemical conditions present in our experiments, we can play with the initial conditions of the differential equations. Some experiments are performed by sending a species, i.e. $N_1$, on the top of another pre-adsorbed species, i.e. $N_2$. The experimental initial conditions, and as a consequence the model initial conditions, can lead to very different results, depending on the reactivity of the species. A practical application on this point is discussed in Sec. 5.2.1. The upper part of Figure 3.2 shows three different initial conditions:

- **a** $N_1(0)=0$ and $N_2(0)=0$ (Nothing on the surface);
- **b** $N_1(0)=1$ and $N_2(0)=0$ (Surface entirely covered with $N_1$);
- **c** $N_1(0)=0$ and $N_2(0)=0.5$ (Half of the surface covered with $N_2$).

![Figure 3.2](image)

**Figure 3.2:** Schematic view of the initial coverages and results of *model 1* for three different initial conditions: blue curves, $N_1(0)=0$ and $N_2(0)=0$; green curves, $N_1(0)=1$ and $N_2(0)=0$; red curves, $N_1(0)=0$ and $N_2(0)=0.5$. The plot shows the surface populations of $N_1$ (solid lines) and $N_2$ (dashed lines) as a function of $N_1$ exposure. All other parameters are fixed, see text. The blue and red solid curves are identical and they have been offset in the figure for the sake of clarity.

The plot of Figure 3.2 shows the results obtained using *model 1* for three different initial conditions. The surface population (the coverage) evolution of the species is plotted as a function of $N_1$ exposure. Both exposure and coverage are dimensionless quantities, and they vary between 0 and 1. This value corresponds to the fraction of the surface covered with the species coming from the gas phase. In order to give a dimension (namely MonoLayer) to both exposure and coverage, the fraction of the surface covered has to be multiplied by the surface density of the sites. In the lower part of Figure 3.2 $N_1$ and $N_2$ coverages are
represented with solid and dashed lines respectively. In the model, all the parameters (fluxes, reaction probability, diffusion coefficients, and desorption rates) are fixed. In particular, $N_1$ flux is 1, $N_2$ flux is 0, the reaction probabilities are 0.5, the diffusion desorption coefficients are 0. In this case the reactions can occur only via ER; as discussed before, the non-mobility of reaction partners is a limiting factor for the LH mechanism.

The first set of initial conditions simulates an experiment in which species are sent onto a bare surface; the second and third ones simulate experiments in which species are sent on a surface entirely or partially covered with $N_1$ and $N_2$ layers, respectively. We note in Figure 3.2 that the $N_1$ curves for the first and the third set of initial conditions are identical (they have been offset in the figure for the sake of clarity). Actually, the difference of $N_2$ initial conditions does not affect the surface-population evolution of $N_1$. The $N_2$ initial conditions cause a shift for $N_2$ population (blue and red dashed lines). On the other hand, $N_1$ initial conditions strongly affect the evolution of $N_1$ and $N_2$ surface population. In fact the presence of a pre-deposited $N_1$, due to ER mechanism, favors a quick $N_2$ formation (dashed green line) and $N_1$ consumption (solid green line). In conclusion the initial conditions allow to simulate experiments in which

a species are sent onto a bare (or non-reactive) surface or

b species are sent on the top of a pre-adsorbed species.

3.1.2 Flux: $\phi_x$

Similarly to the initial conditions of the differential equations, we can vary the incoming fluxes of the species, the so called experimental parameter. The upper part of Figure 3.3 shows three different examples of fluxes:

1. $\Phi(N_1(t))=1$ and $\Phi(N_2(t))=0$;
2. $\Phi(N_1(t))=0.5$ and $\Phi(N_2(t))=0.5$ (co-deposition experiment);
3. $\Phi(N_1(t))=0$ and $\Phi(N_2(t))=1$.

We stress here that the fluxes of the species are constant in our experiments and for this reason we keep $\Phi_x$ constant in the model. The first set of fluxes simulates an experiment in which only $N_1$ arrives from the gas phase and $N_2$ is only formed on the surface. The second set of fluxes simulates an experiment in which both $N_1$ and $N_2$ arrive from the gas phase, the species are co-deposited using the two beamlines (see Sec. 2.1.2). Finally, the third set of fluxes simulates an experiment in which only $N_2$ arrives from the gas phase. The lower part of Figure 3.3 shows the results obtained using model 1 for the three cases. The surface-population evolution of the species is plotted as a function of the exposure of $N_1$ and/or of $N_2$ (sent on the surface). $N_1$ and $N_2$ are represented with solid and dashed lines respectively. In the model, all other parameters (initial conditions, reaction probability, diffusion and desorption coefficients) are fixed. In particular, $N_1(0) = 0, N_2(0) = 0$, the reaction probability is 0.5, the diffusion and desorption coefficients are 0. The flux change allows to simulate experiments in which

1. species are co-deposited on the surface or
2. species are subsequently deposited on the surface;
3. the flux changes in a set of experiments.

We remark that we keep the flux constant since in our experiments $\Phi_x$ does not vary except for a few %. There is nothing, of course, that prevents anyone from using a time dependent flux provided that the conservation law (Eq.3.4) is satisfied.
3.1.3 Reaction probability: $r$

The most important parameter describing the chemistry of a system in our model is the reaction probability. It indicates if a reaction can occur on the surface. It ranges between 0 and 1. In Sec. 3.2, we will explain how this parameter is linked to the energetic parameter, namely the activation energy to overcome the reaction barrier. In the model, we usually distinguish between ER and LH reaction probabilities. For the sake of simplicity, we set here $k_{diff}=0 \text{ s}^{-1}$, and LH has not influence on model results. In this way, we can show how a change in the reaction probability (in this case $r_{ER}$) affects the model results.

Figure 3.3 shows the results obtained using model 1 for five different values of $r_{ER}$: 0, 0.1, 0.2, 0.5, and 1. The surface population of $N_1$ and $N_2$ is plotted as a function of the $N_1$ exposure. $N_1$ and $N_2$ are represented with solid and dashed lines, respectively. In the model, all other parameters (initial conditions, fluxes, diffusion desorption coefficients) are fixed. In particular, $N_1(0) = 0, N_2(0) = 0, \Phi(N_1) = 1, \Phi(N_2) = 0$, the diffusion and desorption coefficients are $0 \text{ s}^{-1}$.

The case $r_{ER}=0$ is a trivial case: $N_2$ formation has a probability equal to zero and its surface population is zero at anytime; the only process that can occur is the adsorption of $N_1$ and its surface population increases linearly. On the contrary, a value of 1 for $r_{ER}$ means that whenever a $N_1$ meets another $N_1$, a $N_2$ is formed. $N_2$ formation depends on the surface population of $N_1$; in fact, the probability for a $N_1$ to find another $N_1$ increases as a function of coverage. This means that $N_1$ (and $N_2$) is consumed (and formed) more rapidly at high

---

Figure 3.3: Schematic view of the incoming fluxes of species and results of model 1 for three different types of fluxes: blue curves $\Phi(N_1(t))=1$ and $\Phi(N_2(t))=0$; green curves $\Phi(N_1(t))=0.5$ and $\Phi(N_2(t))=0.5$; red curves $\Phi(N_1(t))=0$ and $\Phi(N_2(t))=1$. The surface populations of $N_1$ (solid lines) and $N_2$ (dashed lines) are plotted as a function of the $N_1+N_2$ exposure. All other parameters are fixed, see text.
Figure 3.4: Results of model 1 for five different values of $r_{ER}$: 0, 0.1, 0.2, 0.5, and 1. The surface populations of $N_1$ (solid lines) and $N_2$ (dashed lines) are plotted as a function of the $N_1$ exposure. All other parameters are fixed, see text.

coverage, i.e. green curves in Figure 3.4.

3.1.4 Diffusion coefficient: $k_{diff}$

$k_{diff}$ is the parameter describing the mobility of the species on the surface. We remind that $k_{diff}$ represents the fraction of surface scanned each second by a particle. We can find the diffusion coefficient into the usual units, cm$^2$s$^{-1}$, by dividing for the density of sites. The mobility helps the meeting of species and, as a consequence, it increases the reaction rate. The mobility is strictly connected to the LH mechanism, and it is the main limiting step for this mechanism if $r_{LH} \neq 0$. For example, a $k_{diff}=0$ s$^{-1}$ totally hinders LH. Figure 3.5 shows the results obtained using model 1 for six different values of $k_{diff}$: 0, 1, 2, 10, 20, and 100 s$^{-1}$. As usual, the surface populations of $N_1$ and $N_2$ is plotted as a function of the $N_1$ exposure. $N_1$ and $N_2$ are represented with solid and dashed lines respectively. In the model, all other parameters (initial conditions, fluxes, reaction probabilities, and desorption rates) are fixed. In particular, $N_1(0) = 0$, $N_2(0) = 0$, $\Phi(N_1) = 1$, $\Phi(N_2) = 0$, $r_{ER,LH} = 0.5$, and the desorption coefficients are 0.
We stress that only \( N_1 \) can be mobile, while \( k_{\text{diff}} \neq 0 \) for \( N_2 \) would not produce any difference in the results, since \( N_2 \) is an inert species. The results of Figure 3.5 could be summarized with this statement: the higher the mobility, the easier \( N_1 \) is consumed and \( N_2 \) formed. \( N_2 \) formation does not only depend on the surface population of \( N_1 \) (i.e. the probability of a \( N_1 \) to knock another pre-adsorbed \( N_1 \)), but also on diffusion properties of \( N_1 \):

\[
P(\text{reaction}) = P_{\text{ER}}(\text{Surface population}) + P_{\text{LH}}(\text{Surface population, diffusion}).
\]

Mobility opens another reaction route (LH mechanism) with respect to the case of \( k_{\text{diff}} = 0 \), especially at low coverages. In the model, we can distinguish between \( N_2 \) formed via the ER or the LH mechanism. Table 3.1 and Figure 3.6 show the individual contributions in percentage to \( N_2 \) formation by ER (solid lines) and LH (dashed lines) as a function of coverage. The results are obtained using four different values of \( k_{\text{diff}} \): 0.01, 0.1, 1, and 10 \( \text{s}^{-1} \). At left of Figure 3.6 we notice that the point in which LH becomes more efficient than ER shifts to low coverage as the \( k_{\text{diff}} \) increases. Actually, depending on \( k_{\text{diff}} \), there will be a critical surface population \( (N_{1-\text{critic}}) \) for which LH is able to consume efficiently \( N_1 \). \( N_{1-\text{critic}} \) can be roughly evaluated through the ER and LH ratio

\[
\frac{2r_{\text{ER}} \phi_1 N_1}{4r_{\text{LH}} k_{\text{diff}} N_2^2} \leq 1
\]

that, in the simplistic hypothesis that \( r_{\text{ER}} = r_{\text{LH}} \), becomes,

\[
\frac{1}{2k_{\text{diff}} N_1} \leq 1 \Rightarrow N_{1-\text{critic}} = \frac{1}{2k_{\text{diff}}}
\]

For example, if \( k_{\text{diff}} = 1 \text{s}^{-1} \), a surface population higher than 0.5 will make LH more efficient than ER; if \( k_{\text{diff}} = 2 \text{s}^{-1} \), a surface population higher than 0.25 will make LH more efficient than ER, and so on. Moreover, we see that after this critic surface population the ratio ER over LH reaches a steady state, as shown by colored text in Table 3.1. Here again, the value of the ratio at the steady state depends on the value of \( k_{\text{diff}} \) (see right side of Figure 3.6).

Table 3.1: Amounts expressed in percentage of the species produced via ER and LH for four different values of \( k_{\text{diff}} \) (expressed in \( \text{s}^{-1} \)) as a function of exposure. In red the critic surface population for steady state of the ER-to-LH ratio.

<table>
<thead>
<tr>
<th>Exposure</th>
<th>( k_{\text{diff}}=0.01 )</th>
<th>( k_{\text{diff}}=0.1 )</th>
<th>( k_{\text{diff}}=1 )</th>
<th>( k_{\text{diff}}=10 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ER</td>
<td>LH</td>
<td>ER</td>
<td>LH</td>
</tr>
<tr>
<td>0</td>
<td>99.8</td>
<td>0.2</td>
<td>98.7</td>
<td>1.3</td>
</tr>
<tr>
<td>0.05</td>
<td>77</td>
<td>23</td>
<td>63.4</td>
<td>36.6</td>
</tr>
<tr>
<td>0.1</td>
<td>57.2</td>
<td>42.8</td>
<td>63.2</td>
<td>36.8</td>
</tr>
<tr>
<td>0.2</td>
<td>31.9</td>
<td>68.1</td>
<td>57.2</td>
<td>42.8</td>
</tr>
<tr>
<td>0.3</td>
<td>26.1</td>
<td>73.9</td>
<td>31.9</td>
<td>68.1</td>
</tr>
<tr>
<td>0.5</td>
<td>46.8</td>
<td>53.2</td>
<td>46.8</td>
<td>53.2</td>
</tr>
<tr>
<td>0.75</td>
<td>44.2</td>
<td>55.8</td>
<td>44.2</td>
<td>55.8</td>
</tr>
<tr>
<td>1</td>
<td>44.1</td>
<td>55.9</td>
<td>44.1</td>
<td>55.9</td>
</tr>
</tbody>
</table>

Up to now, we have shown how a different \( k_{\text{diff}} \) affects the results as a function of coverage. As discussed in Sec. 1.1.4 the mobility of species changes as a function of temperature. For this reason, in Figure 3.7 we show the individual contributions to \( N_2 \) formation by ER or LH mechanism for four different behaviors of \( k_{\text{diff}}(T_s) \). The laws used for \( k_{\text{diff}}(T_s) \) in Figure 3.7 are

1. \( k_{\text{diff}}(T_s) = k_0 T_s/T_{\text{ref}} \) (black curves),
2. \( k_{\text{diff}}(T_s) = k_0 T_s^3/T_{\text{ref}}^3 \) (red curves),
3. \( k_{\text{diff}}(T_s) = k_0 T_s^4/T_{\text{ref}}^4 \) (blue curves),
Figure 3.6: Individual contributions expressed in coverage (a) and percentage (b) to N$_2$ formation by ER (solid lines) and LH (dashed lines) as a function of exposure. Results of model 1 are obtained for four different values of $k_{diff}$: 0.01, 0.1, 1, and 10 s$^{-1}$.

4. $k_{diff}(T_s) = k_0 \times \exp(-T_{ref}/T_s)$ (green curves),

where $T_{ref}$ is a reference temperature (in this case 10 K) and $k_0$ the diffusion at $T_{ref}$. It must be noted that we have chosen the laws for $k_{diff}(T_s)$ without a particular physical reason. Table 3.2 shows the initial and final value of $k_{diff}$ for the different laws used. From Figure 3.7 we see that N$_2$ formation via LH mechanism increases between 6 and 40 K because of the increase of $k_{diff}$; after 30 K, the main part (> 95%) of N$_2$ is formed via LH as visible in (c) panel in Figure 3.7. On the other hand, the ER contribution decreases as a function of temperature, and the ER contribution arrives at zero in the case of red and blue curves. Here we do not add the information about the desorption temperature, discussed in the following section. In principle, what we can expect is that at higher surface temperatures both ER and LH start to be inefficient because of the desorption of N$_1$ and the decrease of the residence time of species on the surface, thus the N$_2$ production efficiency by this mechanism drops off.

We note here that the three potential laws have, at 10 K, the same value for $k_{diff}$ and in fact the three lines (black, red, and blue) cross at 10 K. We postpone to Sec. 5.3.1 a practical application of this issue (Minissale et al. 2013).

3.1.5 Desorption coefficient: $\alpha_{N_1des}$

The last parameter that we can vary in our model is the desorption coefficient. Figure 3.8 shows the results obtained using model 1 for five different values of $\alpha_{N_1des}$ (in the (a) panel) and $\alpha_{N_2des}$ (in the (b) panel): 0, 0.1, 1, 10, and 100 s$^{-1}$. The evolutions of surface population of N$_1$ and N$_2$ are plotted as a function of N$_1$ coverage. N$_1$ and N$_2$ are represented with solid and dashed lines respectively. In the model, all other parameters (initial conditions, fluxes, reaction probability, diffusion coefficients) are fixed. In particular, $N_1(0) = 0$, $N_2(0) = 0$, $\Phi(N_1) = 1$, $\Phi(N_2) = 0$, the diffusion coefficients are 0 s$^{-1}$. $\alpha_{N_1des}$ and $\alpha_{N_2des}$ are zero in the (b) and (a) panels, respectively. The variation of $\alpha_{N_1des}$ has influence on the surface population of both species; it induces N$_1$ desorption and the lack of N$_1$ prevents the formation of N$_2$. We see from left panel of
Figure 3.7: Model results showing the contribution to $N_2$ formation by either ER (solid lines) or LH (dashed lines) mechanism as a function of temperature for four different laws as described in the text. Contributions to $N_2$ formation are expressed as normalized coverage in the (a) panel, and as percentage in the (b) (ER contribution) and (c) panels (LH contribution).

Figure 3.8 that $N_1$ surface population reaches a steady state

$$\frac{dN_1}{d\theta} = 0 \Rightarrow \phi_1 = 2 \phi_1 r_{ER} N_1 + \alpha_{N_1\text{des}} N_1$$

(3.11)

meaning that the amount of $N_1$ particles arriving from the gas phase is equal to the amount of particles consumed and desorbed. This condition will be satisfied at different coverages depending on the value of $\alpha_{N_1\text{des}}$; increasing the value of $\alpha_{N_1\text{des}}$, the steady state shifts toward low coverage. Moreover, we can evaluate the value of $N_1$(steady state) through the following equation

$$N_1(\text{steady state}) = \frac{\phi_1}{2 \phi_1 r_{ER} + \alpha_{N_1\text{des}}}.$$  

(3.12)

So, the higher the $\alpha_{N_1\text{des}}$ value, the smaller is $N_1$(steady state). The variation of $\alpha_{N_2\text{des}}$

Figure 3.8: Results of model 1 for five different values of $\alpha_{N_1\text{des}}$ ((a) panel) and $\alpha_{N_2\text{des}}$(b) panel): 0, 0.1, 1, 10, and 100 s$^{-1}$. The surface population evolutions of $N_1$ (solid lines) and $N_2$ (dashed lines) are plotted as a function of $N_1$ exposure. All other parameters are fixed, see text.

affects only the $N_2$ surface population. In the case $\alpha_{N_2\text{des}}=10$ or 100 at high coverage this condition is satisfied

$$\frac{dN_2}{d\theta} \approx 0 \Rightarrow \phi_2 + 2 \phi_1 r_{ER} N_1 \approx \alpha_{N_2\text{des}} N_2;$$

(3.13)

we can evaluate the $N_2$ surface population at steady state through the following

$$N_2(\text{ss}) \approx \frac{\phi_2 + 2 \phi_1 r_{ER} N_1}{\alpha_{N_2\text{des}}}$$

(3.14)
and in the case of $\alpha_{N_1,des} \neq 0$, we can substitute $N_1$ by Eq. 3.12

$$N_2(\text{ss}) \approx \frac{\phi_2}{\alpha_{N_2,des}} + \frac{2 \phi_1^2 r_{ER}}{\alpha_{N_2,des}(2 \phi_1 r_{ER}) + \alpha_{N_1,des}}. \quad (3.15)$$

Here the first term depends on the ratio between flux and desorption of $N_2$, the second one depends mainly on the reaction probability. Clearly, $N_2$ does not reach the steady state and increases indefinitely if $\alpha_{N_2,des} = 0$. The evaluation of surface populations of $N_1$ and $N_2$ is more complex in the case $k_{diff} \neq 0$ for $N_1$. We will have, for $N_1$:

$$N_1(\text{ss}) = -\frac{(2 \phi_1 r_{ER} + \alpha_{N_1,des}) + \sqrt{(2 \phi_1 r_{ER} + \alpha_{N_1,des})^2 - 4 \phi_1 k_{diff} r_{LH}}}{8 k_{diff} r_{LH}} \quad (3.16)$$

and, for $N_2$:

$$N_2(\text{ss}) = \frac{\phi_2 + \phi_1 r_{ER} N_1 + 2k_{diff} r_{LH} N_2^2}{\alpha_{N_2,des}} \quad (3.17)$$

We can notice from these two last equations that $k_{diff}$ plays the main role in the steady state values of $N_1$: the higher $k_{diff}$, the lower $N_1$.

### 3.1.6 Conclusion

In this section we have presented the model used to simulate our experiments. The goal of the model is to describe the temporal evolution of the surface populations of the species adsorbed and formed on the cold surface. In the model a rate equation is used for each species. The solution of this rate equation converge to our experimental observables, namely the surface densities of the species deposited and/or formed at the end of each deposition. Each process (i.e. reactivity, diffusion, desorption) is described through a single parameter; an opportune variation of the full set of parameters is able to reproduce our data. In particular, we can vary the following parameters:

1. the initial conditions and the fluxes to describe different experimental procedures and methods;
2. $r_{ER,LH}$ to change the reactivity through the ER and LH mechanisms, these terms are surface temperature independent;
3. $k_{diff}$ to change the diffusion coefficient, this term depends strongly on the surface temperature and it is able to increase the reactivity (through LH);
4. $\alpha_{N_1,des}$ to change the desorption coefficient, this term depends strongly on the surface temperature and it is able to change considerably the surface population of a species.

In conclusion we have to remark that an important condition to find values of a good parameter is that the number of observables is greater than the number of parameters, namely the surface processes. In case this condition is not satisfied, we are not able to give a precise value of the parameter, but only a range of possible values; nonetheless, physical-chemical considerations can railroad, case by case, the parameters. Some practical cases are presented in Chapter 4 and Chapter 5.

### 3.2 From model parameters to physical-chemical quantities

In the previous section, we have discussed the different parameters that can be tuned to fit our experimental data. In this section, we explain how these parameters are linked to physical-chemical quantities.
3.2.1 Reactivity: reaction probability and activation barrier

The two reaction probabilities \( r_{ER} \) and \( r_{LH} \) give the probability that a reaction occurs, thus they have the same physical meaning and can be used to evaluate other physical quantities, namely the activation barrier, discussed in subSec. 1.2.2. By inverting a normalized Arrhenius equation the desorption energy \( E_a \) can be calculated as follows:

\[
E_a = -k_b T_{eff} \ln(r_{ER,LH})
\]  

(3.18)

where \( k_b T_{eff} \) is the energy of the considered system (hereafter, for the sake of simplicity, the \( k_b \) constant will be omitted). In collision theory, this law is derived by considering gas phase particles described through a Maxwell-Boltzmann energy distribution, and assuming that the interactions between the reactants can occur only via head-on collisions (see Atkins&DePaula 2006). For ER reactions, the use of Eq. 3.18 is plausible because the interactions occur between a particle coming from the gas phase (MB(T\(_{gas}\))) and a particle thermalized with the surface MB(T\(_{solid}\)). In this case, somehow similarly to gas phase reactions, the impinging molecules either collide and react with one adsorbate or have enough energy to hop on the surface before thermalizing and accommodating in an empty adsorption site. Gas phase molecules coming from the beam are at around T\(_{gas}\) = 300 ± 20 K while the target particles adsorbed on the substrate are thermalized with the surface at T\(_{solid}\) = 10-60 K. The temperature in Eq. 3.18 represents the average molecular (atomic) kinetic energy \( \bar{E} \) in a gas at thermodynamic equilibrium. \( \bar{E} \) is proportional to the thermodynamic temperature. The problem is to know the exact temperature \( T_{eff} \) to insert in Eq. 3.18.

3.2.1.1 \( T_{eff} \) evaluation

The molecules in a gas at ordinary temperatures (i.e., at room temperature) can be considered to be in ceaseless, random motion at high speeds. The average translational kinetic energy for these molecules can be deduced from the Boltzmann distribution. In a gas at the temperature T\(_{gas}\), it can be expressed for one molecule by the following equations,

\[
\frac{1}{2} m_x v_x^2 = \frac{1}{2} k_b T_{gas} \Rightarrow v_x^2 = \frac{k_b T_{gas}}{m_x},
\]

(3.19)

where \( v_x \) and \( m_x \) are velocity and mass of the particle \( x \), \( k_b \) is the Boltzmann constant.

The conditions present in our experiments are just a little bit more complex. In model 1 the reactions can occur between two N\(_1\) particles. We can consider the N\(_1\)+N\(_1\) system as a two-body problem. We define the reduced mass - the effective inertial mass of the system - as follows

\[
m \rightarrow \mu = \frac{1}{m_1} + \frac{1}{m_2} = \frac{m_1 \cdot m_2}{m_1 + m_2},
\]

(3.20)

and the relative velocity

\[
\vec{v} = \vec{v}_1 - \vec{v}_2,
\]

(3.21)

by taking the square of the relative velocity and by doing the average we obtain

\[
\langle v^2 \rangle = \langle v_1^2 \rangle + \langle v_2^2 \rangle - \langle 2 \vec{v}_1 \cdot \vec{v}_2 \rangle = \langle v_1^2 \rangle + \langle v_2^2 \rangle - 0,
\]

(3.22)

where \( \langle 2 \vec{v}_1 \cdot \vec{v}_2 \rangle = 0 \) because of the isotropy of \( \vec{v}_2 \).

In the simplest case \( m_1 = m_2 \) and all the particles are at T\(_{gas}\) through the equation below

\[
\frac{1}{2} k_b T_{eff} = \frac{1}{2} \mu v^2 = \frac{1}{2} k_b \mu \left( \frac{T_{gas}}{m_1} + \frac{T_{gas}}{m_1} \right) = \frac{1}{2} k_b \mu \left( \frac{2T_{gas}}{m_1} \right) = \frac{1}{2} k_b \mu \left( \frac{2T_{gas}}{m_1} \right)
\]

(3.23)

it is possible to find the effective temperature of the molecules

\[
T_{eff} = T_{gas}.
\]

(3.24)
To generalize our evaluation of $T_{\text{eff}}$ let us consider the following reaction

$$A + B \rightarrow C$$

where $A$ and $B$ are at different temperatures during the reaction

$$\begin{cases} 
B \text{ on adsorbed } A \Rightarrow T_A = T_{\text{solid}} \neq T_{\text{gas}} = T_B \\
A \text{ on adsorbed } B \Rightarrow T_B = T_{\text{solid}} \neq T_{\text{gas}} = T_A,
\end{cases}$$

we will have a reduced mass of

$$\mu = \frac{m_A \ast m_B}{m_A + m_B},$$

then, in the case of $A$ adsorbed and $B$ arriving from the gas phase,

$$\begin{cases} 
\frac{1}{2} m_A v_A^2 = \frac{1}{2} k_b T_{\text{solid}} \Rightarrow v_A^2 = \frac{k_b T_{\text{solid}}}{m_A} \\
\frac{1}{2} m_B v_B^2 = \frac{1}{2} k_b T_{\text{gas}} \Rightarrow v_B^2 = \frac{k_b T_{\text{gas}}}{m_B},
\end{cases}$$

or, in the case of $B$ adsorbed and $A$ from gas phase,

$$\begin{cases} 
\frac{1}{2} m_A v_A^2 = \frac{1}{2} k_b T_{\text{gas}} \Rightarrow v_A^2 = \frac{k_b T_{\text{gas}}}{m_A} \\
\frac{1}{2} m_B v_B^2 = \frac{1}{2} k_b T_{\text{solid}} \Rightarrow v_B^2 = \frac{k_b T_{\text{solid}}}{m_B},
\end{cases}$$

and so

$$\frac{1}{2} k_b T_{1_{\text{eff}}} = \frac{1}{2} \mu v^2 = \frac{1}{2} k_b \mu \left( \frac{T_{\text{solid}}}{m_A} + \frac{T_{\text{gas}}}{m_B} \right), \quad (3.25)$$

$$\frac{1}{2} k_b T_{2_{\text{eff}}} = \frac{1}{2} \mu v^2 = \frac{1}{2} k_b \mu \left( \frac{T_{\text{gas}}}{m_A} + \frac{T_{\text{solid}}}{m_B} \right). \quad (3.26)$$

From these equations, by using $T_{\text{solid}}=25 \text{ K}$, $T_{\text{gas}}=300 \text{ K}$, $m_A=10$, and $m_B=20$ we obtain

$$T_{\text{BonA}} = \mu \left( \frac{T_{\text{solid}}}{m_A} + \frac{T_{\text{gas}}}{m_B} \right) = 208 \text{ K},$$

$$T_{\text{AonB}} = \mu \left( \frac{T_{\text{gas}}}{m_A} + \frac{T_{\text{solid}}}{m_B} \right) = 116 \text{ K}.$$ 

These two $T_{\text{eff}}$ can be used to find a lower and an upper limit for the activation barrier. Moreover, we note that the two reactions $A_{\text{gas}} + B_{\text{solid}}$ and $B_{\text{gas}} + A_{\text{solid}}$ could not have the same probability to occur at different temperatures due to a different residence time on the surface and diffusion coefficient of $A$ and $B$ or strong concurrence with other reactions, for example, $A + A$. These considerations lead us to give a range of values of the activation barrier, rather than an exact value (see Minissale et al. 2013 for a practical application).

### 3.2.2 Mobility: $k_{\text{diff}}$ and surface migration

Here we will focus on the diffusion coefficient $k_{\text{diff}}$ and its physical meaning. In our model, $k_{\text{diff}}$ is treated as a free numerical parameter that simulates the surface migration of the species on the surface. The resulting $k_{\text{diff}}$ values can be used to find the diffusion rate at given temperatures; as already said in subSec. 1.1.4 the different techniques used and the possibility that several surface diffusion mechanisms may be operative can influence the quantitative parameters (in this case $k_{\text{diff}}$) describing the surface diffusion rate. The main issue here is that no information can be inferred about the nature of the diffusive process. The problem can be inverted by using the temperature dependence of $k_{\text{diff}}$ to know what my be the type of the diffusive process. As we have shown in Congiu et al. (2014), diffusion coefficient $k_{\text{diff}}$ vs $T_s$ can be displayed in several ways according to the law used to describe them. For example $k_{\text{diff}}$ may follow
a an empirical law built for fitting the experimental values;
b an Arrhenius-law form, with an activation energy $E_{\text{diff}}$ free to vary;
c a quantum-tunnelling form with a given width and height of the barrier;

A detailed analytical or numerical solution of the dependence of $k_{\text{diff}}$ with $T_s$ can help have some insight into the physical nature of the diffusive process at play. In Chapter 4 we will describe how these argumentations are used to infer the diffusive process of oxygen atoms.

Moreover, beyond the mechanism at play, we stress here that in our model $k_{\text{diff}}$ has the $s^{-1}$ dimension which can be converted into the usual unit cm$^2$ s$^{-1}$ by dividing by the surface density of sites, i.e. $10^{15}$ molecules cm$^{-2} = 1$ ML.

3.2.3 Desorption: desorption probability and binding energy

$\alpha_{N_x\text{des}}$ are the desorption coefficients. In subSec. 1.1.3 we have already presented the theory of thermal desorption. The desorption coefficients are simply the inverse of the residence time. In particular, for $N_x$ the desorption coefficient is

$$\alpha_{N_x\text{des}}(\theta) = \nu_0 \exp\left(-\int \frac{E_b(\theta)}{k_B T} \right)$$

(3.27)

where the $\int E_b(\theta)$ represents the distribution of all the possible binding energies for $N_x$ on a given surface. In fact, as we will see in the next chapter, with the increase in the doses deposited on the surface, the molecules are adsorbed in less tightly bound adsorption sites. In other words, $E_b$ is not a unique value, but a distribution of energies depending on surface-adatom bonds. By multiplying the desorption coefficient by the coverage, we can obtain the desorption rate as follow

$$r_{\text{des}} = -\frac{dN_x}{dt} = \nu_0 \exp\left(-\int \frac{E_b(\theta)}{k_B T} \right) \cdot \theta^n$$

(3.28)

We present a practical example of binding energies evaluation in Sec. 4.2

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There is no quantum world.
There is only an abstract quantum physical description.
It is wrong to think that the task of physics is to find out how nature is.
Physics concerns what we can say about nature.

“The philosophy of Niels Bohr”,
Niels Bohr

Fernanda, en cambio, lo buscó [el anillo] únicamente en los trayectos de su itinerario cotidiano,
sin saber que la búsqueda de las cosas perdidas está entorpecida por los hábitos rutinarios,
y es por eso que cuesta tanto trabajo encontrarlos.

“Cien años de soledad”
Gabriel García Márquez

4.1 Oxygen reactivity and diffusion

In this section, we describe the reactivity and diffusion of oxygen atoms on different surfaces. The reactivity is the study of how O atoms allotropize, or in other words how O\(_2\) and O\(_3\) are formed. In principle, oxygen reactivity should be described in Chapter 5 where we describe the surface chemistry. Nevertheless we treat the oxygen reactivity here because O-atom reactivity and diffusion of oxygen atoms are deeply related. Actually, from a physical point of view, the O-atom diffusion allows O atoms to meet with each other or with other species, and thus diffusion controls reactivity; in other words the allotropization is diffusion-limited. From a practical point of view, our detection instruments are not suitable to follow the evolution with time of fast processes like the diffusion, but they are able to measure the overall and macroscopic effect of these processes. We measure the amount of reactants consumed and products formed, which is a measure of the reactivity of the system. Since this last is determined by the chemical (activation barriers) and physical (diffusion) properties of the system, we can deduce the diffusion by measuring reactivity variation as a function of the experimental conditions used.

4.1.1 Experimental

Experiments were performed using the FORMOLISM set-up. The experimental procedure is very simple: oxygen atoms (and O\(_2\) molecules) are aimed at a cold (6-25 K) sample and the products are probed using TPD and RAIRS. We have varied the following parameters:
• The substrate morphology (Amorphous water ice, porous (p) and compact (np), crystalline (c) ice, amorphous silicate, and graphite)
• The coverage of deposited O/O₂, from 0.1 to 1 ML
• The substrate temperature, from 6.5 to 25 K
• The dissociation rate of O₂ molecules (between 45% and 80%)

It was checked that no O₃ was present in the beam. This control was carried out by two different methods. The first control was performed by placing the quadrupole mass spectrometer (QMS) in front of the beam and by monitoring mass-48 signal of the direct beam, and the one of the beam when blocked by a metallic flag. The signal at mass 48 was always under the detection limit imposed by the electronic noise, and this is a first indication that no O₃ was present in the beam. A second check consisted of irradiating with O+O₂ the surface held at 55 K, then performing a TPD. At this temperature the residence time of O₂ is extremely short and prevents the formation of O₃ through the reaction O+O₂, while gas phase O₃ sticks and remains on the surface. A peak at mass 48 (and mass 32, see below) in the TPD would indicate that O₃ was actually present in the beam. With this second control experiment we could accurately determine that no ozone was present in the O beam.

The energetic state of atoms and molecules was checked before commencing the experiments as described in Sec. 2.2.2.3. We determined that the beam did not contain O or O₂ in an excited state, nor O₃ molecules. The O beam was thus composed of at least 99% ground-state O and O₂. We also recorded the mass 16 signal in all experiments, and did not detect any signal that could be interpreted as O-atom release in the gas phase. Actually, except for the direct beam, or for a very small fraction (<2%) due to cracking of O₂ and O₃ in the QMS, we never detected any signal at mass 16. This indicates that O atoms react and never desorb as such, but exclusively as O₂ and O₃ molecules.

The flux and the determination of O₂ and O₃ monolayer have been discussed in Sec. 2.2.4 and in Minissale et al. (2014a).

4.1.2 Oxygen reactivity

In the previous section, we have implicitly claimed that O₂ and O₃ molecules are formed by sending O atoms on a cold surface. Here, we discuss how the different parameters (substrate, coverage, surface temperature) change the reactivity and, as a consequence, experimental results. Figure 4.1 shows the results of experiments performed by varying the O/O₂ doses. Two desorption peaks are present: O₂ desorption occurs between 35 K and 50 K, and the ozone desorption is observed between 55 K and 75 K (directly, or via the O₂⁺ fragments). We observe, at any coverage or temperature, ozone formation by depositing O and O₂ mixtures on ASW. O desorption is never observed. The shapes and positions of the O₃ peaks are the same as those of O₃ deposited from the gas phase, and are only coverage dependent. We can thus exclude any second order desorption effects, like it should be if O₃ were formed on the onset of or during desorption. By looking at the integrated area of TPD traces of Figure 4.1 we notice that the O₃/O₂ ratio increases with coverage. O₂ reaches rapidly an almost steady state while O₃ rises quite linearly. These experiments suggest that the reactivity of pure oxygen species is limited to two reactions:

\[
\begin{align*}
O + O & \rightarrow O₂ \quad R0.1 \\
O + O₂ & \rightarrow O₃ \quad R0.2
\end{align*}
\]

The O + O₃ → 2O₂ reaction seems not to be competitive with the others, it would not be possible to obtain an almost pure O₃ sample with increasing coverage. About the two reactions R0.1 and R0.2, three questions arise:

1. when do these reactions occur?
2. which mechanism is at play?
3. what are the activation barriers?
As regards the first question, the formation of O$_2$ and O$_3$ can happen during the deposition or during the TPD when the temperature increases. To disentangle this issue, we have followed the evolution of the O$_3$ infrared absorption band intensity from 6.5 K to 35 K as shown in Figure 4.2. Because of a high detection limit (0.3 ML) this method could only be applied to the highest coverage experiment in Figure 4.1. Within experimental uncertainties the O$_3$ infrared band does not vary during the TPD in the high coverage experiment, except at the temperature above which ozone begins to come off the surface (∼ 55K). However, due to the error bars, a small increase of the ozone band could have still been possible. We estimated that an upper limit for the fraction of extra ozone formed during the heating is 15%, a value that we will use below in the discussion. We can fairly say that the majority of O$_3$ is formed during deposition, and the results are consistent with the theory that thermally-induced diffusion during the TPD is a secondary effect compared to diffusion and reactions at the deposition temperature. Aware of this result, we can try to answer the second question (which mechanism is at play). In principle, the two reactions R0.1 and R0.2 may arise from direct reactions between an impinging atom and an adsorbed species (ER mechanism), or may occur by diffusion of the species on the surface (LH mechanism). Moreover, it is also possible that the Hot Atom Mechanism (HAM) has a role as we will discuss in the following. In other words, gaining knowledge about mechanisms at play means to understand what physical processes occur on the surface, i.e., O atoms diffusion. To figure out this matter is the subject of the next section. Finally, as already discussed in Chapter 3 the evaluation of the activation barriers (the third question) is strictly related to the evaluation of the diffusion coefficients of O atoms, presented in the next section. Nonetheless, we anticipate that R0.1 and R0.2 should be barrierless reactions, and in Minissale et al. (2014a) we provide an upper limit of 150 K for the activation energy barriers of both reactions.

4.1.3 Oxygen diffusion

To understand if diffusion plays an effective role in the O$_3$/O$_2$ formation, we have to play with the physical properties of the formation mechanisms. The ER mechanism happens
between a gas phase reactant and a surface reactant: it is by construction not sensitive to the surface temperature and its efficiency depends solely on the coverage. On the contrary, the LH mechanism (as well as diffusion) depends on the temperature of the surface. For this reason, we have performed a second set of experiments in which we varied the deposition temperature of the substrate, but fixing the initial O/O$_2$ dose (coverage). The left panel in Figure 4.3 summarizes the outcome of six TPDs, in which the coverage was fixed (0.29 ± 0.03 ML) and the deposition temperature varied between 8 K and 30 K. We can observe, from curve to curve, a clear change in the O$_3$/O$_2$ ratio. This effect is due to the temperature of the substrate and is a sign of the role of diffusion in the formation of ozone. In fact, with increasing surface temperature, the mobility of O atoms is favored, ozone formation is more efficient, and the O$_3$/O$_2$ ratio increases. Each new adsorbed atom - if the diffusion is fast - is able to scan the surface to react with O$_2$ to form O$_3$, or with another absorbed O atom to form O$_2$ (that, in turn, will also be transformed into O$_3$ by the next incoming and mobile atom). In this scenario, almost all O atoms and O$_2$ molecules are transformed into O$_3$ molecules. On the contrary - if the diffusion is slow - an oxygen atom has not enough time to scan the surface and react with an adsorbed O$_2$. Another O atom then comes and more O$_2$ is formed via the O + O reaction. A reduced mobility leads to the accumulation of O atoms on the surface, the probability for an O atom to meet another O atom rises, and eventually O$_2$ formation is favored. By comparing RAIRS and TPD results, it is possible to see how the diffusion of O atoms changes the O$_3$/O$_2$ ratio. As stated above, we have assumed that an increase of 15 % of the ozone yield may have occurred during the heating from 6.5 to 35 K (see Figure 4.2). From TPD results, however, we obtain a variation of 47 % between the ozone yields after O deposition performed at 8 K and the one performed at 30 K. This indicates that, taking into account the possible 15 % contribution due to the heating, there is still 32 % (47 from TPD, -15 from RAIRS) difference between TPD experiments carried out at T$_s$ = 8 and 30 K. The right panel of Figure 4.3 displays TPD (points) and RAIRS (gray shaded region) normalized peak areas (yields) of ozone and molecular oxygen. TPD variations (also considering the error bars) are greater than the ones in RAIRS data for ozone. This difference is clearly due to T$_s$, i.e., variations of O atom mobility on the silicate surface. As regards O$_2$ yield variations, at 30 K only 15% of the amount of O$_2$ formed at 8 K was observed. In summary,
1. in Sec. 4.1.2 we showed that an incoming O atom is more likely to find O\(_2\) molecules as the coverage increases (Figure 4.1);

2. in Sec. 4.1.3 we showed the increase of the O\(_3\)/O\(_2\) ratio with deposition temperature, which demonstrates the increase in diffusion with temperature (Figure 4.3)

In the next sections, we discuss the role of the substrate on the O\(_3\)/O\(_2\) ratio variation and, through a model, we provide estimations of activation barriers for R0.1 and R0.2 and diffusion coefficients.

4.1.3.1 The role of substrate

The main conclusions of the previous section are that the O\(_3\)/O\(_2\) ratio increases both as function of coverage and as function of surface temperature; but what is the influence of the substrate on the O\(_3\)/O\(_2\) ratio? Figure 4.4 shows integrated areas (in ML) of the TPD peaks of O\(_2\) (red squares), O\(_3\) (green circles), and their sum (blue triangles) as a function of O-atom fluence for four substrates: non-porous ASW ice, crystalline ice, graphite, and silicate (a,b,c, and d panels, respectively). The dashed line corresponds to TPD yields after pure O\(_2\) deposition carried out with the undisassociated beam (the total amount of oxygen atoms deposited on the surface). The O\(_2\) dissociation fraction is 71% ± 4 for all the experiments. We point out two main differences between the four panels:

1. The crossing point between O\(_2\) and O\(_3\) (namely the coverage for which O\(_3\) ≥ O\(_2\)) is at very low coverage, around 0.05 ML, for water ices (np-ASW and crystalline, respectively a and b panels), while it is at a higher coverage, 0.2-0.25 ML for graphite and silicate (respectively, c and d panels).

2. The sum O\(_2\)+O\(_3\) (blue triangles) follows the dashed line in the case of water ices, while it is beneath the dashed line for graphite and silicate.

The first difference can be explained by different O-atom diffusion coefficient on the different substrate; the higher the diffusion, the larger the probability of species encounter, and, as a consequence, the higher the reactivity. The crossing point is in some way a measure of the reactivity and, therefore, of the diffusion coefficients (\(k\)). In particular, \(k_{\text{water-ices}} > k_{\text{bare-substrates}}\) in the plausible hypothesis that activation barriers for R0.1 and R0.2 are the same for all substrates. The second difference can be explained by the different chemical desorption probability of O\(_2\) molecules on the various substrates (Chaabouni et al. 2012;
**Figure 4.4:** Integrated areas (in ML) of the TPD peaks of $O_2$ (red squares) and $O_3$ (green circles) vs O-atom fluency for four substrates: non-porous ASW ice, crystalline ice, graphite, and silicate (a,b,c, and d panels, respectively). Blue triangles: sum of $O_2$ and $O_3$. Dashed lines represent the total amount of oxygen atoms deposited on the surface.
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Figure 4.5: From Congiu et al. (2014). Diffusion constants $k$ of O atoms obtained on np-ASW (open pink circles), on crystalline water ice (black circles), p-ASW (blue triangles), amorphous silicate (red squares), and oxidized HOPG (green stars), plotted as a function of surface temperature. Dashed lines represent a series of Arrhenius-type laws generated by using five values of $E_{\text{diff}}$ (from 150 to 700 K). The two solid lines are best fits of the experimental values obtained through the quantum-tunneling diffusion law for O atoms on compact water ice (black solid line) and amorphous silicate (red solid line); see Table 4.1 for the best fit values of $a$ (barrier width) and $E_a$ (barrier height).

Dulieu et al. (2013). Actually, as discussed in Minissale&Dulieu (2014c), the missing atoms in the case of bare substrates is due to the prompt release of $O_2$ upon formation. This prompt release is apparently impeded on water ices.

4.1.3.2 Model

In this section, we provide an estimation of activation barriers for R0.1 and R0.2 and of the diffusion coefficients on the various substrates. Experimental data are inserted into a model composed by a series of rate equations used to simulate the $O_2$ and $O_3$ formation yields according to coverage and surface temperature. The model includes both LH and ER mechanisms, and it allows reactions to occur during the deposition phase, as well as during the heating phase (TPD). A complete account of our model is given in Minissale et al. (2014a) and in Chapter 3. Here we will focus on the diffusion rates $k$ and the different methods by which they are calculated. In Figure 4.3, we have already demonstrated that reactions mostly occur during the exposure phase. The diffusion of atoms during the heating phase is negligible because not more than a few percent of the deposited O atoms remain available on the surface in the low coverage regime. The effect of any possible diffusion during the TPD lies within the error bars of the experimental data, and can be neglected. For this reason, in what follows, we will address only the diffusion coefficients at a fixed temperature for each one of the substrate investigated.

Other parameters are the dissociation fraction $\tau$, and the chemical desorption rate, that was studied in Dulieu et al. (2013) and Minissale&Dulieu (2014c), it will be discussed in Sec. 4.3. The diffusion coefficients $k$ include two components due to quantum tunnelling and thermal motion:

$$k = k_{\text{qt}} + k_{\text{tm}}. \quad (4.1)$$

In our model, $k$ can be treated as a free numerical parameter during the deposition phase at constant temperature, owing to the fact that the evolution of the coverage with time is known and provides a strong constraint. Therefore, resulting $k$ values are a set of constants giving the diffusion rate at given temperatures, although no information can be inferred about the nature of the diffusive process. In Figure 4.5, the diffusion constants $k$ that we obtained for various substrate compositions are plotted as a function of temperature. An important finding of this comparative study is that diffusion coefficients on water ices (regardless of its morphology) are about one order of magnitude greater than those on silicate and graphite.
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Figure 4.6: From Congiu et al. (2014). Black squares represent diffusion constants of O atoms on amorphous silicate as a function of temperature. The red solid line is a best fit of diffusion constants vs temperature obtained by using the empirical law given in Eq. 4.2; see Table 4.1 for best fit values of $k_0$, $\alpha$, and $\beta$.

Diffusion constants $k$ vs $T_s$ can be displayed in several ways according to the law used to describe them, namely, $k$ may have (a) an empirical law built for fitting the experimental values, (b) an Arrhenius-law form, with an activation energy $E_{\text{diff}}$ free to vary, or (c) a quantum-tunnelling form with a width and height of the barrier. A detailed analytical or numerical solution of the dependence of $k$ with $T_s$ can help have some insight into the physical nature of the diffusive process at play. Case (a), the empirical law we used for fitting the diffusion constant as a function of surface temperature, has the form

$$k_{\text{emp}}(T) = k_0 + \alpha \left(\frac{T}{10}\right)^\beta.$$  (4.2)

Figure 4.6 displays a fit of the experimental values obtained on amorphous silicate according to the empirical law given in Eq. 4.2. $k_0$ can be considered the minimum value of $k$, or the value $k$ must tend to near $T = 0$ K. $\alpha$ is a free parameter with values between 0 and 1, and it accounts for diffusion efficiency differences between the various substrates. $\alpha = 1$ for water ice while it is about 0.1 for graphite and silicate. The dependency on the surface temperature is governed by the factor $(T/10)^\beta$, the exponent $\beta$ can have a value between 3 and 4, with variations due to the surface nature, although the best fits give typical values of 3.5. Case (b), the classical Arrhenius law used to model the diffusion coefficient $k$ is

$$k_{\text{arr}}(T) = \nu_0 \exp\left[-\frac{E_{\text{diff}}(T)}{T}\right].$$  (4.3)

$E_{\text{diff}}$ is the diffusion barrier expressed in kelvin (eV/$k_b$) and $\nu_0$ ($= 10^{12}$ s$^{-1}$), the pre-exponential factor, can be seen as a trial frequency for attempting a new event. In Figure 4.7 we present a fit of the diffusion coefficient $k$ on non-porous ASW obtained by using the Arrhenius law. Figure 4.7 actually displays activation energies for diffusion ($E_{\text{diff}}$) as a function of temperature. In fact, according to Eq. 4.3, a suited set of $E_{\text{diff}}$ can be used to derive one diffusion coefficient for each temperature. It is thus possible to link each of these diffusion coefficients to an Arrhenius behavior, and find one energy barrier at each temperature as shown in top panel of Figure 4.7 (see also dashed lines in Figure 4.5). However, a disordered surface has a complex distribution of adsorption and diffusion barrier energies, and for each surface there exists a unique distribution that can be quite different, even in substrates of the same composition and morphology. We have tried to implement this kind of complication to fit our results. In bottom panel of Figure 4.7 we present an attempt to model the distribution of diffusion energies on amorphous water as a function of surface temperature, calculated assuming an Arrhenius behaviour and according to the experimental values of diffusion coefficients $k$. The colour scale represents the fraction of adsorption sites with energy $E_{\text{diff}}(T)$ populating 1 ML. From bottom panel of Figure 4.7 it is clear that the contour lines are not horizontal, as they should be in a fixed distribution of diffusion energies characterizing a given substrate. This implies that the distribution of diffusion energies cannot be constant in the narrow (6-25 K) temperature interval investigated, but its centre
Figure 4.7: Top panel (from Congiu et al. (2014)): Energy barrier for diffusion on compact water ice as a function of surface temperature in the case of Arrhenius-type diffusion coefficient. The red solid line represents a linear fit of $E_{\text{diff}}(T)$; see Table 4.1 for the interval of $E_{\text{diff}}$ values needed to obtain $k_{\text{Arr}}$ between 6 and 25 K. Bottom panel: Distribution of O-atom diffusion energies on amorphous water ice as a function of surface temperature calculated according to the experimental values of the diffusion coefficients and assuming an Arrhenius (thermal) behaviour. The colour scale represents the fraction of adsorption sites ($1=10^{15}$ sites cm$^{-2}=1$ ML) with $E_{\text{diff}}(T)$ at temperature $T$. 
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has to shift to higher energies with temperature to reproduce the observed trend in diffusion coefficients. We believe that a change in the distribution of barrier energies within such a narrow temperature range is not physically plausible, although not impossible, in the case of “stiff” surfaces such as silicate and graphite, nor in the case of the various morphologies of water ice at such low temperatures. To sum up:

1. an Arrhenius law form in which only one \( E_{\text{diff}} \) exists and is independent of the temperature is not able to fit the data;

2. an Arrhenius law form in which a fixed distribution of \( E_{\text{diff}} \) exists is not able to fit the data;

3. our data are fitted both through a \( E_{\text{diff}}(T) \) or through a temperature dependent distribution of \( E_{\text{diff}} \).

This is why we discarded the Arrhenius-type behavior of \( k \) as it made no physical sense to us. In fact, a systematic increase of the Arrhenius barrier with temperature seemed to us an ad hoc solution. Also, this implies that at low temperatures (6 K) diffusion occurs through low diffusion barriers (e.g., \( E_{\text{diff}} = 170 \) K). If such low barriers actually exist, they represent fast connections between adsorption sites. Why then would these low energy barriers vanish at higher temperatures? To put it in other terms, why and how atoms would diffuse through slow pathways (high diffusion barriers) at high temperatures (>20 K), if faster pathways exist? We consider this unlikely and not physically reasonable.

In Figure 4.8 we show a comparison between the classical behavior (described by an Arrhenius-type law) of the diffusion coefficient as reported by Karssemeijer et al. (2012) for CO molecules on hexagonal water ice, and the trend that we find experimentally for O atoms on amorphous silicate and crystalline water ice. It is clear that our experimental values do not follow an Arrhenius behavior, suggesting that a classical description is incomplete to explain the experimental data (squares and triangles in Figure 4.8). In fact, in a pure thermal diffusion the slope is very different, and if we fit the data by using a classical Arrhenius law, we find values of \( \nu_0 \) and \( E_{\text{diff}} \) not physically acceptable. Therefore, a quantum mechanical approach ought to be used to account for the deviations from the classical trend. Our results on oxygen atoms are consistent with a tunnelling-dominated diffusion as found for H atoms on np-ASW by Senevirathne et al. (2014) in the 6 - 13 K temperature range (the slopes of H- and O-diffusion coefficient behaviors are similar). They also found that diffusion of H atoms is enhanced around 13 K, as occurs to O atoms around 22 K, just where classical thermal motion begins to predominate over quantum processes (Senevirathne et al. 2014; Minissale et al. 2013). Hama et al. (2012) found that this temperature border between quantum and classical diffusion of H atoms is likely to be at \( T_s < 10 \) K. We found that at very low temperatures the diffusion of O atoms is better simulated by quantum tunneling through a square barrier (Messiah 1973). The physical parameters we use to describe such a quantum jump are the width \( a \) and the height \( E_a \) of the barrier. The choice of a square barrier, the simplest shape of a potential, was made purposefully to show that the right trend is obtained if one uses quantum-tunneling diffusion, not because we believed that a square barrier was the right one. We believe that any other more realistic potential shape we could use, would not fundamentally change the results, and it would still be unrealistic given the complexity of the distribution of diffusion barriers. We did not try to obtain the best fit of our data, but tried to show that the right trend is obtained if one uses quantum-tunneling diffusion (see solid lines in Figure 4.3). Hence, we chose to model the quantum diffusion with two parameters which have a simple physical meaning, although they correspond to macroscopic values that come from the interplay of many microscopic different situations. The values of \( k \) and all of the parameters used to fit the diffusion coefficient on each substrate, using the three methods, are listed in Table 4.1. The diffusion coefficients of O atoms calculated on water ices are one order of magnitude greater than those found on amorphous silicate and oxidized HOPG, namely O diffusive mechanism is more efficient on icy grains. Also, as opposed to the case of H atoms, there is no difference between the efficiency of O mobility on the three types of water ices investigated (p-ASW, np-ASW, and c-SW). In the light of our experimental results, we can only observe and simply report this finding. In fact, to deal
Figure 4.8: From Congiu et al. (2014). Comparison between diffusion behaviors of CO molecules, H atoms, and O atoms. Blue squares and green triangles represent O-atom diffusion coefficients as a function of surface temperature on amorphous silicate and crystalline water ice, respectively (this work). The black dashed line represent the thermal diffusion (Arrhenius behavior) of CO molecules on hexagonal water ice found in Karssemeijer et al. (2012). The red solid line and the red dashed line display the H-atom tunnelling (6 - 13 K) and the H thermal diffusion ($T_s > 13$ K), respectively, obtained by Senevirathne et al. (2014) on compact amorphous water ice.

With atoms makes it very difficult to derive key parameters such as the energy barrier for diffusion, or even the energy barrier for desorption, hence no pertinent assumption can be made to explain these findings from a physical chemical point of view. However, to give a physical explanation of our results is beyond the scope of this thesis, since we believe that quantum calculations and simulations will be necessary to thoroughly describe O diffusion mechanisms at low temperatures.

Table 4.1: Best fit parameters of the three methods used to model the diffusion coefficients for O diffusion on five different grain surface analogues

<table>
<thead>
<tr>
<th>Material</th>
<th>A (Å)</th>
<th>$E_a$</th>
<th>$E_{diff}(6&lt;T&lt;25)$ (K)</th>
<th>$k_0 \times 10^{-15}$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous ASW</td>
<td>0.69±0.10</td>
<td>530±70</td>
<td>170&lt; $E_{diff}$&lt;600</td>
<td>1.30</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Non-porous ASW</td>
<td>0.7±0.05</td>
<td>520±60</td>
<td>170&lt; $E_{diff}$&lt;600</td>
<td>1.21</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Crystalline SW</td>
<td>0.69±0.05</td>
<td>500±50</td>
<td>170&lt; $E_{diff}$&lt;600</td>
<td>1.42</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Amorphous silicate</td>
<td>0.67±0.10</td>
<td>720±70</td>
<td>290&lt; $E_{diff}$&lt;740</td>
<td>0.15</td>
<td>0.1</td>
<td>4</td>
</tr>
<tr>
<td>Oxidized HOPG</td>
<td>0.67±0.10</td>
<td>740±60</td>
<td>290&lt; $E_{diff}$&lt;740</td>
<td>0.1</td>
<td>0.1</td>
<td>4</td>
</tr>
</tbody>
</table>

4.1.3.3 The role of amorphyicity and morphology in diffusion processes

The majority of theoretical models describing diffusion consider a potential of the type used in crystalline-like solids (see Oura et al. (2003) and references therein). In reality there is robust observational evidence that an amorphous nature is the most probable structure for grains in space (Leger et al. 1979). Taking this into account, the situation changes dramatically as it can be seen in Smoluchowski (1979, 1981). While in a crystalline solid the atoms are regularly arranged in a lattice, which means that the crystal can be built up by periodic repetition of identical cells, amorphous solid does not show any periodic structure. The number of nearest neighbors of atoms or molecules and the distances between them are
usually very similar in crystalline and amorphous solid, because of atoms (or molecules) have rather well-defined effective radii and the bonds between them are almost unaffected by the degree of crystallinity; in contrast the second, third, etc., neighbors of each site in general will be different in amorphous solids. This difference is described by the so called pair correlation

\[ g(r) = \frac{V}{4\pi r^2N^2} \left\{ \sum_i \sum_{j \neq i} \delta(r - r_{ij}) \right\} \]  

where \( N \) is the total number of particles contained in a volume \( V \). A schematic representation of the \( g(r) \) is shown in Figure 4.9. \( g(r) \) provides a measure of the local spatial ordering in a solid. Using this function one can calculate the spectrum of the binding energies of atoms adsorbed on various sites of the amorphous surface.

Figure 4.10 represents, in a certain sense, the \( g(r) \) function with the contribution for high \( r \) suppressed by the rapid drop-off of the binding energy \( E(r) \). The most important difference between crystalline and amorphous surfaces is that, on a periodic surface (as the crystalline one), the motion of atoms can be represented as a temporary spread of a quantum mechanical wave packet describing the adsorbed atom while on an amorphous surface, and so in a non-periodic sequence of potential wells, this is not possible. Thus, a diffusing atom (for instance of hydrogen) attains accessibility to the whole amorphous surface only at relatively high temperatures through thermal hopping. The most important implication of the breadth of the spectrum shown in Figure 4.10 is that the adsorbed atom will become rapidly localized by tunneling to a site of lowest energy in its proximity; it will diffuse only when the temperature is high enough and thermal hopping is possible.

In this scenario, why do we find similar diffusion coefficients for different morphologies of water ices? The answer can be found in the percolation theory. We know that an amorphous surface has a larger distribution of energy and width of barriers for diffusion with respect to a crystalline surface. If on one hand the amorphicity reduces the fraction of sites accessible (if energy and width of barriers are too large, the atom will be localized), on the other hand it makes other sites more accessible. In other words, on amorphous surfaces diffusion has less sites available with respect to crystalline ones, but between these sites the diffusion is very
fast. The overall effect is that diffusion coefficients do not change as a function of amorphy.

We remark here that we measure average diffusion coefficients and we are not able to measure a specific diffusion coefficient from one to another site. To test this alternative scenario, we develop a very simple model somehow inspired by Wolff et al. (2010). Figure 4.11 displays a sample of the squared grid. We define three different connections between sites:

1. Thick lines correspond to fast connections with diffusion energy $E_{h-d}$;

2. Thin lines correspond to “average” connections with diffusion energy $E_{h}$;

3. No lines correspond to slow connections with diffusion energy $E_{h+d}$,

where $d$ determines in a way the degree of amorphyicity; if $d=0$ the grid represents a crystalline solid. We stress that this model is not intended to be complete. Actually, a distribution for the width of barriers has to be considered too. Nevertheless, we chose to overlook the distribution of width of barriers for a question of simplicity. In this manner, we can show what is the role of amorphyicity in a simple way. The computational procedure is very simple: two atoms fall down randomly on the surface, they are free to migrate, and the code is stopped when they meet and react. We measure the time between the fall and the encounter. Colored points in Figure 4.11 correspond to three different starting conditions: (1) an islet of three connections in red; (2) a deep site in green; (3) a connected grid in blue. The results depends on the initial conditions and Figure 4.12 shows a typical encountering time distribution obtained for a random initial condition and a random degree of amorphyicity $d$. Our free parameters are $E_{h}$ and $d$. In order to understand the role of amorphyicity, we have fixed $E_{h}$. We find generally that the presence of fast and slow connections (with $d=15\%$ of $E_{h}$) decreases significantly reaction times with respect to the case $d=0$. Actually the presence of fast connections prevails over the presence of slow connections. This result is in opposition with the Smoluchowski theory, for which the amorphyicity hinders the diffusion, no matter which type (tunneling or hopping). If we have a look at the probability density function of atoms on the grid built after a complete set of model runs ($\approx 50$), we find that atoms are active and mobile only on well connected network ($E_{h-d}$), as shown Figure 4.13. This is very probably the reason for which when such degree of amorphyicity is introduced, it does not fundamentally change the diffusion. We already claimed that a periodic surface (as the crystalline one) favors the spread of a quantum mechanical wave packet describing the adsorbed atom. On an amorphous surface, the loss of a global symmetry of site energies is compensated for by the presence of an enhanced diffusion on fast connections.
Figure 4.11: Squared grid with three different connections between sites: thick, thin, and no lines correspond to fast, "average", and slow connections, respectively. Colored points correspond to three different starting conditions.

Figure 4.12: Typical encountering time distribution obtained for a random initial condition and a random distribution of sites for two atoms diffusion on the grid presented in Figure 4.11.

Figure 4.13: Probability density function of atoms on the grid. In white and in red well and poorly connected sites respectively.
4.2 Evaluation of desorption energies

4.2.1 Desorption energy of non-reactive species: the case of O$_2$ and O$_3$ molecules

The analysis of TPD spectra is an excellent means to find the desorption energy for a lot of molecules. The shape of the TPD curves is linked to physisorption energies of adsorbate and surface and to the potential structure of the latter. We already stated in Sec. 2.2.2.4 that the disordered nature of a surface entails a wide range of binding energies available on the surface, and as a consequence also a range of desorption temperatures. To take this into account, thermal desorption is described in terms of an Arrhenius expression using a (discrete or continuous) range of desorption energy as

$$R(\theta) = \frac{d\theta}{dt} = \sum_{i=0}^{15} \nu \alpha_i \theta^n e^{-(E_0 + i\sigma)/T} / \beta \Rightarrow R(\theta) = \frac{E_{max}}{E_0} \nu \alpha \theta^n e^{-(E(\theta))/T} / \beta$$  (4.5)

where $R$ is the desorption rate, $\theta$ the adsorbate coverage, $t$ the time, $\nu$ the pre-exponential factor of desorption (the vibrational frequency of the molecules at the surface, $10^{12}$ s$^{-1}$), $n$ the order of the desorption process, $T$ the temperature, $E$ the activation energy for desorption, $\alpha$ are normalization coefficients, and $\beta$ is the heating ramp. The left panel of Figure 4.14 displays the case of desorption of 1 ML of O$_2$ from amorphous silicate. Red points represent the experimental TPD curve and the blue line is obtained by using a discrete distribution of adsorption sites. The right panel of Figure 4.14 shows the distribution of the occupied sites according to their energy. By integrating all columns, we obtain the amount of O$_2$ deposited, 1 ML in this case. Thanks to this figure, we can point out that the choice of only one desorption energy for a molecule is very simplistic. This matter will be discussed in Sec. 6.2. Nevertheless, to give an idea of the desorption energies as a function of coverage, we can choose the peak of the distribution shown in the right panel of Figure 4.14. $\alpha$ and $\beta$ panels of Figure 4.15 show desorption energy distribution for different doses of O$_2$ and O$_3$ desorbing from np-ASW and amorphous silicate. The desorption energy decreases with the coverage, meaning that molecules populate less deep adsorption sites or that intermolecular interactions (i.e., repulsions) have the effect of lowering the binding energy. This behavior is more pronounced on amorphous silicate; for this surface, the difference between low coverage and multilayer desorption energy is larger with respect that present on np-ASW. This is shown in panel $\gamma$ of Figure 4.15 where the normalized (with respect to the monolayer energy) desorption energies are plotted as a function of coverage. This approach can be used to estimate the desorption energy of different molecules. A list of desorption energy for different molecule and substrates determined with this method is shown in Table 4.2.
4.2.2 Desorption energy of reactive species: the case of O atoms

The approach described above to the estimate desorption energy of O$_2$ and O$_3$ can be used only in the case of non-reactive species. This means that once a species has been deposited, it remains inert on the surface up to an increase in surface temperature, namely a TPD. If the species is reactive, a TPD of such species cannot be performed, hence this method cannot be used. This is the case of O and N atoms. They promptly allotropize on the surface and TPDs cannot be used to estimate their desorption energies. Nevertheless the desorption energy can be evaluated by performing a temperature programmed DED (TP-DED). The procedure consists of looking at the products formed as a function of surface temperature. In this way, we can have an idea of the residence time of this species at a given surface temperature. Figure 4.16 displays a particular experiment performed on np-ASW (panel $\alpha$) and oxidized HOPG (panel $\beta$) to determine the O-atom desorption energy. O atoms are sent on the surface and we follow the signal at masses 16, 32, and 48 as a function of surface temperature. Initial surface temperature is 100 K and with a ramp of -1 K/min, the surface reaches 15 K. Figure 4.16 clearly shows three trends for mass 16: (1) a lower plateau ($T < 45$ K for np-ASW and $T < 52$ K for oxidized HOPG) where the majority of O atoms stick on the surface; (2) an upper plateau ($T > 68$ K for np-ASW and $T > 75$ K for oxidized HOPG) where all O atoms desorb from the surface; (3) a transition region ($45$ K $< T < 68$ K for np-ASW and $52$ K $< T < 75$ K for oxidized HOPG) where mass 16 signal falls down from the upper to the lower plateau. Before delving into the details of the transition region, we have to explain the behavior that gives the upper plateau. We notice that between 100 K and 70-75 K the signals of both mass 16 and mass 32 increase. This increase is due to the
**Figure 4.17:** Comparison of experimental (red stars) and model results (green curves) of TP-DED of mass 16 in the 35-85 K region for oxidized HOPG (upper panel) and np-ASW (lower panel).

Different temperature of the desorbing molecules. We know that the detection efficiency of the QMS depends on the particle speed: the higher the speed, the lower the efficiency. At a certain $T_s$, the main part of desorbing molecules have $T_{desorbing} = T_s$. Hence, at $T_s = 100$ K, DED signal is lower than the one at $T_s = 70$ K. The QMS efficiency can be corrected through a factor proportional to $\sqrt{\frac{100}{T_s}}$ through which we obtain the dashed curves in Figure 4.16. We can now focus on the transition region. In the case of a non-reactive species, transition region can be explained only through an increase of the residence time (i.e. $O_2$, red curves), and so it is not difficult to estimate the binding energy of such a species. In the case of a reactive species (i.e. $O$ atoms) a signal decrease during the TP-DED could be due either to desorption or reactivity of the system. This complicates the evaluation of binding energy. By using the same rate equation model used for the diffusion-reactivity of the $O_x$ system, we are able to fit the transition region as shown in Figure 4.17. We consider a thermal diffusion of $O$ and we use the binding energy of $O$ atoms as a free parameter. For instance the green curves on panel $\beta$ of Figure 4.17 (oxidized HOPG) are obtained by using $E_{diff} = 950$ K and $E_b = 1580 \pm 70$, while for panel $\alpha$ (np-ASW) $E_{diff} = 900$ K and $E_b = 1420 \pm 50$. The choice of $E_{diff}$ is not arbitrary but it comes from a previous evaluation by Minissale et al. (2014). Nevertheless, it should be noted that this is only a preliminary evaluation of the $O$-atom binding energy and it has to be improved through further modeling.

### 4.2.3 Conclusion

In this section we discussed how desorption energies can be evaluated:

1. from TPD spectra, following Kimmel et al. (2001) and Amiaud et al. (2006), for pure
non-reactive species (O₂, CO, NO, and so on)

2. from DED measurements of reactive species (O and N)

We present a list of desorption energies for different species adsorbed on np-ASW, amorphous silicate, and HOPG for low coverage and monolayer regime. All the experimental data were recorded during the present thesis work, even if not all the data have been presented.

Table 4.2: List of desorption energies of some atoms and molecules adsorbed on np-ASW, amorphous silicate, and HOPG for low coverage and monolayer regime. Experiments are performed with pure species beam. Where not specified the error bar is ± 40 K.

<table>
<thead>
<tr>
<th>Species</th>
<th>E&lt;sub&gt;des&lt;/sub&gt; K</th>
<th>np-ASW 0.1 ML</th>
<th>np-ASW 1 ML</th>
<th>amorphous silicate 0.1 ML</th>
<th>amorphous silicate 1 ML</th>
<th>HOPG 0.1 ML</th>
<th>HOPG 1 ML</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>± 1420±50</td>
<td></td>
<td></td>
<td>± 1000</td>
<td></td>
<td>± 1230</td>
<td>± 1040</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td>± 1192</td>
<td>± 1000</td>
<td>± 1278</td>
<td>± 1117</td>
<td>± 1250</td>
<td>± 1020</td>
</tr>
<tr>
<td>O₂</td>
<td>± 2200</td>
<td>± 2400</td>
<td>± 2031</td>
<td>± 2500</td>
<td>± 2130</td>
<td>± 2230</td>
<td>± 2040</td>
</tr>
<tr>
<td>NO</td>
<td>± 1510</td>
<td>± 1320</td>
<td>± 1560</td>
<td>± 1440</td>
<td>± 1490</td>
<td>± 1610</td>
<td>± 1650</td>
</tr>
<tr>
<td>NO₂</td>
<td>± 3290</td>
<td>± 2400</td>
<td>± 3900</td>
<td>± 3630</td>
<td>± 3810</td>
<td>± 3610</td>
<td>± 3900</td>
</tr>
<tr>
<td>CO</td>
<td>± 1320</td>
<td>± 2400</td>
<td>± 980</td>
<td>± 1320</td>
<td>± 1100</td>
<td>± 1380</td>
<td>± 1010</td>
</tr>
<tr>
<td>CO₂</td>
<td>± 3290</td>
<td>± 3200</td>
<td>± 3010</td>
<td>± 3420</td>
<td>± 3100</td>
<td>± 3420</td>
<td>± 3100</td>
</tr>
<tr>
<td>H₂CO</td>
<td>± 4330</td>
<td>± 3900</td>
<td>± 3900</td>
<td>± 4220</td>
<td></td>
<td>± 4220</td>
<td>± 4110</td>
</tr>
</tbody>
</table>

(a) The desorption energy evaluation is similar to that discussed for O atoms.

4.3 Chemical desorption

The chemical desorption process starts from the energy excess usually present in radical-radical reactions. The chemical desorption efficiency will depend on how the newly formed molecule dissipates the energy excess. Actually, in order to desorb, the molecule has to convert a fraction of this excess formation energy into kinetic energy, and especially into motion perpendicular to the substrate. In other words, the problem lies on how the newly formed molecule manages the energy excess and interacts dynamically with the surface. The total budget of energy excess (enthalpy of reaction) is the most important parameter describing the chemical desorption. The larger the enthalpy of reaction, the more probable is chemical desorption. On the contrary, the binding energy of the newly formed species should be considered as a limiting factor. Among diverse parameters, the degrees of freedom of the newly formed molecules seem to play an important role: in fact more degrees of freedom lead to an easier distribution to internal modes and thus dissipation. The last parameter that we consider is the interaction with the substrate, namely the phonon propagation. The water ice substrate has larger capabilities to dissipate the excess energy than other substrates (silicate and oxidized graphite), and therefore the probability of chemical desorption is lower. Nevertheless, the “softness” of the water ice substrate is not sufficient to forbid chemical desorption, as shown in Amiaud et al. (2007) and Govers et al. (1980) in the case of H₂. Further works stress - in the case of water - the role of the surface coverage in the inhibition of chemical desorption processes (Congiu et al. 2009).

In this section we present experimental results proving the chemical desorption (CD) of different molecules. All the experiments described in this section are performed using the FORMOLISM set-up and follow a similar experimental procedure described in Sec. 2.2.2.5.
4.3.1 The chemical desorption of the O-H system

The study of CD for the \( \text{O}_2 + \text{H} \) reaction network is quite a complicated case to study, since a plenty of reactions (>20) are involved and several molecules can be formed. For this reason, firstly we have studied separately the case \( \text{O}_2 + \text{H} \) and only then \( \text{O} + \text{H} \).

4.3.1.1 Chemical desorption in \( \text{O}_2 + \text{H} \) experiments

We have studied experimentally the CD for the reaction \( \text{O}_2 + \text{H} \) and subsequent reaction on different surfaces. For the sake of clarity, here we focus our attention mainly on CD and we postpone to Sec. 5.1 the discussion about the chemical network of these experiments. Figure 4.18 shows the results after irradiation with \( \text{D} \) atoms of 1 ML of \( \text{O}_2 \) molecules. We use \( \text{D} \) atoms instead of \( \text{H} \) atoms to increase the signal to noise ratio and to easily distinguish ASW substrate and newly formed molecules. After the deposition at 10 K, the surface temperature is increased up to 200 K and molecules are measured in the gas with a mass spectrometer. Solid, dashed, and dotted lines represent thermal desorption spectra of \( \text{O}_2 \), \( \text{D}_2\text{O} \) (mass 20), and \( \text{D}_2\text{O}_2 \) (mass 36) respectively. Different colors represent the surface in which experiments are performed: red for amorphous silicate, green for graphite, and blue for np-ASW. The black line represents a TPD of 1 ML of \( \text{O}_2 \) deposited on silicate. \( \text{O}_2 \) desorbs as a single peak at around 35 K. When \( \text{O}_2 \) is irradiated with \( \text{D} \) atoms the desorption of \( \text{O}_2 \) is very weak compared to the deposition of \( \text{O}_2 \) only, meaning that most (>90%) of the initial \( \text{O}_2 \) molecules have been consumed. \( \text{D}_2\text{O} \) and \( \text{D}_2\text{O}_2 \) desorption features are observed at 150 K, and before 200 K, respectively. Previous studies showed that \( \text{O}_2 \) reacts quickly with \( \text{D} \), forming \( \text{O}_2\text{D}, \text{D}_2\text{O}_2 \), and finally \( \text{D}_2\text{O} \) (Miyachi et al. 2008; Ioppolo et al. 2009; Dulieu et al. 2010). The area of the desorbed peaks indicates that

1. on graphite only 15% of the oxygen has been included in \( \text{D}_2\text{O} \), meaning that around 85% of the \( \text{O}_2 \) molecules are missing from the surface.

2. on silicate only 25%±5% of the oxygen has been included in \( \text{D}_2\text{O} \) and \( \text{D}_2\text{O}_2 \) formed and \( \text{O}_2 \) not consumed, meaning that around 70% of the \( \text{O}_2 \) molecules are missing from
the surface.

3. on water ice 45% + 16% of the oxygen has been included in the D$_2$O and D$_2$O$_2$ molecules, meaning that around 40% of the O$_2$ molecules are missing from the surface.

The O$_2$ molecules missing in the desorption spectra are believed to be ejected into the gas phase during exposure with D atoms, following chemical reaction. In this sense, once new species are formed, and are unable to thermalize on the surface, they are released into the gas phase (the so called chemical desorption). To prove the existence of this process, we have performed several DED during D irradiation. The measurements are reported in the inset of Figure 4.18 (for the silicate surface) before and during D irradiation for D$_2$O (mass 20), DO$_2$ (mass 34), and D$_2$O$_2$ (mass 36). We observe a direct D$_2$O signal far above the noise level, indicating that D$_2$O is chemically desorbed. On the other hand, we detect a very small increase of the DO$_2$ signal (in the noise) and no increase of the D$_2$O$_2$ signal. OD (mass 18) and O$_2$ (mass 32) are also monitored, but the presence of H$_2$O (mass 18) and O$_2$ as minor contaminants in the vacuum decreases the signal to noise ratio, allowing only a one sigma detection of O$_2$. The DED measurements provide clear evidences of the CD of D$_2$O. We remark that quantitatively DED and TPD experiments cannot be directly compared since the QMS is not located at the same place during these experiments. The possible reactions routes leading to D$_2$O formation and consequent CD are the following

\begin{equation}
O_2 + D \rightarrow DO_2 + D \rightarrow \quad (4.6a)
\end{equation}

\begin{equation}
D_2O_2 + D \rightarrow D_2O + OD \quad (4.6b)
\end{equation}

\begin{equation}
OD + OD + 2D \rightarrow 2D_2O \quad (4.6c)
\end{equation}

Both D$_2$O$_2$ + D (exothermicity ≈ 3.1 eV) and OD + D (exothermicity ≈ 5.2 eV) can contribute to D$_2$O CD but we can not differentiate which contribute is larger. The branching ratio between the two reaction routes can give an idea of contributions. Nonetheless the ambiguous signals of reaction routes marker (D$_2$O$_2$ for the first one, and OD for the second one) do not allow to give a precise evaluation. However, recently, Oba et al. (2013) have shown that H$_2$O$_2$ + H has a high barrier and it is therefore probable that OH+H is the main carrier of H$_2$O CD.

4.3.1.2 Chemical desorption in O$_3$+H experiments

We performed complementary TPD experiments to address the origin of the very important chemical desorption of D$_2$O. In particular we studied the reaction O$_3$ + H. Here we used hydrogen instead of deuterium. Figure 4.19 represents the desorption spectra of water after its formation via 1 ML of O$_2$ with 7 ML of H on silicate held at 10 K (blue); 1 ML of O$_3$ with 7 ML of H on silicates held at 10 K (red); 1 ML of O$_3$ with 7 ML of H on silicate held at 45 K (green). We can see that in the case of O$_3$, there is a higher production of H$_2$O, because the formation of water is made by two sub-routes

\begin{equation}
O_3 + H \rightarrow O_2 + OH \rightarrow \quad (4.7a)
\end{equation}

\begin{equation}
O_2 + H \rightarrow H_2O \quad (4.7b)
\end{equation}

\begin{equation}
O_2 + H \text{ see eq. 4.6a.} \quad (4.7c)
\end{equation}

Performing experiments at 45 K, where O$_2$ is evaporating at a high rate, almost forbid the O$_2$ + H sub-route, so the O$_3$ + H at 45 K is almost like observing the OH + H reaction. Figure 4.19 clearly shows that almost no water seems to be produced in the experiments performed at 45 K, indicating a very strong chemical desorption during exposure through the reaction OH + H. To check that the disappearance of the water signal for O$_3$ + H at 45 K is not due to the fact that the reaction does not proceed, we measured the amount of O$_3$ present on the surface as O$_3$ was exposed to H atoms. We see that the peak of O$_3$, located at 67 K in the TPD, decreases as the exposure with H atoms increases. This shows that even if the residence time of H atoms on the surface is short at 45 K, it is long enough to activate radical-radical reactions, as observed here for the reaction O$_3$ + H and also observed
for NO + H (Congiu et al. 2012). To summarize, we show that the OH + H route is the one responsible for the important amount of water produced during exposure of O$_2$ with H or D. Since most of the water formed through this route is ejected in the gas phase, this allows us to bring further constraints on our first TPD experiment. The reaction O$_2$ + D leads to the formation of D$_2$O and then D$_2$O + OD, or to the formation of 2 OD. Since OD on the surface reacts with a D to form D$_2$O and is ejected in the gas, D$_2$O and D$_2$O$_2$ observed in the TPD are the result of reactions 4.6b and 4.6c. This implies that the 35% of D$_2$O found on the surface comes from reactions 4.6b and 4.6c, and that the branching ratio is $k = 0.35$. Further details about the branching ratio are present in Chaabouni et al. (2012) and Dulieu et al. (2013).

4.3.1.3 Chemical desorption in O+H experiments

The main conclusion of the previous sections is that H-irradiation of O$_2$:O$_3$ ices produces high CD of newly formed water molecules, mainly via the OH + H reaction. Aware of this statement, we have studied the case of O + H reaction. This reaction in theory includes all the possible reaction routes, since once O atoms adsorb on the surface, they can form O$_2$ and O$_3$. We know that

\[ O + H \rightarrow OH + H \rightarrow H_2O \]  
(4.8a)

\[ O + O \rightarrow O_2 + H \rightarrow \text{see eq } 4.6a \]

\[ O_2 + O \rightarrow O_3 + H \rightarrow \text{see eq } 4.7a \]

Figure 4.20 displays DED measurements of masses 17 and 18 during O + H irradiation on oxidized graphite held at 10 K. We note that during the exposure both signal at mass 18 and signal at mass 17 are higher than the background signal. This is evident on right panel of Figure 4.20 where we display signals of mass 17 and 18 normalized to their respective no-deposition signals. The DED measurements provide clear evidence of newly formed molecule CD (H$_2$O and OH). Actually neither mass 18 nor mass 17 are present in the beam and, as a consequence, molecules detected through these masses have to be formed on the surface and released in the gas phase. The allotropization of O atoms complicates the analysis of these results, or at least of mass 18. Actually we have shown that the signal at mass 18 is present.
in O₂:O₃+H experiments. This means that signals at mass 18 can be due to H₂O CD via Eqs. 4.6c, 4.7b, and 4.8a. Conversely, signals at mass 17 are not present in O₂:O₃+H experiments, and thus what we measure is necessarily due to the first step of Eq. 4.6c. We stress here that, H₂O is detected both via masses 17 and 18, due to cracking in the QMS head (see Sec. 2.2.2.1). Their ratio is around 17% in the case of water. Figure 4.21 shows that during no irradiation the M17/M18 ratio is 17%. These signals come from the residual water present in the main chamber. On the contrary, the ratio can reach 40% during irradiation. This indicates that the signal at mass 17 is due to OH CD in the first step of Eq. 4.6c.

4.3.2 The influence of the substrate: CD of O₂

4.3.2.1 Experimental results

The aim of this section is to describe the role and the contribution of the different parameters influencing the chemical desorption. We have chosen to present the case of O atoms reactivity on oxidized graphite for two reasons. First, O atoms reactivity is a well known system (Ward & Price 2011; Minissale et al. 2013; Minissale et al. 2014a; Congiu et al. 2014) and, since only 2 reactions are involved:

\[ O + O \rightarrow O_2 \]  \hspace{1cm} (R0.1)

\[ O + O_2 \rightarrow O_3 \]  \hspace{1cm} (R0.2),

we can immediately realize how the different parameters affect the two reactions. Second, among substrates already studied, the oxidized graphite exhibits the highest chemical desorption efficiency. Some of the experimental results that we analyze here are shown in panel c of Figure 4.4. For the sake of clarity, we replot it in panel a of Figure 4.22. The dashed line corresponds to the conservation of the total number of O atoms: as if all the atoms (in the form of O, O₂, and O₃) desorb during the TPD, therefore the triangles (formed O₂+formed O₃) should overlie this line. This line was determined experimentally using the undissociated beam (pure O₂ beam). We did not detect any signal that could be interpreted as O-atom desorption in the gas phase during the TPD, and the sum O₂+O₃ does not fit the dashed line, as opposed to what observed on a water substrate (see Figure 4.23 and Minissale et al. 2013). The large deficit in O atoms (namely the sum of O₂) is due to the CD. The excess of chemical energy of the newly formed molecule is partly transferred to kinetic energy (by bouncing on the substrate), and the desorption may occur. We can also remark that in panel a of Figure 4.22 the O₂/O₃ ratio depends on the coverage, or more precisely, that the number of missing O is decreased with the coverage.
To get a better proof of the change in chemical desorption efficiency, we re-plot the results of panel a in panel b of Figure 4.22. We use as x-axis the fraction of O$_2$ ($f_{O_2}$) and as y-axis the fraction of O$_3$ ($f_{O_3}$). $f_{O_2}$ is obtained by dividing the yield of O$_2$ ($Y_{O_2}$) by the dose $D_f$ (defined as the flux $\Phi$ multiplied by the exposure time $t_f$), and the fraction of O$_3$ is calculated the same way ($f_{O_3} = \frac{Y_{O_3}}{D_f}$). We can define the efficiency of chemical desorption as $f_{CD} = 1 - f_{O_3} - f_{O_2}$. The equality $f_{O_3} + f_{O_2} = 1$ means that all atoms have remained on the surface before the TPD and so the chemical desorption is fully inefficient. We have represented this case using a broad black line on Figure 4.22. On the contrary, if there is no O$_2$ or O$_3$ desorption during TPD, all the atoms should have gone in gas phase during the reaction, $f_{CD} = 1$, and the chemical desorption is fully efficient. Panel b of Figure 4.22 shows that $f_{CD}$ changes for experiments where the dose has been changed (red stars, same data as in panel a). The lowest coverage case lies just above the dotted line which corresponds to 50% of chemical desorption, while the highest coverage lies above the 18% chemical desorption line. With the increase of the coverage, there is a rather vertical shift upward. This shift illustrates two facts: (i) the O$_2$ production saturates because O$_2$ molecules are transformed in O$_3$ molecules by new incoming O atoms; (ii) the larger the coverage, the lower the chemical desorption efficiency. We want to stress that for increasing doses we need to increase exposure times, keeping the flux of the atomic beam constant. The measurement is made at the end of the exposure, but the coverage evolves during the exposure phase. Any experimental point does not represent a constant coverage, but the evolution from zero to the final coverage. Actually, our experiments represent an integration over the time of events. From stars in panel b of Figure 4.22, it is clear that chemical desorption efficiency is reduced with the coverage, but the experimental method partly conceals the correlation between the coverage and the chemical desorption, because the coverage is not the parameter directly varied. For this reason we performed a second set of experiments. This time, while keeping constant the dose (0.5 ML) - using the same evolution of the coverage (at first approximation) - we incremented the surface temperature for different experiments from 8 to 25 K (above 25 K O$_2$ starts to desorb). A change of the surface temperature varies the diffusion properties, and as a consequence, changes the balance of the two reactions (R0.1) and (R0.2) and the final products. These experiments are represented with blue circles in panel b of Figure 4.22. All these points are located around the 18% dashed line. The O$_2$/O$_3$ balance changes: the higher the surface temperature, the larger is the $f_{O_3}$, as expected. More surprisingly, the
Chemical desorption seems to be rather insensitive to the final-product ratio. In the same way we re-plot data obtained on other surfaces (amorphous silicate and different morphology of water ices), as shown in Figure 4.23. We notice that on water ices all data (vs T_s and vs coverage) are on the no-CD line. Data on silicate show a behavior similar to the ones of graphite: the chemical desorption seems to be rather insensitive to the final product ratio for data vs T_s, while it decreases for data vs coverage. It should be noted that on silicate this decrease is less important than on graphite.

4.3.2.2 Model and discussion

To analyze our experimental results, we can consider how the populations adsorbed on the substrate evolve with time (or coverage). In particular, there are three populations evolving with the deposited dose: O(t), O_2(t), and O_3(t). However, we are only able to measure O_2(t_f) and O_3(t_f) final populations, represented through grey circles on Figure 4.24. The evolution of the two populations has two origins: external incoming fluxes of O and O_2 molecules (represented by broad arrows), and chemical evolution of the populations. O

Figure 4.22: Adapted from Minissale & Dulieu (2014b). Panel a: integrated TPD spectra yields of O_2 (squares) and O_3 (circles) obtained after exposition of different doses of O (75 %) and O_2 (25 %) on oxidized HOPG. The straight dashed line corresponds to a full conservation of the O atoms on the form of O_2 and O_3. Panel b: fraction of O_3 vs O_2. Red stars correspond to experiments shown in panel a (variation of the dose at fixed surface temperature, 10 K), and blue circles correspond to different depositions of fixed dose (0.5 ML) at different surface temperatures (8, 10, 15, 20, 22, and 25 K). Solid, dashed and dotted lines are obtained using f_{CD}=0, 18, and 50 %, respectively.

Figure 4.23: Fraction of O_3 vs O_2 for different experiments on different surfaces. See legend and caption of Figure 4.22 panel b.
atoms undertake the two reactions (R0.1) and (0.2). The branching ratio between (R0.1) and (R0.2) is expressed by the parameter \( a \). If \( a=1 \), only (R0.1) takes place, if \( a=0 \), only (R0.2) takes place. Clearly the balance between the two reactions is dependent on the populations, so from one experiment to another, and even during each experiment, \( a \) varies ranging always between 0 and 1. The parameter \( e \) describes the chemical desorption of (R0.1), and the parameter \( f \) describes the chemical desorption of (R0.2). If \( e=1 \), all the \( O_2 \) formed via \( O + O \) reactions promptly desorb. Parameters \( e \) and \( f \) actually describe the chemical desorption process.

The details of equations are presented in Minissale & Dulieu (2014b); Figure 4.25 shows the comparison of model results (red and green lines, respectively \( O_2 \) and \( O_3 \)) with experimental points (squares and circles, respectively \( O_2 \) and \( O_3 \)). The match is excellent, and the deviation can be attributed to experimental uncertainties rather than to the poor level of the simulations. We note that an excellent match can as well be obtained with a \( f \) parameter frozen to few \%; however, the linear dependence cannot be straightforwardly demonstrated. In fact, the accuracy of the experimental data is not sufficient to analyze the case of \( e \) and \( f \) with values of only a few \%. Model results can be summarized as follows:
a the chemical desorption is mostly carried by the O+O reaction with an efficiency close to 80 % (78 ± 5 %) on a bare oxidized graphite. The other reaction, O+O\(_2\), has a more limited reactive desorption efficiency; set to 5 ± 5%.

b The chemical desorption is highly dependent on the presence of other molecules adsorbed on the substrate and decreases linearly with the surface coverage.

To understand these statements, we have to make clear that the two involved reactions are different in many aspects: the masses and the degrees of freedom of products, the binding energy of reactants, and the enthalpy of reaction. Table 4.3 regroups the different properties of the reactions and their products. From Table 4.3, we can infer why chemical desorption of (R0.1) is larger than that of (R0.2), by looking at each of the following parameters:

1. **Enthalpy of formation.** As already stated, the chemical desorption process requires some energy excess: the source of the energy is certainly the enthalpy of formation, and we can see that (R0.1) has a larger available energy with respect to (R0.2).

2. **Degrees of freedom.** The initial energy shall be spread among more degrees of freedom in the case of O\(_3\) than in the case of O\(_2\). The share of energy available for the motion perpendicular to the surface (required for desorption) is more limited in the case of O\(_3\). So the energy available for desorption favors chemical desorption of O\(_2\).

3. **Binding energy.** It is a limiting factor, since molecules have to overcome a binding energy barrier to desorb. Here again, (R0.1) is favored thanks to a lower binding energy.

4. **Mass of newly formed molecule.** It may have an indirect impact on the chemical desorption. Actually, phonon propagation is dependent on the mass of the colliding molecule with the surface. It is known that light molecules such as H\(_2\) have a rather weak sticking coefficient (about 0.3 at room temperature) with surfaces indicating a poor energy transfer (Chaabouni et al. 2012b). On the contrary, heavier ones, like CO or O\(_2\), have large (> 0.9) sticking coefficients (Bisschop et al. 2006). Of course, it depends on the type of surface, and, in some cases, collisions can be treated classically and an effective mass of the surface can be found. The analysis of measurements of hyperthermal O\(_2\) scattered from a graphite surface shows that the effective mass of 1.8 graphite carbon ring (≃ 130 a.m.u.) can be adopted (Hayes et al. 2012). In our case, we cannot directly use this value since we use oxidized graphite, although treating the graphitic surface as in its entirety can be a good approximation. The collision is not done with a unique carbon atom, or eventually a pair, or even a ring, it is a collective response of the surface. We can use then an effective mass quite larger than the mass of O\(_2\) and O\(_3\).

To estimate the energy transfer for each molecule, we use a classic elastic collision as zero order approximation, and check the kinetic energy transfer. If the impactor has a mass \(m\) and the immobile target has mass \(M\), thus the kinetic energy retained after collision for \(m\) can be written as follows:

\[
\epsilon = \left( \frac{m - M}{M + m} \right)^2
\] (4.9)
Figure 4.26: Adapted from Minissale&Dulieu (2014b). O$_2$ (black squares), O$_3$ (red circles) and their sum (green triangles) obtained after 0.5 ML of beam exposure as a function of the dose of N$_2$ molecules previously deposited on the oxidized graphite sample. The dark cyan dashed line corresponds to no chemical desorption.

Using $m=32$ or 48 a.m.u., and $M=130$ a.m.u., we find $\epsilon_{O_2} = 37\%$ and $\epsilon_{O_3} = 21\%$. Once again, the mass parameter favors the chemical desorption of O$_2$ molecules, because they keep more kinetic energy after the collision with the surface ($\epsilon_{O_2} > \epsilon_{O_3}$).

All the four parameters are in favor of (R0.1) and therefore our first experimental statement (statement $a$) is fully explained. The second one (statement $b$) that deals with the coverage may be explained through the fourth parameter. The energy transfer has higher values if the molecule collides with another adsorbed species: all the energy is transferred in case of equivalent mass molecules, and 0.96 in case of O$_3$-O$_2$ collisions. In other words, all the kinetic energy of the newly formed molecules is transferred to another adsorbed molecule upon collision. Minissale&Dulieu (2014b) have tested successfully this scenario by adding a non reactive molecule (N$_2$) on the substrate. Figure 4.26 shows the influence on CD of a variable amount of pre-deposited N$_2$. Total yields increase with the dose of N$_2$ pre-adsorbed on the surface. The CD process vanishes progressively and disappears between 1 and 2 pre-adsorbed layers of N$_2$. These experiments show the importance of the coverage from a different point of view, that is an efficient energy transfer between newly formed molecules and the molecules adsorbed in the vicinity of the formation site.

4.3.3 Conclusion

In this section, we have described some aspects of the chemical desorption process. We have presented some relevant experiments and we have shown the importance of different parameters for the CD efficiency (substrates, enthalphy, coverage, and so on). Here we report a list of CD efficiencies for different reactions on three different surfaces (np-ASW, amorphous silicate, and oxidized graphite). Some of the reactions used to evaluate CD are presented in the next chapter. Other reactions have been discussed shortly in this thesis and we need further experiments to give a quantitative and precise evaluation of their CD efficiency.

We clearly claim in Sec. 4.3.2 that CD efficiency can be explained by looking essentially at 4 physical parameters of the reaction: (1) exothermicity of reaction ($\Delta H$), (2) mass, (3) degrees of freedom (DF), and (4) binding energy of products. Here we show that using the following law

$$CD = e^{-\frac{E_{\text{binding}} \times \Delta F}{k_B T}}$$

we are able to calculate the CD efficiency. A comparison of model and experimental results for some reactions is shown in Figure 4.27. Model results (red hexagons and green squares)
Table 4.4: List of experimental CD efficiencies for different reactions on three different surfaces (np-ASW, amorphous silicate, and oxidized graphite). For the cases in which we were not able to measure quantitatively the CD efficiency, we provide upper or lower limits. We list theoretical CD efficiencies calculated for a an oxidized graphite.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Method</th>
<th>Reaction</th>
<th>Desorbing product</th>
<th>Experimental CD efficiency</th>
<th>Theoretical CD efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DED</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + H</td>
<td>√</td>
<td>O + H</td>
<td>OH</td>
<td>25±15</td>
<td>50±25</td>
</tr>
<tr>
<td>O + O</td>
<td>√</td>
<td>O + O</td>
<td>O₂</td>
<td>&lt;5%</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>N + N</td>
<td>√</td>
<td>N + N</td>
<td>N₂</td>
<td>&gt;90%</td>
<td>&gt;70%</td>
</tr>
<tr>
<td>CO + H</td>
<td>√</td>
<td>HCO + H</td>
<td>CO</td>
<td>40±20</td>
<td>-</td>
</tr>
<tr>
<td>H₂CO + H</td>
<td>√</td>
<td>H₂CO + H</td>
<td>HCO</td>
<td>-</td>
<td>&lt;8%</td>
</tr>
<tr>
<td>Ar + H</td>
<td>√</td>
<td>Ar + H</td>
<td>Ar</td>
<td>&lt;5%</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>NO + H / N</td>
<td>×</td>
<td>many</td>
<td>many</td>
<td>&lt;8%</td>
<td>&lt;8%</td>
</tr>
<tr>
<td>CO + O</td>
<td>×</td>
<td>HCO + O</td>
<td>CO₂</td>
<td>&lt;10%</td>
<td>&lt;10%</td>
</tr>
<tr>
<td>CH₂OH + H</td>
<td>×</td>
<td>CH₂OH + H</td>
<td>CH₂OH</td>
<td>&lt;8%</td>
<td>&lt;8%</td>
</tr>
</tbody>
</table>

√ and X are used to indicate if the experimental procedure (DED or TPD) have been used or not, respectively; "CD decreases as a function of coverage"; † experiments performed with excited particles (see Sec. 2.2). \( \epsilon \) is the coverage. Moreover, for red hexagons \( \epsilon = 0.4 \) while for green squares it is given by Eq. 19. We remark that this second choice of the \( \epsilon \) value gives a better fit with respect to \( \epsilon = 0.4 \). Nevertheless, some improvements have to be made both from an experimental (to reduce error bars) and a theoretical point of view.

**Bibliography**


Figure 4.27: Comparison between calculated and experimental CD efficiency for the set of reactions investigated in this work.


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5.1 Water formation via $O_2+H(D)$: the effect of the substrate

Oxygen is the third most abundant element in the Universe (Suess & Campbell 1956) after Hydrogen and Helium, and is present in the solid phase of icy grain mantles in the interstellar medium. For this reason, over the last decade a number of independent laboratory experiments involving oxygen has been performed. In particular, in many experimental works (Ioppolo et al. 2008; Dulieu et al. 2010; Mokrane et al. 2009; Coppen et al. 2010; Jing et al. 2011; Obá et al. 2012; Chaabouni et al. 2012) all the possible chemical pathways involving O and H (molecules and/or atoms, i.e., $O$, $O_2$, $O_3$, $OH$, H and $H_2$) in solid phase were investigated. Three different hydrogenation routes for water formation have been identified: $O + H$, $O_2 + H$, and $O_3 + H$. These studies demonstrated that water is the principal product of such reactions. We will not discuss exhaustively the solid state formation of water ice through these routes. The goal of this section is to show the effect of the substrate on water formation efficiency in the submonolayer and monolayer regimes, and the reaction used to achieve this purpose is the $O_2+D$ reaction.

5.1.1 Experimental

Experiments on water formation from $O_2$ and D atoms have been performed at 10 K on different surface samples: (i) silicate (as described above), (ii) non-porous amorphous solid water (np-ASW) ice, and (iii) porous amorphous solid water (p-ASW) ice. The np-ASW ice film with a thickness of about 50 layers is grown at 110 K. The p-ASW ice film with 10 layers of thickness is grown by background vapor deposition on top of the compact water ice substrate kept at 10 K using the same microchannel array doser placed in the remote position. The exposure of $O_2$ molecules and D atoms is always done at 10 K. Under our experimental conditions, 1 ML of D-atoms corresponds to 7 min of D deposition time, while 1 ML of $O_2$ ice is obtained after 6 min of $O_2$ exposure time.
Water formation via O$_2$+H(D)

Figure 5.1: Adapted from Chaabouni et al. (2012). RAIRS spectra of D$_2$O and D$_2$O$_2$ (left panel) and desorption peaks of O$_2$, D$_2$O, and D$_2$O$_2$ (right panel) after the exposure of 1 ML of solid O$_2$ and 2.0 ML of D atoms on different substrates held at 10 K: (a) amorphous silicate, (b) p-ASW ice, and (c) np-ASW ice. The dashed curves at left are gaussian fits. (The adsorption band at 2850 cm$^{-1}$ is due to an impurity.)

5.1.2 Results and discussion

Left panel and right panel of Figure 5.1 show respectively the RAIR spectra and TPD curves after the exposure of 1 ML of solid O$_2$ and 2.0 ML of D atoms on different substrates held at 10 K: (a) amorphous silicate, (b) p-ASW ice, and (c) np-ASW ice. In the RAIR spectra, we assign the broad absorption peak at around 2404 cm$^{-1}$ to the overlapping of D$_2$O and D$_2$O$_2$ -OD stretching vibrations modes. The small peak at around 2107 cm$^{-1}$ is attributed to the $\nu_6$ vibration mode of D$_2$O$_2$ (Jing et al. 2011). In addition, a small peak at around 1215 cm$^{-1}$ is attributed to OD-bending mode of D$_2$O and a second small peak at around 1050 cm$^{-1}$ is attributed to the OD-bending of D$_2$O$_2$. (Miyauchi et al. 2008; Jing et al. 2011) Right panel of Figure 5.1 shows three sets of TPD: between 10 K and 60 K where the O$_2$ desorption occurs, 120 K and 180 K for D$_2$O, and 140 K and 220 K for D$_2$O$_2$. All these results clearly show a difference in the amount of reactants consumed (O$_2$) and products formed (D$_2$O and D$_2$O$_2$). By using RAIRS results (see Chaabouni et al. 2012 for details), we estimated the amount of D$_2$O water molecules formed on each substrate held at 10 K to be $\approx$0.37ML on the silicate surface, $\approx$0.89ML on the p-ASW ice, and $\approx$1.25ML on np-ASW ice surfaces. These results give a lower limit of the O$_2$ consumed (we only have to multiply by a factor of 2). It appears that $\geq$19% of the initial coverage of O$_2$ has to be consumed on the silicate surface, $\geq$45% on the p-ASW ice, and $\geq$63% on the np-ASW ice surfaces. From the TPD results we can independently check the amount of O$_2$, too. We obtained that, on the silicate substrate, most of O$_2$ molecules (96%) are consumed by D-atoms and only 18% of O$_2$ molecules are used to form D$_2$O and 24% to form of D$_2$O$_2$. While in the case of the np-ASW ice substrate, the yield of D$_2$O molecules reaches its maximum of about 55% and that of D$_2$O$_2$ 5% when 85% of O$_2$ molecules are destroyed by D atoms. This difference between consumed reactants and products formed can be explained through the chemical desorption process. Actually RAIRS and TPD experiments showed that the efficiency of D$_2$O water formation depends strongly on the substrate, like the case of O$_2$ formation, discussed before (Minissale&Dulieu 2014c). The fraction of D$_2$O water ice formed on the surface of the silicate at 10 K was found to be $\approx$20%, two and three times lower than the fractions of D$_2$O water molecules formed on the porous amorphous water ice ($\approx$45%) and the nonporous amorphous water ice ($\approx$55%-60%) surfaces, respectively. We can fit our data through the model described in Chapter 3 by using two parameters, the branching ratio ($\alpha$) of O$_2$+D reaction and the chemical desorption probability of D$_2$O (see Figure 5.2 and Chaabouni et al. (2012)). The catalytic effect of the water ice substrate enhances the reaction rates between D and O$_2$. An enhanced diffusion increases the O$_2$+D reaction efficiency by reducing D+D reaction.

1This means that each 100 O$_2$ molecules, 96 are consumed, 2x18 and 24 molecules of D$_2$O and D$_2$O$_2$ are formed, respectively; hereafter percentages refer to the total amount of O$_2$. 
Figure 5.2: Adapted from Chaabouni et al. (2012). Schematic illustration showing the possible reaction routes for the formation of D$_2$O involving O$_2$ and D atoms. The solid and the broken black arrows indicate the reactions without and with activation barriers, respectively. The blue arrow indicates the reaction which is less probable on the bare silicate substrate than on amorphous water ice. Red arrows indicate when the D$_2$O chemical desorption can occur.

The D+OD reaction, due to its high exothermicity and low degree of freedom, is responsible for a high chemical desorption probability for water molecules. The difference between the chemical desorption rate of water molecules on silicate (80%) and on water ices (40%) can be explained in two ways:

1. O$_2$D+D allows ($\alpha \approx 0.7$) the formation of two OD intermediates (that do not recombine) on the silicate surface rather than water ices. On water, more OD recombines to form D$_2$O$_2$. As a consequence more D$_2$O molecules undergo chemical desorption on silicate.

2. If $\alpha$ is constant, the chemical desorption probability changes between the silicate surface and water ices, as proposed in Minissale & Dulieu (2014)

Very probably both mechanisms are at play. In summary the surface (and its morphology) affects surface physics (especially D diffusion and CD efficiency) that in turn modifies surface chemistry favoring some reactions and so formation of some molecules. For example H$_2$O$_2$ formation is favored on multilayer regimes, then on water surfaces, on silicate and finally on graphite. See Sec. 4.3 for a detailed discussion of the chemical desorption of the O-H system.

5.2 Nitrogen oxides chemistry

Inversely to the O/H chemistry, the O/N chemistry is a poorly studied domain. Recently a number of studies involving N/H chemistry have been reported (Hidaoka et al. 1995). The solid state formation of NH$_3$ has been discussed (Hidaoka et al. 2011) and NO ice was shown to be a good starting point in the formation of large molecules such as NH$_3$NO$_3$ or Hydroxylamine, NH$_2$OH (Congiu et al. 2012a, 2012b; Fedoseev et al. 2012), one of the potential precursors of complex pre-biotic species in space (Blagojevic et al. 2003). Both nitric oxide and ammonia are considered important precursor species in the formation of N-containing organics. NO, specifically, is a seed for N- and O-bearing species (Joshi et al. 2012) such as NO$_2$, N$_2$O, HNO, HONO, HN$_2$O$_3$, and NH$_2$OH. In this section, we deal with the O/N chemistry on the solid phase and we present experimental results for NO+O, NO+O$_2$, ...
and NO+O₂ reactions in the solid state that mainly lead to the formation of NO₂. These results could be useful to explain the O/N chemistry in different environments:

- In Earth’s atmosphere (Atkinson 2000), as well as in Venus’ (Watson et al. 1979), nitrogen oxides play a critical role in the tropospheric and stratospheric chemistry of very important compounds such as ozone (O₃) (Toon&Tolbert 1995), the hydroxyl radical (OH), and nitric acid (HNO₃). NO₂, in particular, can deplete ozone in two different ways, as explained in Toon&Turco (1991). NO and especially NO₂ are therefore considered to be very important in the formation and loss of tropospheric ozone and probably bring about climate change and global warming (Hartmann et al. 2000).

Oxidised nitrogen chemistry at high latitudes is very complex (Jones et al. 2001), and it is necessary to study both the background chemistry determining NOₓ concentrations in the polar troposphere and to understand any exchange processes between snow and air.

NOₓ concentrations were studied in many works (Jones et al. 2001; Howrath et al. 1999; Ridley et al. 2000) proposing that NOₓ is produced within the snow pack, Arctic and Antarctic, and in particular upon ice particles. The present work was hence intended to study all the surface reactions involving oxide nitrogen species (NO, NO₂, N₂O etc) and affecting NOₓ concentrations. We will also show that water ice is a good catalyst for these reactions.

- In the interstellar medium, O/N chemistry still remains not fully understood although molecules containing a N-O bond, like NO, N₂O and HNO have been detected in the ISM (Lister/Turner 1978; Zrtrys et al. 1991, 1994; Martin et al. 2003). Astrochemical models predict typical NO abundances in the gas-phase, with respect to molecular hydrogen, of \( f(\text{NO}/\text{H}_2) \approx 10^{-7}-10^{-6} \). The actual observed abundance (Millar et al. 1997) is about a factor 10 lower: \( f(\text{NO}/\text{H}_2) \approx 10^{-8} \). This difference may be due to lacking destruction (i.e., consumption) routes that have not taken correctly into account; actually large amounts of NO (up to 10% of the gas-phase abundance) are likely to accrete on the cold (10 K) dust grains, and therefore to react with H, O, and N atoms arriving from the gas-phase.

In Sec. 4.1.2 we pointed out that the use of a O-atom beam is associated with the presence on the surface of O₂ and O₃ molecules (arriving from the gas phase or formed on the surface). For this reason, any time that we want to study a reaction involving O atoms and a species X, we need to know in advance what is the reactivity of oxygen allotropes with the X species. Therefore, in this section we present firstly NO+O₂ and NO+O₃ reactions and then the NO+O reaction.

### 5.2.1 NO+O₂

In this section, we present the experimental results of NO oxidation by O₂: this reaction leads to NO₂ formation (concurrently to other nitrogen oxides) and it occurs in solid phase via the ER mechanism. The LH mechanism proved to be not efficient under our experimental conditions. This reaction has been discussed in more detail in Minissale et al. (2013a).

#### 5.2.1.1 Experimental

The experiments were performed on four different surfaces: amorphous silicate sample, amorphous or crystalline water ice (see Sec. 2.2.1 for methodology of ice preparation), and oxidized graphite substrate. Experiments were performed through three different procedures:

1. NO deposited on top of pre-adsorbed O₂ (a method in Figure 5.3);
2. O₂ deposited on top of pre-adsorbed NO (b method in Figure 5.3);
3. NO and O₂ co-deposited on the cold sample (c method in Figure 5.3);
Figure 5.3: Schematic representation of our experiments. (a) NO is deposited in a layer of O\textsubscript{2} previously deposited on the cold sample. (b) O\textsubscript{2} is deposited on a layer of NO. (c) NO and O\textsubscript{2} are co-deposited on the cold sample. (d) The products are probed using Temperature Programmed Desorption and Reflection Absorption Infrared Spectroscopy.

Figure 5.4: Adapted from Minissale et al. (2013a). The red trace shows the RAIR spectrum of 5 ML of O\textsubscript{2} and 2.5 ML of NO after co-deposition at 10 K. Seven spectral features due to NO, (NO)\textsubscript{2}, NO\textsubscript{2}, N\textsubscript{2}O\textsubscript{3}, and N\textsubscript{2}O\textsubscript{4} are marked.

All the species are calibrated by saturation of the first layer (Noble et al. 2012). Doses are expressed in monolayers (ML) units, 1 ML corresponding to the surface fully covered with one layer of adsorbate. After deposition of the two reactants, the sample is probed using FTIR, and finally with TPD as shown in Figure 5.3d.

5.2.1.2 Result and discussion

Figure 5.4 shows the RAIRS spectrum obtained after co-deposition of 5 ML of O\textsubscript{2} and 2.5 ML of NO on silicate held at 10 K. We recorded infrared spectra for other doses, deposition methods, and substrates. We decided to show this spectrum because the co-deposition method prevents obvious multilayer screening effects, even though a rather large dose is required to detect without ambiguity the infrared bands already present at sub-monolayer coverage. We assign the band at 1897-1902 cm\textsuperscript{-1} to NO monomer (Fateley et al. 1959), while bands at 1863 and 1776 cm\textsuperscript{-1} are signatures of NO dimer (Consigl et al. 2012a; Fateley et al. 1959). N\textsubscript{2}O\textsubscript{4} is present at 1875 cm\textsuperscript{-1} (Fulsio et al. 2009). We have attributed the broad band at 1311 cm\textsuperscript{-1} to $\nu$(N-O) symmetric s-stretching NO\textsubscript{2} and the one at 1605 cm\textsuperscript{-1} to $\nu$(N-O) asymmetric stretching of NO\textsubscript{2} (Bartram & Koel 1989; Schwakke et al. 1986). Finally, the peak at 1832 cm\textsuperscript{-1} is attributed to the asymmetric stretch of ONNO\textsubscript{2} (Stirling et al. 1984) that very probably contributes to the bands at 1311 cm\textsuperscript{-1} and 1605 cm\textsuperscript{-1}. We explain the
presence of these species through the reaction scheme shown below

\[
\text{NO} + \text{O}_2 \rightarrow \text{NO}_3 \quad R2.1a \\
\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2 \quad R2.1b
\]

together with the following reactions

\[
\text{NO} + \text{NO} \rightarrow (\text{NO})_2 \quad R2.2 \\
\text{NO}_2 + \text{NO}_2 \rightarrow (\text{NO}_2)_2 \quad R2.3 \\
\text{NO} + \text{NO}_2 \rightarrow \text{ONNO}_2 \quad R2.4
\]

Through the spectrum in Figure 5.4 we can point out a few experimental facts:

i. The presence of NO suggests the incompleteness of the reaction NO + O\(_2\)

ii. all listed reactions take place at 10 K

iii. NO\(_3\) is an intermediate species with short solid-state lifetime; it is continuously formed by R2.1a and destroyed by R2.1b and its amount on the surface never increases, so we cannot distinguish its infra-red bands (Jacox & Thompson 2008) from the noise.

(i) and (ii) suggest that the diffusive phase is inefficient for consuming NO and probably the reactivity of R2.1 is mostly happening during the deposition phase via Eley-Rideal mechanism.

We have performed a set of TPD experiments to test the R2.1-R2.4 chemical network. We have studied the NO, O\(_2\), and NO\(_2\) species because we can calibrate separately the doses of these three species as for each we can obtain a pure beam. All the above statements and the R2.1-R2.4 chemical network are confirmed also by results of TPD experiments. Figure 5.5 shows TPD curves of mass 30 u.m.a., 32 u.m.a. and 46 u.m.a. after deposition of 1.0 monolayer (ML) of O\(_2\) and 0.5 ML of NO (O\(_2\) first, then NO) on the silicate sample maintained at 10 K. Three peaks are evident: the first one between 25 and 45 K is due to the O\(_2\) desorption (mass 32), the second one to the desorption of NO (mass 30) (46-65 K) and the last one is due to the NO\(_2\) desorption. This peak is visible at mass 46 (u.m.a), as well as at mass 30 (u.m.a) owing to fragmentation of NO\(_2\) within the QMS. Because of substantial cracking of nitrogen
dioxide in the QMS ionization head (see Sec. 2.2.2.1), only 14% of NO$_2$ is detected via mass 46. In the figure we have added a zoom-in window of the TPD between 100 and 140 K to appreciate the signals of mass 46 and 30, identically shaped and both peaking at 122 K. This is clearly a signature of NO$_2$ molecules as checked with control experiments carried out using a beam of NO$_2$ molecules. A further control has been carried out by studying the temperature evolution of infrared peaks. Figure 5.6 shows a reference spectrum of 2.5 ML of pure NO (in gray) and the temperature evolution of peaks after deposition of 5 ML of O$_2$ and 2.5 ML of NO. RAIR spectra are recorded at 10, 24, 44, 64, 84, 104, 114, 124, 134, 144, and 164 K, from a to j spectrum, respectively. With respect to the signatures shown in Figure 5.4 there is no difference, except for the presence of an additional N$_2$O$_4$ band at 1732 cm$^{-1}$. Figure 5.7 shows the temperature evolution of the integrated area of each peak. We used the “Peak Analyzer” function of ORIGIN software for analyzing overlapped multi-peaks, as shown in Figure 5.8 in the case of overpopulated region between 1810-1920 cm$^{-1}$. In Figure 5.7 we can distinguish three different region:

a before NO desorption (T$_{surface}$ < 60 K);

b between NO and NO$_2$ desorption (60 < T$_{surface}$ < 120 K);

c after NO$_2$ desorption (T$_{surface}$ > 120 K).

In region a all the features are already present. The NO-bond features (NO dimer and monomer, ONNO$_2$ at 1832 cm$^{-1}$) decrease as a function of surface temperature and they go to zero above 64 K, namely the NO desorption temperature. The increase in the NO$_2$-bond features (NO$_2$ and N$_2$O$_4$) corresponds to the decrease in NO-bond in this region. These variations are probably originated from LH process. Surface temperature increase favors surface diffusion of NO and O$_2$ (not yet desorbed) and, as a consequences, R2.1-R2.4 chemical network can occur via LH mechanism. When both NO and O$_2$ have desorbed, no reactions can occur any more, except for R2.4. This corresponds to region b. Finally region c is at temperatures higher than 110-120 K; here both the remaining IR bands start to decrease due to NO$_2$ and N$_2$O$_4$ desorption. In this discussion, the role of ONNO$_2$ is unclear. This molecule is ambiguous because we are not able to measure directly ONNO$_2$ through mass spectroscopy and only an infrared feature (at 1832 cm$^{-1}$) distinguishes ONNO$_2$ from NO$_2$. This feature disappears at 64 K, together with NO features, suggesting that desorption energy of ONNO$_2$
is similar to the NO one. Bartram & Koel (1989) explain this low desorption energy in two possible ways:

1. From a chemical point of view, the most probable configuration of dinitrogen trioxide is ON-NO₂ (NO and NO₂ are bound through nitrogen atoms). From a physical point of view, the physisorption occurs probably through the NO part. Hence, ON-NO₂ has the same desorption energy of NO which dimerizes anyway on the surface.

2. The increase in temperature induces a dissociation of ON-NO₂. The newly formed NO molecule desorbs, while NO₂ remains on the surface (forming N₂O₄ too).

5.2.1.2.a Initial conditions and model

Up to now, we have described only co-deposition experiments, but we have shown in Figure 5.3 that other experimental procedures have been used. In particular, we checked if a different order of deposition of the species changed the final products. The points in Figure 5.9 represent the TPD area under NO, O₂, and NO₂ curves for three different order of deposition of NO and NO₂.
Figure 5.9: $\text{O}_2$, NO and NO$_2$ yields obtained after 1 ML of $\text{O}_2$ and 0.5 of NO by changing sequential order of species deposition on the surface: (a) $\text{O}_2$ deposited first, (b) co-deposition, (c) NO deposited first; solid curves are obtained by fitting experimental data through a rate-equation model.

Figure 5.10: $\text{O}_2$, NO and NO$_2$ yields vs NO dose obtained after irradiation of 1 ML of $\text{O}_2$ with various NO exposures; solid curves are obtained by fitting the experimental data with a rate-equation model.

- panel a: 0.5 ML of NO deposited on 1 ML of $\text{O}_2$;
- panel b: 0.5 ML of NO + 0.5 ML of $\text{O}_2$ co-deposited;
- panel c: 0.5 ML of $\text{O}_2$ deposited on 0.4 ML of NO;

The reactivity is larger when $\text{O}_2$ is deposited first, the lowest when NO is the first species deposited. The results displayed in Figure 5.9 demonstrate that (i) the non-completeness of the reaction NO+O$_2$ and (ii) the reactivity occurs at 10 K, since these results confirm that not all NO is consumed and that reactions have occurred during the deposition phase. The low reaction yield of $\text{O}_2$-on-NO experiments can be explained by the dimerisation of NO (reaction R2.2) and the non-reactivity of the dimer with $\text{O}_2$. R2.1 and R2.3 are actually in competition and the dimerisation prevents from completing the reaction. Solid lines in Figure 5.9 are obtained by using a rate-equation model (see Chapter 3), in which we consider seven different species. Two are deposited on the surface, NO and $\text{O}_2$, and the others, NO$_3$, NO$_2$, (NO)$_2$, (NO$_2$)$_2$ and N$_2$O$_3$ are formed via surface reactions. Results from the model reproduce the experimental data indicating that all reactions happen via ER mechanism and NO$_3$ is the first intermediate as its concentration never increases. In addition, they also reproduce the non-completeness of NO+O$_2$ reaction. In fact, R2.1 occurs with a probability of 60±10%, indicating that the reacting cross section is about 6 Å$^2$, close to the geometrical
size of the molecules. The ER mechanism is the limiting factor for the formation of NO$_3$, and hence of NO$_2$ and other nitrogen oxides. If NO is not directly reacting with species coming from the gas phase, it accumulates and may form dimers, hindering thus NO$_3$ and NO$_2$ production. We have also performed experiments similar to that in Figure 5.5 but with varying NO doses. By measuring the area under the curve for each species and experiments, we can derive the amount of O$_2$ and NO consumed, and NO$_2$ formed. This is shown in Figure 5.10.

Finally Figure 5.10 shows the comparison of model and experiments as a function of NO coverage (same experiments shown in panel a of Figure 5.9). As we can see, all experimental points are well fitted by simulated curves, which confirms that the model is able to reproduce our experimental results and to describe the physics and the chemistry happening on the surface.

5.2.2 NO+O$_3$

5.2.2.1 Experimental

The reaction NO+O$_3$ has been studied using only one procedure: NO has been deposited upon pre-accreted O$_3$, since we do not have a pure beam of O$_3$. Ozone is accreted by sending O+O$_2$ on the surface (Minissale et al. 2014a). This procedure does not allow us to work with high coverages (more than 2 ML) because of layering effects, i.e., for a high NO coverage, the top NO layers will not react with O$_3$ molecules since ozone will be shielded by the underlying NO molecules. Furthermore this procedure maximizes the effect of ER mechanism.

5.2.2.2 Results and discussion

The left panel of Figure 5.11 shows RAIR spectra recorded after irradiation of 1.5 ML pre-deposited O$_3$ with increasing doses of NO at 10 K on oxidized HOPG. The spectrum of curve (a) is obtained after deposition of 1.5 ML O$_3$ (1043 cm$^{-1}$). The NO coverage increases from 0.2 ML (curve b) to 3.5 ML (curve g), while the intensity of the O$_3$ band slowly decreases, and that of the nitrogen oxide bands (NO$_2$, ONNO$_2$, N$_2$O$_4$ and (NO)$_2$) increases. In line with the spectra recorded for NO+O$_2$ we assign the bands at 1874 and 1773 cm$^{-1}$ to the NO dimer.
Figure 5.12: Adapted from Minissale et al. (2014b). Top panel: integrated area of NO\(_2\) (black circles) and consumed O\(_3\) (red triangles) peaks. Red triangles are obtained by subtracting the integrated area of O\(_3\)(NO = x) from O\(_3\)(NO = 0). The green pinstriped zone indicates the zone where reaction R2.1 starts to be efficient. Bottom panel: integrated area of O\(_3\) TPD curves (black circles) as a function of deposited NO, and corresponding fit (green solid line); the red solid line shows the theoretical amount of O\(_2\) formed via the NO+O\(_3\) reaction as if R2.1 was completely inefficient.

Nitrogen oxides (NOx) are found at 1874 cm\(^{-1}\) (Fulvio et al. 2009). The broad band at 1307 cm\(^{-1}\) is attributed to the n(N-O) symmetric stretch of NO\(_2\) (or ONNO\(_2\)) and the band at 1612 cm\(^{-1}\) to the n(N-O) asymmetric stretch of NO\(_2\) (or ONNO\(_2\)) (Bartram&Koel 1989; Schwalke et al. 1986). The band at 1838 cm\(^{-1}\) is due to the asymmetric stretch of ONNO\(_2\) (Stirling et al. 1994). The right panel of Figure 5.11 shows TPD curves after deposition of 1.5 ML pre-deposited O\(_3\) with 3.5 ML of NO at 10 K on oxidized HOPG. Similar experiments have been conducted on a surface of nonporous (compact) amorphous solid water ice and no evident differences - except for small band shifts - have been found.

These results can be explained through the following reactions:

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{R2.5}
\]

Together with the R2.1-R2.4 chemical networks described in the previous section. It is evident that the reaction NO+O\(_3\) is strongly connected to reaction NO+O\(_2\). In fact, when NO and O\(_3\) form NO\(_2\) and O\(_2\) via reaction R2.5, solid O\(_2\) contributes to NO\(_2\) formation via the R2.1 reactions. Two different phases can be distinguished. Initially when the NO coverage is low (\(\ll\)1 ML), O\(_3\) adsorbed on the surface is consumed in Eley-Rideal-like reactions by NO depletion from the gas phase. When NO\(_2\) and O\(_2\) surface densities start to increase, the NO+O\(_3\) reaction probability decreases, and instead, reactions R2.1 and R2.4 become more efficient. At that stage it is unlikely that NO\(_2\) forms via reaction R2.5. The top panel of Figure 5.12 shows the integrated area of the NO\(_2\) and O\(_3\) features as shown in Figure 5.11. The lower panel of Figure 5.12 shows the integrated area of the TPD curves of the infrared inactive O\(_2\) as obtained through a similar set of experiments that are not shown in Figure 5.11. For a coverage lower than 1 ML of NO, the consumption of O\(_3\) and the formation of NO\(_2\) behave linearly. The formation of O\(_2\) follows a similar trend. Gradually (for NO coverages thicker than 1 ML), the formed O\(_2\) (experimental points) starts to separate from the linear regime.
This is expected as the O$_2$ reacts with NO through R2.1 and O$_2$ cannot grow anymore, since the NO molecules cannot react efficiently with the underlying O$_3$. Both effects decrease the O$_2$ abundance. At this point O$_3$ is only partially consumed. This is shown in Figure 5.12 by the saturation of O$_3$ (red triangles, top panel). After this effect of saturation, (between $\approx$ 0.8 and 1.8 ML) NO$_2$ concentration continues increasing (NO coverage > 2 ML) through R2.1 as shown by the green pinstriped zone of Figure 5.12.

5.2.3 NO+O

5.2.3.1 Experimental

The NO+O reaction was studied by co-depositing reactants on different substrates (silicate and gold), and in different ice environments (pure NO+O, NO:H$_2$O+O, and NO:CO+O). In addition, we performed every single experiment under different coverage conditions. The submonolayer regimes cover from 0.1 to 1 ML and the multilayer regimes are in the range of 1 to 10 ML. The experiments were performed by using two different setups: FORMOLISM in LERMA lab at the Cergy-Pontoise University and SURFRESIDE$^2$ in Sackler Laboratory at the Leiden Observatory. Different physical conditions have been used to constrain the reaction mechanisms. Minissale et al. (2014b) have shown that surface temperature and coverage induce no pronounced changes on products. In the case of the submonolayer and multilayer regimes, some reactions change slightly their efficiencies. Furthermore different substrates do not affect strongly the results, but only cause small spectral shifts. For these reasons in the next section we will present only some prime examples of the performed experiments and the results obtained. We will focus on the results obtained on silicate in the submonolayer regime. We refer to Minissale et al. (2014b) for details and further works about NO+O reaction.

In the experiments presented in the next section oxygen atoms were produced through O$_2$ dissociation. Typical values of dissociation are the 70%, meaning that every ten O$_2$, seven are dissociated (14 O) and 3 remain undissociated and reach the surface. Moreover, O$_3$ can be formed on the surface. In other words, the presence of O$_2$ and O$_3$ in the beam and on the surface force us to consider NO+O$_2$ and NO+O$_3$ reactions for the study of NO+O reaction.

5.2.3.2 Results and discussion

Figure 5.13 shows four RAIR spectra recorded after NO+O deposition on a silicate sample held at 10 K. In particular, curve (a) shows the unprocessed spectrum for 1.5 ML of NO;
curves (b) and (c) show the results of a co-deposition resulting in 1.5 and 3.5 ML thick ice of NO + O (+ O$_2$), respectively; finally curve (d) shows the spectrum after the same deposition sequence used in curve (c), but with also annealing to 86 K and cooling to 50 K. In line with spectral assignments of subSec. 5.2.1 and 5.2.2 in curve (a) the NO (dimer) symmetric and asymmetric N-O stretch modes can be seen at around 1861 and 1770 cm$^{-1}$. The other three curves are clearly different with a number of new spectral features. Peaks at 1304-1311 and 1602 cm$^{-1}$ are due to both NO$_2$ and ONNO$_2$ (i.e., N$_2$O$_3$). Peaks at 1878, 1741 and 1256 cm$^{-1}$ are due to N$_2$O$_4$. The peak at 1834 cm$^{-1}$ is also due to ONNO$_2$ (N=O stretch). This latter peak does not show up in curve (d) indicating that ONNO$_2$ is not present at high temperature (>80 K). For this reason, in curve (d), we think that the peaks at 1304-1311 and 1602 cm$^{-1}$ are due to NO$_2$ ice. Here the annealing offers an additional tool for bands assignments. For instance, both NO dimer and N$_2$O$_4$ can contribute to the bands shown in curve (c) between 1890-1850 and 1755-1730 cm$^{-1}$. However, since the spectrum in curve (d) is obtained after annealing to 86 K - at this temperature all NO molecules have desorbed - the peaks at 1878 and 1741 cm$^{-1}$ can only be due to N$_2$O$_4$. This facilitates the overall assignment of all IR bands. We explain the presence of these species by adding the following reaction to the R2.1-R2.5 chemical network:

$$\text{NO} + \text{O} \rightarrow \text{NO}_2 \quad R2.6$$

The reaction NO + O is evidently connected to NO + O$_2$ and NO + O$_3$ reactions, due to oxygen allotropes present in the beam and on the surface. Similarly to the case of NO + O$_2$ and NO + O$_3$, we have performed TPD experiments to study the NO + O reaction and to compare the O$_x$ reactivity with NO. Figure 5.14 shows TPD curves of NO and NO$_2$ for different (co)deposition experiments: 0.4 ML of NO (cyan line), 0.4 ML NO + 1.5 ML of O (green line), 0.4 ML NO + 1.5 ML of O$_2$ (blue line) and 0.4 ML NO + 1.5 ML of O$_3$ (red line). In NO+O experiments almost all NO molecules are consumed. Clearly when O-atoms are produced through O$_2$ dissociation, O$_2$ molecules can still reach the surface. This also means that O$_2$ can react with oxygen atoms to form O$_3$, specifically when the species are co-deposited. So the formation of NO$_2$ can occur via reactions R2.1-R2.5-R2.6. In the case where the O/O$_2$ beam impacts on already accreted NO molecules, R2.5 is less probable and the possible pathways are limited to reactions R2.1 and R2.6. This is the case in Figure 5.14 (green line) where almost all the NO is converted into NO$_2$ (right panel) and only a small number (about
8% of NO molecules do not react. The incomplete conversion of NO into NO$_2$ is not likely to be due to the activation barrier of R2.1. It could be explained by a low penetration depth of O atoms into the NO ice, but it is more probably due to a small mismatch between the areas covered by the two beams (NO and O) in FORMOLISM. Moreover, the blue line in Figure 5.14 shows that O$_2$ is less reactive than O in reactions with NO, and this can further slow down the destruction of NO and concurrent formation of NO$_2$ in NO+O experiments.

These experiments confirm from one side the fast formation of NO$_2$ at low temperature via the NO+O reaction and from the other side, they suggest that the NO-formation reaction

$$\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \quad R2.7$$

is very slow with respect to NO-consumption reactions (mainly R2.6). In other words $k(\text{NO}+\text{O}) \gg k(\text{NO}_2+\text{O})$. For this reason we neglect R2.7 in the present discussion and refer to Ioppolo et al. (2014b) for more details.

5.2.3.2.a Dependence on surface temperature

In Minissale et al. (2014b), we have shown that the different substrates (silicate, compact ASW ice, and gold) and the ice composition used do not visibly affect the final products. They are, however, responsible for small shifts of the IR features. Surface coverage only slightly changes the final products of our experiments. In particular, multilayer regimes facilitate dimerization reactions. In order to investigate any temperature dependence of the NO+O reaction, experiments were performed in which the deposition temperature was varied. Figure 5.15 shows three NO TPD curves after deposition of 0.5 ML NO + 1 ML O on a silicate sample held at 15 K (red curve), 25 K (green curve), and 35 K (blue curve), respectively. The amount of NO left as a function of substrate temperature (calculated by integrating the area of each NO peak) is plotted in the inset of Figure 5.15. Within the experimental error bars, this does not show any substantial temperature dependence. The reaction is already efficient at low temperatures and seems to be essentially barrier free.

5.2.4 NO$_2$ reactivity

The experiments on NO$_2$ reactivity with H, N, and O atoms were carried out with FORMOLISM and the SURFRESIDE (based in Leiden) setups within a collaboration between
Figure 5.16: Scheme involving reactions of NO and NO\textsubscript{2} with H, N, and O\textsubscript{2} particles.

the LERMA-Cergy and the Astrochemistry group at the Leiden Observatory. The NO\textsubscript{2} reactivity has been discussed in Ioppolo et al. (2014b) and the main conclusion are here listed very briefly for the sake of clarity:

1. The final products of NO\textsubscript{2} hydrogenation are NH\textsubscript{2}OH and H\textsubscript{2}O. Hydroxylamine is found to be formed through a series of barrierless surface reactions.

2. N\textsubscript{2}O is formed through the nitrogenation of NO\textsubscript{2}. N\textsubscript{2}O is not destroyed in reactions with H-, O-, and N-atoms. We point out that no experiments of N\textsubscript{2}O irradiations have been performed, and this statement comes rather from indirect verifications.

3. Several nitrogen oxides, such as (NO)\textsubscript{2}, N\textsubscript{2}O\textsubscript{3}, and N\textsubscript{2}O\textsubscript{4}, are formed through surface NO\textsubscript{2} + H/O/N reactions.

5.2.5 Conclusion

We can sum up the results presented in this section and in Congiu et al. (2012a, 2012b), Fedoseev et al. (2012), Minissale et al. (2013a), Minissale et al. (2014b), and Ioppolo et al. (2014b) through the reaction network shown in Figure 5.16 and in Table 5.1 Once we have drawn the different reactions identified experimentally, we can remark that the most stable species (N\textsubscript{2}, N\textsubscript{2}O, NH\textsubscript{2}OH, and H\textsubscript{2}O) seem to be the end of the chemical journey in the O and N world.

5.3 O/C/H chemistry

5.3.1 Carbon dioxide formation on cold surfaces

Carbon dioxide has already been detected in the interstellar medium (ISM) by d’Hendecourt \& Jourdain de Maizon already few decades ago (1989). It represents one of the most common and abundant types of ices, and many astronomical observations (by the Infrared Space
Table 5.1: List of reactions (their final products and their efficiency) studied in the frame of nitrogen oxides chemistry.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Final products</th>
<th>Barrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO+H</td>
<td>NH$_2$OH</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>NO+N</td>
<td>N$_2$</td>
<td>NO$_2$</td>
</tr>
<tr>
<td>NO+O</td>
<td>NO$_2$</td>
<td>ONNO$_2$</td>
</tr>
<tr>
<td>NO+O$_2$</td>
<td>NO$_2$</td>
<td>ONNO$_2$</td>
</tr>
<tr>
<td>NO$_2$+O$_3$</td>
<td>no</td>
<td>ONNO$_2$</td>
</tr>
<tr>
<td>NO$_2$+H</td>
<td>NH$_2$OH</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>NO$_2$+N</td>
<td>N$_2$O</td>
<td>O$_3$</td>
</tr>
<tr>
<td>NO$_2$+O</td>
<td>NO</td>
<td>O$_3$</td>
</tr>
</tbody>
</table>

Observatory and the Spitzer Space Telescope confirm the presence of CO$_2$ in different environments, such as Galactic-centre sources (de Graauw et al. 1996), massive protostars (Gerakines et al. 1999; Gibb et al. 2004), low-mass young stellar objects (Nummelin et al. 2001; Aikawa et al. 2012), brown dwarfs (Tsuij et al. 2011), in other galaxies (Shimonishi et al. 2010; Oliveira et al. 2011), and in comets (Ootsubo et al. 2010). CO$_2$ is predicted to have a low abundance in the gas phase (N$_{CO_2}$/N$_{H_2}$=6.3×10$^{-11}$; Herbst & Leung 1986), and this is confirmed by observations (van Dishoeck et al. 1996). Low abundances in gas phase, together with its observed high abundances in the solid phase, cannot be explained exclusively by formation via gas-phase schemes (Hasegawa et al. 1992), therefore surface reactions are invoked to justify the high abundance of carbon dioxide ices. Extensive experimental studies have been carried out to study formation routes of CO$_2$ formation in solid-phase: on the one hand, irradiation of CO ices (pure or mixed with H$_2$O) with photons, charged particles or electrons, leads to efficient formation of CO$_2$ (Ioppolo et al. 2009; Laffon et al. 2010); on the other hand, Whittet et al. (1998) evoke chemical pathways occurring without the addition of energy to explain CO$_2$ detection in those interstellar environments where a lack of UV photons forbids ice processing (i.e., the molecular cloud Taurus). In this section, we deal with CO$_2$ formation on solid phase through two (non-energetic) pathways:

1. CO+O
2. H$_2$CO+O

5.3.1.1 CO+O

The first successful laboratory investigation of the formation of CO$_2$ by non-energetic processes was performed by Roser et al. (2001), who studied the surface reaction of CO and O atoms. In a first set of experiments they co-deposited the two species at 5 K and performed a TPD. Probably due to the low sensitivity of the quadrupole mass spectrometer they were using at that time, they did not detect any CO$_2$ formation. To prove the formation of carbon dioxide through such a pathway and to give a first estimate of the barrier for such a reaction they subsequently devised an experiment in which the co-deposited layer of CO and O atoms was covered by a layer of porous water ice. The TPD performed under such conditions allowed to detect the formation of CO$_2$ thanks to the reaction of CO and O migrating in the interconnected pores of the amorphous ice. Under the hypothesis that the mobility of species stemmed from thermally activated processes, a reaction barrier of 290 K was obtained that explained the formation of carbon dioxide even in quiescent clouds. Raut&Baragiola (2011) confirmed the formation mechanism of CO$_2$ investigated by Roser et al. (2011). They performed experiments showing the formation of small amounts of CO$_2$ during co-deposition of CO and cooled O and O$_2$ at 20 K, although they did not provide any activation barrier. Here we present further experimental studies for CO+O reaction and we also determined an activation energy of the CO+O reaction and the physical chemical mechanisms occurring on the surface by developing a kinetic model.
5.3.1.1a Experimental

CO$_2$ production on cold surfaces (10 - 40 K) was investigated by concurrent exposures of CO molecules and O atoms. The CO + O reaction is studied in a submonolayer regime on two different substrates: amorphous solid water (ASW) ice and oxidized graphite. The $^{13}$CO molecules and O atoms are sent simultaneously (co-deposition) on the surface via two triply differentially pumped beam lines. We used $^{13}$CO instead of $^{12}$CO to increase the signal-to-noise ratio of the mass signal of the $^{13}$CO reactant and the final $^{13}$CO$_2$ product. Hereafter we refer to $^{13}$CO as CO. The O atoms are produced by dissociation of O$_2$ molecules. The dissociation efficiency of O$_2$ was $\tau = 73\pm5\%$ at the time of the experiments performed on ASW and $61\pm7\%$ when we performed the experiments on graphite. Atoms and undissociated molecules are cooled and instantaneously thermalized upon surface impact with the walls of the quartz tube.

We have calibrated the molecular beam as described in Sec. 2.2.4 and found that the first monolayer (1 ML = $10^{15}$ molecules cm$^{-2}$) of both $^{13}$CO and O$_2$ was reached after an exposure time of about six minutes, which therefore gives a flux $\phi_{O_2,CO} = (3.0\pm0.3) \times 10^{12}$ molecules cm$^{-2}$s$^{-1}$. Once the O$_2$ discharge is turned on, the O-atom flux is $\phi_O = 2\tau \phi_{O_2,off} = 5.4 \times 10^{12}$ atoms cm$^{-2}$s$^{-1}$ and the O$_2$ flux $\phi_{O_2,on} = (1-\tau) \phi_{O_2,off} = 10^{12}$ molecules cm$^{-2}$s$^{-1}$. In addition, we determined that the beam did not contain O or O$_2$ in an excited state by tuning the ionizing electron energy inside the QMS head as described in Sec. 2.2.2.3.

5.3.1.1b Results and discussion

As previously claimed (i.e. in Sec. 5.2) to study CO+O reaction, we need to know what is the reactivity of CO with the other oxygen allotropes (O$_2$ and O$_3$). From an energetic point of view, oxidation of CO to form carbon dioxide may proceed by the following reactions:

\[
\begin{align*}
\text{CO} + \text{O} \rightarrow \text{CO}_2 & \quad \text{R3.1} \\
\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O} & \quad \text{R3.2} \\
\text{CO} + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2 & \quad \text{R3.3}
\end{align*}
\]

for which enthalpies of formation are $\Delta H = -532$, -33, and -425 kJ/mol, respectively (NIST Chemistry WebBook). Roser et al. (2001) and Raut&Baragiola (2011) have already studied reaction R3.1, showing that this reaction can produce carbon dioxide without the intervention of energetic processes. As for reaction R3.2, Mallard et al. (1994) suggested a very high activation energy barrier ($\sim 24000$ K), while reaction R3.3, to the best of our knowledge, has not been studied yet. Panel a of Figure 5.17 shows three TPD spectra of mass 45 for $^{13}$CO$_2$ after deposition on oxidized graphite held at 10 K of 1 ML CO (black squares), co-deposition of 1 ML CO+O$_2$ (red circles), and 1 ML CO+O$_3$ (green triangles). The three TPD curves and integrated areas of the curves are very similar and this suggests that the CO+O$_2$ reaction does not occur or that at least it is very inefficient at producing CO$_2$ in accord with Mallard et al. (1994). We have another indication of the CO+O$_2$ inefficiency by comparing the area of the CO peak with and without O$_2$. In the two cases we do not detect any measurable variations of the CO yield. We get to the same conclusion as far as the CO+O$_2$ reaction is concerned. No difference can be appreciated in the comparison between the peak area of CO, of background CO$_2$ and of O$_3$. This indicates that CO+O$_3$ is not a fast reaction to produce CO$_2$ either. Another control experiment consist into verify that CO$_2$ is really formed on the surface and that it is not present as an impurity in the CO bottle. To check this possibility, we have performed the experiments shown in panel b of Figure 5.17. The TPD spectra of mass 45 shown are recorded after exposure on a graphite surface - held at 10 K - of 4 ML of CO (black squares) and after 4 ML of CO+O (blue stars). The difference between the two TPDs is evident, and comparing the two CO$_2$ signals we find CO$_2$(CO dep)/CO$_2$(CO+O dep) = 8%, which confirms that the majority of the CO$_2$ detected is formed through surface reactions. Figure 5.18 shows the TPD traces resulting from irradiating ASW ice held at 20 K with 0.5 ML of CO+O (i.e., 0.5 ML CO, 0.15 ML O$_2$, 0.7 ML O). Four main peaks appear at masses 29, 32, and 45. The mass-29 peak is clearly due to the CO desorption, which
occurs between 32 K and 55 K and peaks at 41 K. Mass 32 presents two peaks, the first one between 28 and 42 K - peaked at 34 K - is due to O₂ desorption while the second one peaking at around 65 K included between 55 K and 75 K is due to the desorption of O₃ detected in the form of O₂ fragments, as a result of the O₃ cracking in the head of the QMS (see Sec. 2.2.2.1). Finally, the tiny high-temperature peak also shown in the insert comes from the CO₂ desorption occurring between 75 and 95 K and peaking at 83 K.

The experiments performed at different surface temperatures give results similar to the ones just described. In fact, we observe always four peaks (except for the 50 K experiment, where O₂ has already desorbed before starting the TPD), but their intensities change with temperature as shown below. Figure 5.18 indicates that two molecules are actually formed on the surface, O₃ and CO₂. Moreover, O₂ can also be either formed on the surface via the O+O reaction or come from the beam because of the non-total dissociation of O₂ molecules. Considering all reactants and products and remembering that reactions R3.2 and R3.3 can be disregarded, R3.1 is in competition with the two barrierless reaction (Minissale et al. 2013b, 2014a):

$$O + O \rightarrow O_2 \quad R3.4$$

$$O + O_2 \rightarrow O_3 \quad R3.5$$

To understand how efficiently the CO+O reaction proceeds and to derive its activation barrier, we performed several experiments at a fixed coverage and by varying the surface temperature. Temperature, in fact, affects both oxygen atom diffusion and the desorption of species and these two processes give us the key to understand our results (Figure 5.18) and consequently the way CO₂ is formed.

As we can see in Figure 5.19, the CO₂ signal is already present at 10 K, and it reaches a maximum when the surface temperature during exposure is 35 K. Subsequently, for higher temperatures the CO₂ signal decreases and becomes zero at 60 K. This behavior can be explained by considering three different “temperature zones”:

1. before O₂ desorption (below 30 K);
2. between O₂ and CO desorption (30-35 K);
3. after CO desorption (35 K).

Top panel of Figure 5.19 shows that in the range between 10 K and 30 K, the majority of oxygen atoms are used to produce ozone via reaction R3.4 and R3.5, and its production
Figure 5.18: Adapted from Minissale et al. (2013c). TPD curves at mass 29, 32, and 45 after irradiation of 0.5 ML of $^{13}$CO + O on ASW ice held at 20 K. Four peaks are visible. The first peak between 28K and 42K is due to O$_2$ desorption, the second one between 32 and 55K is due to $^{13}$CO desorption. The third peak between 55K and 75 K represents O$_3$ desorption, while the high-temperature peak is the desorption of $^{13}$CO$_2$ (75-95 K).

rises with temperature owing to the increase in O diffusion. In this first temperature zone, only a small amount of oxygen atoms are used to produce CO$_2$, probably via the Eley-Rideal mechanism. When O$_2$ starts to desorb (second temperature zone), O atoms have a lower probability of meeting O$_2$ molecules to form O$_3$. In fact, we see a decrease in the amount of O$_3$ desorbed, while in this range of temperature the probability that an oxygen atom encounters a CO molecule increases (as a consequence of the reduced coverage of O$_2$). Finally at temperatures higher than 35 K, CO desorption begins and the CO$_2$ signal begins to drop with same pattern observed for ozone, as shown in the bottom panel of Figure 5.19. This suggests that also at high temperatures (45 - 50 K) molecules and atoms coming from the beam still have a residence time on the surface long enough to react and form appreciable amounts of ozone and CO$_2$. The shapes of the CO$_2$ and O$_3$ yields suggest that CO$_2$ formation is limited by O$_2$ molecules or, in other words, that reaction R3.1 is in competition with reactions R3.4 and R3.5. In fact, only when the O$_3$ signal decreases (and O$_2$ desorbs) CO$_2$ formation rises. However, presence of O$_2$ apart, CO$_2$ always forms in small amounts, and this very probably indicates the existence of an activation barrier (hereafter $E_a$) for the reaction CO+O. To evaluate $E_a$ and to understand what surface mechanisms are responsible for CO$_2$ formation we used the model described in Chapter 3.

5.3.1.1c Model: evaluation of the CO+O barrier

In this section we present the model used to fit our experimental data. We consider five species: two are coming exclusively from the beam, O atoms and CO molecules, two are formed only on the surface, O$_3$ and CO$_2$, and one, O$_2$, is coming both from the beam and formed on the surface. The free parameters of the model are $r_{ER}$ and $r_{LH}$ probabilities for the reaction CO+O via ER and LH. The additional parameters that we used are:

- $\epsilon$, the chemical desorption probability for O+O reaction. It is equal to zero in the case of a water ice surface while it is 0.5 if the experiments are carried out on graphite.

- $k$, the diffusion coefficient for O atoms. We used the law

$$k = k_0(1 + T^3/T_0^3),$$  \hspace{1cm} (5.1)
Figure 5.19: Adapted from Minissale et al. (2013c). Integrated area under the TPD curves of $O_2$ and $O_3$ (triangles and circles on top panel, respectively), and of $^{13}CO_2$ (stars on bottom panel) as a function of surface temperature. The points are obtained through deposition of 0.5 ML of $^{13}CO+O$ on ASW ice held at different temperatures (10 K, 20 K, 30 K, 35 K, 40 K, 45 K, 50 K, 60 K). The solid line is a fit of the area behavior. The TPD peaks (obtained at $T_{\text{surface}}=20$ K) added in the figure show when $O_2$ and $^{13}CO$ desorb, and this helps interpret the $O_3$ and $^{13}CO_2$ yield behaviors with temperature.
distinguish and quantify the contribution to CO$_2$R, while at high temperatures most CO$_2$ and LH contribution to CO$_2$ decrease of the residence time of species on the surface, however, ER starts to be inefficient because of the desorption and the surface temperatures, however, ER starts to be inefficient because of the desorption and the decrease of the residence time of species on the surface, thus the CO$_2$ production efficiency by this mechanism drops off. On the contrary, the LH mechanism depends on the surface temperature and its efficiency increases going from 10 to 40 K owing to the favored diffusion of atoms. Beyond 40 K, as occurs for the ER case, the probability that O atoms and CO molecules leave the surface is high and the CO$_2$ yield decreases fast with temperature. The ER and LH contribution to CO$_2$ formation is approximately equal at low temperatures (below 20 K), while at high temperatures most CO$_2$ is formed via the LH mechanism. This is not surprising considering the power law dependence on the temperature of the diffusion parameter (Eq. 5.1).

As already claimed in Sec. 3.2, the reaction probabilities $r_{aER}$ and $r_{aLH}$ give the probability that a reaction occurs, in this case CO+O. By inverting a normalized Arrhenius equation, the activation barrier energy $E_a$ can be calculated as follows:

$$E_a = -k_b T_{eff} \log(r_a).$$  

(5.2)

Two alternative strategies can be used to evaluate the activation barrier of the reaction; we can derive the reaction barrier $E_a$ either from $r_{aER}$ or $r_{aLH}$. The problem is to know the

$\text{where } k_0 \text{ is 0.9 and } T_0 \text{ is 10 K.}$

- $E_{O_2}$ and $E_{CO}$, desorption barriers for O$_2$ and CO. We used two energies 1310 K/k$_b$ and 1430 K/k$_b$, even if a distribution of energy could be used.

In our model, we could have added another couple of parameters, $k_{O_2,CO}$, representing the O$_2$ and CO diffusion. However, O diffusion should be dominant with respect to O$_2$ or CO diffusion. The addition of O$_2$ and CO diffusion would cause a quicker consumption of O$_2$ and also because their mobility is likely to be almost zero at $T < 20$ K. Panel a of Figure 5.20 shows the comparison of experimental (points) and model (curves) results. We chose to fit CO$_2$ experimental yields, since they are the most important constraints for our free parameters, namely the reaction probabilities of CO + O reaction (panel b of Figure 5.20). We find that the best couple of reaction probabilities is $r_{aER} = 0.021$ and $r_{aLH} = 0.0019$. As described extensively in Minissale et al. (2013c), the model allows us to distinguish and quantify the contribution to CO$_2$ formation by either ER or LH mechanism. CO$_2$ formation via ER mechanism appears to be constant with temperature between 10 and 40 K also because, in theory, this mechanism is temperature independent. At higher surface temperatures, however, ER starts to be inefficient because of the desorption and the decrease of the residence time of species on the surface, thus the CO$_2$ production efficiency by this mechanism drops off. On the contrary, the LH mechanism depends on the surface temperature and its efficiency increases going from 10 to 40 K owing to the favored diffusion of atoms. Beyond 40 K, as occurs for the ER case, the probability that O atoms and CO molecules leave the surface is high and the CO$_2$ yield decreases fast with temperature. The ER and LH contribution to CO$_2$ formation is approximately equal at low temperatures (below 20 K), while at high temperatures most CO$_2$ is formed via the LH mechanism. This is not surprising considering the power law dependence on the temperature of the diffusion parameter (Eq. 5.1)

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$$E_a = -k_b T_{eff} \log(r_a).$$  

(5.2)

Two alternative strategies can be used to evaluate the activation barrier of the reaction; we can derive the reaction barrier $E_a$ either from $r_{aER}$ or $r_{aLH}$. The problem is to know the
effective temperature (\(T_{\text{eff}}\)) to insert in Eq. 5.2.

**ER case**  In Sec. 3.2, we described how \(T_{\text{eff}}\) can be evaluated. We remember that

\[
T_{\text{eff}} = \mu \left( \frac{T_{\text{solid}}}{m_x} + \frac{T_{\text{gas}}}{m_y} \right) \tag{5.3}
\]

So in the case of ER, for \(T_{\text{gas}}=300\) K and \(T_{\text{solid}}=25\) K, we can consider three different cases for \(T_{\text{eff}}\):

- \(T_{\text{eff}}' = T_{\text{gas}} = 300\) K
- \(T_{\text{eff}}'' = 202 \pm 5\) K
- \(T_{\text{eff}}''' = 123 \pm 10\) K

where \(\mu\) is the effective mass of the CO and O system. These temperatures correspond to the velocity of the center of mass of the system. Evidently, we do not take into account the case \(T_{\text{eff}} = T_{\text{solid}}\), because that means to consider molecules already thermalized with the surface, as in a pure LH process.

In the first case (\(T = T_{\text{gas}} = 300\) K) we obtain a barrier of 1200 K. Clearly, in our experiments we cannot consider CO and O as two gases at the same thermodynamic equilibrium so the temperature is likely to be lower than 300 K. This means that \(E_a = 1200\) K is only an upper limit of the activation barrier.

The second and third cases give a CO+O reaction barrier \(E_{a,ER}\) in the range 780-475 K/\(k_b\).

**LH case**  The Eq. 5.2 has to be used with care in the case of LH, since the temperature dependence of \(r_{\text{LH}}\) is not as simple as in the Arrhenius case. Moreover, the temperature dependence cannot be derived from the experimental values because they do not provide enough constraints, hence we give a mean value \(r_{\text{LH}}(T) = 0.0019\) across the whole temperature range investigated (10 - 60 K). We then try to estimate the reaction barrier by taking into account the two following considerations:

i  although O-atoms diffusion is predominant with respect to that of \(O_2\) and CO, at high temperatures \(O_2\) and CO diffusions have to be taken into account if a proper evaluation of \(r_{\text{LH}}(T)\) is required.

ii  Non-exponential behaviour of the \(CO_2\) formation rate due to occurrence of tunneling at very low temperatures (Goumans & Andersson 2010).

Figure 5.21 displays a comparison between experimental and theoretical values of \(r_{\text{LH}}\), by considering tunneling for CO+O reaction and \(O_2\)-CO diffusion. These considerations suggest that \(r_{\text{LH}}(T)\), for \(T < 25\)K, is better described by this law:

\[
r_{\text{LH}}(T) = \exp(-E_a/k_b T_{\text{eff}}) + r_{\text{tunn}}(E_a, T), \tag{5.4}
\]

where \(r_{\text{tunn}}(E_a, T) \geq 0\) represents the rate of tunneling of the CO+O reaction, and it is able to increase the reaction probability value at low temperature. By inverting Eq. 5.4 we have

\[
E_a = -k_b T_{\text{eff}} \log(r_{\text{LH}}(T) - r_{\text{tunn}}(E_a, T)) > -k_b T_{\text{eff}} \log(r_{\text{LH}}) \tag{5.5}
\]

By putting \(T_{\text{eff}} = 25\) K in Eq. 5.5, \(r_{\text{LH}}(25\text{K}) = 0.0019\) and \(r_{\text{tunn}}(E_a, T) = 0\), thus we obtain a lower limit for \(E_a\) of 160 K/\(k_b\). This value is underestimated for two reasons:

- At 25 K the tunneling term could become dominant with respect to the classical term (Arrhenius law), and clearly is not zero.
- \(r_{\text{LH}}(T)\) is a mean value, and very probably \(r_{\text{LH}}(T)\) presents a minimum around 25 K

This means that \(r_{\text{LH}}(25\text{K}) < 0.0019\) and \(E_a > 160\) K/\(k_b\) are consistent with the values obtained for \(r_{\text{ER}}\).
5.3.1.1.d Conclusions

We have described above how we evaluated the activation barrier of the CO+O reaction. Our model allows us to distinguish which mechanisms (Eley Rideal or Langmuir-Hinshelwood) is at play in different temperature regimes and we are able to give a range of values of the activation barrier of reaction CO+O of 780-475 K/k_b. We have to make clear that these values make sense only in the range of validity of Eq. 5.5. Finally, it should be noted that the range of activation energy barriers given in this work are only apparently inconsistent with the 290 K/k_b value of Roser et al. 2001. In fact, they provide an estimation (not a measure) of the barrier by using only the classical LH mechanism (very low T_eff), but on the other hand the ER mechanism (high T_eff) with the same barrier would produce more CO_2 than that they observed. Their estimate can thus be considered a lower limit of the barrier which is included in our study of the LH case.

5.3.1.2 H_2CO+O

Formaldehyde (H_2CO) was the first polyatomic organic molecule detected in the interstellar medium (Zuckerman et al. 1970). It can be detected through 1_11 - 1_10 ground-state rotational transition at 4830 MHz (Snyder et al. 1969), and its distribution is found similar to that of HI and CO in different environments, i.e. our Galaxy (Davies & Few 1979; Tang et al. 2013, and references therein), and in Galactic radio sources (Downes et al. 1980).

H_2CO has been observed both in some comets (Crovisier & Bockelé-Morvan 1999; Mumma et al. 2005), and in interstellar ices (Keane et al. 2001). Its abundance with respect to water ice varies from 1% to 6% in high- (Keane et al. 2001; Dartois 2005) or low- (Boogert et al. 2008) mass protostars, or hot cores (Maret et al. 2004). Gas-phase reactions (Shalabiea & Greenberg 1994), and UV photolysis of H_2O-CO ice (Allamandola et al. 1988; Schutte et al. 1996; Watanabe et al. 2007) can produce efficiently formaldehyde, but surface reactions, as hydrogenation of CO ice (Hirao et al. 1994; Watanabe & König 2002; Watanabe et al. 2004; Madzunkov et al. 2009) are needed to explain the observed abundances in the solid phase.

Formaldehyde is a key species in the grain-surface chemistry in interstellar clouds (Schutte et al. 1993, 1993b). Hidaka et al. (2004) and Fuchs et al. (2009) show that formaldehyde can form methanol (CH_3OH) through H-atom additions, and we show that it can produce CO via H-atom abstraction. Moreover H_2CO is involved in the formation of large molecules.

Figure 5.21: Adapted from Minissale et al. (2013c). Temperature dependence of \( r_{LH}(T) \) between 10 and 60 K. The two pin-stripped regions indicate how different parametrization of tunneling for CO+O reaction (red zone) and of O_2 and CO diffusion (green zone) can change our estimation of \( r_{LH}(T) \). Blue circles represent our experimental data. Solid line is an example of a pure Arrhenius behavior.
containing C-H, C-O, O-H, and C-N bonds (Schutte et al. 1993b): during the warm-up of the ice on grains, formaldehyde can react with NH$_3$, H$_2$O, and itself (H$_2$CO) to form respectively amine, diols or [-CH$_2$O$_2$]$_n$ groups (Noble et al. 2012b; Theulé et al. 2013; Mispelaer et al. 2013); for this reason, it could be considered a primary precursor of some complex organic materials (Schutte et al. 1993b). In this section, we show experimentally that formaldehyde is also reactive with ground-state O($^3P$) atoms to form CO$_2$, one of the most abundant species in interstellar ices. Formaldehyde seems to play a crucial role in the chemistry of interstellar ice, and in particular in the balance between CO$_2$, CH$_3$OH, and CO.

### 5.3.1.2.a Experimental

All the experiments were performed by sending O atoms on formaldehyde ices previously grown on the cold sample. The two species are deposited by using, at different times, the same triply differentially pumped beam line. As described in Sec. 2.2.2.2, formaldehyde gas is obtained by depolymerization of paraformaldehyde. The resulting gas contains a little part of CO. To avoid CO adsorption we deposit formaldehyde at 60 K. Moreover, we used different isotopes of formaldehyde to better constrain our findings: H$_2^{12}$CO, D$_2^{12}$CO, and H$_2^{13}$CO. In the case of D$_2^{12}$CO the purity is of about 98%, while for H$_2^{13}$CO is of 99%. Hereafter we refer to $^{12}$C simply as C. Oxygen atoms are generated (in the $^3P$ ground state) by dissociating O$_2$ molecules and typical values of 70±5% are used for the dissociation efficiency. From calibrations we have found that, the first monolayer (1 ML=10$^{15}$ molecules cm$^{-2}$) of formaldehyde was reached after an exposure time of about 12 minutes while for O$_2$ the same dose was reached after six minutes, which gives respectively a flux of $\phi_{H_2CO}=(1.6\pm0.4)\times10^{12}$ and $\phi_{O_2off}=(3.0\pm0.3)\times10^{12}$ molecules cm$^{-2}$s$^{-1}$. Once the O$_2$ discharge is turned on, the O-atom flux is $\phi_O=2\tau \phi_{O_2off}$=5.4$\times10^{12}$ atoms cm$^{-2}$s$^{-1}$ and the O$_2$ flux $\phi_{O_2on}=(1-\tau)\phi_{O_2off}$=10$^{12}$ molecules cm$^{-2}$s$^{-1}$.

CO$_2$ formation was investigated on two different surfaces, ASW and an oxidized slab of HOPG. During each phase (ices growth or O-atom deposition) the surface is held at a given constant temperature. After each O-atom deposition, the products are probed through RAIRS technique. When about 5 ML of oxygen atoms were deposited on the surface, the surface was heated with a linear temperature ramp of 10 K/min until the adsorbate had fully desorbed from the surface (around 200 K). For both substrates (ASW ice and graphite), we used two surface temperatures (10 and 60 K). We also performed an experiment to check the H$_2$CO reactivity with O$_2$ and O$_3$ to form CO$_2$. For this purpose, we performed two sets of TPD experiments. First, the H$_2$CO+$O_2$ reaction was checked by depositing 2 ML of O$_2$ on top of H$_2$CO ices. The H$_2$CO+$O_3$ reaction was studied through a similar experiment except that we had previously produced ozone via the O+$O_2$ reaction occurring on the surface, subsequently we eliminated the residual O$_2$ by heating to 50 K, and only then, deposited H$_2$CO at 60 K.

### 5.3.1.2.b Results and discussion

The main aim of the experiments (and their results) described in this section is to know if H$_2$CO is able to react with O$_2$ (O, O$_2$, and O$_3$).

As said in the previous section, O$_2$ is present in the O beam and therefore O$_3$ can be formed on the surface at temperatures lower than < 55 K (Minissale et al. 2014a). For this reason, at first, we have studied separately the reactions H$_2$CO+$O_2$/O$_3$ and only then the reaction H$_2$CO+$O$. Figure 5.22 shows TPD curves of mass 30 a.m.u. (H$_2$CO) in panel a and of mass 44 a.m.u. (CO$_2$) in panel b after deposition, on oxidized HOPG held at 10 K, of:

1. 2 ML of H$_2$CO (black squares),
2. 5 ML of O (cyan circles),
3. 2 ML of H$_2$CO + 5 ML of O atoms (blue stars),
4. 2 ML of H$_2$CO+$O_2$ (red triangles),
5. 2 ML of H$_2$CO+O$_3$ (green triangles). The TPD curves shown in panel b and their integrated areas suggest that H$_2$CO is not consumed by O$_2$ or O$_3$. Actually this is not a surprising result since reactions

$$
\text{H}_2\text{CO} + \text{O}_2 \rightarrow \text{HCO} + \text{HO}_2 \hspace{1cm} \Delta H = +160 \text{ kJ/mol} \hspace{1cm} \text{(R3.6)}
$$

$$
\text{H}_2\text{CO} + \text{O}_3 \rightarrow \text{HO}_2 + \text{HCO}_2 \hspace{1cm} \Delta H > 200 \text{ kJ/mol} \hspace{1cm} \text{(R3.7)}
$$

are endothermic (NIST Chemistry WebBook) and present high (> 1600 K/k$_b$) activation barriers (Michael et al. 1999; Brashsvy&Heicklen 1976). Moreover, the inefficiency of R3.6-7 is confirmed by the absence of newly formed species.

On the other hand, we argue that H$_2$CO ice is consumed after the oxygen irradiation (blue stars in Figure 5.22) to form CO$_2$. The experiments in which only O atoms are deposited has been carried out to make sure that CO$_2$ is not present in the O beam, and it is truly formed on the surface, following H$_2$CO oxygenation. Actually, a signal at mass 44 (CO$_2$) is visible in panel a of Figure 5.22 (cyan circles), and could come either from O beam or be formed via oxygenation of residual CO. In any case, it is ten times smaller than mass-44 signal coming from H$_2$CO oxygenation experiment (blue stars).

Further evidence of H$_2$CO consumption and CO$_2$ formation are provided by RAIR spectra. Figure 5.23 shows RAIR spectra recorded after deposition at 10 K (top panel) and 55 K (bottom panel) on ASW ices of 2±0.5 ML of H$_2$CO with increasing doses of oxygen atoms (0, 0.5, 0.8, 1.2, 2, 3.8 ML, respectively, from spectrum a to f). We assign the band at 1732 cm$^{-1}$ to the CO stretch of H$_2$CO. The peak between 2349-2345 cm$^{-1}$ is assigned to anti symmetrical stretch of CO$_2$. The band peaking at 1047 cm$^{-1}$ is due to the $\nu_3$ asymmetric stretching mode of O$_3$. Moreover we assign the weak and broad band at 1502 cm$^{-1}$ to the CH$_2$ scissoring of H$_2$CO. Minissale et al. (2013b, 2014a) show that solid-state formation of O$_3$ is efficient at temperatures lower than 55 K. Actually, temperatures higher than 55 K prevent O$_2$ adsorption on the surface and, as a consequence, O$_3$ is no longer formed. These differences become evident by comparing top and bottom panels of Figure 5.23. The two sets of spectra differ for two main differences: O$_3$ band is not present and the feature at 2347 cm$^{-1}$ increases steadily with O-exposure. These two pieces of evidence, as discussed in detail in the model section, make the evaluation of H$_2$CO+O activation barrier easier.

Similar results are obtained when the experiments are performed on graphite. The different substrates (HPG or compact ASW ice) are responsible for small shifts of the IR features, as well as for a change in the band intensities; actually, under the same conditions (equal amount of O sent on H$_2$CO), HOPG facilitates CO$_2$ formation with respect to the formation of O$_3$ and vice versa on ASW. This is a consequence of two effects:

- different diffusion constants of O atoms for oxidized HOPG and ASW ice,
- $k_{diff-\text{HOPG}} < k_{diff-\text{ASW}}$ (Congiu et al. 2014);
**Figure 5.23:** Adapted from Minissale et al. (2014). Six RAIR spectra obtained after deposition on a ASW ice held at 10 K (top panel) and 55 K (bottom panel) (H$_2$CO was always deposited at 60 K) of: (a) 2±0.5 ML of H$_2$CO; (b) 2±0.5 ML of H$_2$CO + 0.5±0.1 ML of O atoms; (c) 2±0.5 ML of H$_2$CO + 0.8±0.1 ML of O atoms; (d) 2±0.5 ML of H$_2$CO + 1.2±0.2 ML of O atoms; (e) 2±0.5 ML of H$_2$CO + 2.0±0.3 ML of O atoms; (f) 2±0.5 ML of H$_2$CO + 3.8±0.3 ML of O atoms. In bottom panel one more spectrum is present: (e2) 2±0.5 ML of H$_2$CO + 2.8±0.3 ML of O atoms.

- different probabilities of chemical desorption for O$_2$, $\epsilon_{\text{diff-HOPG}} > \epsilon_{\text{diff-ASW}}$ (Dulieu et al. 2013; Minissale&Dulieu 2014c).

On the one hand, fast diffusion of O atoms and low probability of chemical desorption of O$_2$ on ASW allow O atoms to allotropize into O$_2$ and then into O$_3$ (O$_3$ ≫ CO$_2$). On the other hand, on HOPG, surface density of O$_2$ decreases due to chemical desorption. O atoms stay longer on the surface, and thus have a higher probability to react with H$_2$CO and form CO$_2$ (O$_3$ ≈ CO$_2$), due to the lack of O$_2$ and the slower diffusion constant.

All the experiments presented up to now show the consumption of H$_2$CO and the formation of CO$_2$.

These results are very similar to those obtained experimentally by Chang&Barker (1979) at high temperature (> 300 K) in gas phase and theoretically by Dupuis&Lester (1984). The simplest explanation for CO$_2$ formation is the O-atom addition to the doubly-bonded carbon atom in H$_2$CO and the following formation of a vibrationally excited triplet of methylenebis(oxo),

$$H_2CO + O(^3P) \rightarrow H_2CO_2(^3B_3 - ^3B_2) \quad R3.8a$$

that, following the decomposition process

$$H_2CO_2 \rightarrow CO_2 + H_2 \quad R3.8b,$$

leads to CO$_2$ formation (for details on the solid-state network see Minissale et al. (2014c)).

### 5.3.1.2.c Model: evaluation of the H$_2$CO+O barrier

In this section we present the model used to fit our experimental data and in particular to evaluate the activation barrier of H$_2$CO+O reaction. In the model (see Chapter 4 for details), we have considered only the most abundant species present on the surface (O, H$_2$CO, O$_2$, CO$_2$,...).
O$_{3}$ and CO$_{2}$, and the reactions R3.4, R3.5, and R3.8. H$_{2}$ is not considered in our model, since our experiments are performed at high temperature and H$_{2}$ desorbs very quickly from the surface. In any case, H$_{2}$ is inert at low temperature and it cannot change the surface density of the other species. The above-mentioned surface reactions can occur through two mechanisms: the Eley-Rideal (ER) and the Langmuir-Hinshelwood (LH) mechanisms. In the ER mechanism one molecule is already adsorbed on the surface and the other comes from the gas phase (i.e., the beam line); it becomes more efficient as the surface coverage increases. In the LH mechanism, both molecules are bound to the surface and by diffusion they can meet each other and react. LH is highly dependent on the surface temperature. Aware of these facts, we have chosen to fit the data of Figure 5.23 (bottom panel) to give a more precise evaluation of the H$_{2}$CO+O barrier. Actually, physical-chemical conditions in these experiments allow us to simplify our model and reduce the errors:

- O-atom diffusion is very fast, and the main part of adsorbed O atoms are consumed through R3.4;
- R3.5 can be neglected, since it is prevented by O$_{2}$ desorption;
- R3.8 is most likely to occur via ER, since O atoms are deposited on the H$_{2}$CO ice.

Clearly the last point does not exclude that R3.8 could occur via the LH mechanism and, in fact, it is the main source of error in the barrier determination. The LH mechanism depends strongly on O-atom diffusion barrier (E$_{O\text{diff}}$), one of the free parameters of the model. E$_{O\text{diff}}$ is a thermal diffusion and quantum effects are negligible at this temperature (Minissale et al. 2013). It has an upper limit of 900 K/k$_{b}$ (Cazaux et al. 2010), and a lower limit given by ozone formation in our experiments (< 0.05 ML). A value lower than 600 K/k$_{b}$ for E$_{O\text{diff}}$ increases the efficiency of R3.4, and produces more than > 0.05 ML of ozone. These two limits change the amount of CO$_{2}$ formed via LH by 20 % of the total if E$_{O\text{diff}}$ =900 K/k$_{b}$, and by 5 % if E$_{O\text{diff}}$ =600 K/k$_{b}$. This indetermination, as we will see below, complicates the evaluation of the activation barrier of reaction R3.8 (E$_{a}$), the second free parameter of the model. A priori, E$_{a}$ is a positive real number and becomes equal to zero in the case of a barrierless reaction. Figure 5.24 shows the results of the model (lines) compared with experimental data (symbols). We have used four values for E$_{a}$: 550 K/k$_{b}$ (panel α), 300 K/k$_{b}$ (panel β), 280 K/k$_{b}$ (panel γ), and 200 K/k$_{b}$ (panel δ). We have varied E$_{O\text{diff}}$ in the 600-900 K/k$_{b}$ range, and Figure 5.24 shows four cases: 600 (dash-dotted line), 700 (dashed line), 800 (dotted line), and 900 K/k$_{b}$ (solid line). Panel α shows that a too high value (> 550 K/k$_{b}$) for E$_{a}$ is not able to fit our data for any value of E$_{O\text{diff}}$; actually small amounts of CO$_{2}$ and H$_{2}$CO are respectively formed and consumed. Moreover, a big amount of ozone is formed. On the other hand, a value too small (< 200 K/k$_{b}$) for E$_{a}$ has an opposite effect, CO$_{2}$ is formed too rapidly and H$_{2}$CO too quickly consumed by O atoms (panel δ). Couples of values of E$_{a}$ and E$_{O\text{diff}}$ ranging in 300-280 K/k$_{b}$ and 600-900 K/k$_{b}$ respectively (panels β and γ) give excellent fits of the experimental data. Since the fit depends on two parameters, we are not able to give a precise value of the activation barrier of R3.8. Anyway, we have to stress that a determined value for E$_{O\text{diff}}$ automatically railroads the value of E$_{a}$: by using E$_{O\text{diff}}$ =700±150 K/k$_{b}$, we find E$_{a}$ =335±55 K/k$_{b}$.

5.3.1.3 Conclusion

In this section we have shown that carbon dioxide can be formed efficiently through CO+O and H$_{2}$CO+O reactions on cold surfaces, such as amorphous water or oxidized graphite. We have estimated, through a model, values of 630±100 K and 335±55 K for their activation barrier. These reactions are relevant to astrochemistry to explain CO$_{2}$ abundances, as well as the CH$_{3}$OH ones, in interstellar ices as we will explain in the last chapter. As shown in Table 5.2 another non-energetic route competes in the CO$_{2}$ formation, namely the CO+OH reaction (some experimental works have already been conducted by Oba et al. 2011, Noble et al. 2011, Ioppolo et al. 2013). The CO+OH pathway seems to be facilitated by the low
barrier of the reaction, but it has an other type of hindrance. In fact, it requires OH formation first (see Chaabouni et al. 2012; Cuppen et al. 2010, and references therein for details on OH formation in space). In H-rich environments, OH can be formed easily, although it can be very quickly destroyed to form water. These facts suggest that the efficiency of the three reaction strongly depends on three parameters:

- the O/H ratio, very probably the most important parameter;
- the grain temperature: the higher the temperature, the shorter the H residence time on the grain and thus the probability of OH formation;
- H and O diffusion on the surface: since only H diffusion is usually considered in models (e.g., Garrad&Pauly 2011), the CO+O contribution is, in our opinion, underestimated.

### 5.3.2 The cycle of the CO-H chemistry

CO hydrogenation has been the subject of study by many experimental groups (Hirao ap et al. 1994, 2002, Watanabe&Kouchi 2002, Watanabe et al. 2004, and Fuchs et al. 2009). Nevertheless experimental results of these works seem to lead to different conclusions. Briefly Watanabe et al. (2002, 2004) and Fuchs et al. (2009) found that the CO+H reaction leads to formaldehyde and methanol formation, while formaldehyde is the only species formed in Hirao ap et al. (1994, 2002). To disentangle this problem and due to the fundamental importance of the CO-H chemistry in astrochemistry, we have decided to restudy the problem, with the awareness that we can use different experimental conditions. Table 5.3 lists the
Figure 5.25: Comparison of our experimental fluence regimes (blue bands) with the ones of Watanabe & Kouchi (2002) and Fuchs et al. (2009).

Table 5.3: List of publications about the solid state reaction CO+H with experimental conditions and products.

<table>
<thead>
<tr>
<th>Article</th>
<th>Flux</th>
<th>Fluence</th>
<th>CO initial thickness</th>
<th>Major products of CO+H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hirao et al.</td>
<td>10^{13}</td>
<td>3.6 x 10^{16}</td>
<td>36 ML</td>
<td>H₂CO</td>
</tr>
<tr>
<td>Watanabe et al.</td>
<td>2 x 10^{15}</td>
<td>&gt;10^{17}</td>
<td>&lt; 100 ML</td>
<td>H₂CO and CH₃OH</td>
</tr>
<tr>
<td>Fuchs et al.</td>
<td>5 x 10^{13}</td>
<td>&gt;10^{17}</td>
<td>&lt; 100 ML</td>
<td>H₂CO and CH₃OH</td>
</tr>
<tr>
<td>This work</td>
<td>5 x 10^{12}</td>
<td>6 x 10^{15}</td>
<td>6 ML</td>
<td>CO</td>
</tr>
</tbody>
</table>

The probability of H-atom recombination increases as a function of H-atom flux; hence H atoms have larger time of residence in our experiments. On the other hand, the total amount of H atoms sent on CO ices is two order of magnitude smaller with respect to Watanabe et al. (2004) and Fuchs et al. (2009), as shown in Figure 5.25. Our experimental conditions are somewhat similar to those of Hirao et al. (1994, 2002).

5.3.2.1 CO+H

Figure 5.26 shows the TPD curves of mass 28, 29, 30, 31, and 32 u.m.a. after deposition of 2.5 ML of CO (red curves), and 2.5 ML of CO + 6 ML of H (green curves) on graphite maintained at 10 K. For both depositions it is present a peak at mass 28 between 25 and 60 K due to CO desorption; it is shown in logarithmic scale in the zoom-in inset. Similar peaks are present at mass 29 and mass 30. These two peaks are very probably due to the desorption of isotopes of carbon monoxide (¹²CO and ¹³CO respectively): we find that the ratio (the area under the peak) of ¹³CO/CO=1.3% is not far from 1.1% found in IUPAC 1998. Similarly, the ratio C¹⁸O/CO=0.3% fits exactly with that found by Cook & Lauer (1968). The comparison between the two depositions (pure CO vs CO+H) suggests that only a small part of CO ice reacts with H atoms. Actually, the initial ice layer thickness is 2.5 ML and at the end of irradiation with 6 ML of H, 0.4 ML of CO is consumed (around 16% of the initial ice coverage). Hirao et al. (2002), Watanabe et al. (2004) and Fuchs et al. (2009) have found a slower reactivity of CO with H atoms. For example Fuchs et al. (2009) found that a fluence of H atoms of ≈2 x 10^{16} cm⁻² s⁻¹ is needed to consume 15% of initial CO ice
Figure 5.26: TPD traces for mass 28, 29, 30, 31, and 32 obtained after deposition on oxidized HOPG held at 10 K of: 2.5 ML of CO (red curves), and 2.5 ML of CO + 6 ML of H (green curves). The pinstriped TPD curves added in the figure show when H$_2$CO and CH$_3$OH desorb. The TPD spectra displayed in the bottom panel are offset for clarity.

compared to $2 \times 10^{16}$ cm$^{-2}$s$^{-1}$ to consume 16\% in our experiments. CO hydrogenation can lead to formaldehyde and methanol formation through the following hydrogenation scheme:

$$
	ext{CO} + \text{H} \rightarrow \text{HCO} \rightarrow \text{H}_2\text{CO} \quad \text{R3.9a} \\
	ext{H}_2\text{CO} + \text{H} \rightarrow \text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH} \quad \text{R3.10}
$$

where in red we indicate undetected species. Reactivity of CO+H is limited to R3.9a in Hiraoka et al. (2002), and continues to R3.10 in Watanabe et al. (2004) and Fuchs et al. (2009). In our experiments, only R3.9a takes place on the surface. Figure 5.26 shows two pinstriped TPD curves of H$_2$CO and CH$_3$OH obtained after deposition of 1 ML of H$_2$CO and CH$_3$OH respectively. H$_2$CO can be detected via mass 30 and 29, and CH$_3$OH via mass 32, 31, 30, and 29. None of these masses present a peak at desorption temperatures of H$_2$CO and CH$_3$OH for CO+H experiment. We can sum up our experimental results through the following statements:

a the reactivity of CO with H atoms seems to be higher (more CO consumed, with the fluence being equal) with respect to that found in Watanabe et al. (2004) and Fuchs et al. (2009);

b the two products found by Watanabe et al. (2004) and Fuchs et al. (2009), namely formaldehyde and methanol, have not been detected;

c Initial reactants $> \text{unreacted reactants + final products, something is lost.}$

How can we explain these differences? To give an answer to this question we decided to study separately the hydrogenation of H$_2$CO and CH$_3$OH. The H$_2$CO+H experiments are treated in the next section while we determined that experimentally

d methanol hydrogenation does not occur.
5.3.2.2 $\text{H}_2\text{CO}+\text{H}$

Figure 5.27 shows the TPD curves of mass 28, 29, 30, 31, and 32 u.m.a. after deposition 1.8 ML of $\text{H}_2\text{CO}$ (red curves), 1.8 ML of $\text{H}_2\text{CO} + 3.6$ ML of H (blue curves), and 3.6 ML of H (green curves) on graphite maintained at 10 K. Three main peaks are visible in the figure: between 25 and 60 K due to CO desorption; between 85 and 130 K due to $\text{H}_2\text{CO}$ desorption; between 130 and 160 K due to $\text{CH}_3\text{OH}$ desorption; each one of these peaks is detected via different masses depending on the cracking pattern of each molecule (see Sec. 2.2.2.1). We notice by comparing the TPD curves after 1.8 ML of $\text{H}_2\text{CO}$ and 1.8 ML of $\text{H}_2\text{CO} + 3.6$ ML of H that a large part of formaldehyde is consumed; after H-atom irradiation, 1.4±0.3 ML of initial formaldehyde ice is consumed and only 0.4±0.2 ML remains unreacted. By looking at the CO and $\text{CH}_3\text{OH}$ peaks, we estimated that 0.25±0.2 ML of CO and 0.3±0.1 ML of $\text{CH}_3\text{OH}$ are formed. We can explain these products through the following hydrogenation scheme,

$$\begin{align*}
\text{H}_2\text{CO} + \text{H} &\rightarrow \text{HCO} + \text{H}_2 \quad \text{R3.9b} \\
\text{H}_2\text{CO} + \text{H} &\rightarrow \text{CH}_3\text{O} + \text{H} \quad \text{R3.10}
\end{align*}$$

although we cannot explain the lack of CO (under the form of CO, $\text{H}_2\text{CO}$, and $\text{CH}_3\text{OH}$ molecules) at the end of the irradiation, like in the case of CO+H experiment. We can sum up our experimental results through the following statements:

- the reactivity of $\text{H}_2\text{CO}$ with H atoms seems to be quicker than CO+H;
- $\text{H}_2\text{CO}+\text{H}$ has two products: CO and methanol;
- initial reactants $\succ$ unreacted reactants + final products, something is lost.

Coming back to the question of the previous section, we can affirm that the total hydrogenation of CO leading to $\text{CH}_3\text{OH}$ is not necessarily the only process occurring on the surface. Actually, in these experiments, we have shown that a dehydrogenation of $\text{H}_2\text{CO}$ can lead to CO formation. The difference between our results and the results of Watanabe et al. (2004) and Fuchs et al. (2009) can be explained by looking at the different physical-chemical conditions used, namely H-atom fluxes and fluences and CO ice thickness. As we already claimed, the higher the flux, the smaller the residence time of H atoms, thus the smaller the probability of the CO+H reaction. This is consistent with the comparison of ours and Fuchs et al.'s results if we consider equal fluences. If H-atom flux explains CO consumption, fluence and CO ice thickness explain the reactivity and the final products. Roughly the higher the fluence, the higher the probability for R3.9a and R3.10 to occur. Also this point is coherent with all experimental results; in fact we know that

$$\text{Fluence}_{\text{This work}} < \text{Fluence}_{\text{Hiraoka}} < \text{Fluence}_{\text{Fuchs and Watanabe}}$$

and the products are, respectively, CO (this work), $\text{H}_2\text{CO}$ (Hiraoka et al. 2002), $\text{H}_2\text{CO}$ and $\text{CH}_3\text{OH}$ (Watanabe et al. 2004; Fuchs et al. 2009). Finally the “apparent” no-conservation of matter (initial reactants $\succ$ unreacted reactants + final products) can be explained through the third physical-chemical parameter, CO ice thickness. Watanabe et al. (2004) have performed their experiments for large CO ice thickness (120 Å $> 10$ ML), while Fuchs et al. (2009) have used variable CO ice thickness (from 1 to 10 ML) showing that the efficiency of $\text{H}_2\text{CO}$ and $\text{CH}_3\text{OH}$ formation increases as a function of CO ice thickness. The natural question is “why should the ice thickness have an influence on the reactivity?” The answer can be found in the chemical desorption pumping process.

5.3.2.3 Chemical desorption pumping process

Figure 5.28 shows DED of mass 28 during the exposure of H atoms on 2.5 ML of CO ice and on 1.8 ML of $\text{H}_2\text{CO}$ on the graphite substrate held at 10 K. Both DED experiments would suggest the presence of CD process on graphite of CO molecules. An overview of chemical desorption is shown in Table 5.4 where we have considered DED of different masses, in
Figure 5.27: TPD traces for mass 28, 29, 30, 31, and 32 obtained after deposition on oxidized HOPG held at 10 K of: 1.8 ML of H$_2$CO (red curves), 1.8 ML of H$_2$CO + 3.6 ML of H (blue curves), and 3.6 ML of H (green curves). The TPD spectra are offset for clarity.
Figure 5.28: Mass 28 monitored with the QMS during the exposure of H atoms on 2.5 ML of CO ice (top panel) and on 1.8 ML of H$_2$CO (bottom panel) on the graphite substrate kept at 10 K.

Table 5.4: List of CD signal for different masses in CO/H$_2$CO/CH$_3$OH+H experiments.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Mass 28</th>
<th>Mass 29</th>
<th>Mass 30</th>
<th>Mass 31</th>
<th>Mass 32</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO+H</td>
<td>Strong</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>H$_2$CO+H</td>
<td>Strong</td>
<td>Weak</td>
<td>Weak</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>CH$_3$OH+H</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>

CO/H$_2$CO/CH$_3$OH+H experiments.

Figure 5.29 shows the whole CO-H network leading from CO to CH$_3$OH and passing from the pivotal H$_2$CO molecule. We can sum up our finding considering three processes:

1. Methanol is formed via H$_2$CO hydrogenation. It is the only inert and stable (in the sense that it cannot be consumed by H atoms) molecule in the CO-H chemistry;

2. H$_2$CO can be both hydrogenated to form methanol or dehydrogenated to form CO. In the dehydrogenation process the chemical desorption can occur. Its efficiency could be high, probably around 40%.

3. CO can be hydrogenated to form formaldehyde but, even in this case, chemical desorption can occur, due to dehydrogenation reactions or due to H$_2$CO CD.

As we already discussed in the Sec. 4.3, chemical desorption depends strongly on the substrate and, recurring to this argument, we can explain the difference between our results and the results of Watanabe et al. (2004) and Fuchs et al. (2009). The balance of these processes depends on the ice thickness; in other words the balance of these processes depends on the possibility that reactions occur into the bulk or on the surface:

1. into the bulk, the chemical desorption occurring in the CO-H$_2$CO system is not efficient. Gradually, the CO-H$_2$CO system evolves toward a more stable system, that is CH$_3$OH.

2. on the surface, the chemical desorption occurring in the CO-H$_2$CO system is efficient. Chemical desorption is continuously pumped and it leads to a loss of material. In this case the CH$_3$OH formation becomes less probable.

5.3.3 Preliminary results of CH$_3$OH and HCOOH irradiation with H/O atoms

In these section, we present preliminary results on the reactivity of methanol (CH$_3$OH) and formic acid (HCOOH) with H or O atoms. These two molecules have been observed in

\[\text{We have obtained only qualitative results so far after testing the reactivity of CH}_3\text{OH and HCOOH.}\]
Figure 5.29: Scheme of the CO-H chemistry. The molecules in red are not detected in our experiments.

interstellar ices, and these experiments are intended to test their possible consumption routes. Experiments regarding CH$_3$OH are very trivial about the analysis: CH$_3$OH irradiations with H or O atoms produce no effects. Experiments were performed on oxidized graphite; CH$_3$OH ices are irradiated with different doses of H or O and TPDs spectra with or without irradiation are exactly alike. We can exclude solid-state consumption routes for CH$_3$OH: the importance of this finding will be illustrated in the astrophysical conclusions. On the other hand, formic acid presents a more lively surface chemistry. Figure 5.30 displays results after irradiation of 1.5±0.5 ML of HCOOH with 4.2±1 ML of H. First of all, we remind that formic acid is detected mainly via mass 29 and also via masses 46, 45, 44, and 28, while methanol is detected via mass 31 as well as via masses 32, 15, and 29 (see Sec. 2.2.2.1). By comparing blue and red curves in Figure 5.30 we notice that

1.5 ML HCOOH = Mass 29 (red) > Mass 29 (blue) = HCOOH + 0.45×Mass 31 (CH$_3$OH)

with

\[
\frac{\text{Mass 29}}{\text{Mass 31}} = 0.45
\]

being the cracking factor of methanol. We can conclude that a part of the deposited formic acid is consumed. By looking at the products, we notice in TPDs performed after H-irradiation a peak of mass 18 coming from H$_2$O desorption, a peak of mass 28 (between 30 and 60 K) due to CO desorption, and evident peaks of masses 31 and 32 due to methanol desorption. Finally a minor peak of mass 44 (between 70 and 100 K) could be due to CO$_2$ desorption. In summary

\[
\text{HCOOH} + \text{H} \rightarrow \text{H}_2\text{O} + \text{HCO}
\]

\[
\rightarrow \text{HCO} + \text{H} \Rightarrow \text{CO} + \text{CH}_3\text{OH}.
\]

HCOOH + O experiments are presented in Figure 5.31. In this case, we still see consumption of HCOOH, and the products are limited to H$_2$O and CO$_2$. We reiterate that through these experiments (HCOOH + H / O) we provide only qualitative estimations of HCOOH + H / O reactivities and we are able to suggest only roughly branching ratios and reaction barriers. In particular, to estimate the reaction barrier we compare the rate of consumption ($k_{\text{HCOOH}+\text{H}}$) of HCOOH ($k_{\text{HCOOH}+\text{H}}$) (irradiated both with H and O) with the rate of consumption of CO and H$_2$CO ($k_{\text{CO}+\text{O}}$ and $k_{\text{H}_2\text{CO}+\text{O}}$) irradiated with O atoms:

\[
\text{k}_{\text{CO}+\text{O}} \ll k_{\text{HCOOH}+\text{X}} < k_{\text{H}_2\text{CO}+\text{O}}
\]

hence, since the following relation is valid for the activation barrier:

\[
630 \text{K} = E_{\text{CO}+\text{O}} \gg E_{\text{HCOOH}+\text{X}} > E_{\text{H}_2\text{CO}+\text{O}} = 335 \text{K},
\]

we can conclude that $E_{\text{HCOOH}+\text{X}} \approx 450 \pm 100$ K.
Figure 5.30: TPD curves of different masses after deposition of $1.5\pm0.5$ ML of HCOOH (blue curves) and irradiation of $1.5\pm0.5$ ML of HCOOH with $4.2\pm1$ ML of H (red curves) on oxidized graphite held at 10 K.
Figure 5.31: TPD curves of different masses after deposition of $1.5 \pm 0.5$ ML of HCOOH (blue curves) and irradiation of $1.5 \pm 0.5$ ML of HCOOH with $2 \pm 0.3$ ML of O (red curves) on oxidized graphite held at 10 K.

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In this thesis we have reviewed some important results of recent experimental investigations relative to physical-chemical processes occurring on cold surfaces. The main part of these results can be framed in an astrophysical context, particularly in astrochemistry, where they could be relevant to help astronomers understand the formation of interstellar ices, the increase of molecular complexity, and the equilibrium between gas and solid phase. In the following we will present briefly the astrophysical context in which we apply our findings, and we will discuss their influence on the physical-chemistry of molecular clouds.

6.1 Astrophysical conclusion

6.1.1 Astrophysical context

More than eighty years ago, Robert Julius Trumpler noted that the brightness of the more distant open clusters was lower than expected, and the stars appeared more red (Trumpler 1930). He supposed that something in the space between stars and us weakened starlight, by an amount proportional to the distance it travelled, so that light from more distant clusters was extinguished more than that from nearby clusters. This hypothesis was revealed to be true. Space among stars is not empty, observations show that it is filled with rarefied gas, dust particles, magnetic field, and relativistically moving electrons, protons and other atomic nuclei. Such diffuse matter is called the Interstellar Medium (ISM). The total mass of the ISM in the Milky Way is about 10% of the visible mass of Galaxy; 99% is made of gas, intermixed with it there is a 1% consisting of tiny dust grains. The ISM is present in different phases (see Table 6.1) characterized by different densities and temperatures, that depend on the physical
and chemical characteristics of the gas and dust and on the physical condition which lead to condensation in clouds. To simplify the description, interstellar clouds may be subdivided in two main types:

- Diffuse clouds (density \( \leq 10^2 \text{ cm}^{-3} \)), in which UV photons penetrate. The UV radiation causes the breaking of complex molecules (Gas is composed above all of H\(_2\), CO and CH) and inhibits the formation of ice mantle in the dust (substantially silicate and a-Carbon).
- Dense clouds, (density \( \approx 10^4 \text{ cm}^{-3} \)) in which photons do not penetrate. In these clouds molecules more complex than H\(_2\), CO and CH can form, as for example formaldehyde, alcohols and so on up to H\(_3\)CN. The fact that photons do not penetrate permits the formation of ice mantles on dust grains.

Moreover it must be clarified that cloud morphology changes continuously; its density varies (in the range of million of years) from dense to diffuse and vice versa, because of different energy budgets from surrounding environments:

1. clouds tend to expand and become more diffuse when radiation pressure is larger than gravity;
2. clouds tend to contract and become more dense when radiation pressure is smaller than gravity;
3. cloud collapses (in certain conditions fragmentation occurs, see Cabrit (1994) and Bate 2000) and star formation begins when radiation pressure is not strong enough to prevent gravitational collapse (the Jeans instability is reached Jeans 1902).

It is know that 1% of the ISM mass is in the form of dust grains, with sizes ranging from nanometric to micrometric. For several decades, dust grains were thought to be only passive and annoying entities present towards any astrophysical objects that astronomers wanted to observe. Only in the 1946, Oort and van de Hulst (Oort & Hulst 1946) revealed the real nature of dust, showing that dust grains could be a powerful interstellar catalyst. Actually today around 200 molecular species have been identified in interstellar space[1] ranging in complexity from molecular hydrogen (H\(_2\)), which is by far the most common molecule in space, through other familiar ones, such as water, hydrogen cyanide (HCN), nitrous oxide (N\(_2\)O), and ethanol (CH\(_3\)CH\(_2\)OH), to esoteric carbon-chains known as cyano-polyynes, the biggest known of which is H\(_{11}\)C\(_3\)N. Although most of the molecules detected in the interstellar clouds appear to be formed via sequences of gas-phase reactions (Smith et al., 2004; Herbst, 2001), this is not true for all species in all types of sources: the presence of dust grains is crucial to synthesis of these species. Grains both shield molecules from stellar ultraviolet light that would otherwise disrupt the chemical bonds and provide a surface on which atoms, radicals, and molecules can congregate and interact. A well studied example is the formation of molecular hydrogen from precursor hydrogen atoms adsorbed in cold surfaces. Today the formation of several other molecules by surface reactions has been studied. Among them there are carbon dioxide, water, formaldehyde, methanol and carbonic acid (Hage

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Table 6.1: List of different components of an interstellar cloud, with the respective temperature, density of particle and mass in SMU (solar mass unity).

<table>
<thead>
<tr>
<th>Phase</th>
<th>( \text{T}_g ) (K)</th>
<th>density (cm(^{-3}))</th>
<th>( M ) (10(^9)M(_\odot))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular</td>
<td>20 - 30</td>
<td>( 10^3 - 10^6 )</td>
<td>( \approx 2.5 )</td>
</tr>
<tr>
<td>Cold neutral medium</td>
<td>50 - 100</td>
<td>10 - 50</td>
<td>( &gt; 6.0 )</td>
</tr>
<tr>
<td>Warm neutral medium</td>
<td>8000</td>
<td>0.2 - 0.5</td>
<td>( \approx 2.8 )</td>
</tr>
<tr>
<td>Ionized warm medium</td>
<td>8000</td>
<td>0.2 - 0.5</td>
<td>( \approx 1.5 )</td>
</tr>
<tr>
<td>Warm coronal gas</td>
<td>( 10^6 )</td>
<td>0.003</td>
<td>-</td>
</tr>
</tbody>
</table>

---

et al. 1998; Zheng&Kaiser 2007). Laboratory studies have shown that not only simple molecules can be made in this way but elaborate molecules (yet to be detected in space) that may be important in the origin of life itself. Among the molecules of biochemical interest already detected in the Sagittarius B2 cloud, near the center of the Galaxy, is glycolaldehyde (CH$_2$H$_2$O$_2$), a simple sugar that can combine with other molecules to form more complex sugars i.e. ribose and glucose. Ribose is a building block of nucleic acids such as RNA and DNA, which carry the genetic code of living organisms. One observation also suggests the presence of glycine, the simplest amino acid (a chemical unit of proteins), in Sag B2 (Kuan et al. 2003), even if we have to say that such a detection has not been yet confirmed by other observations.

6.1.2 O diffusion

In Sec. 4.1.3 we have deduced O-atom diffusion coefficients on different surfaces (see Table 4.1 for details). Aside from the diffusion mechanism at play, we have found the a very efficient diffusive process exists; this has an impact on the chemistry occurring at the surface of dust grains. In fact, either the formation of some species may be enhanced, or at least the relative abundances of the final products affected. The implications for solid-state astrochemistry are of major importance. It was usually thought that the chemistry was mostly driven by H diffusion, and therefore the final products were mostly hydrogen saturated species such as H$_2$O, NH$_3$, CH$_4$, and CH$_3$OH. We can affirm that O addition chemistry is competitive with H additions because of the comparable budget of O atoms and H atoms in dense and UV protected interstellar environments (Caselli et al. 2002). An important example of how O-atom mobility can modulate the abundances of key species of ices in dense quiescent molecular clouds is the case of the H$_2$O : CO$_2$ ratio. Most of the molecular variety observed in interstellar ices has long been considered the outcome of H-atom addition reactions involving O, O$_2$, O$_3$, CO, N, and NO. Water, for example, is the final and most stable species of all the chemical networks between H and O, O$_2$ and O$_3$, which justifies its role as the most abundant ice in the Universe. If the reactive partner of H is CO, then CH$_3$OH is obtained via a series of successive hydrogenations. On the other hand, if H is the only mobile species able to scan the entire surface of the grain (Matar et al. 2008), it may be difficult to explain the abundance of CO$_2$, the second most abundant condensed species. Even if CO$_2$ can be formed via energetic processes by irradiating ice mixtures of H$_2$O and CO with UV photons or ions (Ioppolo et al. 2009; Laffon et al. 2010, and reference therein), these processes are less efficient in dense core of molecular clouds, and CO$_2$ can only be formed via non-energetic mechanisms, i.e., the reactions CO + OH, CO + O, and H$_2$CO + O. If these chemical routes leading to CO$_2$ involved only species which are not mobile at 10 K, then CO$_2$ formation would be greatly hindered by the rate of accretion and the high mobility of H atoms, which are able to reach CO, OH, and O long before these species can meet to form carbon dioxide. Our present and previous works introduce strong arguments to suggest that O atoms too are mobile at very low temperatures. This implies that the formation rate of CO$_2$ in dense clouds is governed by a balance between the accretion rate of H atoms and the diffusion rate of O atoms on the surface of dust grains. We carried out some calculations to show the evolution of the relative abundances of H atoms and O atoms on the surfaces of dust grains and - assuming that both species are mobile at low temperatures - how this balance can affect the chemistry within interstellar clouds of various densities. In fact, different environments are characterized by different densities; the abundances of species in the gas phase change and this entails a change in the accretion timescales of particles on dust grains. In diffuse clouds, hydrogen is mainly present in its atomic form and is by far the most abundant atomic species. In dark clouds, hydrogen is mainly present in its molecular form, so H atoms become a rather rare reactant, with [H] : [H$_2$] = 10$^{-3}$ (Li&Goldsmith 2003). The number density of H atoms is mostly governed by the destruction of H$_2$ due to cosmic rays. This value, almost independent of the density of the cloud, is of the order 1 H cm$^{-3}$. On the other hand, the [O] : [H$_2$] ratio remains approximately constant (10$^{-4}$), thus the number of atomic O, unlike H, is proportional to the density of the cloud (see, for example, Table 1 in Caselli et al. 2002). For a cloud with number density of $10^4$ cm$^{-3}$, the [H] : [O] ratio is 1 : 0.75, while for
a denser cloud with a density of $10^5$ cm$^{-3}$, the [H] : [O] ratio is 1 : 7. Therefore, for very dense clouds, O is the most abundant species in atomic form, can accrete on grains and, provided the O atoms are mobile, can subsequently react with other species before these become fully saturated by H-additions. The accretion rates of H atoms and the diffusion coefficients of O are then the key factors to be compared in order to determine at what density of the medium oxidation reactions become comparable to H atom additions. Figure 6.1 shows the time interval between two impacts of particles of the same species (H or O) on a single dust grain, as a function of the density $n$ of the cloud. The time intervals between the two arrivals are derived from the actual particle flux of a given species. The interstellar flux of a species accreting on dust grains can be calculated as follows:

$$\Phi_x = \frac{1}{4} n_x v_x$$

where $n_x$ is the density of species $x$ in the gas phase and $v_x = (8 k_B T / \pi m_x)^{0.5}$ is its mean velocity. $\Phi_x$ is thus expressed in particles cm$^{-2}$ s$^{-1}$. For our calculation, we can approximate the dust grains to spheres with a typical radius $r=0.1$ mm, with accessible surface area $A = 4 \pi r^2$. The time interval between the impacts of two particles is then:

$$t = \left( \frac{n_x v_x A}{4} \right)^{-1}$$

The grey solid line in Figure 6.1 represents the time interval between the impact of two hydrogen atoms, calculated by assuming a constant density of H atoms, $n_H = 2.3$ cm$^{-3}$ (Li & Goldsmith 2003). The density of O atoms is proportional to the density of the clouds, $n$, namely, $n_O = 5 \times 10^{-4} n$. The time interval between the arrival of two O atoms is displayed as a red solid line, which clearly shows that the arrival of oxygen atoms becomes more frequent (shorter time between the two impacts) with the increasing density of the cloud. The grey and red lines cross at a density $n$ of around $10^4$ cm$^{-3}$. This suggests that for cloud densities of $\approx 10^4$ cm$^{-3}$ the accretion rates of H and O are comparable, and, given that both species can diffuse, oxidation reactions on the grains may play a role, although H-atom additions are still dominant due to the higher mobility of H. In Figure 6.1 we also indicate the mean time O atoms need to complete a scan of all the adsorption sites on the surface of one typical grain as used above, with radius = 0.1 $\mu$m and $10^6$ absorption sites ($10^{15}$ sites cm$^{-2}$). The mean times needed for a complete scan of the grain surface were calculated for a surface temperature of 10 K by using the diffusion constants $k$ of O atoms on each substrate presented in this work.
taking into account that \( k = 10^{-15} \text{ cm}^2 \text{ s}^{-1} \) corresponds to one jump per unit time. For H atoms, the mean time for scanning the entire surface of water ice was derived by the energy barrier for diffusion of 255 K (at 10 K) given by Matar et al. (2008). It is interesting to observe the intersection occurring at \( n = 10^5 \text{ cm}^{-3} \) between the red line and the band giving the mean time H atoms employ to scan the whole surface of the grain. This implies that at cloud densities of \( \approx 10^5 \text{ cm}^{-3} \) or greater, the diffusion and accretion rates of H atoms are smaller than the accretion rate of O atoms. Therefore, in very dense clouds, oxygen atoms may become the dominant reaction partner, able to react with CO and produce CO\(_2\), as well as reacting with H to produce OH. Since H atoms are rare in this environment, OH will not be readily transformed into water via hydrogenation, and the hydroxyl radical is likely to react with the abundant CO molecules to form CO\(_2\).

6.1.3 Chemical Desorption

For a long time the role of dust as interstellar catalyst has been well recognized. On the contrary, mechanisms that allow the formed species on the surface to populate the gas phase are still poorly known. This is a real paradox and issue of modern astrochemistry: to reconcile almost non-observable solid phase dust catalysis to observable products in the gas phase. In Sec. 1.1.3 we have listed some of the processes leading to gas phase release of adsorbed species. In particular three types of non-thermal desorption can be considered: photodesorption, sputtering, and chemical desorption. This last has been discussed in depth in Sec. 4.3. Here we try to pinpoint what is the impact of CD on the chemistry of ISM. To estimate the impact of chemical desorption on the gas phase composition of astrophysical environments, we used a theoretical model (Cazaux et al. (2010); Meijerink et al. (2012)), by adding CD yields derived from the experiments presented in Sec. 4.3 (Dulieu et al. 2013; Minissale & Dulieu 2014). In this sense, we quantify the direct impact of the chemistry on dust on the gas phase. For some reactions occurring on the surface, an important amount of the formed species are ejected in the gas phase. Therefore, within the parameter range at which these reactions dominate the chemistry on the dust surface, an important contribution in the gas phase is expected. Figure 6.2 displays the calculated efficiencies of the conversion rate of gas phase atomic oxygen into another gas phase species (OH, H\(_2\)O, and O\(_2\)) by the use of grain surface chemistry. In Dulieu et al. (2013) efficiency has been calculated for binding energy of \( E_{\text{Oxygen}} = 1100 \text{ K} \) (left panel of Figure 6.2). The formation efficiency is on the order of 30\% for OH (below 15 K) and 70\% for water (below 25 K). For O\(_2\), there are two main temperature ranges where desorption into the gas phase is important. The first one, located around 17 K, has an efficiency of about 4\%, while the second one, located around 35 K, has an efficiency of 0.2\%. If a strong UV field is considered in our calculations, then the species on the surface can be photo-dissociated and reform. We consider a strong radiation filed.
Astrophysical conclusion

$G_0 = 100$, which corresponds to 100 times the ambient UV radiation field), and show that the efficiency of $O_2$ formation is increased by a factor of 5. On the other hand, the formation of OH and $H_2O$ is unchanged. In the right panel of Figure 6.2 we have calculated efficiency for binding energy of $E_{binding} = 1800$ K, that is the value found in Sec. 4.2. Even in this case the formation efficiency is on the order of 30% for OH and 70% for water, while for $O_2$ efficiency has a value of 12%. Moreover the $T_{dust}$ dependence is somewhat different: water and OH efficiency are zero at 44 K and 48 K (instead of 33 K and 21 K), and $O_2$ efficiency has no longer two peaks, but only one that falls down at zero at around 52 K. By comparing the formation rates of species via gas or dust routes, we note that the formation of OH (and water) on dust surfaces dominates by 12 (9) orders of magnitude the gas phase route for a gas at 100 K, while this becomes of 0 (2) for a gas at 500 K. These estimations are made considering the dust temperature in the range (0-15 K for left panel and 0-31 K for right panel) for OH and (0-25 K for left panel and 0-30 K for right panel) for water (for calculation details see Dulieu et al. (2013)). Searches of $O_2$ with ground based telescopes and space missions such as SWASS and ODIN indicated that $O_2$ has a widespread low abundance. $O_2$ remained unseen allowing to derive some upper limits $X(O_2) \leq 10^{-7}$ (Goldsmith et al. 2000; Pagani et al. 2003). However, while recent Hershel observations confirmed the general trend that $O_2$ has very low abundances (detection of $O_2$ towards rOph, $X(O_2) \approx 10^{-8}$, Lisseau et al. (2012)), one isolated high abundance of $O_2$ has been reported towards ORION (Goldsmith et al. 2011). This high abundance has been attributed to the presence of warm dust, or to shocks. In this work, our model shows an alternative efficient way to form $O_2$ in the gas phase through chemical desorption from dust. This efficiency is important only for very specific conditions ($T_{dust}$,30-40 K and high UV field), which could explain why the detection of $O_2$ is seen only in isolated cases. We note that a single variation of one of model parameters (i.e. O atom binding energy) produces a substantial change in model results, and thus of their astrophysical interpretation. In other words, the prediction power of a theoretical model lies, for a big part, on the right choice of (experimental) physical-chemical parameters, and not only on model degree of sophistication.

Finally we want to stress that the existence of CD not only impacts the chemical composition of our Universe, but affects the way stars form. Actually in regions where stars are forming, the presence of dust dramatically influences the gas phase composition, changing the abundances of molecules available to cool the gas. Therefore, a cloud that undergoes gravitational collapse to form a star will cool more or less rapidly, depending on the available coolants, and this impacts the efficiency and characteristics (mass, binariy) of star formation.

6.1.4 H/C/N/O chemical network

In Chapter 5 we have presented many reactions pointing out their final products and their efficiency. Here we report a list of reactions studied in this thesis by providing products and energy barrier. We have not been able to find a precise value of energy barrier in all the studied reactions, but we provide anyhow an estimation.

6.1.4.1 Interstellar ices

Thanks to infrared observations we know that interstellar dust grains are covered with an ice mantle formed in molecular clouds. Temperatures in these regions can be as low as 10 K, allowing molecules that collide with grains to form an icy mantle. Thereafter, atoms undergo thermal motion across the surface, eventually forming bonds with other atoms. This results in the formation of water and other molecules (i.e. carbon dioxide, carbon monoxide, methanol, ammonia). The composition of interstellar ice varies along the line of sight of different objects and Table 6.3 lists abundances of interstellar ices ($CO$, $CO_2$, and $CH_3OH$) expressed as percentages of the $H_2O$ abundance. We note that

1. carbon dioxide is the most common and abundant types of ice after water. It presents an abundance $N(CO_2/H_2O) \approx 30$ in all objects.

2. carbon monoxide has very variable abundance ranging from 12 to 47% of $H_2O$ abundances.
**Table 6.2:** List of reactions (their final products and their efficiency) studied in this thesis.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Energy Barrier</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O + H</td>
<td>OH</td>
<td>bl</td>
<td>Dulieu et al. (2010)</td>
</tr>
<tr>
<td>OH + H</td>
<td>H$_2$O</td>
<td>bl</td>
<td>Dulieu et al. (2010)</td>
</tr>
<tr>
<td>O$_2$ + H</td>
<td>O$_3$H</td>
<td>bl</td>
<td>Chaabouni et al. (2012)</td>
</tr>
<tr>
<td>O$_2$H + H</td>
<td>H$_2$O$_2$</td>
<td>bl</td>
<td>Chaabouni et al. (2012)</td>
</tr>
<tr>
<td>O$_2$ + H</td>
<td>2 OH</td>
<td>bl</td>
<td>Chaabouni et al. (2012)</td>
</tr>
<tr>
<td>O$_3$ + H</td>
<td>O$_2$ + OH</td>
<td>bl</td>
<td>Makmune et al. (2009)</td>
</tr>
<tr>
<td>O + O</td>
<td>O$_2$</td>
<td>bl$^a$</td>
<td>Minissale et al. (2013, 2014)</td>
</tr>
<tr>
<td>O$_2$ + O</td>
<td>O$_3$</td>
<td>bl$^a$</td>
<td>Minissale et al. (2013b, 2014a)</td>
</tr>
<tr>
<td>N + N</td>
<td>N$_2$</td>
<td>bl$^a$</td>
<td>This work</td>
</tr>
<tr>
<td>HCOOH + H</td>
<td>H$_2$O + CO + CH$_3$OH</td>
<td>s</td>
<td>This work</td>
</tr>
<tr>
<td>HCOOH + O</td>
<td>H$_2$O + CO$_2$</td>
<td>s</td>
<td>This work</td>
</tr>
<tr>
<td>NO + H</td>
<td>NH$_2$OH</td>
<td>bl</td>
<td>Congiu et al. (2012)</td>
</tr>
<tr>
<td>NO + N</td>
<td>N$_2$ + NO$_2$ + O$_3$</td>
<td>s</td>
<td>Minissale et al. (2014b)</td>
</tr>
<tr>
<td>NO + O</td>
<td>NO$_2$</td>
<td>bl</td>
<td>Minissale et al. (2014b)</td>
</tr>
<tr>
<td>NO + O$_2$</td>
<td>NO$_2$</td>
<td>1.66 17.2 200</td>
<td>Minissale et al. (2013a)</td>
</tr>
<tr>
<td>NO + O$_3$</td>
<td>NO$_2$</td>
<td>small</td>
<td>Minissale et al. (2014b)</td>
</tr>
<tr>
<td>NO$_2$ + H</td>
<td>NH$_2$OH + H$_2$O</td>
<td>bl</td>
<td>Ioppolo et al. (2014b)</td>
</tr>
<tr>
<td>NO$_2$ + N</td>
<td>N$_2$O + O$_3$</td>
<td>high</td>
<td>Ioppolo et al. (2014b)</td>
</tr>
<tr>
<td>NO$_2$ + O</td>
<td>NO + O$_3$</td>
<td>high</td>
<td>Ioppolo et al. (2014b)</td>
</tr>
<tr>
<td>NO$_2$ + NO</td>
<td>(NO)$_2$</td>
<td>bl</td>
<td>Minissale et al. (2013a, 2014b)</td>
</tr>
<tr>
<td>NO$_2$ + NO$_2$</td>
<td>N$_2$O$_3$</td>
<td>bl</td>
<td>Minissale et al. (2013a, 2014b)</td>
</tr>
<tr>
<td>NO$_2$ + NO$_2$</td>
<td>N$_2$O$_4$</td>
<td>bl</td>
<td>Minissale et al. (2013a, 2014b)</td>
</tr>
</tbody>
</table>

$^a$ These reactions should be barrierless, and we estimate an upper limit of 150 K. $^b$ For some experiments we are not able to give a precise evaluation of the barrier; we use bl (barrierless) for reactions with barrier ($E_b$) smaller than 150 K, s (small) for 150 $\leq E_b < 500$ K, h (high) for 500 $\leq E_b < 800$ K, vh (very high) for $E_b > 800$ K.

3. methanol presents low abundances ($<6$) with unexpected peak at $30\%$ of H$_2$O ices.

How to explain these abundances? To give an answer to this question, we have to know how these molecules are formed and consumed.

**CO$_2$:** its high abundances observed in interstellar ices are explained through some solid-phase reactions. Energetic formation processes leading to efficient formation of CO$_2$ include irradiation of CO ices (pure or mixed with H$_2$O) with photons, charged particles or electrons (Ioppolo et al. 2009; Laffon et al. 2010). On the other hand, Whittet et al. (1998) invoke chemical pathways occurring without the addition of energy to explain the CO$_2$ detection in those interstellar environments where a lack of UV photons forbids ice processing (i.e., molecular cloud Taurus). To date, three (non energetic) pathways are considered:

- **a** CO + OH → CO$_2$ + H
- **b** CO + O → CO$_2$
- **c** H$_2$CO + O → CO$_2$ + H$_2$

Noble et al. (2011) and Oba et al. (2011) showed experimentally the CO$_2$ formation through reaction (a), but no consistent values were obtained for the activation barrier (barrier between 0 and 400 K). Roser et al. (2001) and Rault&Baragiola (2011) successfully showed that the formation of CO$_2$ is possible through reaction (b). Recently in Minissale et al. (2013b)
Table 6.3: Abundances of interstellar (CO, CO$_2$, and CH$_3$OH) ices expressed as percentages of the H$_2$O abundance. Data are based on infrared spectroscopy of Whittet et al. (2011) and references therein$^a$. Each value is obtained by averaging observations of different interstellar objects (Dark clouds, low-mass YSO, and high-mass YSO). y (yes) and n (not) indicate evidence for thermal processing of ices.

<table>
<thead>
<tr>
<th>Species</th>
<th>Field Stars</th>
<th>Low-mass YSOs</th>
<th>High-mass YSOs</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>100</td>
<td>y</td>
<td>n</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>30.7±9.2</td>
<td>27.1±4.5</td>
<td>34.3±4.3</td>
</tr>
<tr>
<td>CO</td>
<td>26.0±15.1</td>
<td>14.4±6.1</td>
<td>47.2±14.9</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>&lt;6.7±3.1</td>
<td>&lt;5.4±3.4</td>
<td>&lt;5.7±4.3$c$</td>
</tr>
</tbody>
</table>

$^a$ Whittet et al. 2011 and references therein: Boogert et al. (2000, 2008); Pontoppidan et al. (2003, 2004, 2008); Bottinelli et al. 2010; Cook et al. (2011); Zasowski et al. 2009; Chiar et al. (1996, 1998); Thi et al. (2002, 2006); Gerakines et al. 1999; (13) Öberg et al. 2011; Graham 1998; Gibb et al. (2004). $^b$ This value has been obtained by considering only one object; $^c$ the average has been obtained by counting out two objects with N(CH$_3$OH/H$_2$O)=30;

we confirmed these results, and we estimated an activation barrier of about 600 K. Finally in Minissale et al. (2014) we have studied reaction (c) by showing that also reaction (c) can efficiently form CO$_2$ in the ISM. Up to now there is a lack of knowledge on efficient reaction routes able to consume CO$_2$, except for irradiation of energetic cosmic rays not very likely to occur in molecular clouds.

CO: its abundance is explained only via gas-phase reactions and subsequent accretion on dust grains (Glover et al. 2013); up to now, it is known that solid-phase reactions are at a certain degree able to consume CO (i.e. to form CO$_2$ or CH$_3$OH).

CH$_3$OH: CH$_3$OH is formed via four CO hydrogenations (with a total energy barrier > 800 K/kb, Fuchs et al. 2009), leading to the formation of two unstable radicals, HCO and CH$_3$O, and one stable molecule, namely, H$_2$CO. This process can occur only in very H-atom-rich environments (see Sec. 5.3.2). CH$_3$OH can be formed through energetic processing of icy mantles (Hudson&Moore 1990; Ioppolo et al. 2009, and references therein). As for CO$_2$, no efficient routes of consumption are known.

Abundances of Table 6.3 can be explained on the basis of formation and consumption routes. H$_2$O, CO, CO$_2$, and CH$_3$OH are the principle molecules in the solid phase of the H-C-O system. In this system we have three inputs (species arriving from the gas-phase): H, O, and CO (in red in Figure 6.3). By combining two by two inputs we obtain: H-O→H$_2$O, H-CO→CH$_3$OH, O-CO→CO$_2$ (broad arrow in Figure 6.3). This is true only in first approximation; in fact OH and H$_2$CO break the symmetry of the system. Reaction (a) (CO+OH) does not influence very much H$_2$O formation, due to the abundance of H atoms and the

Figure 6.3: Simple schemes of ices formation in ISM. Species are denoted in red and in blue if they are in the gas-phase and in the solid-phase respectively.
barrierless reactions leading to H$_2$O formation; on the other hand reaction (c) (H$_2$CO+O) and the large CO hydrogenation energy barrier could hinder CH$_3$OH formation, and favor CO$_2$ formation. In other words, except for H-rich environments CH$_3$OH formation is not a very likely event. These considerations can be summarized up as follows (right panel of Figure 6.3):

1. $N$(CO$_{gas}$)$\ll N$(H$_{gas}$) and $N$(CO$_{gas}$)$< N$(O$_{gas}$) favors H$_2$O$_{ice}$
2. $N$(O$_{gas}$)$\approx N$(H$_{gas}$) favors CO$_2$−$ice$
3. $N$(O$_{gas}$)$\ll N$(H$_{gas}$) favors CH$_3$OH$_{ice}$

From an astrophysical point of view, these conditions would suggest that a segregation of interstellar ices may develop (see Figure 6.4), the first condition is met when the dust cools down, at $40^\circ<T_{dust}<25$ K. Under this regime, CO cannot stick while O atoms are able to stick on dust ($E_{b-CO} \approx 1000 K < 1500 K \approx E_{b-O}$). Hydrogen is prevalently in its atomic form and it is able to hydrogenate O atoms to form water ices; neither CH$_3$OH nor CO$_2$ can be formed. At $T_{dust}<15$ K all species stick. Part of the hydrogen is in molecular form ($N$(H$_2$$_{gas}$) increases), thus $N$(H$_{gas}$) decreases and the second condition is satisfied. These two conditions basically explain observations of ices in field stars and low-mass YSOs, where water and carbon dioxide are the most abundant ices. The third condition is met only in some peculiar cases. Actually, this condition requires that, at least locally, $N$(H$_2$$_{gas}$) decreases to favor the $N$(H$_{gas}$) increase. In high-mass YSOs the high photon fluxes could cause photodissociation of H$_2$. This produces a temporary increase of $N$(H$_{gas}$) and thus conditions for CH$_3$OH formation. In other words, indirect photochemistry increases CH$_3$OH abundance in high-mass YSOs. This schematic scenario is quite coherent with observations of interstellar ices; in fact, it seems that a sort of depth (i.e., age) segregation exists between the three most abundant ices (H$_2$O, CO$_2$, CO) (Gibb et al. 2004; Öberg et al. 2011) water tends to be concentrated in the layers forming the inner (and older) part of the mantles, while CO$_2$ and CO abundance increases in the outer (and more recent) layers.

6.2 Perspectives

6.2.1 Ice growth: MonteCarlo Model

The growth of ice mantle can be simulated by using a microscopic Monte Carlo (MMC) method. Atoms and molecules (essentially H/O/CO) accrete on dust from the gas-phase and their rates of accretion vary over time simulating interstellar evolution. In collaboration with S. Cazaux (University of Groningen) and V. Cobut (University of Cergy-Pontoise) we are developing a MMC to study the ice mantle growth. The model is very similar to the one used in Cuppen&Herbst (2007) or Cazaux et al. (2010), but it differs essentially in two points: (1) massive use of experimental data; (2) continuous comparison with experimental results. We assume that the physics acting on interstellar ices is the same of the physics we observe in the laboratory. Hence, we think that a MMC has to reproduce laboratory results in order to provide reliable predictions. The match between theoretical and observational data (scheme in Figure 6.5) should be improved by increasing the degree of model sophistication and using a different “physics”, as the more consistent physics adopted, the more reliable the match will be. For this reason, first of all, we will implement in our MMC all the experimental results that we have found (i.e. activation barriers for reaction, energy barriers for diffusion, CD efficiencies, binding energies), and subsequently we will test the physics used in the model by comparing model results with experimental data. Model parameters are tuned to find a reasonable match. Only after determining that the model can reproduce the experimental values it will be used for predicting physical chemical properties of the ISM and for drawing astrophysical conclusion (see scheme b in Figure 6.5). One way for comparing model results with experimental data could be reproduce experimental TPDs with MMC as shown in Figure 6.6. In this case, the parameters we have to adjust, to find a good match is the addition of binding energies and the transition from monolayer to multilayer description.
**Figure 6.4:** Temperature of dust as a function of evolution time for ices in molecular clouds towards field stars, and ices observed near low-mass YSOs and high-mass YSOs. Pinstriped zones indicate, respectively H$_2$O, CO$_2$, and CO snow-lines. Colored arrows indicate moments at which each condition is met (see text). On the right side schematic representation of interstellar ices for their respective regions of observation.

**Figure 6.5:** Schematic representation of classical MMC approach sequence (a) and our own MMC for deriving physical chemical properties of ISM (b).
Figure 6.6: Comparison between TPDs of O\textsubscript{2} obtained experimentally (panel at left) and through two different versions (central panel, preliminary version; panel at right, improved version) of the MMC model.

Once TPDs of different molecules and simple reactivity cases are checked, the MMC model could also be used to study the properties of icy mantles.

6.2.2 Further perspectives

1. Comparison of O-atom isotopic diffusion: the use of an isotope of the O atom (i.e., \textsuperscript{18}O\textsubscript{2}) could give further experimental constraints about the O atoms diffusion and could help to demonstrate the mass effect predicted in Allen et al. (1980).

2. N-atom and C-atom diffusion: N and C atoms could reveal mobility properties similar to those of O atoms. If we scale the diffusion for these atoms, on the basis of their polarizability alone - the main parameter for physisorption - there is a reasonable range of temperatures (5-20 K) where the mobility of O, C and N is activated. For this reason, the production of O, C, and N bearing molecules can grow, avoiding saturated chemical traps. This could also be one of the mechanisms leading to complex nonvolatile organic compounds observed in meteorites, such as amino acids.

3. Molecular complexity, H-C-N-O: in Chapter 5 we presented many reactions by using not more than a 3-dimensional matrix of species (H-C-O, H-N-O). What molecule can be formed using a 4-dimensional matrices?

4. Phase transition, from gas to solid and vice versa: the gas and solid phases are almost sealed off and a bridge between them would help to understand chemistry and dynamics of the ISM. Some key questions already stand on robust pillars, but some other questions are still open:

   - What are the parameters ruling the phase transition?
   - What is the energy distribution of desorbing molecules (thermal and non-thermal)?
   - How phonons dissipation occurs?
Bibliography


6.08 Congiu, E., Minissale, M., Baouche, S., Chaabouni, H., Moudens, A., Cazaux, S., Manicò, G., Pirronello, V., and Dulieu F., Efficient diffusive mechanisms of O atoms at very low temperatures on surfaces of astrophysical interest, Faraday Discussion 168 (2014)


6.29 Minissale, M., Congiu, E., and Dulieu, F., Oxygen diffusion and reactivity at low temperature on bare amorphous olivine-type silicate, The Journal of Chemical Physics, Volume 140, pp.074705 (2014a)


6.32 Minissale, M., Baouche, S., Chaabouni, H., Congiu, E., Moudens, A., and Dulieu, F., Solid-state formation of CO2 via the H2CO + O reaction, submitted to Astronomy and Astrophysics (2014s)


6.42 Trumpler, R. J., *Preliminary results on the distances, dimensions and space distribution of open star clusters*, Lick Observatory Bulletin, Volume XIV, Number 420, pp. 154-188 (1930)


Appendix A. Atomic and molecular term symbols

Atomic and molecular term symbols specify electronic energy levels of atoms and diatomic molecules, respectively. The form of the symbols imply Russell-Saunders coupling and consist of four parts: spin multiplicity, azimuthal angular momentum, total angular momentum, symmetry and parity. In the atomic case, the whole notation has the general form

\[ 2S+1L(S, P, D, F, \ldots)_J \]  

where

- \( L \) is the total orbital quantum number; The first 4 symbols of are S, P, D, F corresponding to a value of 0, 1, 2, 3;
- \( S \) is the total spin quantum number. \( 2S + 1 \) is the spin multiplicity;
- \( J \) is the total angular momentum quantum number.

For homonuclear diatomic molecules, or symmetric molecules with an inversion centre the following notation is used:

\[ X(A, B, \ldots, a, b)2S+1\Lambda(\Sigma, \Pi, \Delta, \Phi, \ldots)^{(\pm)}_{h,(g,u)} \]

where

- \( \Lambda(\Sigma, \Pi, \Delta, \Phi, \ldots) \) is the projection of the orbital angular momentum along the internuclear axis; \( \Sigma=0, \Pi=1, \Delta=2, \Phi=3 \), and so on;
- \( S \) is the total spin quantum number;
- \( \Omega \) is the projection of the total angular momentum along the internuclear axis;
- \( \pm,\ldots \) indicates the reflection symmetry along an arbitrary plane containing the internuclear axis
- \( g,u \) indicates the parity (reflection through an inversion center). \( g \) means \textit{gerade} (German for even), \( u \) means \textit{ungerade} (odd).
- \( X(A, B, \ldots, a, b) \) indicates the electronic states. \( X \) is for the ground state, excited states of the same multiplicity (i.e., having the same spin quantum number) are labelled in ascending order of energy with capital letters \( A, B, C, \ldots \); excited states having different multiplicity than the ground state are labelled with lower-case letters \( a, b, c, \ldots \).

\( J \) and \( \Omega \) are usually omitted in atomic and molecular orbital notations.
Appendix B. List of publications

1 Water formation through $O_2+D$ pathway on cold silicate and amorphous water ice surfaces of interstellar interest,
Journal of Chemical Physics, 137, 234706 (2012)

2 Chemical desorption source of observable molecules in our Universe,
F. Dulieu, E. Congiu, J. Noble, S. Baouche, H. Chaabouni, A. Moudens, M. Minissale and S. Cazaux,

3 Formation of nitrogen trioxide and nitrogen dioxide via NO + O$_2$ gas-solid reaction on cold surfaces,
M. Minissale, E. Congiu, S. Baouche, H. Chaabouni, A. Moudens, F. Dulieu, G. Manicó and V. Pirronello,

4 Quantum tunneling of oxygen atoms on very cold surfaces,
M. Minissale, E. Congiu, S. Baouche, H. Chaabouni, A. Moudens, F. Dulieu, M. Accolla, S. Cazaux, G. Manicó, and V. Pirronello,

5 CO$_2$ formation on interstellar dust grains: a detailed study on the barrier of the CO+O channel,
M. Minissale, E. Congiu, G. Manicó, V. Pirronello, and F. Dulieu,

6 Efficient diffusive mechanisms of O atoms at very low temperatures on surfaces of astrophysical interest,
E. Congiu, M. Minissale, S. Baouche, S. Cazaux, H. Chaabouni, G. Manicó, A. Moudens, V. Pirronello, and F. Dulieu,
Faraday Discussion 168 “Astrochemistry of Dust, Ice and Gas” (2014)

7 Oxygen diffusion and reactivity on bare silicate interstellar grains,
M. Minissale, E. Congiu, and F. Dulieu,
Journal of Chemical Physics, 140, 074705, (2014)

8 Nitrogen chemistry on cold surfaces - Part I: The surface consumption of NO,
M. Minissale, G.S. Fedoseev, E. Congiu, S. Ioppolo, F. Dulieu, and H. Linnartz,
Physical Chemistry Chemical Physics, 16, 8257 (2014)
9 Nitrogen chemistry on cold surfaces - Part II: The surface consumption of NO\textsubscript{2},
S. Ioppolo, G.S. Fedoseev, M. Minissale, E. Congiu, F. Dulieu, and H. Linnartz,
Physical Chemistry Chemical Physics, 16, 8270 (2014)

10 Influence of surface coverage on the chemical desorption process,
M. Minissale, and F. Dulieu,
Journal of Chemical Physics, 141, 014304 (2014)

11 CO\textsubscript{2} formation via solid state H\textsubscript{2}CO + O reaction,
M. Minissale, E. Congiu, S. Baouche, H. Chaabouni, and F. Dulieu,
submitted to A&A
List of Acronyms

**AMU** : Atomic Mass Unit

**ASW** : Amorphous Solid Water

**CD** : Chemical Desorption

**Cps** : Counts per second

**DED** : During Exposure Desorption (or Detection)

**EID** : Electron impact desorption

**ER** : Eley-Rideal

**ESD** : Electron-stimulated desorption

**FIR** : Far InfraRed

**FL** : Focal Length

**FT** : Fourier Transform

**FUV** : Far UltraViolet

**HAM** : Hot-Atom Mechanism

**HOPG** : Highly Ordered Pyrolytic Graphite

**IR** : InfraRed
**ISM**: Interstellar Medium

**LERMA**: Laboratoire d’Etudes du Rayonnement et de la Matière en Astrophysique et Atmosphères

**LH**: Langmuir-Hinshelwood

**MCT**: Mercury Cadmium Telluride

**ML**: Monolayer

**OFHC**: Oxygen-Free High thermal Conductivity

**p-np**: porous - not porous

**QMS**: Quadrupole Mass Spectrometer

**RAIRS**: Reflection Absorption InfraRed Spectroscopy

**TD**: Thermal desorption

**TDS**: Temperature Desorption Spectroscopy

**TPD**: Temperature Programmed Desorption

**UHV**: Ultra High Vacuum

**UV**: UltraViolet
A thesis is not the result of only one person’s work (mine) but that of many people. Clearly not all of them have contributed in the same way, by plotting a graph or writing a formula. Many of these have been very helpful in non-working times and for extra-working reasons, but it does not mean they were less crucial to who I am, and what this thesis is. These lines could not start with anyone else other than François Dulieu. Without him, I would probably still be drafting the first chapter. He was my supervisor, but also a colleague and a friend giving and asking for advice. Then, it is the turn of the seraphic Emanuele Congiu, who had to hear my chatter, in the laboratory and in the office, on the train and on soccer fields. So much time spent with him to have any doubts of his “genius”. I want to thank Valerio Pirronello and Giulio Manicò, whose distance has certainly decreased the number of contacts, but certainly not their intensity. I thank my referees Stephen Price and Pascal Parneix for their wise counsel and for the pleasant words used to describe my work. With them, I would like to thank the rest of the jury of my thesis (Paola Caselli, Cécile Engrand and Olivier Pluchery) for not having asked bad questions during the defense. Thanks, from the bottom of my heart, to Stephanie Cazaux, one of the few people with whom to work with seriously becomes synonymous of fun. She was able to make me work when I would have probably preferred to be partying or drinking in a pub. I would also like to thank Henda Chaabouni, whose constant presence has often helped me in the deafening silence of the laboratory. Then Saoud Baouche that I cannot forget on one hand for the skillful mastery with bolts and connections, and on the other hand for the curses due to broken pumps or American screw stripped. Next is Audrey Moudens, with her delicious cakes, cakes that I missed even more at the time of the thesis redaction when I desperately needed more sugar. Fortunately, Henri Lemaitre was able to make up for this lack, thanks to interesting discussion and by raising the alcohol content in our office. I have to thank Stephan Diana, for his help with computers, as well as Eric Somson, François Lacheve and Gilles Remy for the debates over crépes and cafes about French culture, movies and football.

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A fool sees not the same tree as the wise man sees.

“The Marriage of Heaven and Hell”
William Blake
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Avec le temps...
Avec le temps, va, tout s’en va
On oublie les passions et l’on oublie les voix

“Àvec le temps”
Léo Ferré
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