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Non-linear astrochemical kinetics: theory and applications

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1 | INTRODUCTION

1.1 Astrochemistry

Astrochemistry is the study of the abundance and reactions of atoms and molecules in the Universe, both in the gas phase and in the solid state, and involves interaction with energetic particles and radiation. This field of research has played crucial roles in a wide range of applications, broadening our understanding of its influence on the structure, dynamics, and evolution of astronomical objects. Molecules are found throughout the Universe, from the first carbon-bearing specie detected (CH, C₂, CN, CO) in the interstellar medium by Swings & Rosenfeld (1937) to nowadays observations, that comprise detections of both small and tall species, stable and reactive, and comprising a remarkably large number of so called COMs, complex organic molecules. A large panel of molecules have been observed in relatively close objects like comets, solar photosphere, planetary atmospheres, or further objects like protoplanetary disks, evolved stars, and in particular molecular clouds. McGuire (2021) gives a recent and extended list of molecules detected, including the observational facility, wavelength range, transitions, and enabling laboratory spectroscopic work, as well as listing tentative and disputed detections. In summary, 241 individual molecular species, with two to seventy atoms, have been observed in the interstellar medium (ISM), spanning a remarkably large variety in chemical appearances.

The primary focus in this thesis will be on astrochemical processes taking place in the ISM. The ISM is an important part of stellar life cycles, it is considered as a repository of polyatomic molecules in between stars, recycling elements from supernova explosions and the winds of late type stars through different cloud stages toward proto- and planetary systems (Figure 1.1). This environment is mainly gaseous, with molecular hydrogen, H₂ being the most abundant molecule by far. Ionizing sources such as hot stars Cosmic-Rays (CR) and Ultra-Violet (UV) are also present, coming from supernova remnants. Interstellar chemistry is controlled by a wide range of physical and chemical parameters (temperatures, visual extinctions, densities). In accordance with their values, combined with other interstellar phenomena (gravity, turbulence, magnetic fields), the ISM region can be classified in different categories, referred as interstellar clouds (Table 1.1). Even in the darker and cooler environments, the CR ionize interstellar molecules, primarily reacting with H₂ to produce H₂⁺, and

$\text{H}_2 + \text{H}_2^+$ reaction leads to the formation of a highly reactive ion, H_3^+ . Thereafter, H_3^+ reacts with other species, leading the way to sequences of protonation reactions which yield carbon- and oxygen-bearing molecular ions. Dissociative recombination with electrons then produces neutral abundant molecules. The different types of elemental gas phase reactions are listed in Table 1.2. The ISM consists also of 1% of dust grains. They are mainly composed of silicate and carbonaceous material with an average size of $0.1 \mu\text{m}$. Depending where the grains resign in the interstellar clouds, inclined by temperature, density and radiations, they can be covered by layers of ice, that are regarded as interstellar catalysts on which solid state reactions can take place. The interaction between icy dust grains and gas phase species in the ISM is currently an area of intense research.

The cold and dense molecular clouds are often formation sites for solar-type stars (and presumably planets). Single clouds may have masses of a few hundred solar masses (M_\odot), while dense cores within such clouds may be as small as one to a few M_\odot . The low temperature and lack of embedded high-luminosity sources make these regions ideal testing grounds for models of gas-phase ion-molecule chemistry. Mostly because the physical conditions of this type of environment allow the system to be in a stationary state and it is computationally easier with simple thermodynamic processes (isothermal, adiabatic and isochoric). Furthermore, it is a standard and well used physical condition in experimental studies to demonstrate the behavior of specific chemical reactions on grain surfaces.

All chapters of this PhD focus on dense molecular cloud environments. The results presented are all based on modeling studies, and linked to observational and laboratory based data.

Table 1.1: Cloud types in the ISM with typical sizes, temperatures, number densities and visual extinction commonly used to probe physical conditions as noted in Millar (2015).

Cloud Type	Size (pc [†])	T (K)	n (cm ⁻³)	A_μ (mag)
Diffuse	1-3	70-100	10-100	1
Dark	1-5	8-15	10^4 - 10^6	10-20
Hot Core	0.01-0.1	100-300	10^7 - 10^9	5000
Giant Molecular	100-500	30-70	10^3	-

[†] 1 pc = 3.086×10^{18} cm.

1.2 Astrochemical kinetics

In theoretical studies, the chemical evolution of interstellar or planetary objects is analyzed through the calculation of abundances of species present in the environment as a function of different physical parameters (temperatures, densities, visual extinction)

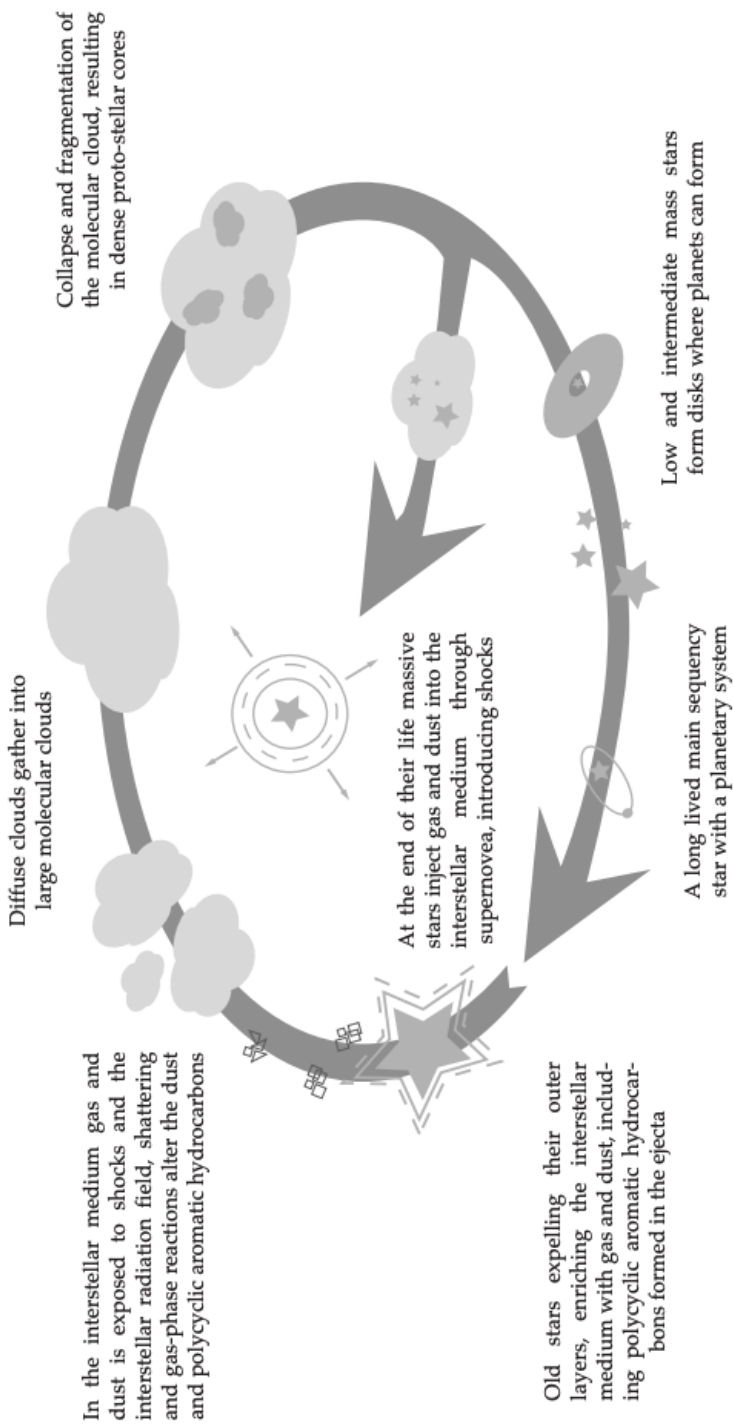


Figure 1.1: Cartoon of the Galactic life cycle, as shown in J. Bouman thesis dissertation (1979). After Steven Simpson (Verschuur 1992, Sky Telescope Magazine) by Christiaan Boersma.

and radiation parameters (CR ionization rate, UV rate) characteristic for an astronomical object. Before starting to simulate the chemical evolution, we need to establish the interstellar synthesis happening in a designated environment and consider which kinetics methods should be favored.

1.2.1 Interstellar synthesis

Historically, molecules and chemical reactions have been listed and documented, from the pioneering work of L. Gmelin (1816-1819) in inorganic chemistry or the list of K. Weltzien, published in 1860, comprising 3000 organic substances, to the Beilstein database (1886), becoming the largest database in the field of organic chemistry. In 40's-50's of last century scientists started to implement electronic libraries and archives, when the first basic computers became available, but it was not until the Digital Revolution happened (70's-80's) that chemical databases became historically important. Nowadays they are everywhere and are used to enhance our day-to-day life. It took chemists a few decades to digitize all the molecules and chemical reactions already registered in the literature. It took some extra decades for astrochemists to create their own databases, in part because of the exotic conditions involved, such as extreme low densities and temperatures as well as intense radiations fields. These databases are now accessible internationally. Depending on the main field of research in astrochemistry, you can find a panel of databases. For astrochemical modeling, the chemical network chosen initially, based on databases, is crucial for the simulation of astrochemical environments.

Coming back to the focus of this thesis research, the UMIST (University of Manchester Institute of Science and Technology) Database for Astrochemistry (UDfA), launched in 1991, was the world's first public chemical kinetic database for Astrochemistry. Millar et al. (1991) publishing the first version called Rate91, followed by Millar et al. (1997), called Rate95, then Le Teuff et al. (2000) with Rate99, Woodall et al. (2007) with Rate06 and finally a fifth version by McElroy et al. (2013) with Rate12. Each version was updated with new species as well as new chemical reactions. In parallel, Prasad & Huntress (1980) elaborated a chemical network specific for interstellar clouds, available in the OSU (Ohio State University) database. From 2012, another research group (Wakelam et al. (2012)) created KInetic Database for Astrochemistry (KIDA). This database also consists of chemical reactions with rate coefficients and uncertainties. Besides providing kinetic information for the interstellar medium, KIDA contains data for planetary atmospheres and for circumstellar envelopes. A subset of the reactions in the database has been provided as a network for the simulation of the chemistry of dense interstellar clouds with temperatures between 10 K and 300 K. Two main points need to be touched on before continuing to the next section.

First, all astrochemical kinetic databases listed above describe gas-phase reactions. Besides for KIDA, including progressively surface reactions. As pointed out by Woodall & Gray (2007), the role of surface chemistry in the synthesis of interstellar

molecules was a matter of much debate, but is largely accepted nowadays, also given the astronomical identification of a number of ices and the elaborate laboratory work over the last decades illustrating the chemical potential of solid state astrochemical reactions. Most arguments to support the influence of grain reactions start from the failure of gas-phase chemistry to reproduce abundances of particular molecules or classes of molecules detected in various interstellar environments. In this regard, it is important to have a system of gas-phase reactions as complete as possible to describe molecular synthesis combined with the appropriate ice-interactions. Tielens (2005) describes astrochemistry as a cosmic dance of the elements in which atoms are constantly reshuffled from one species to another. The variety of steps involved can be separated in three classes: the gas phase processes, the interaction between the gas and the grain surface and processes occurring in the bulk ice mantle. As introduced in the previous section, the elemental gas phase processes are listed in Table 1.2. Experiments have shown that on the surfaces, a single atom, after accretion, can react following three main mechanisms : Langmuir-Hinshelwood (LH), Eley-Rideal (ER), and “hot atom” (HA) (Wakelam et al. (2017b)). In the Langmuir-Hinshelwood mechanism, atoms from the gas phase first become accommodated on the surface and then, via diffusion, they encounter each other and react. The resulting molecule might or might not leave the surface, depending on how the energy gained in the reaction is partitioned. In the Eley-Rideal reaction, an incoming atom interacts directly with a partner on the surface; the incident atom is not accommodated on the surface. The resulting molecule is likely to leave the surface retaining much of the energy gained in the reaction. The “hot atom” mechanism is similar to the Eley-Rideal one, but here the atom first lands on the surface, without becoming fully accommodated, and proceeds to sample the surface at supra-thermal energy until it finds and reacts with a partner species. The schematic formation of molecules on grain surfaces is shown in Figure 1.2. Thanks to experimental (Linnartz et al. (2015); Öberg (2016); Qasim (2020)) and observational studies (Boogert et al. (2015); Chu et al. (2020); Aikawa et al. (2020)) correlated with the theoretical ones (Tielens & Hagen (1982); D’Hendecourt et al. (1985); Brown & Charnley (1990); Charnley (1998, 2001); van Dishoeck & Blake (1998); Garrod et al. (2008); Cuppen et al. (2013); Vasyunin & Herbst (2013); Ruaud et al. (2016); Simons et al. (2020)) we now have a better understanding of the importance of the contributions and interactions between these three classes¹.

Second, we cannot mention astrochemical kinetic databases without acknowledging the National Institute of Standards and Technology (NIST) being a basic reference for further study in chemistry in general. This site provides thermochemical, thermo-physical, and ion energetics data compiled. It has been created in 1996 and continues to implement new features for observational, experimental, and theoretical research. An astrochemical kinetic database has also been implemented. As a side note, PubChem is a younger database (2004) specialized on molecules and their activities that can be useful for astrochemist experimentalist.

¹A more extended list of articles is shown as the theoretical review is lacking.

In this thesis, Chapters 2, 3 and 4 will use gas-phase chemical networks, based on Rate12, with implementation of few grain-surface processes interactions. These chapters will be focusing on chemical bistability from an astrochemical modeling perspective (see section 1.2.3). The final chapter, Chapter 5, combines to a greater extent gas-phase chemistry with surface chemistry and computes the composition of ice mantles on dust. This chapter extends an existing chemical network to focus on the ISM formation of small COMs, including methanol.

Table 1.2: Generic gas phase reactions as listed in Tielens (2005).

	Reaction
Photodissociation	$AB + h\nu \longrightarrow A + B$
Neutral-Neutral	$A + B \longrightarrow C + D$
Ion-molecule	$A^+ + B \longrightarrow C^+ + D$
Charge-transfer	$A^+ + B \longrightarrow A + B^+$
Radiative dissociation	$A + B \longrightarrow AB + h\nu$
Dissociative recombination	$A^+ + e^- \longrightarrow C + D$
Collisional association	$A + B + M \longrightarrow AB + M$
Associative detachment	$A^- + B \longrightarrow AB + e^-$

1.2.2 Methods

When choosing a specific astronomical environment, the chemistry needs to be tailored, taking into account the considerations mentioned before. Once the chemical network is fixed, multiple methods exist to analyze the chemical evolution. Different methods can be applied but not all are equally suited. This time, we can talk about a computational dance, trying to find which equations will be relevant, with a lower approximation error, and a shorter-term simulation time. Figure 1.3 shows an overview of the different methods.

Due to its fast simulation time, the rate equations method is the most used one in astrochemistry, it is well established in the study of gas phase processes but more controversial in the study of surface chemistry. The rate equations method is a time dependent method that allows to study the evolution of interstellar chemical abundances by solving a set of nonlinear differential equations (ODEs):

$$\dot{y}_i = G_i = n_H \left[\sum_j \sum_m k_{jm} y_j y_m - y_i \sum_s k_{is} y_s \right] + \sum_u \beta_u y_u - y_i \sum_w \beta_w; \quad i = 1, \dots, N \quad (1.1)$$

where n_H is the density of hydrogen nuclei ($n_H (= n(\text{H}) + 2n(\text{H}_2))$); fractional abundance of species i , $y_i(t)$, is equal to n_i/n_H , for number density n_i ; and k_{jm} , β_u , β_w are reaction rate coefficients for various bimolecular and unimolecular processes. If the ice

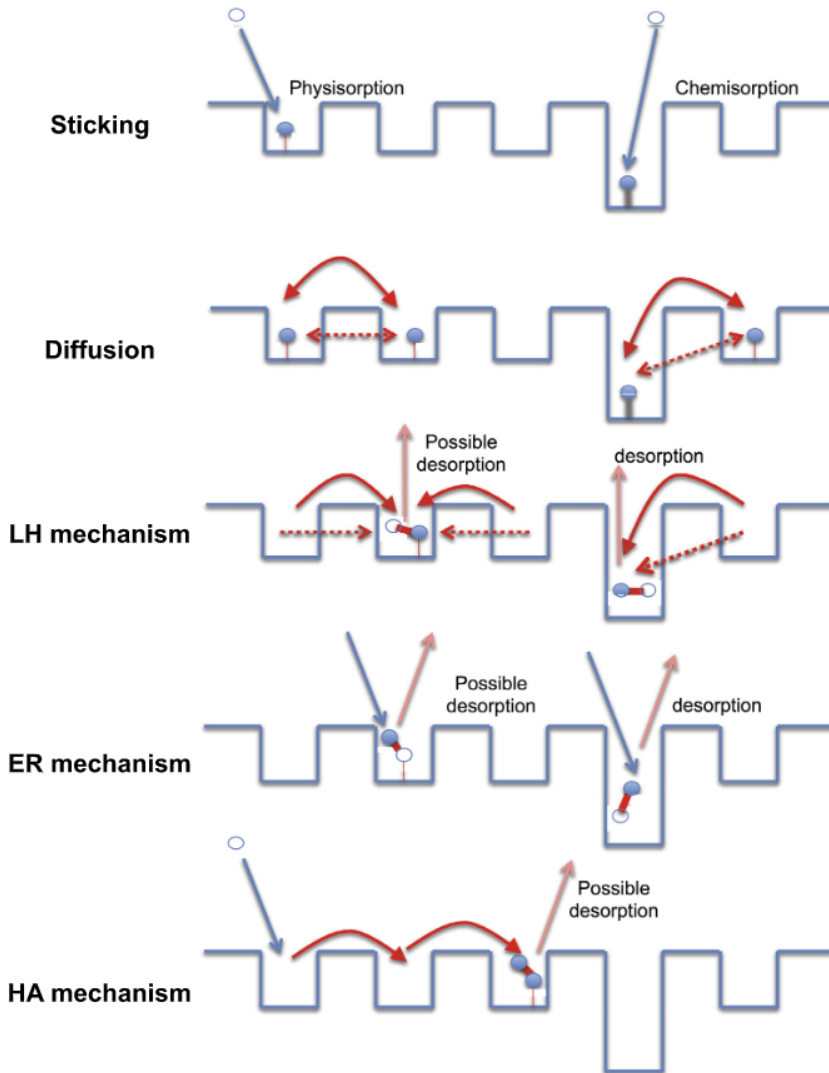


Figure 1.2: Schematic illustrated in Wakelam et al. (2017b) showing the key surface processes involved in the formation of H_2 . These basic processes are also at play in the surface formation of other and larger species in the ISM. Dotted red arrow : Tunneling. Full line arrow : Thermal Hopping.

chemistry is included in the model, then another approach is taken on the rate equation (Hasegawa et al. (1992); Wakelam et al. (2013)). For each neutral species i , the coupled evolution of gas and grain-surface abundances is described by the differential equations

$$\dot{y}_i = G_i - \lambda_i y_i + \xi_i g_i \quad (1.2)$$

$$\dot{g}_i = \lambda_i y_i - \xi_i g_i \quad (1.3)$$

where g_i is the fractional abundance of species i currently resident on dust. Sticking collisions of gaseous species with dust occur at the accretion rate, λ_i , and surface species leave the dust grain at the desorption rate, ξ_i (e.g. Brown & Charnley 1990).

Another method, providing precise results and well known in ice chemistry research, is the Kinetic Monte Carlo method (KMC). It consists in studying the evolution of interstellar chemical abundances by solving the master equation:

$$\frac{\partial}{\partial t} P(\mathbf{x}; t) = \sum_{\mu}^{M_d} [W_{\mu}(\mathbf{x} - \mathbf{s}_{\mu}) P(\mathbf{x} - \mathbf{s}_{\mu}; t) - W_{\mu}(\mathbf{x}) P(\mathbf{x}; t)] \quad (1.4)$$

Gaseous atoms and molecules collide and stick to the surface giving rise to an instantaneous population of species on the dust surface, described by population vector $\mathbf{x} = X_i$ for $i = 1, 2, \dots, N_d$. $P(\mathbf{x}; t)$ is the probability that the surface is in state X_i at time t . $W_{\mu}(\mathbf{x})$ is the probability per unit time of process μ occurring in the infinitesimal time interval $[t, t + dt]$, given that it is in state \mathbf{x} at time t . The stoichiometry of reaction μ is accounted for by the vector \mathbf{s}_{μ} . The different ways to solve this equation led to the sub-method listed in Figure 1.3. Cuppen et al. (2013) explain in detail all listed sub-methods.

Concerning the physical movements of atoms and molecules (molecular dynamics) or the behavior of interstellar dust, different computer simulation methods are used. The further discussion on physical processes needed for both methods will not be mentioned here. However, an analytical technique not listed in Figure 1.3, less common in astrochemical models of molecular clouds, needs to be addressed here due to its application to the bistability analysis. The Newton-Raphson method is an algorithm that can be employed directly to find the steady-state solutions of the system of ODEs. It finds solutions of a system of non-linear equations by producing successively better approximations to the roots (or zeroes) of a real-valued function. For N chemical species, these are the solutions of the system

$$\mathbf{G}_i(\mathbf{y}; \epsilon) = 0 \quad i = 1; \dots; N, \quad (1.5)$$

where \mathbf{y} is a vector of chemical fractional abundances or concentrations, \mathbf{F} is a non-linear function expressing the production and loss rates of each species i and ϵ is the list of control parameters needed in interstellar chemistry (Charnley & Markwick (2003); Dufour & Charnley (2019)). This method is necessary for the calculation of the unstable branch found in the bistability phenomenon.

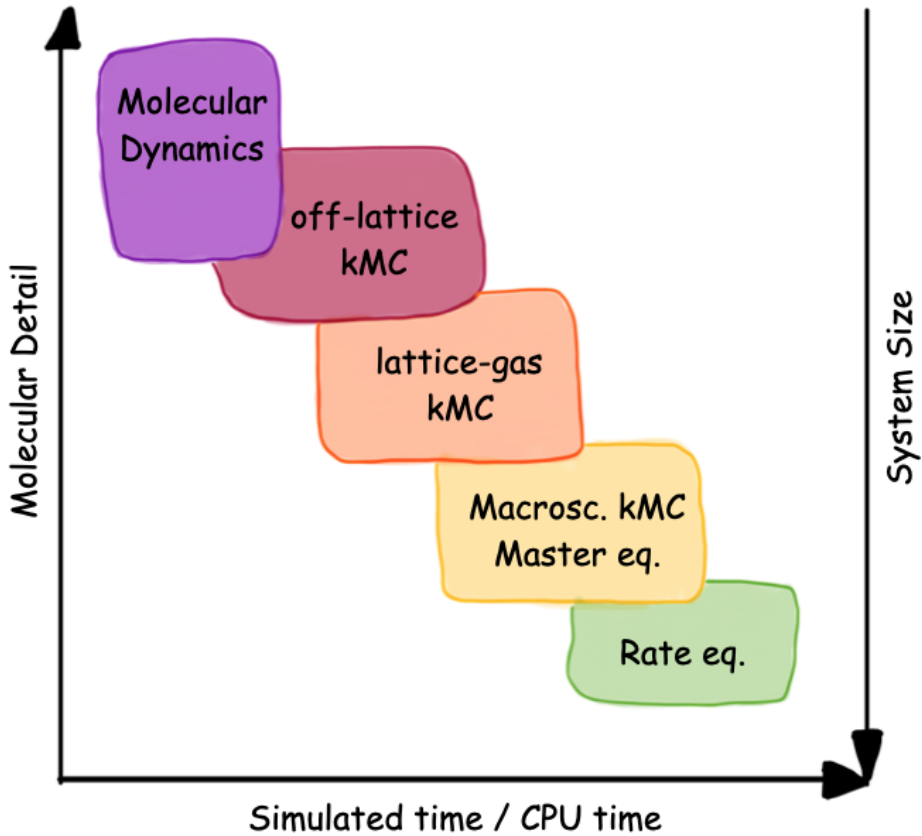


Figure 1.3: Overview of the different simulation method, as mentioned in Cuppen et al. (2013).

As a remark, Wakelam et al. (2006a) describe the effect of uncertainties in the chemical model of dark clouds. It is an important point to not forget in the interpretation of results and in the comparison with observations or experiments. Each field includes a certain set of approximations and uncertainties that could lead to contradictions, debate but positively also motivate to construct more accurate tools.

For the work on chemical bistability in Chapters 2, 3 and 4, the rate equations combined with the Newton-Raphson has been used. For Chapter 5, focusing on the surface chemistry analysis, a kMC method is chosen.

1.2.3 Non-linear dynamical phenomena

Chaotic behavior has been widely recognized as a fundamental aspect of many nonlinear dynamical systems. Then, it is not surprising to find some of the standard feature's

characteristics of these systems. Multiple fixed points for a given set of control parameters have been demonstrated. Pineau des Forets et al. (1992) were the first group to describe the "two-chemical phases". Le Bourlot et al. (1993), called the phenomenon bistability. Bistability is special as it indicates that a chemical evolution can develop in completely different directions. In order to understand chemical compositions in space, it is important to characterize these processes theoretically. Both groups show steady state models of dark interstellar clouds following two different types of chemistry, leading to very different predictions of atomic and molecular abundances. Figure 1.4 shows how the bistability phenomenon can be understood, and we can point out the coexistence of two stable states connected by an unstable branch. The occurrence and relevance of this phenomenon is extensively described in Chapters 2 and 3.

To further focus on the concept of astrochemical bistability, it is useful to look to the ongoing debates discussed since the earliest discovery from Pineau des Forets et al. (1992). First, observed abundances from molecular clouds, as well as nearby supernova remnants, have shown discrepancy with the results obtained with astrochemical models (Le Bourlot et al. (1993); Ceccarelli (2011)). Following this issue, bistability is of interest due to the drastic change of abundance observed within a close range of density, leading for example to an explanation of high CI/CO ratios and low O₂ abundances in molecular clouds (Viti et al. (2001)). Second, to substantiate the bistability phenomena, various modeling uncertainties were needed to be addressed. The earliest models discovering bistability included only gas phase chemistry, focusing on molecular clouds. While an ionization instability connected to the respective rates of radiative and dissociative electron recombination of H⁺ and H₃⁺ was suggested to be responsible of the creation of this unstable environment (Pineau des Forets et al. (1992); Le Bourlot et al. (1993)) others suggested that the effect of gas-grain interaction suppresses the bistability (Boger & Sternberg (2006)). Chapters 2 and 3 touch on each of the arguments concluded in previous studies.

Two nonlinear phenomena rarely discussed among astrochemical modelers are limit cycle oscillations and chemical chaos. This is rather surprising, as such behavior is another normal feature of nonlinear sets of chemical equations (see Gray & Scott (1990)). Even more recently, Roueff & Le Bourlot (2020) have shown various oscillatory behaviors in an isochoric model where the thermal balance is solved concomitantly with the chemistry. They did not identify the triggering mechanism of the oscillations but the detailed analysis of the differential behavior of the various species points to the role of long chains of deuterium fractionation reactions. Chapter 4 shows the limit cycle and chemical chaos oscillations.

1.3 This thesis

The elaboration of more models with the knowledge of different methods participates actively in the methodical interpretation of already detected interstellar chemistry as well as for future predictions using new instruments like James Webb Space Telescope

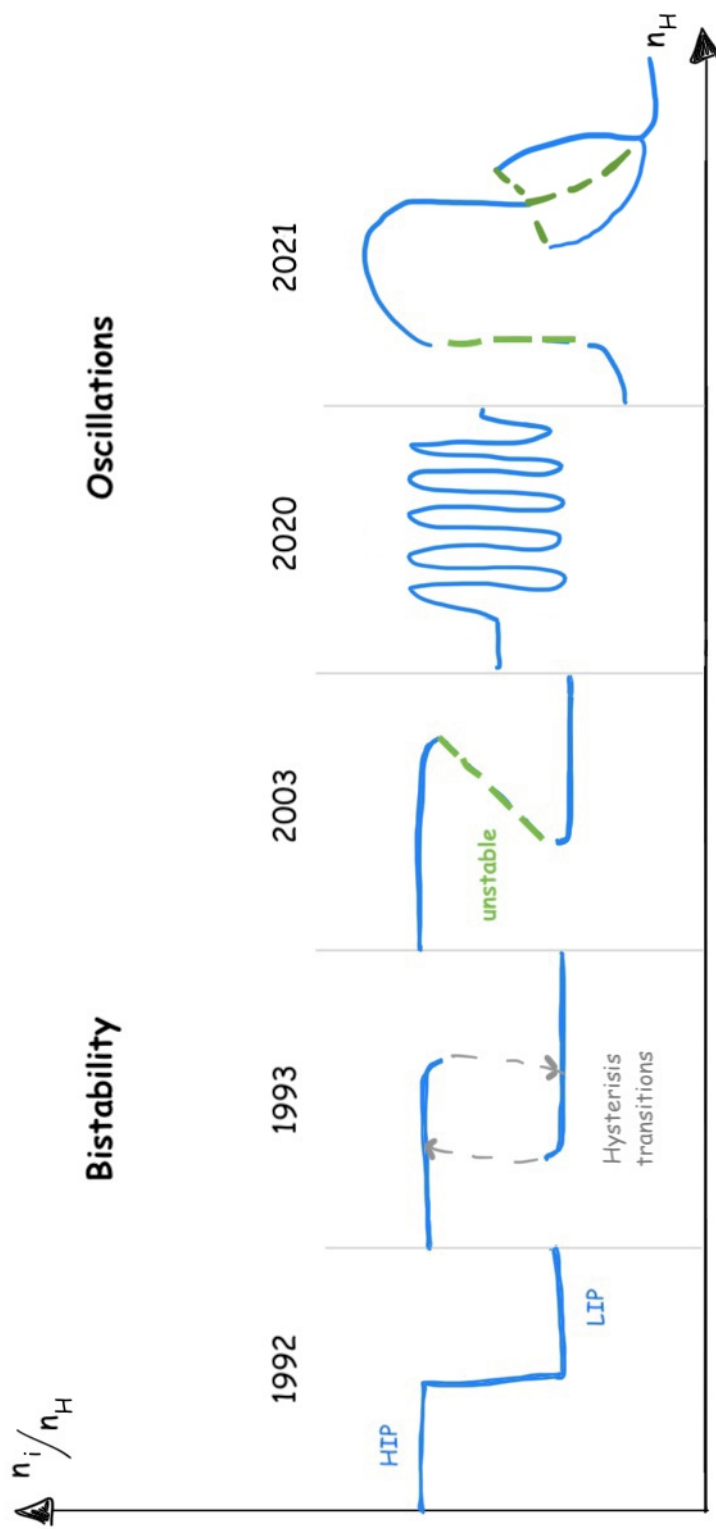


Figure 1.4: Schematic cartoon of the fractional abundance of a species i as a function of density. The different solutions obtained by non-linear dynamical system discovered overtime are shown.

(JWST). The motivation of this thesis is first and for all to acknowledge the presence of chaotic behavior in astrochemical models. Then to pursue the analysis of different theoretical cases for a better understanding of the underlying processes causing unstable solutions. Even in the study of ice-chemistry using a stochastic method, it is relevant for future work in non-linear systems.

Chapter 2 demonstrates that interstellar chemistry is bistable due to the interaction of several autocatalytic processes involving molecular oxygen (O_2). By deconstructing a known bistable solution into ever simpler reduced models through omission of chemical elements, and then artificially removing selected reactions, four distinct modes of autocatalysis are identified. These processes are driven respectively by reactions of H^+ , He^+ , C^+ , and S^+ with O_2 . The theoretical results show that these processes can produce the bistable solutions found in previous studies, as well as the dependence on various model parameters such as the helium ionization rate, the sulfur depletion and the H_3^+ electron recombination rate. The bistable solutions present in dense cloud chemistry are due to autocatalysis and not an ionization instability.

Chapter 3 follows the work of Chapter 2, finding new bistable solutions in reduced chemical sets comparable to simplistic gas-phase chemical models of dense molecular clouds. Several autocatalytic cycles in the ion–molecule chemistry of the major volatile elements: O, N, and C, have been found. The applicability of these results to astronomical environments is briefly discussed. The bistable solutions found for carbon chemistry occur for low densities and high ionization fractions that are not compatible with those found in cold, dense clouds. Bistability in the pure nitrogen chemistry occurs for conditions that are relevant for prestellar cores in which significant CO depletion has taken place.

Chapter 4 is complementary to Chapters 2 and 3, we have studied gas-grain chemical models of interstellar clouds in the context of nonlinear dynamical systems. A prescription is given for producing oscillatory solutions when a bistable solution exists in the gas-phase chemistry and we demonstrate, for the first time, the existence of chaotic solutions in astrochemistry. As the autocatalytic chemical processes underlying these solutions are common to all models of interstellar chemistry, the occurrence of these solutions should be widespread. We briefly discuss the implications for interpreting molecular cloud composition with time-dependent models and some future directions for this approach.

Chapter 5 focuses on recent theoretical and experimental information on solid state astrochemical reaction networks. This new data is gathered in an extended astrochemical model, based on Charnley (1998, 2001), with a specific focus on the carbon chemistry of smaller species. The results are primarily compared to recent astronomical observations of dense cloud environments. Then a sensitivity analysis of an

extended grain surface reaction network is performed. Based on the conclusions and remarks of the analysis, an optimized model is provided. A kinetic Monte Carlo model is used, based on stationary stochastic simulation techniques including both gas and grain chemical evolution. Two main findings are also discussed. First, the reaction $\text{H}+\text{HCO}$, which forms CO and H_2CO , is found to strongly impact the amount of CO available in the system, which subsequently regulates the amount of CH_3OH . Second, the reaction CH_3+OH is confirmed as the main formation pathway of methanol before CO freezes-out in the optimized model.

This thesis shows discoveries in nonlinear astrochemical kinetics as well as a deeper analysis of dark clouds chemistry. The results and discussion of the five chapters allow further understanding of the chemical evolution in a gas phase system and in a gas-grain environment, giving better prediction with observations. The use of high analytical methods such as Newton-Raphson and kMC are a challenge but beneficial for more accurate results, encouraging to apply the research not only to molecular clouds but to other environments.

