Non-linear astrochemical kinetics: theory and applications

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Summary

Dense molecular clouds are an ideal environment for astrochemical modeling, because of the typically low temperature and the long time period of "rest". The chemistry is estimated to evolve toward a stationary state after some 10^7 years. This chemical stability allows more complex theoretical analyses to be done as well as the accuracy of recurrent models to be tested, comparing results with those derived from astronomical observations. To date, about 240 molecules have been identified in interstellar space, from the smallest carbon-bearing molecule CH^+ (methylidynium) to remarkable species such as CH_3COCH_2OH (hydroxyacetone), a so called COM (Complex Organic Molecule), and even fullerenes, such as C_{60}, C_{60}^+ and C_{70}. Experiments and astrochemical models aim at a better understanding of the formation pathways of these and other, still unobserved molecules. Over the last decades thousands of reactions have been investigated, both in the gas phase and in the solid state, and the relevant parameters are now available in online databases such as UMIST (University of Manchester Institute of Science and Technology), KIDA (KInetic Database for Astrochemistry) or PubChem. The extended lists of formation and destruction pathways are used as initial input for astrochemical modeling. Depending on the exact environment under study, the chemistry selected will differ in accord with the physical parameters such as the temperature, the density, the visual extinction and how much the environment is ionized by energetic radiation, such as (vacuum) ultraviolet (VUV) photons or cosmic rays (CR). Subsequently, to simulate the chemical evolution in interstellar space over time, we need to select which theoretical method is best suited to calculate the absolute abundances of species. The most common method is a set of ordinary differential equations (ODEs) for each species of the system, derived as a function of time. ODEs are a well known tool to study gas-phase chemistry but are not that common to study "mixed-chemistry", including processes on icy dust grains. Another prominent method, efficiently describing the gas-grain interaction, is the kinetic Monte Carlo method (kMC). It studies the evolution of interstellar chemical abundances by solving the "master equation". This equation describes the gaseous atoms and molecules colliding and sticking to the surface giving rise to an instantaneous population of species on the dust surface. The goal of this thesis is to use theoretical methods to further improve our knowledge of the chemical processes taking place in space. The focus is on two different topics, chemical bistability and the formation of methanol, the smallest COM by definition. The first topic is described in chapters 2, 3 and 4 in which ODEs are used to simulate interstellar cloud evolution. The second

topic is described in chapter 5 and uses the kMC method.

Bistability

This thesis deals with studying non-linear processes in dense interstellar clouds. The first chapters focus and extend on chemical bistability. Here bistability means that a slight variation of relevant physical parameters (e.g. temperature or density) results in complete different chemical distributions, despite starting from (nearly) the same initial chemical conditions. Similar this complex dynamical behavior is a common phenomenon found in different fields of research, for example in optical studies, dealing with laser beam counter-propagation, as well as in bio-chemical work where it is repeatedly visible in the cell cycle mechanism. Concerning astrochemistry, Pineau des Forêts et al. were the first to point out this chemical bistability in 1992. We define bistability as the coexistence of two stable states connected by an unstable branch (see Figure 1). The stable states occur in a molecular hydrogen gas and comprise a high ionization phase (the so-called HIP) in which the saturated species are under-abundant and protonation reactions are less efficient, as well as a low ionization phase in which saturated molecular ions are more abundant (the LIP). In order to calculate the unstable branch, it is needed that astrochemical models are treated in detail and in this Thesis this is realized by implementing the so called Newton-Raphson (NR) method. This 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. The undesired alternative of using only ODEs without coupling with NR-method, is that only a "gap" in the abundance profiles will be detected (see Figure 1).

Chapter 2 demonstrates that interstellar chemistry is bistable due to the interaction of several autocatalytic processes involving molecular oxygen. Four distinct modes of autocatalysis that can occur in dense molecular clouds are identified to be responsible to create instabilities in the system. (1) O^+ pathway initiated by $He^+ + O_2$; (2) O atom initiated by $H^+ + O_2 \longrightarrow O_2^+ + H$ and $O_2^+ + e^- \longrightarrow O + O$; $C^+ + O_2$ forming (3) O^+ and (4) O. The bistable solutions discovered in dark clouds are controlled by ζ/n_H (ζ being the CR-ionization rate; n_H being the density), the relative elemental depletions, and the value of the H_3^+ electron recombination rate. Coupling ionized grains, estimated to have a negative charge, to the system has been suggested as a solution to remove the instability in the gas-phase chemistry but our study proved that the bistable solutions present in dense cloud chemistry are due to autocatalysis and not an ionization instability.

Gas-phase bistability is possible when an autocatalyst can form a dimer that is subsequently destroyed in an autocatalytic step followed by reformation of the dimer. We can see this autocatalytic behavior also in the nitrogen and carbon chemistry, similar to what previously has been found in the oxygen chemistry. In Chapter 3 it is

shown that both, N and C chemistry, have bistable solutions. In the nitrogen chemistry two possible autocatalytic processes have been found. An autocatalytic cycle driven by the reaction of He^+ with N_2 produces bistability. (1) N atom initiated by He^+ + N_2 forming the ion N_2^+, followed by N_2^+ electronic recombination; (2) N^+ and N also formed by He^+ + N_2. The simplified model, including only the nitrogen chemistry, has bistable solutions at high densities ($n_H > 10^5 cm^{-3}$) which are present at all values of the elemental N abundance considered. In the carbon chemistry three possible autocatalytic processes have been identified. We find that two autocatalyses occur in the acetylene chemistry with CH, rather than atomic C, being the autocatalyst. These involve $C_2H_2^+$ and C_2H_2 in processes similar to those found in the oxygen autocatalysis. (1) CH obtained by the hydrogenation process $C_2^+ \longrightarrow C_2H^+ \longrightarrow C_2H_2^+$, followed by $C_2H_2^+$ electronic recombination; (2) CH^+ and CH initiated by He^+ reacting with C_2H_2. As there are no bistable solutions for the appropriate densities ($n_H > 2 \times 10^3 cm^{-3}$) and elemental carbon depletions, these bistable solutions are unlikely to be relevant for realistic models of dense clouds. The work presented in this thesis accounts for the simplest bistable solutions that can occur for O, C and N chemistries in cold, dark molecular gas irradiated by cosmic rays; it is very well possible that more bistable solutions can be discovered through the coupling of these autocatalytic processes. Figure 2.a. shows how bistability is seen in abundance profiles of different species present in a dense cloud model.

Oscillations

Now following the study of a dark cloud environment, Chapter 4 shows that introducing accretion and desorption of atomic and molecular oxygen on grain surfaces into a model of interstellar chemistry, with known autocatalytic pathways and bistable solutions, leads to chemical oscillations. Chemical oscillation is seen easily in different crystalline gel or lyotropic liquid experiments found to be driven by specific reactions. The results have shown the substance to change the composition or color. The clear change in the chemistry is expected to be found as well in different astrochemical environments. No observable evidences have been seen yet, but as discussed in Chapter 4, it is highly probable that sustained oscillations are present in dense cloud chemistry. We explained that it is intrinsic of the chemical behavior. Even when using a simple reduced model, containing only hydrogen, helium and oxygen, as previously studied in Chapter 2 and 3, oscillations are found. The difference of adding the grain defines the total of oxygen initially present in the system to be set by the accretion and desorption of oxygen atoms. In chapter 4 kMC is applied as ODEs are not sufficient for this purpose. Then we can see the system transitions from stationary to bistable at lower density (as seen in the previous chapters), then to stationary to periodic solutions for higher density, called Hopf bifurcations (see Figure 1). For a dense cloud model, we find that slightly higher grain temperatures (few Kelvin) are required for oscillations to appear than in the pure oxygen chemistry because the presence of other

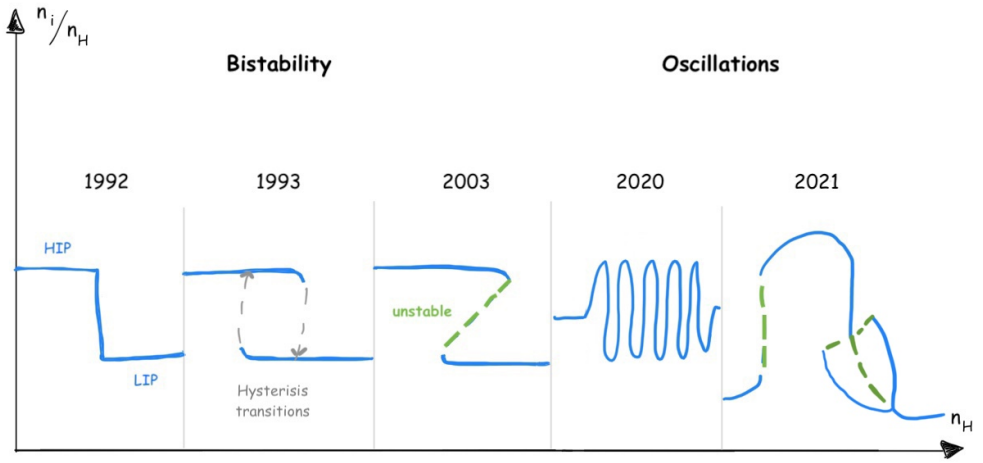

Figure 1: Schematic cartoon of the fractional abundance of a specie *i* as a function of density. The different solutions obtained by non-linear dynamical system discovered overtime are shown.

elements (C,N,S) can shift the range of bistability to even higher density (as seen in Chapter 2). Dense environments as molecular clouds, with the drop of temperatures causing the gas phase species to accrete onto the dust grain, provide conditions that are suited for a rich ice chemistry, leading to both small and large species, including COMs. In the models describing these steps, it is important to take into account that the interaction of gas-grain chemistry can result in bistable or periodic solutions (oscillations) for specific parameters. Figure 2.b. shows how oscillations are seen in the oxygen chemistry abundance profiles in a dense cloud model.

Grain chemistry

New theoretical and experimental information on solid state astrochemical reaction networks and the involved rate constants has become available recently. In Chapter 5, this new data is gathered in an extended astrochemical model, based on Charnley et al. 1998 and 2001, with a specific focus on the carbon chemistry of smaller species as these play a key role in the formation of larger carbon bearing species. A common way to consider the formation and evolution of larger carbon-bearing molecules is through the study of complex organic molecules (COMs) and polycyclic aromatic hydrocarbons (PAHs). In Chapter 5, the focus is on COMs, specifically methanol, the smallest COM by definition and known to be a precursor of larger COMs. An updated astrochemical model is presented here in a dense cloud environment, calculated by stochastic methods. As mentioned above, the difference with the gas-grain model from the previous chapter, is given by the astrochemical methods used

to calculate the evolution of the interstellar cloud. The formation of ice monolayers is included as well. The results are linked to recent astronomical observations of dense cloud environments. The primary goal of this work is to update the surface chemistry network in a dense cloud environment by performing a sensitivity analysis of an extended grain surface reaction network, and to provide an optimized model. The formation/destruction pathways of several molecules important in the interstellar medium, i.e. H_2O, CH_4, CO_2, HCOOH, H_2CO, CH_3OH is extensively studied. We find that HCO plays a major role in CO and CH_3OH chemistry through the reaction, H+HCO. By changing the branching ratio of this reaction, i.e., to favor the formation of CO over H_2CO, we see CO becoming highly abundant overtime and the formation of methanol, through the hydrogenation pathway, being diminished. From the results obtained, we derive an optimized model, allowing the abundance ratios to become in close agreement with recent theoretical and observational results. Finally, we show that in a H_2O-rich ice environment, methanol is formed predominantly by CH_3+OH at early times, and afterwards being mainly formed by the hydrogenation pathway. Given the relevance of understanding how methanol and other COMs may form in the solid state in space, quite some modeling studies have been reported in the literature, recently. The work described in this thesis differs from those approaches using ODEs as the method to study the gas and grain evolution, and adds to the existing literature for those using kMC. Chapter 5 compares the similarities and differences with recent laboratory and theoretical studies and provides an outlook for upcoming observational work.

This Thesis shows discoveries in non-linear astrochemical kinetics as well as a deeper analysis of dark clouds chemistry. It is concluded that autocatalysis in interstellar gas-phase chemistry leads to bistability but when coupled with the gas-grain exchange of key species, the system can show Hopf bifurcation and lead to the appearance of complex chemical oscillations. 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, providing better predictions to steer future 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 also to other environments, such as diffuse interstellar medium or even asymptotic giant branch (AGB) star regions.

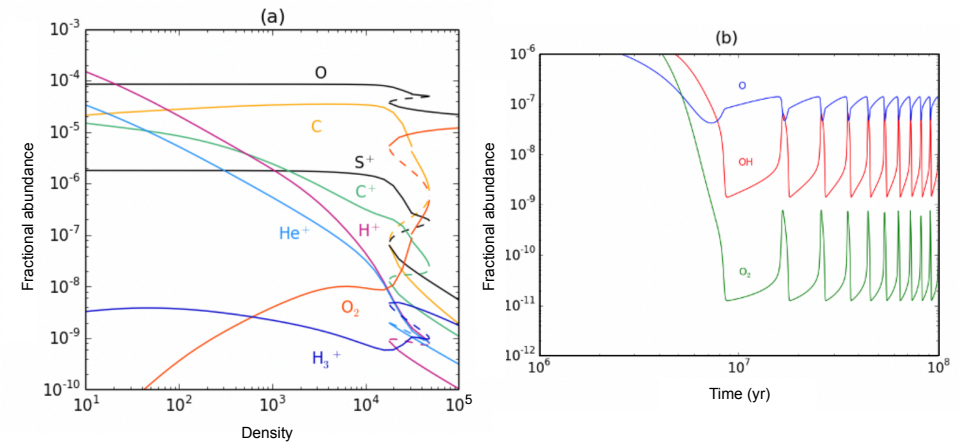

Figure 2: (a) Fractional abundances of the abundant species in a dense cloud environment as a function of the cloud density. Bistability is shown, using ODEs and NR-methods. The complete description is given in Chapter 2 (Figure 2.2.a); (b)Fractional abundances of the abundant species in a dense cloud environment as a function of time. Oscillations are shown, using ODEs method. The complete description is given in Chapter 4 (Figure 4.1.b).