

ASTROCHEMISTRY OF STAR FORMATION

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ABSTRACT. Star formation is one of the key processes governing the evolution of the Universe. It is accompanied by significant transformations in the chemical composition and the physical state of the interstellar medium. Combining observations in infrared and radio bands, we obtain a wealth of observational data on the star formation both in continuum and spectral lines. These lines mostly belong to molecules, from simple diatomic species to complex organic compounds. However, interstellar molecules are not well-mixed with the bulk interstellar gas (molecular and atomic hydrogen) and possess a complex evolution of their own. Thus, a straightforward interpretation of observational data is seldom possible. One needs sophisticated chemical and physical models to decipher processes occurring in star-forming regions.

Key words: star formation, ISM, astrochemistry, numerical modeling, databases for astrochemistry

1. Introduction

For more than a century astronomers know that the space between stars is not empty. Since first guesses on calcium clouds [1] our knowledge on the interstellar medium (ISM) has expanded significantly. Thanks to powerful new observatories, both ground-based and space-based, and a great amount of spectroscopic data, we have got new insights on the chemical composition of the interstellar matter. One of the key discoveries of the second half of XX century was a detection of numerous molecular species, extending from simple diatomic molecules, like CO or OH, to complex organic compounds, with tentative detection of a simplest amino acid, glycine, in the ISM.

The molecular composition of the interstellar medium (ISM) has become a subject for the new branch of astronomy which is called astrochemistry. The field of astrochemistry goes well beyond the ISM and molecular clouds. Molecules are observed in comets, planets, their satellites, planetary nebulae, and even in stars. However, we can assume with certainty that it is the star formation theory that benefits most from the development of astrochemical models. The

lifecycle of species observed in star-forming regions is of great interest, as molecules are not just passive witnesses of the star formation. Often, they play a significant role in the formation of stars and planetary systems and eventually in the origin of life itself, by affecting the thermal balance in the ISM, defining its interaction with magnetic fields, and providing raw materials for organic synthesis in young planetary systems.

The Universe started as an almost pure mixture of hydrogen (70%) and helium (30%), with small amount of lithium and beryllium. All the other elements were synthesized later in stars and then ejected in the ISM. It was long believed that beyond planets these elements may only exist as atoms or ions as molecules cannot form in harsh interstellar conditions. However, since late 1930's it has become apparent that at least simple species like CH, CN, CH⁺ are abundant in the general ISM (by the way, the problem of their formation and survival is still far from being solved). Development of radioastronomy after the Second World War opened a new chapter in studies of the ISM. Vast cold clouds of interstellar gas have been discovered that are dense and opaque to UV photons. So, they present much more favorable conditions for formation and survival of molecules.

Molecular clouds are dense ($> 10^2 \text{ cm}^{-3}$) and cold ($\sim 10\text{K}$) components of the ISM that are known to be sites of the ongoing star formation. The chemical composition of nearby molecular clouds is typical for the general interstellar medium in the Solar vicinity. The most abundant elements are hydrogen and helium. All the other elements are significantly less abundant, with oxygen abundance being less than 10^{-3} (by number relative to H atoms). Also, many elements (like sulfur, magnesium, iron, silicon, and others) are depleted into dust grains so that their gas-phase abundances have values of the order of $10^{-9} - 10^{-8}$. The distinctive feature of molecular clouds is that hydrogen is almost totally in molecular form.

First interstellar molecules have been detected in absorption, producing very thin lines in spectra of background stars. But the real start of astrochemistry and star formation studies is also related to the advent of radioastronomy. As molecules possess additional de-

degrees of freedom related to their internal motions, they are able to emit and absorb photons not only in electronic transitions, but also in vibrational transitions, rotational transitions, etc. Low-energy rotational transitions are most important in cold molecular clouds, having their wavelengths in millimeter and centimeter ranges.

Radioastronomical studies of the ISM have started with the seminal paper by Ewen & Purcell [2], describing the detection of the 21 cm atomic hydrogen line. The first interstellar molecule, hydroxyl, has been found in 1963 [3], ammonia, water, and formaldehyde followed in late sixties. Since then, a few molecules are discovered each year. One of the most important of them, CO, has been detected by Wilson et al. [4]. This molecule is very abundant and easy to observe. It is now believed to be a proxy for molecular gas in general, as molecular hydrogen has no transitions that would be observable in molecular clouds.

It must be kept in mind that molecular clouds are not uniform, and no single molecule may serve as a true tracer of the bulk molecular gas. The star formation process starts with a formation of dense clumps ($n \sim 10^4 \text{ cm}^{-3}$) in molecular clouds. These clumps are most often traced by CO and NH_3 lines. Later, some isolated cores ($n \sim 10^6 \text{ cm}^{-3}$) form inside the clumps. These are observed in lines of HCN, CS, HCO^+ and some other. The birth of a star is accompanied by powerful outflows that can be seen in emission lines of CO, water, SO, SO_2 . Finally, a planetary system forms around a star, and it definitely borrows some molecules from a parent molecular cloud.

Molecular lines are a valuable source of information on various stages of the star formation process. Of course, some data can also be extracted from dust observations, but the utility of these data is limited. Basically, one can infer grain surface density, the radiation field (heating the grains), and grain temperature.

Molecular lines are much more diverse. Their analysis allows estimating both surface and volume gas density, velocity field, gas temperature, magnetic field (using the Zeeman effect). Only with molecular lines one can detect that a given molecular core is indeed collapsing, that is, is truly going to become a star in the future.

There is a complication, though. None of more than 150 molecules found up to date is well mixed with molecular hydrogen, that is, with gas in general. Also, molecular abundances are extremely low, typically being much less than 10^{-5} relative to molecular hydrogen. In fact, we try to infer conditions in molecular clouds using tiny admixtures that are non-evenly distributed in the parent cloud. Obviously, one cannot interpret observations of molecular lines without knowing chemical reactions that operate in a studied object.

2. Chemical reactions

To build an astrochemical model one specifies the list of compounds and reactions between them, along with the physical parameters in the medium and element abundances. In the overwhelming majority of astronomical situations only two-body processes should be taken into account. Reactions are divided into gas-phase reactions and surface reactions, occurring on dust grains. Accretion and desorption are responsible for the exchange of species between gas and dust. The contribution of each reaction type depends on the conditions in the cloud. In general, gas-phase reactions mostly produce simple molecules, while complex compounds are synthesized on grains and then returned to gas-phase by some desorption mechanism. Exceptions are possible. Some simple molecules, like CO_2 , NH_3 , water, are effectively produced on dust surfaces, while gas-phase formation routes have been proposed for a number of organic species.

2.1. Gas-phase reactions

Gas-phase reactions are usually divided into reactions of chemical bond formation, reactions of chemical bond destruction, and reactions of chemical bond rearrangement. Depending on reactants, reactions are classified as neutral-neutral, ion-molecular, recombination reactions (with electrons), photoreactions (with photons), and reactions with cosmic rays.

Rates of most neutral-neutral reactions depend on the temperature and may have potential barriers. Thus, their rates at low temperatures of molecular clouds are mostly very low. Apart from some specific cases, neutral-neutral reactions do not influence the chemical evolution of a molecular cloud significantly. On the other hand, ion-molecular reactions are free from barriers and less temperature dependent. They were recognized almost forty years ago as a main contributor to the chemical evolution of the ISM ([5]; [6]), especially, at early stages. For ion-molecular reactions to start operating, there must be some ions in the medium. The initial ionization is provided by cosmic ray particles.

Quite recently, ion-ion reactions started to be considered in astrochemical networks, as negatively charged ions have been discovered that can interact with positive ions. As soon as negatively charged ions are taken into account, reactions of associative detachment also should be included in the network. Interaction of a molecular ion with an electron results in recombination or dissociative recombination. Photoreactions lead to ionization or dissociation (or both) of a species.

2.2. Surface reactions

Gas-phase reaction networks allow explaining abundances of many molecules, but they fail in the most important case of H₂ formation. Molecular hydrogen cannot form in the gas phase, or, more accurately, gas-phase reactions of H₂ formation are extremely slow. It is widely assumed now that two H atoms unite into a molecule on a surface of a grain.

Other molecules may stick to dust grains or form on grain surfaces as well. Colliding with a grain at low temperature, a molecule freezes to its surface. It may be held by van der Waals forces (physical adsorption) or chemical bonds (chemisorption). If a molecule is chemisorbed, it cannot move over the grain surface. So, the only way for it to interact with another molecule is the direct accretion of this other molecule to the very same site on the grain. Probability of such an event is quite low.

Physical adsorption gives a molecule more freedom. It may move over the grain surface via thermal hopping. Still, at low temperatures only the lightest species can migrate this way. When migrating species encounter other (may be, heavier) species, they may combine to form some new molecule. A heavy molecule remains at the same site for a long time, so it may grow bigger than in the gas phase. Surface chemistry is invoked to explain the formation of complex molecules [7], along with the formation of molecular hydrogen.

Surface species are returned to gas via desorption processes. Desorption can be thermal, with the evaporation rate depending on the grain temperature, or non-thermal, via collision with a cosmic ray particle, UV photon absorption, or due to energy generated by exothermic surface reactions [8].

2.3. Mathematical representation

The mathematical representation of the chemical evolution is given by

$$\frac{dn_i^g}{dt} = \sum_j \sum_l K_{lj}^g n_l^g n_j^g - n_i^g \sum_j K_{ij}^g n_j^g - k_i^{\text{acc}} n_i^g + k_i^{\text{des}} n_i^d \quad (1)$$

for gas phase reactions and

$$\frac{dn_i^d}{dt} = \sum_j \sum_l K_{lj}^d n_l^d n_j^d - n_i^d \sum_j K_{ij}^d n_j^d + k_i^{\text{acc}} n_i^g - k_i^{\text{des}} n_i^d \quad (2)$$

for surface reactions. In that approach dust is considered to be continuous medium, which is not correct, generally speaking. But a more rigorous approach would require rather difficult methodology (e.g. [9]). Factors k^{acc} k^{des} are rates of accretion and desorption, respectively. Coefficients K_{ij}^g and K_{ij}^d are used to com-

pute binary reaction rates. They have different meanings for different reactions, depending on reactants.

According the Arrhenius law, for a two-body reaction

$$K_{ij} = \alpha_{ij} \left(\frac{T}{300}\right)^{\beta_{ij}} \exp(-\gamma_{ij}/T) \quad (3)$$

for reactions where both reactants are chemical species. Parameters α , β and γ should be found either by theoretical computations or by experiments. Next, for photo-reactions

$$k = G_0 \alpha \exp(-\gamma A_V), \quad (4)$$

where α is a rate coefficient for the unshielded UV field, γ accounts for an extinction of the UV field, A_V is the extinction in visual band. The intensity of the radiation field is described by the dimensionless factor G_0 expressed in units of the mean interstellar field in the solar vicinity [10]. Finally,

$$k = \alpha \zeta \quad (5)$$

for direct ionization by cosmic rays. Here ζ is the cosmic ray ionization rate per H₂ molecule, typically assumed to be of the order of 10^{-17} s^{-1} [11].

This formulation allows describing rates for all the reaction types with only three parameters, α , β , and γ . In this approach the set of reactions is a set of ordinary differential equations (ODE) and can be solved by some publicly available solvers, like DVODE or VODE.

3. Databases for astrochemistry

Modeling chemical evolution requires a physical model of an object, an ODE solver to track the changes in component abundances and a database that contains information on relevant chemical reactions together with α , β and γ parameters. Modern databases mostly include only binary reactions. The reactants are molecules, ions, radicals, atoms, electrons, photons, cosmic ray particles and, sometimes, grains (in reactions of dissociative recombination). Also some additional information can be included, like the temperature range for adopted α , β , and γ or information on heat of formation. There are several databases created for special purposes, like databases for deuterium chemistry, a subset of reactions for sulfur chemistry ([12], [13]), a database for shock models [14], a database for photon-dominated regions [15]. But in modeling of the chemical evolution of the ISM, more general purpose databases are common. The two most widely used databases are the UMIST Database for Astrochemistry (UDFA) and KIDA (Kinetic Database for Astrochemistry). Another useful resource is the NIST compilation of reaction parameters that summarizes information from literature.

3.1. UDFA

The UMIST database for astrochemistry started with the work of Millar et al. [16]. The initial reaction set, called the UMIST ratefile included rate coefficients of 2880 gas-phase reactions among 313 species. The next version of the database (UMIST95; [17]) contained rate coefficients for 3864 gas-phase reactions relevant to interstellar and circumstellar chemistry that involved 395 species and 12 elements. Also heats of formation were added. The version of 1999 was updated, and its format was revised. The database contained rate coefficients, temperature ranges, and the temperature dependence of 4113 gas-phase reactions among 396 species. Also there was a new table listing the photoprocess cross sections (ionization, dissociation, fragmentation) for a few species for which these quantities are available. The version of 2006 [18] contains 4572 binary gas-phase reactions among 420 species. Major updates have been made to ion-molecular reactions, neutral-neutral reactions, particularly at low temperature, and dissociative recombination reactions. Also it includes reactions with fluorine.

The most recent update is published in early 2013 [19] as the Rate12 ratefile. It contains purely gas-phase network of reactions between 467 components. The new release includes 22 new negative ions participating in 1280 reactions. Data on dissociative recombination for 18 components are updated. Newer or better data are given for 74 neutral-neutral reactions. The network includes 174 new ion-molecular reactions. A major upgrade is also performed for a set of photoreactions. The latest version can be downloaded from the web-site <http://www.udfa.net/>.

The UMIST database is very popular and was used for modeling different objects, like protoplanetary disks ([20]; [21]; [22]), protostellar disks [23], dense cores ([24]; [25];[26]), comets ([27]; [28]).

3.2. The OSU database

The OSU (Ohio State University) database has a long history that started in the 1980's. It was partially based on the paper by Prasad & Huntress [29] that included the basic chemical model and a library of chemical reaction that contained more than 1400 gas-phase reactions among 137 species. Leung & Herbst [30] updated the reaction network, and since that time E. Herbst's group went on updating the database. The latest version of OSU appeared under that name in 2009. It contains 6046 gas-phase reactions between 468 species and is supplied by the network of surface reactions. The ratefiles can be downloaded from <http://www.physics.ohio-state.edu/~eric/research.html>.

The OSU network is also widely used. Hot cores

([31]; [32]), cold cores ([33]; [32]), protoplanetary disks [32] were modeled using this database.

3.3. KIDA

KInetic Database for Astrochemistry [34] is a new network of gas-phase reactions which is being developed in the University of Bordeaux since 2009 [35] and is derived from the OSU database. It is declared to be designed for the chemical modeling of the ISM and planetary atmospheres. One of the most remarkable features of the network is its constant development. The version of 2010 contained 6215 gas-phase reactions among 666 species. An up-to-date version can be downloaded from <http://kida.obs.u-bordeaux1.fr/>. Also KIDA contains recommendations concerning rate coefficients and uncertainties for them.

3.4. Problems and perspectives

Though the discussed networks are all relevant, sometimes they lead to different results. This is demonstrated in Wakelam et al.[34] where *kida.uva.2011*, *osu-01-2009*, and *udfa06* networks are compared. Even KIDA, initially based on OSU, shows results slightly different from the parent network. The difference stems from sources used for compiling the network, namely, literature, laboratory measurements, theoretical calculations, and other estimations. Selection of sources and their reliability are up to authors of the databases. KIDA was established as an attempt to create a uniform database, so it may become the network of choice in the future. Problems related to numerical implementation of astrochemical models are discussed in detail in Röllig [36].

Yet another problem is related to the incompleteness of databases. In particular, most researchers admit that surface reactions are very important, but the databases mentioned above still do not include them in a general way. The chemical difference of ortho- and para-hydrogen is also not yet incorporated systematically. That hampers the proper account of the deuterium chemistry. Some sets of reactions with deuterated species exist ([37],[38]; [39]) independently. Deuterium is most obvious, but not the only isotope that should be taken into account. Chemistry of isotopologues may become one of the main perspectives in the further development of databases [40].

4. Chemical models

As soon as both the reaction database and a solver for ODE are chosen, they can be used to create the

chemical model itself. The overall design of the model depends on the scientific problem and an object to be modeled. Models can be pseudo-time-dependent ([41]; [42]; [43]) that ignore changes in an object physical structure or in its physical conditions during the chemical evolution, or truly time-dependent (e.g. [44]). While most often researchers tend to create models themselves, there are some publicly available codes.

4.1. *Nahoon*

Nahoon is a pseudo-time-dependent 0D and 1D gas-phase chemical code created by the authors of KIDA [45] and written in Fortran90. The solver DLSODES from the ODEPACK package is used. The code is available online since 2007. The latest version (October 2001) can be downloaded from <http://kida.obs.u-bordeaux1.fr/models/>.

The code [34] is designed for work with KIDA and uses all its advantages. In particular, it checks the temperature range for rate coefficients and checks for duplication of chemical reactions, defined over complementary temperature ranges. Some important processes (formation of molecular hydrogen) are not included, so that the user has to do it additionally. Grains are defined as chemical species and participate in reactions of charge transfer.

4.2. *Astrochem*

Astrochem is “a code to compute the abundance of interstellar species”, written in C and distributed under the terms of the GNU General Public License (GPL). The official web-page for the code is <http://smaret.github.com/astrochem/>. The solver chosen by the author is CVODE [46] from the SUNDIALS library [47]. The code is very fast, as a Jacobian matrix of the system is computed explicitly to speed-up computations. *Astrochem* works with a number of gas-phase chemical processes as well as gas-grain interactions that are described in the manual. *Astrochem* comes with a program *Plabun* that makes plots of abundances computed by *Astrochem* and presents results of computations in a graphic form.

5. Astrochemistry and star formation studies

Suppose we constructed an astrochemical model that predicts molecular abundances as a function of location within a modeled object. There are currently two major strategies to utilize this information in star formation studies. First, one can invoke some simple considerations to relate line intensities to column densities and then compare these observed column densities with

theoretical ones. The simple line analysis also allows deriving some approximate values for gas temperature and density, that are, as a rule, represent values averaged over the line of sight. Considering Doppler shifts of various lines, one can make general conclusions on the kinematics in the studied objects.

The major advantage of this approach is its relative simplicity. It is also less demanding to the quality and amount of observational data. This opens the possibility to use it in surveys and other studies of wide areas with complex and diverse morphology.

The other approach is to use results of astrochemical (and hydrodynamical) modeling as an input for a radiation transfer model that allows computing line profiles for different molecules and transitions at various directions toward the object and then making *direct* comparison with observed profiles. This approach is definitely more adequate but this comes at a price. A good radiation transfer model even in 1D (to say nothing about 3D) is in itself a very complicated and resource-consuming numerical problem. Also, it requires some additional data on molecules, like collisional transition rates, which are not always available.

In very general terms, the mere presence of certain molecular lines is often considered as a marker of a certain evolutionary stage. We have already mentioned in Introduction that CO lines are used as a general “Universe-wide” tracer of moderately dense molecular gas. In denser clumps its utility is lessened due to significant self-absorption. While less abundant CO isotopologues (^{13}CO , C^{18}O) can still be useful, starless (prestellar) cores are more often observed in ammonia and CS lines. These lines in a core that does not show a presence of a compact infrared source indicate the earliest phase of the star-formation process. Additionally, line spectroscopy can be used to select so called infall candidates among such cores. A specific asymmetric line profile shape in these cores is a marker of inward gas motion (presumably, the beginning of a protostellar collapse).

When a protostar appears in the center of the core, it starts to warm up dust grains and evaporates icy mantles, so that complex molecules, having been synthesized on grains, are released into the gas phase where their lines can be observed. The presence of formaldehyde, methanol, methylformate lines is an evidence of a more advanced star formation phase that is called a hot core or a hot corino, depending on a protostar mass.

Yet another signposts of advanced star formation phases (as a rule, in massive star forming regions) are masers in various molecular tracers, most often methanol, water, and hydroxyl masers.

Molecular line observations may help to make a choice among the two most widely accepted paradigms of star formation. According to the “standard” star formation theory, birth of a star is a slow process which

is mainly governed by the magnetic field. Specifically, a single star history starts in an individual dense clump that is initially supported against gravitational collapse by the magnetic field. Due to a gradual loss of magnetic support, the core slowly contracts for a few million year until its density becomes high enough so that gravity wins over magnetic field. Afterwards, the core collapses rapidly and becomes a protostar.

In the gravoturbulent model, both clumps in molecular clouds and the clouds themselves are transient objects born due to collisions of turbulent flows. A density fluctuation arising in a turbulent medium may become gravitationally unstable if its density is high enough. Thus, it appears and collapses in a dynamical timescale that is generally shorter than 1 Myr.

Different timescales involved into these star formation paradigms should leave different imprints into the core molecular content as various molecules also evolve with different timescales. This gives rise to a concept of a chemical clock according to which abundance ratios of rapidly evolving molecules and slowly evolving molecules (for example, CS vs NH₃) can be used to estimate the core age.

While this concept sounds simple and logical, its practical implementation encounters many complications, mostly related to a vast number of unknown parameters. To name a few, our knowledge of CR ionization rate in molecular clouds can be incomplete; description of molecule accretion onto dust grains with a single value of a sticking probability is definitely an oversimplification, and so on. This results in degeneracy of protostellar object parameters determined from observations of only a few molecules [48]. To make model-based inferences more sound, one needs to use observations of as many molecules as possible, which implies a great demand for observing time.

On the other hand, while this information is available it can be used to validate a model and to infer object parameters with a significant certainty. For example, Kochina et al. [49] have shown that a UMIST-based model with surface chemistry allows reproducing column densities in a TMC-1 core for 46 out of 55 species for which this information is available. Among these 46 species are both diatomic molecules and complex organics, like methanol and methyl formate. However, such a detailed analysis is only possible for a limited number of individual objects.

An astrochemical modeling of molecular clouds as 3D evolving objects is still in its infancy as available resources only allow considering very limited reaction networks that are mainly focused on the formation of H₂ and main molecular tracers, mostly, CO.

On the other end of spatial scales we find protoplanetary disks that become more and more attractive from the astrochemical point of view. While only a dozen of molecules is detected in protoplanetary disks so far (compare to more than 150 molecules in interstellar

and circumstellar medium), great expectations are related to the ALMA array that currently operates in Chile. Two most advanced modern astrochemical and physical models of protostellar disks are PRODIMO [50] and ANDES [51].

6. Conclusions

Observations of molecular lines provide a powerful diagnostics of the interstellar medium and protostellar objects at various stages of the star formation process. However, due to the complex nature of interstellar chemistry and molecular emission, these observation cannot be adequately interpreted without equally detailed models. Moved by this necessity, astrochemistry has grown into the powerful and self-sustained branch of astronomy. We can now say that we understand formation and destruction pathways of all the primary molecules in various phases of the ISM, including star-forming regions.

Among the next necessary steps, incorporation of chemical networks into 3D hydrodynamical models can be listed supplied with proper radiation transfer model. This would allow making a complete transition to synthetic observations, that is, to the most rigorous way of comparing theoretical and observational data.

Other vital problems include uncertainties in various molecular parameters, including reaction rates, that can be solved with theoretical modeling and in astrochemical laboratories. Also, chemical models should include reactions with isotopologues. This is needed not only to interpret observations, but also to relate the interstellar chemistry to the chemical composition of the Solar System.

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