

MINI-REVIEW

The Modeling of Grain Surface Chemistry[†]Long-fei Chen^{a,b*}, Fang-fang Li^a, Qiang Chang^c*a. Xinjiang Astronomical Observatory, Chinese Academy of Sciences, Urumqi 830011, China**b. School of Astronomy and Space Science, University of Chinese Academy of Sciences, Beijing 100049, China**c. School of Physics and Optical Engineering, Shandong University of Technology, Qingdao 255000, China*

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Astrochemistry has made great progress in recent years. Especially the grain surface chemistry played important roles in the explanation of the formation of the interstellar molecules. In this review, we will discuss the progress, including the different numerical methods to simulate the ice mantles in the astrochemical models. We will also introduce the laboratory astrochemical experimental results, and their contributions to the grain surface chemistry in the review.

Key words: Astrochemistry, Molecules, Surface chemistry, Solid-state

I. INTRODUCTION

In the past few decades, astrochemistry has been paid attention gradually. This is because of the detection of more and more molecules in the interstellar medium. Molecules existing in the interstellar medium are in the state of rotation, vibration, or rot-vibration, so that they could emit the radiations in the range from radio to infrared wavelength. Those frequencies are unique for each molecule, and thus can act as the fingerprint for its identification. Since the first detected molecule, CH, in the interstellar medium [1], there are more than 200 molecules that have been identified (<https://cdms.astro.uni-koeln.de/classic/molecules>). On the other hand, molecules that were observed in the various of astronomical sources also present diversity. From then on, the evolution of molecules in the astronomical environments is more and more studied, including the theoretically calculated abundances of molecules, the formation and destruction mechanisms of molecules in the interstellar medium. Historically, the modeling of astrochemistry undergoes the developments from the pure gas-phase chemistry to gas-grain chemistry to the more complicated multi-phase chemistry.

Pure gas-phase chemistry has achieved a great success because many molecular abundances predicted by pure gas-phase chemical model are in good agreement with the observational data [2]. However, some molecules do not fall into this category. For instance, the most

abundant species, molecular hydrogen, cannot be synthesized by atomic hydrogen in the gas phase [3]. So, most of the modern astrochemical models consider the influence of the cosmic dust grains. In those models, gas phase species can deplete onto the surface of the grains, while species on the grain surface can also desorb into the gas phase. On the grain surface, species can diffuse among the binding sites, so that they recombine to form new species.

In this review, we will focus on the grain surface chemistry, discuss its recent development and its importance for the explanation of the observational data.

II. BASIC CONCEPTS OF GRAIN SURFACE CHEMICAL MECHANISMS

For most astrochemical models that include the grain surface chemistry, dust grain is approximated to be spherical with a radius of $a=0.1\ \mu\text{m}$, and is constituted with silicate. The grain density is $\rho=3\ \text{g/cm}^3$, the dust-to-gas mass ratio is assumed to be 0.01, and the dust-to-gas number ratio is set as 10^{-12} . There are approximately $N=10^6$ sites on the surface for such a grain. Different type of reactions could occur on the grain surfaces. The following are the details for those reactions and their reaction rates.

Firstly, for a gas phase species, i , which can deplete onto the grain surface, its depletion rate is represented by

$$R_i = k(i)n(i) \quad (1)$$

$$k(i) = \sigma\langle v(i)\rangle n(d) \quad (2)$$

where $k(i)$ is the rate coefficient, $n(d)$ is the number density of dust grains, and $n(i)$ is the number density

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of species i . In the rate coefficient k_i ,

$$\sigma = \pi a^2 \quad (3)$$

$$\langle v(i) \rangle = \left(\frac{8k_B T}{\pi m(i)} \right)^{1/2} \quad (4)$$

where $\langle v(i) \rangle$ is the average thermal velocity of species i , k_B is the Boltzmann's constant, T is the gas temperature, and $m(i)$ is the mass of species i .

Secondly, as opposite to the depletion, species on the grain surface can also desorb back to the gas phase. The desorption rate $k_{\text{des}}(j)$ for a grain surface species j is as follows

$$k_{\text{des}}(j) = \nu \cdot \exp\left(\frac{-E_D(j)}{T_d}\right) \quad (5)$$

where $\nu=10^{12} \text{ s}^{-1}$ is the typical vibrational frequency, $E_D(j)$ is the desorption energy of species j , and T_d is the grain temperature.

Thirdly, the species on the grain surface can hop among the sites. For a grain species, m , its hopping coefficient from one site to another site is represented by

$$k_{\text{hop}}(m) = \nu \cdot \exp\left(\frac{-E_b(m)}{T_d}\right) \quad (6)$$

where $E_b(m)$ is the diffusion barrier energy of species m . Most astrochemical models assume that when the total visited sites of the two species are equal to N which is the total sites of the surface, those two species will meet each other on the same site eventually. So the reaction coefficient for the two species, m and n , is as the following

$$k_{m,n} = P(m,n) \frac{k_{\text{hop}}(m) + k_{\text{hop}}(n)}{N} \quad (7)$$

where $P(m,n)$ is determined by activation energy (E_a). If $E_a=0$, then $P(m,n)=1$; if $E_a>0$, then

$$P(m,n) = \exp\left\{-2\left(\frac{b}{\hbar}\right)[2k_B\mu(m,n)E_a]^{1/2}\right\} \quad (8)$$

where $b=1 \text{ \AA}$ is the barrier thinness, \hbar is the reduced Planck's constant, and $\mu(m,n)$ is the reduced mass of species m and n . Thus the reaction rate $R_{m,n}$ between species m and n is as follows,

$$R_{m,n} = k_{m,n} N_m N_n \quad (9)$$

where N_m and N_n are the numbers on the grain surface for species m and n respectively. In the astrochemical models that include the gas-grain reactions, the units for surface species abundances must be consistent with those for gas phase species (cm^{-3}), thus the above rate coefficient [4] becomes

$$k'_{m,n} = \frac{k_{m,n}}{n(d)} \quad (10)$$

III. PROGRESSES OF THE ASTROCHEMICAL MODELS

Although the astrochemical models that include the grain surface chemistry solved many problems that pure gas-phase models cannot, three main issues also appear in front of us. The first is the numerical method for the simulation of the evolutions of the grain surface chemistry, the second is the chemical modeling of the grain ice mantles, and the third is the modeling of dust grains. The following are the current progress about those three aspects.

A. Numerical methods of grain surface chemistry

For the earlier gas-grain chemical models, the rate equation is always used to calculate the abundances evolution of various species versus time. Due to the rapid calculation of the rate equation, this method is still the most used one. However, there is a problem for the rate equation. When the number of a species on the grain surface is less than one, the results of the rate equation may bring a significant error compared with the more accurate method [5]. This is the so-called finite size effect. For example, if there is only one atomic hydrogen on the grain surface, it will not be synthesized to molecular hydrogen. However, the reaction rate predicted by the rate equation for the synthesis of molecular hydrogen is non-zero even if there is only one atomic hydrogen on the grain surface. Actually, the rate equation method assumes an infinite size of dust grain. Under the reality of the finite size of the dust grain, the number of some species, especially the most chemically active species, such as H, may be less than one. Thus, the rate equation method may introduce some calculation errors.

To solve this finite size effect, many new numerical methods have been introduced. The first is the modified rate equation method [6]. The main concept of this method is that it limits the surface reaction rates caused by the diffusion of grain surface species to the depletion or desorption rates of those reactants. Although this method is semi-empirical, it is more approachable to the strict method developed lately when compared with the rate equation method. At present the widely used method is the advanced modified rate equation [7] where it not only modified the reaction rates caused by diffusion, but also modified the formula form of the rate equation.

Master equation is a more rigorous method to take into account the finite size effect. The newly developed method is mostly around how to solve the master equation [8]. Similar to the rate equation, master equation is also a gain-loss equation. The difference is that, in the rate equation method the change of abundance over time of each species is equal to the rate at which the species is produced minus the rate at

which the species is consumed, while the master equation no longer describes the change of species abundance over time, but describes the change of probability of the number of species in a reaction network over time. The master equation can directly solve the ordinary differential equation to obtain the probability of species number over time which is similar to rate equation. However, with the increase of the complicity of the reaction network, there will be many approximations in order to directly solve the master equation [9]. To decrease the computational complicity of the master equation, an approximate method which is called moment equation is developed [10]. Basically, the moment equation is also an ordinary differential equation, so that it can be solved by the existing codes. Initially, the moment equation was only used for the grain surface simulations, and then Du *et al.* [11] developed a hybrid moment equation method to simulate the gas-grain chemical evolutions.

The Monte Carlo method, also called Gillespie method, is the strictest method to solve the master equation [12]. This method treats every chemical reaction in the reaction network as a random event. When a random event that is a chemical reaction occurs, the number of the reactants and products in the system will be updated. When the evolutionary time reaches the final time, the simulation terminates. At present, the Monte Carlo method has achieved great success in solving the master equation, it can perform a complete gas-grain chemical network to do the simulation [13]. However, the Gillespie method encounters a great difficulty in dealing with the high-density and high-temperature environments, because too many depletion and desorption events which consume the most CPU time occur, leading to the calculation very slow. To solve this problem, a modified Gillespie method based on quasi-steady-state assumption is proposed [14]. This method effectively accelerates the simulation speed under high-temperature and high-density physical conditions.

The above introduced numerical methods solved the finite size effect quite well, but the complicity of surface chemistry is not limited to the finite size effect. On one hand, the surface reaction rate is under an assumption which is that a species doesn't repeatedly visit a site. On the other hand, different sites may have different diffusion barriers or desorption barriers. To solve those two problems, Chang *et al.* [15] developed a microscopic Monte Carlo method. This method remembers the site where each species diffuses on the grain surface, and then it decides whether the reaction could occur or not when two species diffuse to the same site. So, the microscopic Monte Carlo method solved the above problems very well. However, the disadvantage of this method is the huge computational cost, and so far this method has been only performed to the cold core chemical evolutions [16]. The microscopic Monte Carlo method proposed by Chang *et al.* pre-defined the location of each site. This approximation is accurate when the number

of species on the grain surface is relatively small and not all of the sites are occupied. However, with the accumulation of ice on the grain surface, the pre-defined site is not necessarily the lowest potential energy. To solve this problem, Garrod [17] proposed a more precise microscopic Monte Carlo method which is called off-lattice microscopic Monte Carlo method. This method dynamically searches for the lowest potential energy in the process of calculating the chemical evolution instead of using the pre-defined lowest potential energy.

B. The structure of grain ice mantles

The initial gas-grain astrochemical models are two-phase models, which include the gas phase and the grain surface. In 1992, Hasegawa *et al.* [4] proposed an improved model, which is called the three-phase model. In that three-phase model, the grain surface chemistry is only applied on the upper-most one layer of the ice mantles. Thus, the three-phase includes the gas-phase, the active grain surface, and the inner inert ice mantles. Although the three-phase model conforms to our physical intuition, it doesn't predict the species abundance in the molecular clouds better than the two-phase model. Thus, this model is ignored for a long time, until the microscopic Monte Carlo method is used by Chang *et al.* [15]. Because the microscopic Monte Carlo method can divide the grain surface from the inner ice mantles automatically so that the three-phase model is paid attention gradually. Subsequently, many improved three-phase models were proposed, and the improvement of these models mainly focused on the chemical modeling of the inert ice mantles.

The initially three-phase model assumed that the inert ice mantles are uniform, whereas Taquet *et al.* [18] constructed a three-phase model that the inner inert ice mantles are porous. They found that the holes in the porous structure could limit the radicals to the ice mantles. Garrod [19] proposed a model that different species can exchange within the ice mantles, and the species inside the inert ice mantles could run into the active layers by the exchange. Vasyunin *et al.* [20] also developed a multi-phase model. This model takes into account the sequence of the formation of the ice mantles. When the temperature of the molecular clouds warms up, the latter formed ice is desorbed firstly. Because the microscopic Monte Carlo method can track the position of each species thus the models calculated by this method are a multi-phase model. Recently, photolysis of the inert ice mantles by ultraviolet (UV) photons is gradually paid attention [16, 21, 22]. In this new model, UV photons could penetrate into the upper layers of the grain surface and photodissociate the species inside the inert ice mantles. The products of the photolyzed species could diffuse in the inert ice mantles and participate in the chemical reactions. The most interesting result of this model is that the produced radicals by the photol-

ysis species could freeze inside the ice mantles, which is consistent with the laboratory experiments. When the temperature of the molecular clouds increases, those radicals could diffuse and recombine to form complex organic molecules. The model results predicted by Lu *et al.* [22] showed the abundances of complex organic molecules in the protostars could be over one order of magnitude higher than that from the simple two-phase model, and gave a solution for the problem of underestimating the complex organic molecules in the previous models.

C. Modeling of dust grain

Finally, as for the dust grains used in the general astrochemical models, the assumed size of the grains is uniform, and the grain temperature is identical with each other. However, this assumption is not accurate because there is a dust grain size distribution in the interstellar medium certainly [23, 24]. Recently, some astrochemical models begin to be used to study the effect of grain size distribution on the chemical evolution. Acharyya *et al.* [25] found that the chemical model containing the grain size distribution doesn't make the predicted results in more agreement with the observational results. Ge *et al.* [26] found that the molecules number density on the smaller grains is larger than that on the larger grains in the dark clouds. Pauly *et al.* [27] not only introduced the grain size distribution but also considered the size-dependent grain temperature. They found that CO₂ is easier synthesized on the smaller grains because the smaller grains are warmer than larger grains. Recently, Chen *et al.* [28] discussed the effect of the grain temperature fluctuations of small grains (with radius around 0.00687 μm) on the chemistry of cold cores. The grain temperature fluctuations are mainly caused by the absorbed photon energy of the interstellar radiation field. Infrared wavelength photons can heat the grain temperature up to several to over ten Kelvins depending on the size of the grains and the extinction of the clouds [29], whereas cosmic-ray induced UV photons can heat the grain temperature much higher. Higher grain temperature can increase the diffusion of the species on the grains more quickly, thus increase the reaction rates between two species. Under this effect, their results showed that the temperature fluctuations of those small grains caused by interstellar radiation can help some complex organic molecules formed on the grain ice mantles.

IV. LABORATORY ASTROCHEMICAL EXPERIMENTS

Another approach for the study of the astrochemistry is the laboratory experiments. Like the gas-phase and grain surface chemistry in the astrochemical models, there are also gas-phase and solid-state experimental

setups in the laboratory. Readers can refer to the literature reviewed by Smith [30] for the laboratory gas-phase astrochemical processes. In the following, we mainly and briefly summarize the setups and processes of the solid-state experiments, and their implementations for the astronomical grain surface chemistry.

A. Setups of the experiments

The experiments rely on several ultra-high vacuum chambers to simulate the cosmic environments, and the temperature can be programmed in a range of values. Pure gas is prepared in one of the chambers and can be imported into the main chamber which contains a gold-coated cooper or silver substrate where the gas can be deposited to form multilayer ice analogs to simulate the interstellar ice mantles on the dust grain. To experiment the possible chemical process in the ice samples, some methods can be performed on those ice analogs which we will describe in the following. During the experiments, some diagnostic equipment are performed to monitor the changes, such as using the Fourier transform infrared absorption spectroscopy to analyze the species present in the ices either in embedded, formed, or consumed, or using the temperature programmed desorption quadrupole mass spectrometry to analyze the thermally desorbed ice species [31].

One of the chemical processes that may increase the compositional complex of the ice samples is that radicals can diffuse in the ices and recombine with other species to form new species. This process does not need external energy input, thus is the so-called non-energetic process. In the experiments, H atoms together with CO gas, or with CH₃OH gas co-deposited on the substrate under temperature of a few ten Kelvins [31–33]. Those experiments showed that CO and H₂CO can be hydrogenated to form H₂CO and CH₃OH ices respectively, or reversely from H₂CO and CH₃OH ices to produce CO and H₂CO species by H atom abstraction [31]. Those experiments also showed that more complex molecules can be synthesized too [31–33], such as HCOOCH₃, CH₂(OH)CH₂OH, or CH₂OHCHOHCH₂OH.

On the other hand, mimic with the dust grains exposed in the interstellar radiation field, the ice samples in the laboratory could be irradiated with a broad-band UV hydrogen microwave-discharge lamp or electron gun to simulate the irradiation of the cosmic environment [34, 35]. This is the so-called energetic process. Reactive intermediates, such as radicals, could be formed in the ice samples upon the irradiation. Thus, more complex molecules could be synthesized by radical-radical recombination in the ices. For example, in the experiments performed by Oberg *et al.* [35], CH₂OHCHO and CH₂(OH)CH₂OH were detected by the irradiation of CH₃OH ices. The two isomers of C₂H₆O, CH₃CH₂OH and CH₃OCH₃, were detected by irradiation of CH₃OH

and CH₄ ice mixture in the experiments performed by Bergantini *et al.* [36].

B. Implementations on the astrochemistry

Complex organic molecules (COMs) as defined in astronomy are carbon-containing molecules with at least six atoms [37]. The origin of the interstellar COMs is one of the interesting questions in astrochemistry. One of the simplest and most important COM is methanol (CH₃OH), which is believed to originate from the grain surface, and is the mother molecule for the production of the more complex molecules.

Many COMs have been detected in the astronomical environments both in hot cores and in cold dense cores [38–40], including those presented above. The formation of those molecules has gotten a lot of discussions [38, 41, 42]. Grain surface chemistry is at least an important link for the detected gas phase COMs, either those molecules could be directly formed on the grain ice mantles and then sublimated to the gas phase, or the precursors that formed those molecules are firstly produced on the grain ice mantles and then sublimated to the gas phase to synthesize those complex molecules.

On the other hand, the composition of the grain ice mantles is quantified by the observations of the infrared absorptions toward the background stars. Boogert *et al.* [43] showed that the abundance of CH₃OH ices can be as high as 30 percent with respect to H₂O ices. And the CO ices can be as high as 31 percent with respect to H₂O ices in cloud cores showed by Oberg *et al.* [44]. Interstellar grains are exposed in the cosmic environments, and they could be bombarded by the high energy photons, such as UV photons and cosmic-rays, thus the radicals could be produced by the photolysis of the species in the grain ice mantles so that complex species could be synthesized by the radical-radical recombination.

As introduced above, the experimental results confirmed that COMs indeed could be produced on the grain ice mantles under the cosmic environments. Thus, those experimental results are useful for us to understand the origin of the interstellar COMs. The mechanisms for the synthesis of COMs on the grain ice mantles, together with the possible formation pathways and reaction branching ratios revealed by those experiments could help us to build a more complete reaction network in order to give a better constrain on the explanation of the observational data.

As a conclusion, the laboratory astrochemical experiments are important for the verification and improvement of the grain surface chemistry.

V. SUMMARY AND OUTLOOK

In this review, we described the developments of the modeling of the astrochemistry, and concentrated on the current progress related with the grain surface chemistry, including the different methods of the chemical models, the modeling of the grain ice mantle structure, and the role of dust grain playing in the astrochemistry. We also briefly summarized the highlights from the laboratory astrochemical experimental results, and their possible influences on the astrochemistry.

At present, most rate coefficients of the gas-phase reactions in the reaction network are based on the estimation. More precise measurements and calculations are needed by the laboratory experiments and computational quantum chemistry in the future. The modeling of the grain surface chemistry also has a large uncertainty. Currently, the grain surface chemical models do not include all of the important physical processes. The parameters used for the grain surface chemistry, such as the desorption energy of a species, also exist in a large uncertainty. All of those uncertainties need the precise measurements of the laboratory astrochemistry. Last but not least, the chemical models are promoted by the observations, so that different chemical models could be tested and verified by the constantly detected interstellar molecules.

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