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Suprathermal particles in astrochemistry

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The kinetic Monte Carlo method, used in astrochemistry to investigate suprathermal (hot) particles at the molecular level, is presented. Different modifications of this method, aimed at studying the influence of suprathermal particles in the processes occurring in gas and dust envelopes surrounding astrophysical objects — prestellar and protostellar cores of molecular clouds, planets, their moons, and comets in the Solar and extrasolar planetary systems — are considered. The important role of the fraction of suprathermal particles in astrochemical applications of this approach is demonstrated. The presence of these particles leads to local changes in the chemical composition; causes non-thermal emissions in gas and dust envelopes; enhances the chemical exchange between the gas and dust fractions of envelope; leads to the formation of extended hot coronae of planets; increases non-thermal atmospheric losses, thus determining the evolution of planetary atmosphere on astronomical time scales; and facilitates the formation of complex molecules in gas and dust envelopes of astrophysical objects.
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1. Introduction

One of the fundamental issues of modern astrophysics concerns the life cycle of molecular matter in the Universe. The study of the origin of heavy elements in stars; their transformation into molecular matter in interstellar clouds; incorporation into planet-forming bodies; and, finally, the origin of life is one of the most important lines of research of astronomers, planetologists, and biologists. Our efforts to understand the origin of life on the Earth and estimate the possibility of its existence in other planetary systems is related to a great extent to the question about the source of prebiotic and protobiotic molecules. Extraterrestrial organic matter continues to be supplied to the Earth with meteorites and interplanetary dust particles. The inventory of molecular matter in the Universe makes it possible to trace the propagation of chemical elements in Galaxy: from stars to planetary bodies in our Solar system (see, *e.g.*, Fig. 1).

About more than 40 years ago, a prevailing opinion was that the molecules present in interstellar gas can hardly be more complex than diatomic. Indeed, the interstellar medium, filled with a cold and rarefied gas, was considered to be too unfavourable for maintaining active chemical processes. Taking into account the low particle density [1, 2] ($\sim 10^0 - 10^2$ cm^{-3}) and the inevitable dissociation and ionization of molecules under UV irradiation from neighbouring stars, it was shown that polyatomic molecules cannot be formed in the interstellar medium.

To date, the concept of dense interstellar medium has radically changed (mainly due to the observations of molecular spectral lines in the radio, millimetre, and submillimetre wavelength ranges), because $\sim$200 chemical compounds have been reliably identified in the interstellar and circumstellar media (http://astrochemistry.net). Some molecules† have been found by observing their electronic spectra in absorption lines against the stellar background (examples are CH, CH^+, and NH) or the rotational – vibrational transitions in the IR region (examples are HCCH, CH_4, and SiH_4). In addition, some polyatomic molecules

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† Historically, in the studies of interstellar medium, the term 'molecules' is applied not only to true molecules but also to radicals, anions, and cations, *i.e.*, chemically active particles.

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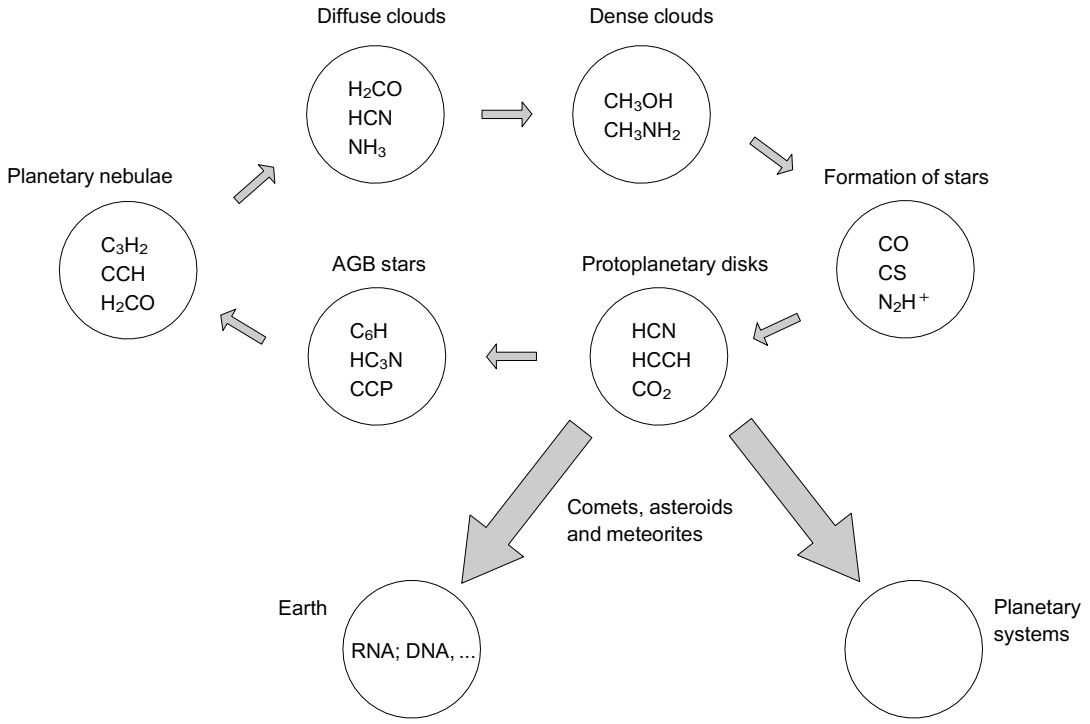


Figure 1. Life cycle of interstellar matter (constructed based on the data of Refs 1 and 2).
Each cycle stage is presented with indication of some characteristic molecules, in lines and bands of which these evolution stages of interstellar matter are observed by modern ground-based space astronomy instruments. AGB stars are stars in the asymptotic branch of giants, *i.e.*, in the region of the Hertzsprung – Russell diagram that is filled with evolving small and intermediate-mass stars.

(C_8H^-, $HC_{11}N$) were revealed in a lower frequency (microwave) spectral range.

Thus, the observations of molecular lines in the radio, millimetre, and submillimetre wavelength ranges gain much insight into the nature of the phases of transformation of interstellar matter (from the chemical evolution of the galaxy and to the chemical composition of planets and their atmospheres), which makes possible the development of various forms of life on planets that are similar to the Earth.[1–4] The molecules present in these media (see Fig. 1), are very useful indicators of the structure of circumstellar envelopes, planetary nebulae, dense and diffuse clouds, prestellar and protostellar cores of molecular clouds, and protostellar disks. They also allow one to trace the composition of bodies of the Solar system, in particular, planets, their natural moons, asteroids, and comets. It follows from the established unique relationship between the molecular lines and the aforementioned astrophysical objects that the development and refinement of the concepts of the chemistry of interstellar molecules is of decisive importance for evaluating the life cycle of interstellar matter and, especially, for understanding the processes of formation of stars and planetary systems.

The chemical variety in the interstellar medium is the object of study in astrochemistry: a young, intensively developing interdisciplinary science at the junction of astronomy, astrophysics, and chemistry, which is aimed at studying the mechanisms and rates of the chemical processes dominant in the Universe. The differences between astrochemical and chemical processes (the latter occur in terrestrial and technogenic media) are as follows:

— because of the low density, characteristic of interstellar medium, the time scale of the chemical evolution of astronomical objects may be several tens of thousands (or even millions) of years;

— astrochemical reactions occur at extremely low temperatures in comparison with the temperatures typical of the Earth, and these reactions often have paths free of energy barriers or occur with participation of particles possessing excess kinetic energy;

— chemical compounds that are rare on the Earth play a key role in astrochemistry; for example, chemical changes in cold molecular clouds are initiated by molecular ions H_3^+ (see below).

The concepts of the evolution of protoplanetary systems and the planet formation processes have radically changed in the last decade. This change is mainly caused by the following two 'observation breakthroughs' in planetary cosmogony:

— discovery of extrasolar planetary systems;

— onset of wide-scale observations of protoplanetary disks around young stars.

Astrochemical methods are more and more widely applied in this field of astrophysical research. Previous observations and studies of 'primitive building blocks' in the Solar system proved convincingly the presence of complex organic material in the early Solar nebula.[5,6] Most likely, complex molecules are also present in other protoplanetary disks; however, until now, only few their forms were found using modern submillimeter and millimeter interferometers. Such observations make it possible to impose limitations on the radial and vertical physicochemical structures of disks and yield information about the

molecular composition of their external regions. In the nearest future, one would expect the use of the Atakama Large Millimeter Array ALMA (Chile) with a high sensitivity and spatial resolution, the space James Webb telescope with a high spectroscopic potential in the IR range, and the space telescope Spectrum-UV to yield new information about the structure and chemistry of circumstellar disks. These data will provide a better insight into the global chemical evolution and dynamics of disks. The growth of planets and simultaneous disk evolution occur under various factors (stellar radiation and corpuscular plasma fluxes interacting with dust, gas, and plasma components of each circumstellar disk) and processes (hydrodynamic, caused by gravitational and magnetic hydrodynamics, as well as chemical and physical collisions), which themselves depend strongly on the physical nature and chemical composition of the solid and gas disk phases. The modern comprehension of the ways leading to the formation of planetesimals from the initial population of micrometre-sized dust grains is hindered by the absence of observational limitations and models, capable of representing this variety of physical and chemical processes.[7, 8]

To date, it has been generally understood that there are two main scenarios [primary atmospheres (or protoatmospheres] captured from the disk and secondary atmospheres) and three sources (gas accreted from the disk, degassing of the magma ocean, and delivery of volatile components under giant impacts) for forming the atmosphere of protoplanets. However, both these scenarios are characterized by a significant degree of uncertainty.

In the first scenario, exact mechanisms and quantitative effects of gas accretion from the disk, which is an integral part of planetary accretion, have not been completely understood. The stability of the atmosphere formed as a result of accretion depends on the efficiency and time constants of different processes of particle escape from atmosphere and its erosion, which are responsible for the atmosphere dissipation. These processes have been poorly studied for exoplanets[9] and only partially investigated for the planets of the Solar system.[10] In addition, the known uncertainties in the characterization of planets hinder clear understanding of the types of planets for which this scenario may be dominant. To overcome these difficulties, it is necessary to improve significantly the observational determinations and the models of exoplanet atmosphere structure.

According to the second scenario, secondary atmospheres arise due to the combined action of degassing and external bombardment. Improved estimates of the magnitudes and chemical composition of these two sources are urgently needed; however, they are characterized by great uncertainty even for the Earth. A key parameter, controlling the possibility of forming an ocean *via* water condensation from a vapour atmosphere, is the characteristic surface cooling time and solidification of primitive magma ocean, which likely depends strongly on the distance to the host star. Taking into account the current limitations of our knowledge about the ways in which these processes are implemented on exoplanets, it is reasonable to move ahead using maximally the knowledge gained by studying the planets of the Solar system, for which quantitative investigations can be performed in a simpler way and atmosphere models of higher accuracy can be developed.[9, 10] To gain more information about the exoplanet atmospheres, hydrogen-rich atmospheres, or secondary atmospheres formed during degassing, observations are performed mainly in the following two lines:

— discovery of exoplanets at bright nearby stars;

— high-precision observations of the spectra of exoplanet atmospheres.

Stars must be sufficiently bright to measure exactly their radii, masses, and atmospheric spectra. Suprathermal particles play an important role in the formation and evolution of the gas and dust envelopes of astrophysical objects.[9 – 12] Suprathermal (hot) particles are generally considered as particles with kinetic energies significantly exceeding the thermal energy of the surrounding gas. They are formed in various physicochemical processes, whose products have excess kinetic energy. If the formation rate of suprathermal particles is sufficiently high in comparison with their thermalization rate in elastic collisions, a stable fraction of suprathermal particles is formed, which may perturb significantly the locally equilibrium distribution of the thermal energy of gas and dust envelopes surrounding astrophysical objects: prestellar and protostellar cores of molecular clouds, planets, and their moons and comets in the Solar and extrasolar systems.

The main difficulty in studying the formation, kinetics, and transport of excited suprathermal atoms and molecules is the necessity of considering these processes at the molecular level. Indeed, suprathermal particles are formed in a thermodynamically open system: gas and dust envelope, which is forced by the high-energy particle fluxes. Correspondingly, their further evolution is determined using the kinetic Boltzmann equations for chemically reacting rarefied gas and dust media. Promising approaches for studying the kinetics and transport of suprathermal particles are those based on the development of discrete mathematical models, using the probabilistic interpretation of collisions in an ensemble of model particles. The approaches of this class include the kinetic Monte Carlo method and its modifications, which are used to study the nonequilibrium processes in chemically active gas and dust envelopes of astrophysical objects.[10, 11]

In this review we present the kinetic Monte Carlo method (KMCM) for studying the role of suprathermal particles in astrochemistry at the molecular level. Different modifications of KMCM, aimed at determining the role of suprathermal particles in the chemical processes occurring in planet atmospheres and on icy surfaces of astrophysical objects, are considered. The important role of the fraction of suprathermal particles in astrochemical applications of this approach is illustrated. The presence of these particles leads to the following effects:

— local changes in the chemical composition, because the rates of nonequilibrium chemical reactions (especially with high activation energy) between suprathermal particles and surrounding gas and dust envelopes are much larger than those of chemical reactions at thermal energies;

— occurrence of non-thermal emissions from the gas and dust envelope;

— enhancement of chemical exchange between the gas and dust fractions of the envelope;

— formation of extended hot coronae around planets in the Solar and extrasolar systems, which leads to an increase in the non-thermal atmospheric losses determining the evolution of planet atmosphere on the astronomical time scale.

Glossary of special terms:

— astrochemistry: a field of research studying chemical reactions in space;

— kinetic Monte Carlo method: a numerical method for solving the kinetic Boltzmann equation based on the dynamic and stochastic description of gas at the molecular level;

— suprathermal (hot) particles: particles with kinetic energies greatly (by a factor of 5 – 10) exceeding the thermal energy of the particles of surrounding gas (thermal particles);

— planetesimals: celestial bodies with sizes from several metres to several kilometres, which are formed in the stage of condensation of the gas and dust fractions of the protoplanetary disk and serve as the initial 'building material' for planet formation;

— atmospheric sputtering: a physical process induced by impact of high-energy ions on the planet atmosphere, as a result of which particles with suprathermal energies (capable of escaping from the atmosphere) are formed;

— physisorption: a physical process in which atoms are adsorbed from the gas phase on the surface of cold dust grains and are bonded by weak forces with it;

— Knudsen number (Kn): the ratio of the characteristic micro- and macroscopic scales of the rarefied-gas state; this parameter determines the mode of atmospheric gas flow: from free molecular ($\mathrm{Kn} \gg 1$) through transient ($\mathrm{Kn} \approx 1$) to hydrodynamic ($\mathrm{Kn} \ll 1$);

— XUV radiation: solar (stellar) photons in the soft X-ray (from 1 to 10 nm) and extreme UV (from 10 to 100 nm) ranges.

The following designations are used below:

SSA is the stochastic simulation algorithm,

A_i, B_i, and C_i are constants characterizing, respectively, the frequency of strong collisions, the pre-exponential temperature dependence, and the activation energy of the ith chemical reaction;

α_i is the ith component of a gas envelope under study;

$a_0(\boldsymbol{N})$ is the full function of gas reactivity;

$a_m(\boldsymbol{N})$ is the partial (for the chemical reaction m) function of the gas reactivity;

$\boldsymbol{C}$ is the gas state vector in the numerical stochastic system;

$\boldsymbol{C} \to \boldsymbol{C}'$ are jump-like transitions between the states of numerical system;

$\boldsymbol{C}(t)$ is a homogeneous Markovian jump-like process;

${}^{(s_t)}\boldsymbol{C}$ is a homogeneous Markovian chain, equivalent to the homogeneous Markovian jump-like process $\boldsymbol{C}(t)$;

$\boldsymbol{c}_i$ is the velocity of the ith-component particle;

$\mathrm{d}\sigma_m$ is the differential scattering cross section for the chemical reaction;

e_m is the normalization factor in the Boltzmann equation, which takes into account the phase volume conservation in chemical reactions;

E_H^{dif} are energy barriers for thermal (diffuse) displacements on the dust grain surface;

g_{ij} is the relative velocity;

$\Gamma_{ij}^{+}(\Gamma_{ij}^{-})$ are the transition probabilities, leading to the appearance (or disappearance) of particles at an active lattice site i;

$\{\Gamma_{ij}(\mathbf{X})\}$ is the transition probability matrix;

F_α is the distribution function of ith-component particles over velocities and internal excitation states;

$F^{\mathrm{surface}}(E)$ is the energy distribution for the molecules knocked out from an icy surface under heavy-ion bombardment;

$f_\alpha(\boldsymbol{c}, t)$ is the single-particle (*i.e.*, normalized to unity) distribution function of ith-component particles over velocities;

$J_m(F_{\alpha i}, F_{\alpha j})$ is the collision integral for the chemical reaction m;

J_{mt} are the integrals in the Boltzmann equation for elastic and inelastic collisions of hot atoms with atmospheric particles;

Kn is the Knudsen number;

k_{B} is the Boltzmann constant;

k_i is the rate constant for the ith chemical reaction;

m_i is the ith-component mass;

$n_\alpha(\boldsymbol{z}, t)$ is the numerical density of ith-component particles in the internal excitation state with a set of quantum numbers $\boldsymbol{z}_i$;

T is temperature;

t_{H} is the residence time of atom on the dust grain surface;

$t_{h\nu}$ is the time scale of photon absorption by a dust grain;

L_i^{plasma} is the rate of neutral component loss due to the charge exchange reaction with corotation ions of magnetospheric plasma;

N is the number of particles;

$\boldsymbol{N}$ is the state vector of a discrete stochastic system;

N_{p} is the total number of processes occurring at an active site i;

$Q_i^{(\nu)}$, $Q_i^{(\mathrm{e})}$ are sources of neutral and ionized particles during photolysis and electron impact;

Q is the absorption efficiency;

$\mathbf{Q}_{\mathrm{Oh}}$ is a function specifying the energy spectrum of the formation rate of hot oxygen atoms in exothermic reactions;

$\boldsymbol{r}_i$ is the position of ith-component particle in the configuration space;

V is the physical volume;

Φ is the UV photon flux;

$\mathbf{X}_i(t)$ is the state vector of numerical system at active site i on the dust grain surface;

$\boldsymbol{z}_i$ is the set of quantum numbers for each possible level of internal excitation of ith-component particle;

$\varphi(\boldsymbol{C},t)$ is the probability density distribution function for the gas state $\boldsymbol{C}$ at instant t;

ν is the frequency of thermal vibrations of active sites on the dust grain surface;

ξ is the fraction of hydrogen atoms colliding with a dust grain that are adsorbed on its surface;

X is the solid scattering angle;

η is the recombination efficiency of hydrogen atoms on the dust particle surface;

$\omega(\boldsymbol{C} \to \boldsymbol{C}')$ are the transition probabilities;

$\tau(\boldsymbol{C} \to \boldsymbol{C}')$ is the time interval between successive transitions;

$\{\varepsilon_{ij}\}_{j=1}^{N_p}$ are the participation indices for active site i on the dust grain surface;

σ is the geometric cross section of dust grain.

2. Basic concepts

2.1. Astrophysical objects and their gas and dust envelopes

The astronomical observations of interstellar and circumstellar spaces have made it possible to identify several hundreds of different molecules and ions, most of which

have an organic nature.‡ Correspondingly, the mechanisms of the formation of complex chemical species under space conditions must be theoretically explained.[2, 13] Interstellar dust grains are distributed over sizes: from several nanometers to several hundreds of nanometers. A number of unique physicochemical processes are related to the existence of dust grains in the interstellar medium. Many of these processes affect or even determine the astrophysical phenomena on macroscopic scales, including the formation of stars and planets. In particular, the surfaces of interstellar dust grains are important as catalytic ones for the formation of the most widespread interstellar molecule: the hydrogen molecule. At the same time, it is known that the formation of molecular hydrogen in the gas phase under interstellar medium conditions is hindered. Actually, molecular hydrogen may arise on interstellar dust grains if hydrogen atoms from the gas phase are adsorbed on the dust-grain cold surfaces and bonded with them by weak forces; this process is known as physisorption. These bonds are formed on the so-called active lattice sites, corresponding to the free energy minima on the surface of the system.

Weakly bound hydrogen atoms can move over surface during thermal diffusion through the potential barriers of active sites. If two hydrogen atoms find themselves at the same active site, molecular hydrogen is formed without activation energy. An opposite process is the desorption of hydrogen atom from the dust grain surface *via* thermal evaporation or some non-thermal mechanism: cosmic ray sputtering, photoevaporation, *etc*. In the interstellar medium, molecular hydrogen is formed basically in diffuse molecular clouds. The presence of molecular hydrogen in the gas phase is responsible for the subsequent appearance of the H_3^+ ion, which, in turn, is involved in a complex network of astrochemical ion-molecular reactions leading to the formation of more than a hundred of molecules that have been found in interstellar and circumstellar media.[2]

Many of astrophysical objects are surrounded by gas and dust envelopes. If the gas and dust motion in an envelope is limited by the gravitational field of astrophysical object, the envelope is referred to as an atmosphere; if the gas and dust motion is not limited by the celestial body gravity, the envelope is referred to as a coma. In the case of exoplanets with orbits located close to the parent star, one can observe complex asymmetric gas and dust envelopes, which include both the planetary atmosphere and clouds and tori of the gas escaping from the atmosphere, maintained by the stellar wind plasma.[9] The chemical evolution of the gas and dust envelopes of astrophysical objects with different masses and sizes (dust grains, planetesimals, protoplanets, prestellar and protostellar cores, *etc*.) is determined by the total action of many interrelated processes, including catalysis on the surface, chemical metabolism between the dust and gas fractions, and the change in the envelope composition. Chemical processes are initiated by the field of extreme UV radiation from the interstellar medium, protostar, or a star with a planetary system; they are characterized by significantly different time scales and degrees of deviation from equilibrium. Correspondingly, astrochemical studies of gas and dust envelopes must be performed applying numerical methods based on solving chemical kinetics equations on micro- and macroscopic scales, with allowance for the UV radiation transfer.

The practice of astrochemical studies of the interstellar medium showed[2, 14 – 16] that such problems must be solved applying both the macroscopic methods of chemical kinetics and the methods for describing chemical reactions at the molecular level. In the latter case an efficient approach is the method of stochastic simulation of nonequilibrium physicochemical processes in rarefied gas media.[11] The kinetic Monte Carlo method is used to study the chemical evolution of gas and dust envelopes of astrophysical objects of different masses, with detailed consideration of the contribution of suprathermal particles.[10, 17 – 20] Accelerated algorithms of this method for stochastic astrochemical models on the dust-grain surface and chemical exchange between the gas and dust fractions have been developed. A hybrid numerical model[18, 20] taking into account different time scales of chemical evolution has been developed. Within this model, fast chemical reactions can be described using the macroscopic chemical kinetics equations, while slow chemical reactions, which determine the chemical evolution of the object, can be described with the aid of microscopic stochastic kinetics equations.

One of the most important applications of the developed technique is the study of the formation of polyatomic molecules on the surface of dust grains in prestellar and protostellar cores of dense and cold molecular clouds.[19 – 22] In view of the rarefaction ($\sim 10^3 - 10^5$ cm^{-3}) and low temperatures ($\sim 10 - 30$ K), the synthesis of both simple and polyatomic molecules in dense molecular clouds occurs on the surface of dust grains.[2] Note that these chemical processes (also in view of the rarefaction of the surrounding gas medium and the discrete structure of dust grain surface) have a stochastic character.[14]

As was noted above, the formation of molecular hydrogen in the gas phase under interstellar medium conditions is hindered, and molecular hydrogen should be formed on interstellar dust grains in the following way: hydrogen atoms from the gas phase are adsorbed on the surface of cold dust grains and bound with the surface *via* weak forces (physisorption). The efficiency of hydrogen molecule formation on dust grains of olivine and amorphous carbon was investigated using the kinetic Monte Carlo method.[19, 20] The chemical pathways of the formation of water, formaldehyde, and methanol molecules on icy surfaces of interstellar dust grains in prestellar cores of molecular clouds were investigated applying the stochastic method for solving the main master equation of astrochemical kinetics.[21, 22] The molecules of the aforementioned species are very important links in the formation of complex molecules with a prebiotic potential in the interstellar medium.[2]

2.2. Astrochemistry of gas and dust envelopes of astrophysical objects

The chemical complexity of interstellar matter is described using the astrochemical systems including physical models of the objects under study and a network of chemical processes, which link many chemical compounds *via* an as wide as possible set of reactions. The astrochemical models of various astrophysical objects include generally the following groups of chemical processes:[23, 24]

— reactions in the gas phase;

— diffusive reactions on the surface of dust grains;

‡ The lists of observed interstellar molecules can be found, *e.g*., at the website http://astrochemistry.net.

— chemical exchange between the gas and dust fractions *via* adsorption and desorption processes.

2.2.1. Chemical reactions in the gas phase

Astrochemistry deals mainly with the reactions that may occur efficiently under conditions of low temperatures and densities, which are characteristic of cold and dark molecular clouds. These unusual reactions should be exothermic and pass without energy barriers (*i.e.*, without activation energy); at the same time, most of chemical processes are characterized by fairly high activation energies and occur rapidly only at room temperature. One of the main parameters of a chemical reaction is its rate coefficient, which is generally written in the form [23–25]

$$k_i = A_i\left(\frac{T}{300}\right)^{B_i}\exp\left(-\frac{C_i}{T}\right) \quad (1)$$

Here, T is the gas temperature and the constants A_i, B_i, and C_i characterize, respectively, the frequency of strong collisions, the pre-exponential temperature dependence, and the activation energy of the ith chemical reaction. One can select five classes of interactions [25] occurring without activation energy, specifically: ion – molecule, radiative association, dissociative recombination of molecular ions, radical – radical, and radical – stable molecule.

Ion-molecular reactions mainly increase the chemical complexity of interstellar medium. For example, the processes

$$H_2^+ + H_2 \xrightarrow{k_1} H_3^+ + H \quad (2)$$

$$CH_3OH_2^+ + CH_3OH \xrightarrow{k_2} (CH_3)_2OH^+ + H \quad (3)$$

tend to occur with relatively high rates ($k_1 = 10^{-9}$, $k_2 = 10^{-11}$ cm^3 s^{-1}) [23–25] in the so-called collisional limit, when almost all strong collisions lead to the reaction.

Radiative association reactions occur most often under the conditions where reaction products cannot be formed through conventional exothermic channels. Examples are the processes

$$C^+ + H_2 \longrightarrow CH_2^+ \quad (4)$$

$$C^+ + H_2 \longrightarrow CH^+ + H \quad (5)$$

whose rate coefficients are, respectively, 10^{-15} and $10^{-16}\,(T/300)^{5/4}\exp(-4700/T)$ cm^3 s^{-1} (Refs 23–25). Having collided, reactants form a complex, which then either decomposes into the initial reactants or becomes stable due to the emission of excess energy. Statistical theories show that the rate coefficients of these reactions may change from the collisional limit to values many orders of magnitude smaller. Larger values are associated with more complex ions, lower temperatures, and deeper potential wells for the complexes. Process (5) is a characteristic example of a reaction characterized by an energy barrier ($\sim$0.4 eV). A necessary condition for its occurrence under interstellar medium conditions is the existence of an external source of kinetic energy. The role of this source can be played by hydrogen molecules, ejected from dust grains with suprathermal kinetic energies,[26] or turbulent pulsations in diffuse molecular clouds.[27]

In dissociative recombination reactions, molecular ions recombine with electrons to form neutral products of smaller size. For example, for the processes

$$H_3^+ + e \longrightarrow \begin{cases} H + H + H \\ H + H_2 \end{cases} \quad (6)$$

the rate coefficient is $\sim 10^{-7}$ cm^3 s^{-1} (Refs 25 and 28), which is several orders of magnitude larger than that for ion-molecular reactions. An important feature of these reactions is the yield of recombination products with an excess thermal energy, *i.e.*, suprathermal atoms and molecules. Recently, significant progress has been made in the study of the rates of these reactions and the distribution of their products owing to the experiments with molecular ions.[25, 28] Note that the dissociative recombination reactions of molecular ions are an important source of chemical complexity in the interstellar medium.

A necessary condition for the occurrence of most reactions with participation of neutral atoms and molecules is the supply of activation energy; however, neutrals with an odd number of electrons, referred to as radicals, have a rather high chemical activity. In particular, for low-temperature interactions,

$$CN + C_2H_2 \longrightarrow HC_3N + H \quad (7)$$

$$C + O_2 \longrightarrow CO + O \quad (8)$$

the rate coefficients are, respectively, 10^{-10} and $10^{-11}\,(T/300)^{0.5}$ cm^3 s^{-1}; these values are only several times smaller than the rate coefficients for fast ion-molecular reactions.[29]

Simplified schemes of chemical interactions of hydrogen with the most important admixture elements relative to hydrogen (C, N, and O) in the gas phase are presented in Fig. 2. It follows from these schemes that simple diatomic molecules consisting of hydrogen and carbon, nitrogen, or oxygen are formed in ion-molecular reactions with participation of H_3^+ ions, which, in turn, arise in the chemical processes involving hydrogen. These cycles are generally completed by dissociative recombination of saturated hydrogen ions with electrons, which leads to the formation of both radicals and simple chemically neutral molecules.

Hydrogen chemistry is initiated by the ionization and dissociation of the main components (H, H_2) under impact of cosmic rays and interstellar UV radiation. It should be noted that some likely primary chemical processes, such as $C^+ + H_2$, $N^+ + H_2$, and $O + H^+$, are endothermic;[30] correspondingly, the rates of these reactions at temperatures of $T \approx 10 - 100$ K are very low. With allowance for this fact, we should emphasize the fundamental role of the H_3^+ ion in the formation of the chemical complexity of prestellar and protostellar cores of molecular clouds and, possibly, the important role of the reactants with suprathermal kinetic energies (see, *e.g.*, Ref. 26).

The chain of reactions (II) indicates that the formation of hydrocarbons is implemented either through a fairly slow association process $C^+ + H_2 \rightarrow CH_2{}^+$ or *via* the ion-molecular reaction $C + H_3^+ \rightarrow CH^+ + H_2$. The rates of these reactions, which are determined by the concentrations of C^+ and H_3^+ ions, are maximum in the diffuse envelope of prestellar core.

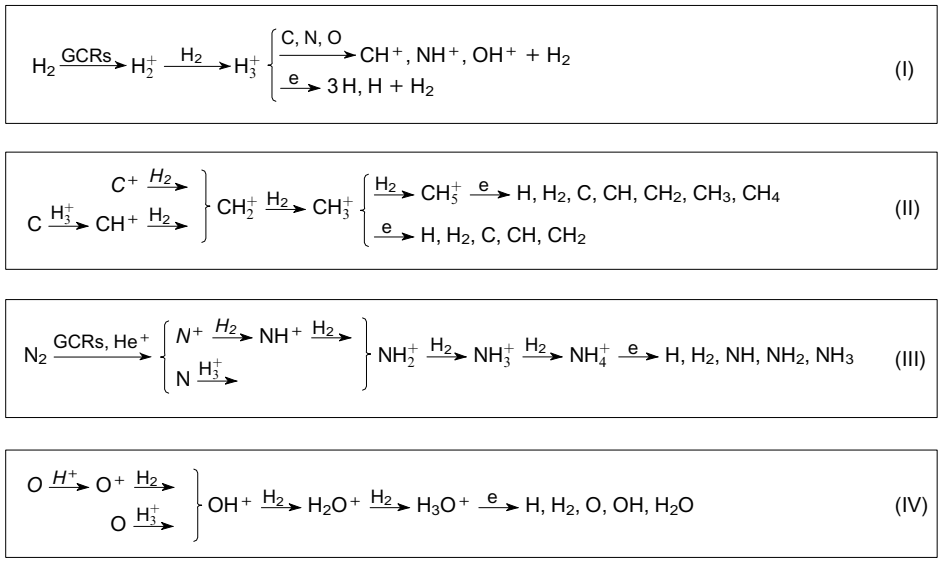


Figure 2. Simplified schemes of chemical reactions between hydrogen and its most important intrinsic elements (C, N, and O), occurring in the gas phase.[30]
In these schemes, endothermic reactions (which must involve suprathermal particles) are given in italics; all other reactions are exothermic. GCRs stands for galactic cosmic rays.

The initial reactions in the chain of chemical transformations (III) depend on either the endothermic reaction with a low reaction threshold, $N^+ + H_2 \rightarrow NH^+ + H$, or on the poorly studied interaction of atomic nitrogen with the H_3^+ ion. Apparently, the catalytic processes of the formation of ammonia and molecular nitrogen (which are fairly inert chemically) on the surface of dust grains also play an important role. Note also that the freezing out of water vapour and carbon oxide with simultaneous dissociative ionization of molecular nitrogen by He^+ ions facilitates the synthesis of polyatomic nitrogen-containing molecules, such as polyynes and cyanopolyynes.[2]

The gas-phase processes (IV) with participation of oxygen in dark prestellar cores are also determined by the reaction with participation of the H_3^+ ion. The free atomic oxygen in the external envelope is fairly efficiently saturated with hydrogen on the surface of interstellar dust grains and returns to the gas phase. Correspondingly, a relatively high concentration of chemically active hydroxyl radicals is observed. As a consequence, this region (transition with respect to the collapsing core) may also contain a relatively high concentration of evaporated water, which is one of the final (*i.e.*, chemically neutral) products of the chain of chemical transformations involving oxygen. However, the processes of accretion on the surface of dust grains; the reactions of catalytic surface chemistry; and, finally, the processes of icy mantle formation begin to play an important role in the region of collapsing core.

Gas-phase chemical models of astrophysical objects are generally constructed by writing several thousands of reactions of the aforementioned classes and simultaneous solution of the balance equations of chemical kinetics. A new database has been compiled recently: Kinetic Database for Astrochemistry (KIDA, http://kida.obs.u-bordeaux1.fr),[23, 31] which accumulates the rate coefficients for the network of chemical reactions in the gas phase and, in contrast to above-mentioned astrochemical networks, contains uncertainty coefficients and tools for estimating the corresponding calculation errors. This database is open for new experimental data and theoretical estimates of rate coefficients of astrochemical reactions that were not studied under laboratory conditions. These networks of chemical reactions in the gas phase with allowance for the processes of adsorption – desorption on interstellar dust grains are most often used to analyze the chemical evolution of dense, cold, and quiet prestellar cores and their condensation into giant molecular clouds.[2, 24, 32]

2.2.2. Chemical reactions on the surface of dust grains

Astronomical observations of dense and cold prestellar and protostellar cores give evidence of chemical complexity of the icy mantle coating interstellar dust grains.[33] Correspondingly, the catalytic reactions on the surface of dust grains are most important in the astrochemistry of various (basically cold) astrophysical objects. Indeed, molecular hydrogen — the main component of cold interstellar medium — is efficiently formed mainly on the dust fraction (Fig. 3).[34]

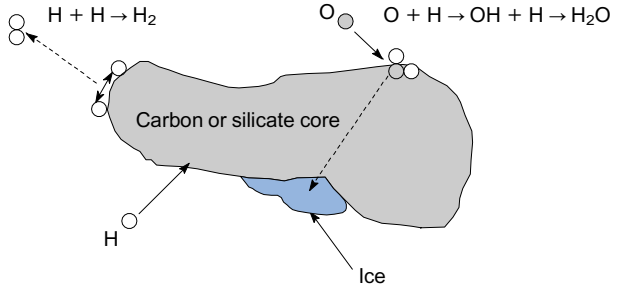


Figure 3. Schematic of an interstellar dust grain.[13]
Atoms and molecules are adsorbed on the dust grain surface, where H_2 and H_2O molecules arise due to the chemical diffusion, and an icy mantle is formed.

In astrophysical media at very low temperatures ($\sim$10 K), atoms of light elements, such as hydrogen or deuterium, after being adsorbed on an interstellar dust grain and captured in a potential well of the surface lattice, can move over the grain surface either due to the thermal diffusion or by means of quantum-mechanical tunnelling through potential barriers. During the diffusive displacement of hydrogen atoms over the surface, there may be reactions with heavier and almost immobile atoms and molecules (the so-called Langmuir – Hinshelwood mechanism). Other known mechanisms of chemical reactions, for example, the Eley – Rideal mechanism or an impact of a hot atom are apparently less efficient under conditions of cold and rarefied gas of prestellar cores.[16] Correspondingly, under conditions of cold molecular cores, the most widespread reactions on the surface of dust grains are those of saturation of heavier atoms and molecules with atomic hydrogen, for example,

$$O + 2H \longrightarrow OH + H \longrightarrow H_2O \qquad (9)$$

An analysis of the chemical interactions on the surface of dust grains in these cold cores showed that the gas phase contains generally free atomic hydrogen, and, because of its accretion on the grain surface, the relatively fast association reactions lead to the formation of hydrogen-saturated chemically neutral molecules: CH_4, NH_3, and H_2O. These molecules are accumulated on the surface and form icy mantles with many molecular monolayers [16, 35, 36] (see, *e.g.*, Fig. 4).

Another important process is the saturation of carbon monoxide with hydrogen. Carbon monoxide is rapidly formed in the gas phase in cold cores and adsorbed on the dust grain surface. The saturation with hydrogen (see, *e.g.*, Fig. 5),

$$CO + 2H \longrightarrow HCO + H \longrightarrow H_2CO + H \longrightarrow \longrightarrow H_3CO + H \longrightarrow CH_3OH \qquad (10)$$

occurs apparently on icy mantles due to the quantum-mechanical tunnelling of hydrogen atoms through potential barriers, in which CO molecules and their derivatives are captured.[16, 22, 37] This mechanism of methanol formation in dense and cold cores is very important, because formaldehyde and methanol are building blocks for more complex organic molecules,[2] which are necessary for abiogenesis.

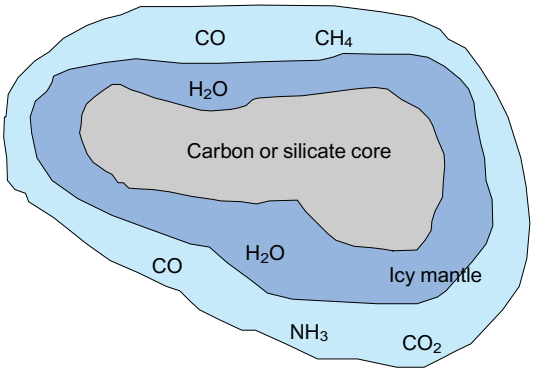


Figure 4. Schematic of the formation of the multilayer structure of icy mantle on a dust grain in the late evolution stages of cold prestellar core.[13]

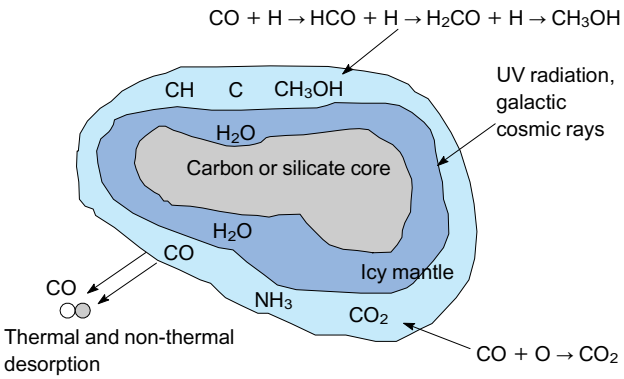


Figure 5. Schematic of the methanol formation on icy mantles of dust grains in the late evolution stages of cold prestellar core.[13] The chemical reactions in icy mantles and non-thermal desorption processes are initiated by interstellar UV radiation and galactic cosmic rays.

At the same time, astrochemical studies showed that the chemical ways of methanol formation in the gas phase are inefficient. Indeed, methanol is observed in the gas phase in some astrophysical objects with the following relative contents: 10^{-6} – 10^{-7} in hot protostellar cores, 10^{-9} in dark prestellar cores, and $<10^{-9}$ in the diffuse molecular gas.[2, 38] In the gas phase, methanol is formed mainly in the dissociative recombination reaction

$$CH_3OH_2^+ + e \longrightarrow CH_3OH + H \qquad (11)$$

The corresponding molecular ion is the product of very slow radiative association reaction

$$CH_3^+ + H_2O \longrightarrow CH_3OH_2^+ \qquad (12)$$

Correspondingly, the observable methanol contents cannot be reproduced in the astrochemical models of chemical gas-phase reactions.[23, 32] At the same time, interstellar methanol is observed in icy mantles of dust grains in prestellar and protostellar cores, and its content varies from several percent to several tens of percent with respect to the water ice content — the main mantle component.[39] These relatively high methanol concentrations in the icy mantles of dust grains are a weighty argument in favour of the aforementioned mechanism of saturation of CO molecules with hydrogen on the grain surface.[35] Recent observations confirmed the fact of methanol formation on the icy surfaces of dust grains in prestellar and protostellar cores of molecular clouds.[40]

Astrochemical networks on the surface of dust grains are generally simulated by analogy with simulation of chemical processes in the gas phase using balance equations.[41] This approach is known to be valid only when the surface concentration of reactants greatly exceeds unity and the discrete structure of the dust grain surface can be neglected. If these concentrations are low (a conventional situation in the astrochemistry of cold objects), this approach becomes invalid, and one must take into account the probabilistic nature of chemical reactions and the discrete structure of dust grain surface.[14]

The stochastic description of surface chemical reactions and processes is based on the so-called chemical master equation: a linear equation characterizing the probability density of occupation of possible states of atoms and molecules on the surface.[16, 22, 42] The master equation generates a random Markovian process, which exactly imitates the evolution of a chemically reacting system on the surface. Astrochemists use both the direct method for solving the master equation[22, 43] and the Monte Carlo method for simulating the chemical kinetics on the surface of dust grains.[21] The advantages and drawbacks of each of these stochastic approaches were discussed.[14]

It should be noted that, when problems of chemical kinetics on surface are solved using stochastic methods, the requirements to computational resources are rather stringent, and only limited chemical reaction networks on the dust grain surface can currently be considered.[22] In particular, the above-described processes of saturation of carbon and oxygen atoms and carbon monoxide molecules with hydrogen on the surface of dust grains in quiet and dense molecular cores were considered.[21, 22] It was shown that the chemical kinetics can rigorously be described only within stochastic approaches. Concerning the practical realization, the most promising approach appears to be the development of hybrid models,[14, 19 – 22] within which the components that are fairly abundant on the surface are described deterministically, *i.e.*, using modified balance equations of chemical kinetics, whereas the chemically active components with average abundance on the order of unity are described stochastically, *i.e.*, within the Monte Carlo method. Specifically this scheme should be applied when developing complete astrochemical models, in which the kinetics of reactions in the gas phase and on the surface of dust grains is considered using mixed deterministic and stochastic approaches.[16, 20, 36]

2.2.3. Chemistry of suprathermal atoms

Since particles with an excess of kinetic and internal energy (*i.e.*, suprathermal particles) have nonequilibrium properties, the processes of their formation and subsequent evolution should be considered at the microscopic (kinetic) level. First attempts of theoretical description of the chemistry of hot (suprathermal) atoms were made in Refs 44 – 47, where reactions of hot atoms were considered as a perturbation in the theory of neutron cooling. The main concept of the proposed kinetic theory is to trace hot atoms during their life cycle, having calculated the number of collisions of each atom with a specified energy. This information was integrated into the parameter referred to as the collision density, which was then combined with the reaction probability per collision for calculating the total number of reactive collisions of a given type. This approach made it possible to calculate directly the yields of hot-atom reaction products. Thereafter this approach was applied to photochemically induced reactions, in which hot atoms are formed.

In the stochastic theory proposed in Ref. 45, the emphasis was made on the initial energy dependence of the reaction yields rather than on the collision density. This dependence can be found by solving some integral equations. It was shown that this theory is reduced in the corresponding limit to the Estrup – Wolfgang kinetic theory. Time-dependent distribution functions of hot atoms over velocities were obtained for the first time using the Monte Carlo method.[48, 49] The distribution function of hot atoms was found to be highly nonequilibrium: the distribution of hot atom velocities reaches high- and low-temperature stationary states, although the distribution of stationary states differs significantly from the equilibrium Maxwell function.

The approaches used to study the hot-atom chemistry turned out to be in demand when analyzing the role of suprathermal particles in the physics and chemistry of gas and dust envelopes of astrophysical objects. The interest in these studies has significantly increased in the last years. The suprathermal particles formed in the upper atmospheric layers play an important role; specifically, they[11, 50]

— lead to local changes in the chemical composition, because the rate coefficients of nonequilibrium chemical reactions (especially those with a high activation energy) between suprathermal particles and surrounding atmospheric gas are much larger than in the case of chemical reactions at thermal energies; this is explained by the higher particle concentrations in the range of suprathermal kinetic energies than in the case of locally equilibrium distributions;

— cause non-thermal atmospheric emissions;

— populate hot planetary coronae and enhance non-thermal atmospheric losses, thus determining the atmosphere evolution on astronomical time scales.

In the first studies in this field,[51 – 54] possible contributions of suprathermal nitrogen atoms to the chemistry of odd nitrogen[55 – 57] and oxygen atoms to the formation of non-thermal emissions in the upper atmosphere of the Earth[52, 58] were noted. The next important step was to investigate the role of suprathermal oxygen atoms in the hot oxygen corona of the Earth, which is formed both due to the reactions of exothermic atmospheric chemistry[59, 60] and as a result of atmospheric sputtering[61, 62] of high-energy oxygen ions and protons precipitating from the magnetosphere. The results of further studies of the role and contribution of suprathermal particles to the formation of hot planetary coronae[11, 12, 50] were confirmed by spacecraft observations and measurements, *e.g.*, the first *in situ* measurements of the suprathermal fractions of nitrogen and methane molecules in Titan's upper atmosphere, performed by the NASA's Cassini mission instruments.[63] The possibility of formation of these suprathermal fractions was predicted theoretically (see, *e.g.*, Refs 11 and 64).

Below we consider the formalism of the kinetic Monte Carlo method, which is used in astrochemistry to study the suprathermal particles, and show examples of its application in the analysis of the role of suprathermal atoms and molecules in the gas envelopes of some objects, such as planetary atmospheres of the Solar and extrasolar systems, the surface atmospheres of ice moons of giant planets, and the surface of interstellar dust grains.

3. Kinetic Monte Carlo method for simulating the astrochemical kinetics

The main sources of suprathermal particles in a rarefied gas and dust envelope of an astrophysical object are the following processes:

— charge exchange of high-energy ions of stellar wind plasma during their interaction with the neutral components of atmospheric gas;

— dissociative recombination of molecular ions with thermal electrons;

— dissociation and dissociative ionization under impact of UV radiation and stellar wind plasma;

— exothermic ion-molecular and neutral chemical reactions;

— charge exchange reactions and atmospheric gas sputtering by stellar wind plasma;

— non-thermal desorption from the surfaces of aerosol particles and dust grains.

Photochemical sources, such as dissociative recombination, dissociation induced by stellar (XUV) photons in the soft X-ray (1 – 10 nm) and extreme UV (10 – 100 nm) ranges and high-energy electrons, as well as exothermic chemical reactions, are accompanied by energy release on the order of several electron volts; a part of this energy can be stored as the internal excitation of reaction products.[65] For example, Fig. 6 shows as an illustration the calculated distribution function of oxygen atoms — the main component in the transition (from thermosphere to exosphere) region of Mars' upper atmosphere.[66] As can be seen, in the suprathermal energy range, the concentration of oxygen atoms formed due to the photochemical source (red line) — dissociative recombination of molecular oxygen ion — greatly exceeds the concentrations of thermal oxygen atoms (blue line) according to the Maxwell distribution. A detailed analysis of the contribution of suprathermal oxygen atoms due to the dissociative recombination of the main ionospheric ion O_2^+ to the population of Mars' hot oxygen corona is given below (see Section 4).

Plasma sources include the charge exchange of high-energy ions and atmospheric gas sputtering by stellar wind plasma. These processes are characterized by high energy transfer efficiency and accompanied by the formation of hot particles with energies up to several hundreds of electro volts.[12]

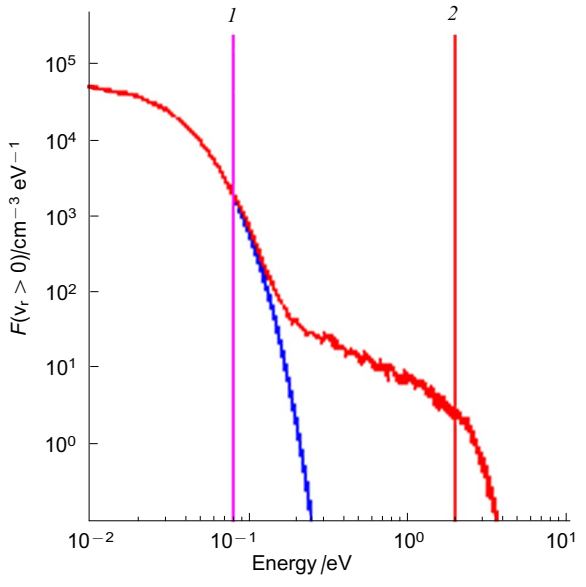


Figure 6. Calculated and thermal (red and blue lines, respectively) kinetic-energy distribution functions [$F(v_r > 0)$] of oxygen atoms at an altitude of 230 km in the upper atmosphere of Mars.[66]
The thermal distribution function was calculated at an altitude of 230 km at a Martian exosphere temperature of 205 K under conditions of moderate solar activity. The vertical lines indicate the conditional boundary of suprathermal energy range (*1*) and the escape energy from the Martian atmosphere (*2*). $v_r > 0$ means positive radial velocity.

The newly formed suprathermal particles lose their excess kinetic energy in elastic and inelastic collisions with the surrounding atmospheric gas. These processes are generally considered in the linear approximation, which implies that the surrounding gas is in thermal equilibrium and perturbations of its state by suprathermal particles are small. If the formation rate of hot particles is high, one must use the nonlinear kinetic approximation, because secondary particles are also formed with suprathermal energies. Therefore, their further collisions with the surrounding gas lead to cascade formation of new hot particles and, as a consequence, to significant perturbations of the thermal state of atmospheric gas. Therefore, when the Boltzmann equation is used, the hot-particle kinetics can be described rigorously only at the microscopic level.

3.1. Kinetics of suprathermal particles in a reacting gas

Let us consider a chemically reacting gas, consisting of K chemically different atoms, molecules, and their ions [*i.e.*, α_i ($i = 1, \ldots, K$) components] in a limited physical volume V with concentrations n_i and gas temperature T. Each of the particles of component α_i (atom, molecule, ion) is characterized by its mass m_i, position $\boldsymbol{r}_i \in V$, velocity $\boldsymbol{c}_i$, and set of quantum numbers $\boldsymbol{z}_i$ for each of possible internal excitation levels. These chemically different components are involved in $m = 1, \ldots, M > 1$ chemical reactions in correspondence with the following dynamic collision schemes:

$$m: \ \alpha_i(\boldsymbol{c}_i, \boldsymbol{z}_i) + \alpha_j(\boldsymbol{c}_j, \boldsymbol{z}_j) \longrightarrow \alpha_k(\boldsymbol{c}'_k, \boldsymbol{z}_k) + \alpha_l(\boldsymbol{c}'_l, \boldsymbol{z}_l) \qquad (13)$$

For the generality of description of a given chemically reacting system, reaction (13) will be considered as a set of different types of collisions, including elastic ($\alpha_i = \alpha_k$ and $\alpha_j = \alpha_l$), inelastic [$\alpha_i = \alpha_k$, $\alpha_j = \alpha_l$, but internal excitation levels are different: $\boldsymbol{z}_i \neq \boldsymbol{z}_k$ and(or) $\boldsymbol{z}_j \neq \boldsymbol{z}_l$], and reactive [$\alpha_i \neq \alpha_k$ and(or) $\alpha_j \neq \alpha_l$] collisions.

The probabilities of reactions (13) are determined by the functions

$$g_{ij} \mathrm{d}\sigma_m = |\boldsymbol{c}_i - \boldsymbol{c}_j| \mathrm{d}\sigma_m(|\boldsymbol{c}_i - \boldsymbol{c}_j|, \boldsymbol{\Omega}) \mathrm{d}\boldsymbol{\Omega} \qquad (14)$$

where $\mathrm{d}\sigma_m$ is the differential scattering cross section for the reaction occurring according to scheme (13); g_{ij} is the relative rate, and $\boldsymbol{\Omega}$ is the solid scattering angle. The scattering functions depend on the interaction potential of the reactants; they are generally calculated by quantum mechanics methods or measured in laboratory experiments.[67]

Evolution of a chemically reacting system at the molecular (microscopic) description level is determined by solving the system of kinetic Boltzmann equations

$$\frac{\mathrm{d}F_{\alpha_i}}{\mathrm{d}t} = \sum_m \sum_j J_m(F_{\alpha_i}, F_{\alpha_j}), \quad \alpha_i = 1, \ldots, K \qquad (15)$$

with the initial and boundary conditions for atmospheric gas in a volume V and on certain physical assumptions, such as rarefied gas and finite or rapidly decreasing interaction radii of particles during collisions. Here we used a microscopic description of the gas state by distribution functions of gas particles over velocities and internal excitation states:

$$F_\alpha = n_\alpha(\boldsymbol{z}, t) f_\alpha(\boldsymbol{c}, t)$$

The collision integrals on the right-hand side of the kinetic equations, which describe the changes in the gas state due to the chemical reactions, can be written as

$$J_m(F_{\alpha_i},\, F_{\alpha_j}) = \qquad (16)$$

$$= \int g_{ij} \mathrm{d}\sigma_m \, \mathrm{d}\boldsymbol{c}_j [e_m F_{\alpha_k}(\boldsymbol{c}'_k) F_{\alpha_l}(\boldsymbol{c}'_l) - F_{\alpha_k}(\boldsymbol{c}'_l) F_{\alpha_j}(\boldsymbol{c}'_j)]$$

Here, e_m is the normalization factor of phase volume conservation in chemical reactions.

The chemical kinetics of rarefied reacting gas at the microscopic level is completely determined by the dynamic and probabilistic (scattering functions) characteristics of molecular collisions, as well as the distribution functions of colliding particles over translational and internal degrees of freedom. Correspondingly, the chemical evolution of the reacting gas is characterized by complex exchange between the translational and internal energies. Astrochemical kinetics is often considered in the approximation of local or global thermal equilibrium,[17, 22] which corresponds to solution of a system of kinetic Boltzmann equations in zero approximation. In this case the gas thermal state is characterized by equilibrium Maxwell distributions of particles over velocities:

$$f_\alpha^{(0)}(c,\, T_\alpha) = \left(\frac{m_\alpha}{2\pi k T_\alpha}\right)^{3/2} \exp\left(\frac{m_\alpha c^2}{2k T_\alpha}\right) \qquad (17)$$

where T_α is the local or global gas temperature. After averaging kinetic equations (15) over equilibrium distributions (17), we arrive at the balance equations of chemical kinetics rates [67]

$$\frac{\mathrm{d}n_{\alpha_i}}{\mathrm{d}t} = \sum_m \left(n_{\alpha_k}, n_{\alpha_l}\, q_{\alpha_k \alpha_l} - n_{\alpha_i}\, n_{\alpha_j}\, q_{\alpha_i,\alpha_j}\right) \qquad (18)$$

Here, the functions

$$q_{\alpha_i \alpha_j} = \int g_{ij} \mathrm{d}\sigma_m f_{\alpha_i}^{(0)} f_{\alpha_j}^{(0)} \mathrm{d}\boldsymbol{c}_i \mathrm{d}\boldsymbol{c}_j \qquad (19)$$

are kinetic coefficients of the rates of chemical reactions occurring according to scheme (13).

3.2. Stochastic kinetics

The chemical kinetics of rarefied atmospheric gas can be formulated as a stochastic evolution of an ensemble of atoms, molecules, and ions. The stochastic approximation is based on the relationship between two approaches to description of the evolution of a chemically reacting rarefied gas:

— using the dynamic Liouville equation and the corresponding kinetic equations;[68]

— applying stochastic laws (the theory of Markovian processes and stochastic Kolmogorov equation);[11, 69, 70] for example, the evolution of a spatially uniform rarefied gas is presented as a homogeneous Markovian process:[69] changes in the gas state are caused by the instantaneous and time-separated collisions, and the description of this interactions is equivalent to the use of a homogeneous Markovian jump-like process.[71, 72]

The transition probabilities between the states of a random process are determined by the kinetic rates of chemical reactions, and the conservation laws specify the phase-space region where changes in this random process occur. The stochastic simulation method implies in the general case construction of a physical and probabilistic analogue of discrete media with collisional physicochemical processes [72, 73] and is used to simulate chemically reacting multicomponent gases at the molecular level. This approach has been developed when studying the generation, kinetics, and transport of suprathermal particles both in the photochemistry of planetary atmospheres[17] and in the analysis of the formation of hot coronae of planets and moons.[10, 18]

3.3. Stochastic master equation for suprathermal particles

The probabilistic description of the chemical kinetics of a rarefied atmospheric gas is based on the theory of random processes.[69, 74] Proceeding from the definitions of this theory, the evolution of a chemically reacting gas is described by the kinetic equation [10, 17, 18, 72]

$$\frac{\mathrm{d}}{\mathrm{d}t}\varphi(\boldsymbol{C}, t) = V^{-1} \sum_m \sum_{i,j} \int g_{ij} \mathrm{d}\sigma_m \left[e_m \varphi(\boldsymbol{C}_{ij}^m, t) - \varphi(\boldsymbol{C}, t)\right] \qquad (20)$$

This equation, linear with respect to the distribution $\varphi(\boldsymbol{C},\, t)$ of the probability density of gas state $\boldsymbol{C}$ at the instant t, is referred to as the stochastic (or basic) master equation of the chemical kinetics of rarefied gas in the stochastic approximation. In the case of pair elastic collisions, it coincides with the well-known Prigogine – Katz equation for an N-particle distribution function over velocities.[68, 69]

Stochastic master equation (20) describes the evolution of a homogeneous Markovian jump-like process in correspondence with the following definitions.

Gas state: within the stochastic approximation, the concentrations of rarefied gas components in a specified physical volume V are considered as random variables. Correspondingly, the rarefied gas can be presented by a numerical system of a finite number of $N = N^0 + \ldots + N^\alpha + \ldots + N^K$ particles; the particles from the subset $1, \ldots, i, \ldots, N^\alpha$ have velocities $\boldsymbol{c}_1, \ldots, \boldsymbol{c}_i, \ldots, \boldsymbol{c}_{N^\alpha}$ and correspond to the αth gas component. The state of this numerical system, characterized by discrete images of distribution functions $F_\alpha = n_\alpha(\boldsymbol{z}, t) f_\alpha(\boldsymbol{c}, t)$, can be written as

$$\boldsymbol{C} = \bigcup_{\alpha=0}^{K} \boldsymbol{C}^\alpha, \;\; \boldsymbol{C}^\alpha = \bigcup_{i=1}^{N^\alpha} \boldsymbol{c}_i^\alpha = \left\{N^\alpha;\, \boldsymbol{c}_1, \ldots, \boldsymbol{c}_{N^\alpha}\right\} \qquad (21)$$

Jump transitions $\boldsymbol{C} \to \boldsymbol{C}'$ between the states of the numerical system occur as instantaneous changes in the particle characteristics in correspondence with the dynamic schemes of chemical reactions (13)

$$\boldsymbol{C} \to \boldsymbol{C}' = \boldsymbol{C}_{ij}^m = \qquad (22)$$

$$= \left\{\boldsymbol{C}^{\alpha'},\, \alpha' \neq \alpha_i, \alpha_j, \alpha_k, \alpha_l;\, \boldsymbol{C}_i^{\alpha_i} \setminus \boldsymbol{c}_i,\, \boldsymbol{C}_j^{\alpha_{ji}} \setminus \boldsymbol{c}_j;\right.$$

$$\left.\boldsymbol{C}^{\alpha_k} \cup \boldsymbol{c}'_k,\, \boldsymbol{C}^{\alpha_l} \cup \boldsymbol{c}'_l\right\}$$

The velocities of particles after the reaction are determined from the conservation laws, and their directions are statistically determined by the differential scattering cross sections.

The transition probabilities $\omega(\boldsymbol{C} \to \boldsymbol{C}')$ are discrete representations of the rate coefficients (19) of the chemical reactions

$$\omega(\boldsymbol{C} \to \boldsymbol{C}') = \omega_{ij}^{m} = V^{-1} g_{ij} \sigma_m(g_{ij}) \tag{23}$$

The probabilistic time distribution between the successive transitions $\tau(\boldsymbol{C} \to \boldsymbol{C}')$ is set by the exponential law

$$P\{\tau(\boldsymbol{C} \to \boldsymbol{C}') \leqslant \tau\} = \tag{24}$$
$$= 1 - \exp\left(- \tau \sum_{m} \sum_{i,j} \omega_{ij}^{m} \right) = 1 - \exp(-\tau\omega(C))$$

because $\boldsymbol{C}(t)$ is a Markovian jump process.

Expressions (21) – (24) yield a rigorous definition of the random process $\boldsymbol{C}(t)$, describing the chemical kinetics of rarefied gas in the stochastic approximation. An important advantage of the stochastic approach is the linearity of the stochastic kinetic equation, due to which one can develop efficient schemes of simulation of the evolution of a chemically reacting gas [see Eqn (20)] based on the Monte Carlo method.[17, 18]

3.4. Chemical master equation

If the state of rarefied reacting gas is close to local and(or) global thermal equilibrium, the number of variables in the stochastic master equation (20) can be reduced. It follows from the thermal equilibrium condition that gas is well-mixed, *i.e.*, elastic collisions occur much more often than reactive ones. In other words, this circumstance makes it possible to average the evolution of chemically reacting gas on the fast dynamics scales in the velocity space. Therefore, the state of a chemically reacting gas can be presented by numbers of molecules of each type, considered as random variables in a specified physical volume V.

Within the accepted assumptions, the state of the gas as a stochastic system is described by vector (21) integrated over particle velocities, specifically,

$$\boldsymbol{N}(t) = \{N_1(t), \ldots, N_i(t), \ldots, N_K(t)\} \tag{25}$$

Here, $N_i(t)$ is the number of atoms or molecules of component α_i in the considered gas volume at an instant t. Correspondingly, the changes in the state vector $\boldsymbol{N}'$ induced by chemical reactions (13) correspond to the changes in the number of molecules in correspondence with the stoichiometric schemes of the reactions

$$\boldsymbol{N} \to \boldsymbol{N}' = \{\ldots, N_i - 1, \ldots, N_j - 1, \ldots, N_k + 1, \ldots, N_l + 1, \ldots\} \tag{26}$$

Thus, the stochastic evolution of a chemically reacting rarefied gas within the thermal equilibrium approach is described by a homogeneous Markovian jump-like process on an integer N-size lattice of natural numbers. The evolution equation of this random process, describing probabilistic fluxes to the state $\boldsymbol{N}'$ and from the state $\boldsymbol{N}$, is the result of integration (over the velocity space) of stochastic master equation (20)

$$\frac{\mathrm{d}}{\mathrm{d}t}\phi(\boldsymbol{N}, t) = \sum_{m=1}^{M} \left[a_m(\boldsymbol{N}^m)\phi(\boldsymbol{N}^m, t) - a_m(\boldsymbol{N})\phi(\boldsymbol{N}, t) \right] \tag{27}$$

This equation is often referred to as the chemical master equation.[75, 76] Here, the functions $a_m(\boldsymbol{N})$ are analogues of the chemical reaction rate coefficients (19) used in chemical kinetics. The main and most important property of this equation is its linear dependence on the probability density $\phi(\boldsymbol{N}, t)$. The chemical master equation (27) is generally used to analyze strongly nonlinear and nonequilibrium chemical systems.[76]

3.5. Analogue Monte Carlo algorithm for solving the stochastic master equation

Direct methods for solving the stochastic master equation imply compilation and simultaneous solution of the system of equations for the probabilities of all possible trajectories of a state of chemically reacting rarefied gas. Unfortunately, this procedure can be implemented for only very simple chemical systems,[76] whereas in the case of real astrochemical systems this approach encounters great computational difficulties.[14, 22]

The Monte Carlo method, which implies generation of a sample of individual trajectories of a state of chemically reacting gas, is an efficient tool for studying complex chemical systems in the stochastic approximation. The procedure of generating an individual trajectory is much simpler: one must sample a sequence of transitions between the states of chemically reacting gas and the time intervals between the transitions, proceeding from correct probability distributions. To perform this procedure, the homogeneous Markovian jump process $\boldsymbol{C}(t)$ is replaced with the equivalent homogeneous Markovian chain ${}^{(s_t)}\boldsymbol{C}$, where s_t is the number of transitions (22) between states (21) for a time t. This equivalent correspondence is the basis of algorithmic realization, because the procedure of numerical realization of the chain ${}^{(s_t)}\boldsymbol{C}$ is strictly determined by relations (21) – (24). This procedure is an analogue algorithm of the Monte Carlo method for solving the stochastic master equation (20).

The rigorous scheme of simulating the Markovian chain ${}^{(s_t)}\boldsymbol{C}$ on the discrete time network $t_\delta = \delta\Delta t$, $\delta = 0, 1, \ldots$ includes, in correspondence with definitions (21) – (24), the following operations at a time step Δt, beginning with the state ${}^{(0)}\boldsymbol{C} = \boldsymbol{C}(t_{\delta-1})$ at the instant $t_{\delta-1}$:

(*a*) a current transition s is chosen, the transition frequency is calculated (23), and expectation time $\tau^{(s)}$ of this transition is randomly determined from the probabilistic distribution (24); this time is fixed in the transition counter

$$T^{(s)} = T^{(s-1)} + \tau^{(s)} \tag{28}$$

(*b*) if the transition counter satisfies the condition $T^{(s-1)} \leqslant \Delta t \leqslant T^{(s)}$, the new state is assumed to be $\boldsymbol{C}(t_\delta) = {}^{(s-1)}\boldsymbol{C}$; in the opposite case, the next transition is chosen [in correspondence with the probabilities (23)], and all operations are repeated beginning with the step *a*.

The set of algorithmical steps *a* and *b* is an exact analogue of the Monte Carlo method for solving the stochastic kinetic equation of a chemically reacting gas.[17, 18] Due to the linearity of Eqn (20) and, correspondingly, the analogue Monte Carlo algorithm for its solution, the dynamic, physical, and chemical gas characteristics are calculated by averaging the realizations of trajectories of the random process $\boldsymbol{C}(t)$.

3.6. Stochastic simulation algorithm

If the state vector $\boldsymbol{C}(t)$ is averaged over the velocity space with allowance for the equilibrium distribution (17), we obtain a stochastic simulation algorithm for the chemical reactions in a locally equilibrium (well-mixed) gas from the above-considered analogue algorithm of the Monte Carlo method for solving Eqn (20). This algorithm is an explicit and exact procedure of numerical realization of the above-

described stochastic process $\boldsymbol{N}(t)$. According to the theory of discrete Markovian processes, it includes the following operations:

— when a chemically reacting gas is in the state N at the instant t, the full chemical activity function is calculated:

$$a_0(\boldsymbol{N}) = \sum_{m=1}^{M} a_m(\boldsymbol{N}) \tag{29}$$

— two random numbers (r_1 and r_2), uniformly distributed over the unit interval, are chosen, and the expectation time τ is calculated from the equality

$$\tau = -\frac{1}{a_0(\boldsymbol{N})} \ln r_1 \tag{30}$$

and the number m of the next chemical reaction is calculated as the least integer satisfying the condition

$$\sum_{k=1}^{v} a_k(N) > r_2 a_0(\boldsymbol{N}) \tag{31}$$

— the result of the chosen chemical reaction (the new time $t \to t + \mathrm{d}t$ and state $\boldsymbol{N} \leftarrow \boldsymbol{N}^m$) is calculated;

— the new state is recorded, and all operations are repeated if the final time is not reached.

This algorithm and its different modifications were proposed by Gillespie.[75,77] The above-described algorithm is an analogue algorithm of the Monte Carlo method for solving the chemical master equation (27). However, from the computational point of view, it is fairly laborious, because one must sample all time-separated chemical reactive collisions. This laboriousness is especially pronounced if the amount of one of the reactants in the chemical reaction network is very large.[77]

4. Applications of the kinetic Monte Carlo method for studying suprathermal particles in astrochemistry

4.1. Suprathermal atoms in the upper atmospheres of planets of the Solar and extrasolar systems

In this subsection we present kinetic Monte Carlo models for studying the contribution of suprathermal hydrogen and oxygen atoms to the coronae and dissipation of atmospheres of the terrestrial planets. The rarefied gas of the upper planetary atmosphere is described using the kinetic Monte Carlo method,[10] which is equivalent to the solution of kinetic Boltzmann equations and provides dynamic and stochastic description of gas at the molecular level. The models take into account the most important photochemical and plasma sources of suprathermal atoms.

4.1.1. Suprathermal fractions of hydrogen, carbon, and oxygen atoms in the upper atmosphere of terrestrial-group planets

The thermosphere, exosphere, and ionosphere of Mars form a thin upper boundary (hot planetary corona). The solar energy and matter should either pass through it or be deviated from it. The Martian neutral corona, ionosphere, and residual magnetic fields interact directly with the leaked-in solar wind plasma to form a high-dynamic induced magnetosphere, which affects the structure and variability of the upper atmosphere and causes various plasma processes. In addition, atmospheric particles are excited under the action of radiation energy and solar wind plasma; the kinetic energy of some of them becomes sufficiently high to escape the planet. The immediate proximity of solar wind with the Martian ionosphere, as well as the significant extension of exosphere with respect to the planet size, cause precipitation of both neutral and ionized particles into the atmosphere. Neutral particles may have a sufficiently high energy to escape independently in view of their thermal distribution [thermal escape and(or) evaporation of atmosphere], or obtain a suprathermal energy necessary for escape from solar radiation and in subsequent chemical reactions (photochemical escape) or from collisions with the particles entering the atmosphere from outside [from above; for example, *via* sputtering and(or) precipitation of solar wind protons]. The escape rate of neutral particles was numerically estimated by combining measurements and simulation of atmospheric reservoirs for dissipation.[10,78] The total atmospheric dissipation due to ions and neutral particles is varied, depending on the same drivers that are observed at changes in the region of solar wind interaction with atmosphere. These variations can be extrapolated to estimate the total atmospheric loss during the Martian history using the scaling parameters or adjusting the models to make them consistent with the modern changes in the atmospheric loss rate.[78]

The kinetic Monte Carlo models for studying the distribution of suprathermal hydrogen and oxygen atoms in the Venus and Mars coronae were presented with sufficient completeness.[66,79–82] These models consider the elastic, inelastic, and superelastic (quenching of metastable excitation levels) collisions of suprathermal hydrogen and oxygen atoms with the atmospheric gas; the consideration is performed using the differential scattering cross sections, determining the scattering angles in these processes. Very important components of the numerical model are the photochemical and plasma sources of suprathermal atoms, such as dissociation of hydrogen and oxygen molecules under the action of UV radiation and the corresponding photoelectron flux, dissociative recombination of molecular ions, exothermic ion-molecular reactions, and charge exchange of hydrogen atoms with solar wind protons at exospheric altitudes.

The exothermic ion-molecular reactions (and especially dissociative recombination of molecular oxygen ions) are very important sources of suprathermal oxygen atoms in the upper atmospheres of terrestrial-group planets.[58,59,83] Some photochemical reactions responsible for the formation of hot oxygen were investigated.[60,84] These exothermic reactions, used in our models, are supplemented with a refined scheme of channels and energy yields for dissociative recombination of the molecular ion O_2^+:

$$O_2^+ + e \longrightarrow \begin{cases} O(^3P) + O(^3P) + 6.99\,eV \\ O(^3P) + O(^1D) + 5.02\,eV \\ O(^1D) + O(^1D) + 3.06\,eV \\ O(^1D) + O(^1S) + 0.84\,eV \end{cases} \tag{32}$$

Oxygen atoms are formed in the ground (^3P) and metastable (^1D, ^1S) electronic states with kinetic energy excess. The energy yields are calculated provided that oxygen ions occupy the ground vibrational level. Proceeding from the measurements performed,[85] the realization probabilities of channels (32) were taken to be, respectively, 0.22 : 0.42 : 0.31 : 0.05.

The precipitation of magnetospheric electrons with high kinetic energies, as well as the effect of photoelectrons, are accompanied by excitation, dissociation, and ionization of the atmospheric components; the corresponding processes are incorporated into the network of exothermic photochemical reactions used by us. In particular, the dissociation and dissociative electron-impact ionization (e_a) were considered as additional sources of hot oxygen atoms,

$$O_2 + e_a \longrightarrow \begin{cases} O(^3P) + O(^3P, ^1D, ^1S) + e_a + \Delta E_{O_2}^{dis} \\ O^+(^4S) + O(^3P, ^1D, ^1S) + e + e_a + \Delta E_{O_2}^{dis-i} \end{cases} \quad (33)$$

which are formed again in the ground (^3P) and electronically excited (^1D and ^1S) states with a kinetic energy excess of several electronvolts. The distributions of the excess kinetic energy of oxygen atoms at dissociation ($\Delta E_{O_2}^{dis}$) and dissociative ionization ($\Delta E_{O_2}^{dis-i}$) of oxygen molecules by an electron impact were estimated based on the measurements [86] and calculation results.[87] The cross sections for the dissociation processes were also taken from those studies.

The interactions of high-energy magnetospheric protons (precipitating in high latitudes) with atmospheric components are accompanied by the momentum and energy transfer in elastic and inelastic collisions, ionization, and charge exchange and electron capture in collisions with the main atmospheric molecules and atoms. Hot hydrogen atoms, formed under a proton impact, also affect the atmospheric components, transferring momentum and energy to them in elastic, inelastic, and ionization processes. The collisions, accompanying the penetration of high-energy protons and hydrogen atoms into the upper atmospheres of terrestrial-group planets, can be written as

$$H_f^+(H_f) + M \longrightarrow \begin{cases} H_{f'}^+(H_{f'}) + M^* \\ H_{f'}^+(H_{f'}) + M^+ + e \\ H_{f'}(H_{f'}^+) + M^+(M) + e \end{cases} \quad (34)$$

Here, M are the main atmospheric components: O_2, CO_2, CO, N_2, and O. The secondary fast hydrogen atoms $H_{f'}$ and protons $H_{f'}^+$, arising as a result of charge exchange and ionization, repeat the above-described cycle of impact processes. Correspondingly, the precipitation of magnetospheric protons and(or) solar wind protons into the atmosphere should be considered as a cascade process, accompanied, in particular, by the formation of constantly increasing fraction of suprathermal excited atoms M* of the atmospheric gas. This process is known in the literature as the atmospheric sputtering induced by high-energy ions.[88]

To study the penetration of a flux of high-energy protons and hydrogen atoms into the upper atmospheres of Mars and Venus, we used the kinetic Boltzmann equations,[89,90] because specifically these equations describe the scattering in elastic, inelastic, and ionization collisions and in the processes of charge exchange with the surrounding atmospheric gas, as well as the flux transport for the particles under consideration. An important consequence of the penetration of high-energy flux of protons and hydrogen atoms into the upper atmosphere is the formation of suprathermal oxygen atoms (O_h) due to the momentum transfer in elastic and inelastic collisions of the $H^+(H)$ flux with atmospheric atomic oxygen (O_{th}):

$$H^+(H) + O_{th} \longrightarrow H^+(H) + O_h \quad (35)$$

Under these conditions, the hot oxygen atoms moving upwards populate the corona, and their fraction with energies exceeding the gravitational binding energy with the planet forms a non-thermal escape flux.[62]

The hot oxygen atoms formed in the processes (32) – (35) lose their excess kinetic energy in collisions with the surrounding atmospheric gas and are height-distributed in the transition (from thermosphere to exosphere) region; their kinetics and transport are described by the Boltzmann equation

$$\boldsymbol{v}\frac{d}{d\boldsymbol{r}}f_{O_h} + \boldsymbol{s}\frac{d}{d\boldsymbol{v}}f_{O_h} = Q_{O_h}(\boldsymbol{v}) + \sum_{\substack{M=O,N_2,\\O_2,CO_2,CO}} J_{mt}(f_{O_h}, f_M) \quad (36)$$

where $f_{O_h}(\boldsymbol{r},\boldsymbol{v})$ and $f_M(\boldsymbol{r},\boldsymbol{v})$ are the velocity distribution functions of hot oxygen atoms and components of surrounding atmospheric gas, respectively. The left-hand side of the equation describes the transport of suprathermal oxygen atoms in planetary gravitational fields; the function Q_{O_h} in the right-hand side specifies the energy spectrum of the formation rate of hot oxygen atoms in the processes (32) – (35). The integrals J_{mt} for elastic and inelastic collisions of hot atoms with atmospheric particles are recorded in the standard form (16) on the assumption that the velocity distribution of the particles of surrounding atmospheric gas corresponds to locally equilibrium Maxwell distribution functions.

The thermalization rate of suprathermal oxygen atoms is determined to a great extent by the cross sections of collisions with the surrounding atmospheric gas. A key aspect of this numerical model is the stochastic interpretation of the distribution of scattering angles of hot oxygen atoms in elastic and inelastic collisions with atmospheric components. We used the calculations of differential scattering cross sections for elastic and inelastic collisions of suprathermal oxygen atoms with atomic oxygen [91] and molecular nitrogen.[92]

Similarly developed Monte Carlo models of the transport and kinetics of high-energy electrons were used to determine the dissociation rates of hydrogen and oxygen molecules under electron impact in CO_2-dominant [93] and H_2-dominant [94] atmospheres. The formation rates of suprathermal hydrogen and oxygen atoms at dissociative recombination of molecular ions and in exothermic photochemical reactions were calculated using the stochastic model.[79] After finding the formation rates of suprathermal hydrogen and oxygen atoms in the aforementioned photochemical and plasma sources, it became possible to calculate the kinetics and transport of hydrogen and oxygen atoms in the transition (from thermosphere to exosphere) regions of the atmospheres of Venus and Mars using the 1D or 3D versions of the stochastic model of planetary corona.[18,80]

Models based on the kinetic Monte Carlo method make it possible to investigate the structure of hot oxygen coronae of Venus, Earth, and Mars, formed due to the exothermic reaction: dissociative recombination of molecular oxygen ions. The calculated distributions of hot oxygen atoms in the upper atmosphere of Mars are presented in Fig. 7. The distributions of these atoms over kinetic energy (see Fig. 7 *a*) clearly demonstrate dominance of the fraction of atoms with suprathermal energies up to 2 eV (escape energy of oxygen atoms from the atmosphere) above the thermal fraction. Local thermal distributions of oxygen atoms

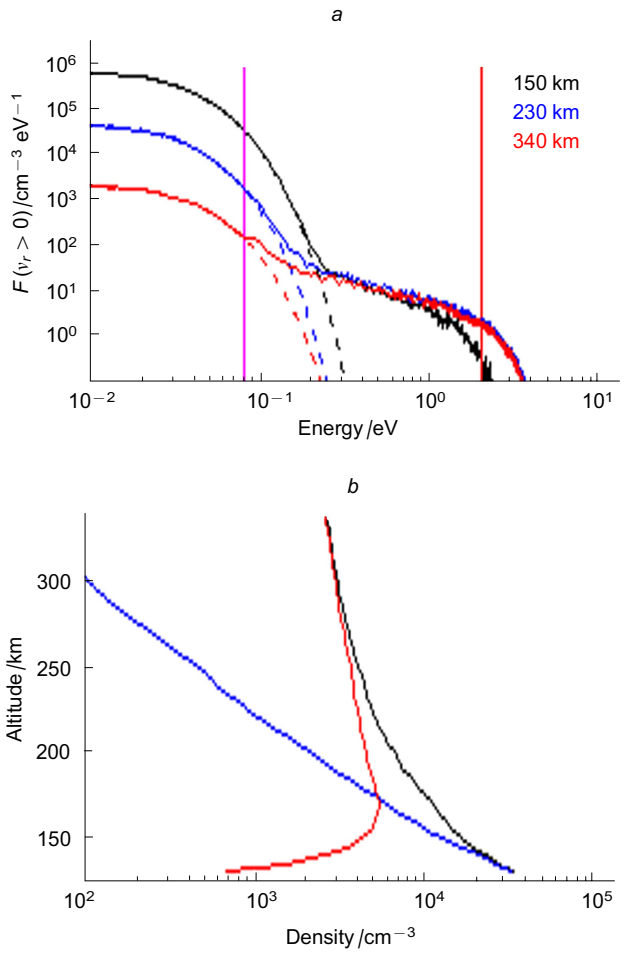


Figure 7. (*a*) Distribution functions of atomic oxygen in the upper atmosphere of Mars at different altitudes and (*b*) distribution of hot oxygen in the Martian corona;[66] (*a*) dashed lines are locally equilibrium distributions of thermal oxygen atoms; the atoms with energies enclosed between two verticals populate the hot corona; (*b*) altitude distributions of hot thermal and non-thermal (blue and red lines, respectively) oxygen atoms; the black line is the total distribution of hot oxygen atoms.

(dashed lines in Fig. 7 *a*) were calculated for Martian upper atmosphere temperatures of 190, 205, and 220 K at altitudes of 150, 230, and 340 km, respectively. Actually suprathermal atoms are of photochemical origin; they populate the hot oxygen corona of Mars (see Fig. 7 *b*). Moreover, dissociative recombination is now the main source of the non-thermal photochemical escape of oxygen atoms from the Martian atmosphere, which, correspondingly, makes up for loss of significant amounts of water for geological scale times.

The formation of a fraction of suprathermal hydrogen atoms due to the collisions of thermal hydrogen atoms with hot oxygen atoms was also investigated.[94] To this end, the kinetic Monte Carlo model of hot oxygen coronae[79] was modified by taking into account the elastic collisions between atmospheric hydrogen atoms and suprathermal oxygen atoms (formed due to the dissociative recombination of molecular oxygen ion) based on the general technique of stochastic simulation of the sources, kinetics, and dynamics of suprathermal particles in planetary atmospheres.[18] An important novel element of the developed model is the use of the total and differential scattering cross sections at collisions of hydrogen and oxygen atoms with suprathermal kinetic energies, which were calculated.[95] The differential collision cross sections of H and O atoms are known to determine the scattering angles in these processes and, finally, the efficiency of excess kinetic energy transfer from suprathermal oxygen atoms to thermal hydrogen atoms. New data on the scattering cross sections made it possible to investigate in detail the thermalization kinetics of newly formed suprathermal hydrogen atoms in elastic and inelastic collisions with the main atmospheric components. A large amount of experimental data on the upper atmosphere and ionosphere of Mars was obtained from the Viking spacecraft observations in 1976 in the period of very low solar activity; for this reason, the calculations presented below are based on input data for only low solar activity conditions.

Numerical realizations of the stochastic model of hot hydrogen and oxygen corona of Mars accumulated statistics of the velocity distributions of suprathermal hydrogen and oxygen atoms in all computational cells. These data made it possible to estimate the local fluxes of hot oxygen atoms in the transition region of the upper atmosphere of Mars. The energy spectra of hot oxygen atoms moving upwards at altitudes of 160 and 200 km are presented in Fig. 8 *a*. Hot particles are generally considered to be particles with kinetic energies exceeding the average thermal energy by a factor of 5 – 10. One can see that the suprathermal energy range up to 2 eV is significantly populated. Specifically these suprathermal oxygen atoms form the hot corona.

As calculations showed, the hot corona in the region above the exobase consists mainly of suprathermal oxygen atoms of photochemical origin, because the exosphere is populated by a large number of these particles due to the transport from lower layers. Correspondingly, the number of particles with energies exceeding the escape energy in the exosphere, becomes larger than that at altitudes below the exobase, where hot particles are efficiently thermalized in collisions with oxygen atoms and carbon dioxide molecules. The escape flux of suprathermal oxygen atoms from the atmosphere under low solar activity conditions was estimated to be 2.3×10^7 cm^{-2} s^{-1}, which is 30% lower than the escape flux for the models,[79, 81, 96, 97] disregarding the energy transfer from hot oxygen atoms to thermal hydrogen atoms in the transition region of the upper atmosphere of Mars. Therefore, this value should be considered as more representative.

The energy spectra of hot hydrogen atoms moving upwards at altitudes of 160 and 200 km are presented in Fig. 8 *b*. These atoms acquire excess kinetic energy in collisions with newly formed suprathermal oxygen atoms due to the momentum and energy transfer. Calculations showed that this process is an efficient source of hot hydrogen atoms in the thermosphere-to-exosphere transition region of the upper atmosphere of Mars. Indeed, significant nonequilibrium tails arise in the distribution of hydrogen atoms over kinetic energy in the suprathermal energy range. At the same time, due to the low escape energy of hydrogen atoms from the Martian atmosphere, the occupancy of the suprathermal energy range >0.08 eV by hot hydrogen atoms is much lower than for hot oxygen atoms in the regions above the exobase.

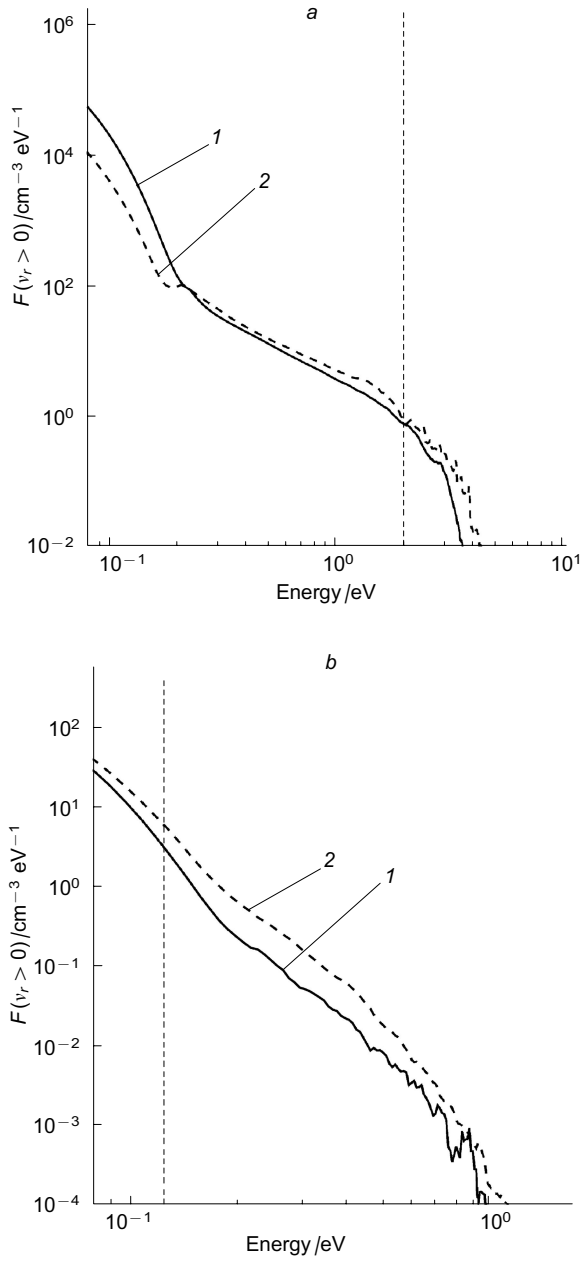


Figure 8. Kinetic energy distribution functions $F(v_r > 0)$ of upwards moving thermal and suprathermal (*a*) oxygen and (*b*) hydrogen atoms at altitudes of (*1*) 160 and (*2*) 200 km in the transition region.[82]
The vertical dotted lines indicate the escape energies of (*a*) ~2 eV for oxygen atoms and (*b*) ~0.12 eV for hydrogen atoms from the Martian atmosphere. The ordinate axis corresponds to the energy of 0.08 eV, above which oxygen and hydrogen atoms are considered as suprathermal.

The developed models made it possible to estimate the escape rates of hot oxygen and carbon atoms from the modern Martian atmosphere at low and high levels of solar activity. The most complete set of possible photochemical and plasmachemical sources of suprathermal carbon and oxygen atoms is taken into account, and the motion of these particles through the upper layers of atmosphere was investigated by the stochastic simulation method. It was shown [81, 82] that the dissociative recombination of molecular ions O_2^+, CO_2^+, which is the main source of hot atoms, leads to a loss rate of oxygen atoms from the atmosphere equal to $(2.5-3.0)\times10^{25}$ s^{-1}. It was shown for the first time [81, 82] that the escape velocity of oxygen atoms due to the dissociative recombination of the CO_2^+ ion is in the range from 1.0×10^{25} to 0.9×10^{25} s^{-1} for the same levels of solar activity. It was established [81, 82] that the non-thermal losses of carbon atoms are mainly due to the CO photodissociation with rates ranging from 0.8×10^{24} to 3.2×10^{24} s^{-1} for low and high solar activities, respectively. Depending on the solar activity level, the calculated loss of suprathermal carbon atoms turned out to be ~35 times higher than the loss of the CO_2^+ ion, obtained in recent measurements using the Analyzer of Space Plasma and Energetic Atoms (ASPERA-3) on the board of ESA Mars Express (MEX) spacecraft. The estimated losses of suprathermal carbon and oxygen atoms also exceed the loss of the Martian atmosphere due to the atmospheric sputtering by solar wind plasma and captured ionospheric ions.

The formation processes, kinetics, and transport of suprathermal and superthermal hydrogen and oxygen atoms in the transition (from thermosphere to exosphere) region of the upper atmosphere of Mars under precipitation of high-energy protons and hydrogen atoms were also investigated. Calculations showed that the distribution functions of oxygen atoms are essentially nonequilibrium in comparison with the thermal fraction of oxygen corona, because there is a large number of oxygen atoms in the suprathermal energy range (>0.08 eV). It is known [81, 82] that the non-thermal flux of escape oxygen atoms due to exothermic photochemical processes lies in the range of $(2.3-3.0)\times10^7$ cm^{-2} s^{-1} in dependence of the level of solar activity, whereas the escape flux of these atoms due to the precipitation of protons and hydrogen atoms from the solar wind is much lower: it is in the range of $(0.7-3.0)\times10^5$ cm^{-2} c^{-1} (Ref. 10) for the spectra of precipitating protons measured by MEX/ASPERA-3 under conditions of low solar activity. However, the preliminary measurements by Solar Wind Ion Analyzer (SWIA) on the board of NASA's Mars Atmosphere and Volatile Evolution (MAVEN) spacecraft showed that, in the case of high solar activity and (especially) at solar flares, the precipitation spectra are more kinetic-energy extended, and the differential fluxes may be several orders of magnitude higher than those measured by MEX/ASPERA-3 under conditions of low solar activity.

A modified kinetic Monte Carlo model of precipitation of protons and hydrogen atoms into the upper layers of the Martian atmosphere was used recently [98] to estimate the escape of hot oxygen atoms from the atmosphere, caused by the precipitation at high solar activity. The input data for the upper boundary of the model, located at a distance of 500 km, were the energy spectra of high-energy particles penetrating the atmosphere measured by MAVEN/SWIA.[99] Calculations revealed that the escaping flux of suprathermal oxygen atoms from the atmosphere lies in the range of $(1.7-0.8\times10^7$ cm^{-2} s^{-1} for the precipitation spectra of protons from the magnetosheath (model *1* in Fig. 9) and hydrogen atoms from unperturbed solar wind (model *2* in Fig. 9). One can see that the escape of neutral oxygen due to the precipitation of H^+ and H particles may compete with the photochemical escape under conditions of extreme solar events. Correspondingly, the dissipation of the upper atmosphere of Mars due to the precipitation of fluxes of

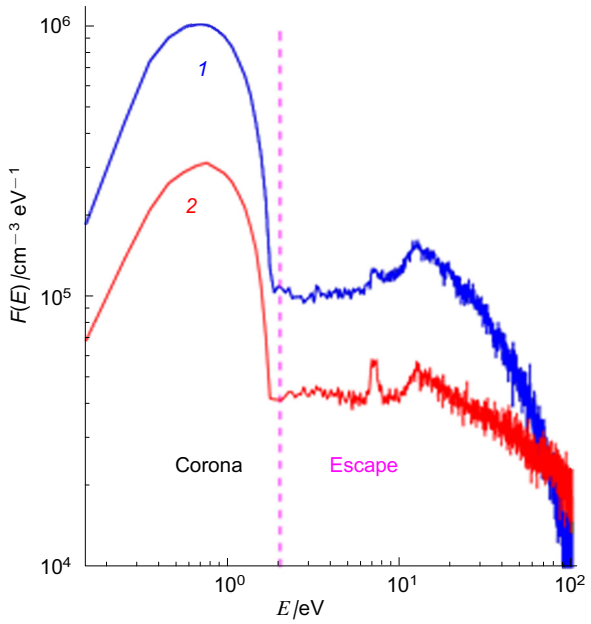


Figure 9. Energy spectra of the distribution function of upwards moving thermal and suprathermal oxygen atoms, calculated at an altitude of 300 km using the kinetic Monte Carlo model of precipitation of high-energy protons and hydrogen atoms in the upper atmosphere of Mars.
The measurements (SWIA on MAVEN) of the energy spectrum of (*1*) protons precipitating from the magnetosheath and (*2*) hydrogen atoms after the charge exchange with protons from unperturbed solar wind are used as the upper boundary condition. The vertical dashed line shows the escape energy of oxygen atoms from the Martian atmosphere.

high-energy protons and hydrogen atoms during solar flares can be dominant for the Martian atmosphere loss on astronomical time scales.[78]

The analysis of the distribution of suprathermal hydrogen, carbon, and oxygen atoms, formed in the upper atmospheres of terrestrial planets (Venus, Earth and Mars) is an important fundamental problem of comparative planetary aeronomy. The spacecraft investigations of the energy transfer in the solar wind – ionosphere – neutral Martian atmosphere systems confirmed the simulation results, according to which suprathermal hydrogen, carbon, and oxygen atoms are formed in large numbers in the upper atmospheres of terrestrial planets. One of the first results of the MAVEN spacecraft observations was confirmation of the presence of extended corona from the above atoms, which was observed using the Imaging UV Spectrograph (IUVS).[78] Indeed, the solar effect on the upper atmospheres of terrestrial planets *via* absorption of UV radiation and atmospheric sputtering by solar plasma leads to the formation of an extended neutral corona populated by suprathermal atoms. In turn, a hot corona causes variations in the flux of solar wind plasma at exospheric altitudes, which affects the long-period evolution of the planetary atmosphere. Therefore, the important components of extended neutral coronae are suprathermal H, C, and O atoms, which determine the processes of thermal and non-thermal atmospheric dissipation and characterize the space around the planet. A detailed analysis of the observational manifestations of suprathermal atoms in the upper atmospheres of terrestrial planets and interpretation of the observation results in theoretical models can be found, for example, in Refs 10, 11, 78 and 81. Data on the thermal and non-thermal dissipation of the upper atmospheres of Mars and Venus make it possible to draw important conclusions about the key processes of evolution of Earth's neighbouring planets and, correspondingly, about possible unfavourable trends in the Earth's evolution.

The significant contribution of suprathermal particles to the formation of hot planetary coronae[11,12,50] was confirmed by spacecraft observations and measurements, for example, the first *in situ* measurements of the suprathermal fractions of nitrogen and methane molecules in the upper atmosphere of Saturn's moon Titan, performed by the instruments of NASA's Cassini space mission;[63] the possibility of forming these suprathermal fractions was predicted theoretically (see, *e.g.*, Ref. 64). In particular, it was shown that, in order to approximate correctly the Titan exosphere density, measured by the Ion and Neutral Mass Spectrometer (INMS/Cassini), one must take into account the occupation of the high energy ranges in the distribution function and thus present the suprathermal particles generated below the exobase.[10,11,64] In this case the complete distribution function can be described by a Maxwell function combined with a power-law distribution for high energies. A detailed description of the results of measuring suprathermal methane and nitrogen molecules in the upper atmosphere of Titan and their interpretation in theoretical models can be found in reviews.[11,63]

4.1.2. Suprathermal hydrogen atoms in the upper atmospheres of exoplanets

One of the most significant achievements in the space research of the last two decades is the discovery of exoplanets and extrasolar planetary systems. The observations performed using ground-based and space telescopes in the IR and UV ranges provided first estimates of very important characteristics of planetary atmospheres in extrasolar planetary systems: their composition and thermal state. Currently, the processes of formation, stability, and evolution of the atmospheres of exoplanets are being actively studied using observations in ground-based and space telescopes and mathematical simulation. Important data on the nature of exoplanets have been obtained. Some unique features were revealed for the planetary systems of single and double stars with bodies radically differing from the planets of the Solar system (for example, hot Jupiters).

Soon after the first observation of an extended hydrogen cloud around a giant exoplanet — transit hot Jupiter HD 209458b (Ref. 100) — several research teams developed independently models[101–107] for studying the hydrodynamic escape from atmospheres of hot Jupiters. Despite the difference in their details, all these models are in satisfactory agreement with the observations of the hydrogen gas envelope of this exoplanet (whose orbit is close to the parent star) but do not make it possible to study its history on large time intervals. Similar to the impossibility of using time reversal for studying the evolution of planets in the early Solar system, including the loss of atmosphere by terrestrial-group planets, one cannot either find the sources of atmosphere formation for a specific exoplanet; however, one can compare the specific features of similar planets in different stages of their evolution.[9]

Because of the proximity of hot Jupiters to the host star, their atmosphere is affected by intense plasma and radiation fluxes. The latter heat the upper atmosphere to high temperatures, change significantly its chemical composition, and affects strongly the character of the planet evolution *via* high escape fluxes hydrogen atoms from the atmosphere. The excess thermal energy of the hydrogen atoms formed as a result of dissociation of molecular hydrogen is found from calculated and experimental distributions. They contain a fraction of relatively slow hydrogen atoms with kinetic energies of 0 – 1 eV and a peak near the thermal energy and a fraction of fast hydrogen atoms with kinetic energies of 1 – 10 eV and a peak near 4 eV. In the case of suprathermal hydrogen atoms, the efficiency of energy transfer from hot to thermal atoms and hydrogen molecules in elastic collisions is determined by the phase functions: scattering angle distributions. As follows from the experimental and calculation data, phase functions are generally characterized by the presence of peaks in the range of small scattering angles at relatively large elastic-scattering cross sections. Correspondingly, the, energy transfer efficiency depends strongly on the collision energy. These specific features of the elastic scattering of suprathermal hydrogen atoms from the thermal components of H_2, He, and H determine to a great extent the parameters of the suprathermal hydrogen fraction in the upper atmosphere of exoplanet.[94]

The kinetic Monte Carlo model[94] takes into account that the hydrogen atoms formed as a result of H_2 dissociation have excess kinetic energy; therefore, their distribution in the $H_2 \rightarrow H$ transition region of exoplanet's upper atmosphere is determined by solving the kinetic Boltzmann equation with a photochemical source of suprathermal hydrogen atoms. The functions of the source of suprathermal hydrogen atoms were determined from the rates of atmospheric gas photolysis caused by XUV radiation from the star and the related photoelectron flux.

The photoprocesses of absorption of XUV radiation from the star by exoplanet's atmospheric gas, which are accompanied by excitation, dissociation, and ionization of atmospheric components, as well as the formation of a photoelectron flux with energies sufficient for subsequent excitation and ionization of atomic and molecular hydrogen, were considered within this numerical model. To calculate the rates of photoprocesses, transfer, and collisional kinetics of photoelectrons in exoplanet's upper atmosphere, the Monte Carlo model[93] adapted to hydrogen atmospheres was applied. This model realization used the experimental and calculated data on the cross sections and scattering angle distributions in elastic, inelastic, and ionization collisions of electrons with the main components: H_2, He, and H.

The model made it possible to estimate for the first time the formation rate and energy spectrum of the hydrogen atoms with excess kinetic energy that arose as a result of H_2 dissociation in the upper atmosphere of the exoplanet HD 209458b (Fig. 10). The numerical stochastic model of a hot planetary corona,[18] adapted to hydrogen atmospheres of exoplanets on orbits close to the parent star, was applied to analyze in detail the kinetics and transport of suprathermal hydrogen atoms in the $H_2 \rightarrow H$ transition region of the extended upper atmosphere of HD 209458b. Calculations of the distribution functions showed[94, 108] that the processes of molecular hydrogen dissociation are accompanied by the formation of an ascending flux of suprathermal hydrogen atoms with kinetic energies exceeding the local escape energy and their transport to the most upper layers of the $H_2 \rightarrow H$ transition region. The escape flux was estimated to be 5.8×10^{12} cm^{-2} s^{-1} for a moderate level of stellar activity (XUV radiation), which leads to a rate of 5.8×10^9 g s^{-1} for the atmospheric loss caused by H_2 dissociation. These estimates are close to a value of $\sim 10^{10}$ g s^{-1}, which is the atmospheric loss rate for HD 209458b found from the observations.[100] Therefore, the calculated estimate of the atmospheric loss rate for this exoplanet can be considered as a lower value, because the calculations were performed for the XUV radiation levels corresponding to moderate stellar activity. Obviously, in the case of high stellar activity, the contribution of the H_2 dissociation under hard XUV radiation from the star and the corresponding photoelectron flux to the generation of hydrogen atoms escaping from the atmosphere should increase. Therefore, the processes of H_2 dissociation as a source of suprathermal hydrogen atoms must be considered in modern aeronomic models of physical and chemical processes occurring in the upper atmospheres of exoplanets.[108]

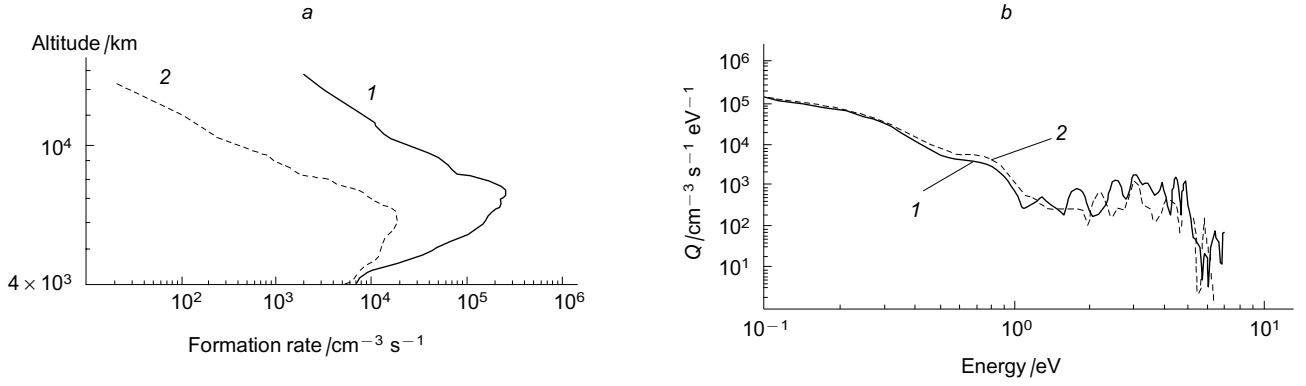


Figure 10. (*a*) Change in the formation rate of suprathermal hydrogen atoms upon dissociation of molecular hydrogen induced by (*1*) XUV photons and (*2*) photoelectrons in the upper atmosphere of hot Jupiter HD 209458b and (*b*) energy spectrum (Q) of the hydrogen atoms formed at altitudes of 5000 (*1*) and (2) 8000 km upon dissociation and dissociative ionization of H_2 by photoelectrons.[94]

Observations revealed that the atmospheres of hot Jupiters extend beyond the Roche lobe, which causes an intense hydrodynamic outflow of atmospheric material.[100] The upper hydrogen atmosphere is heated due to the absorption of XUV radiation from the parent star in the range of 1 – 100 nm. This radiation is absorbed mainly in the reactions of ionization of atomic hydrogen and helium, as well as the ionization, dissociation, and dissociative ionization of molecular hydrogen. Correspondingly, the heating efficiency is determined as the ratio of the total rate of atmospheric-gas local heating to the absorption rate of stellar radiation energy. This parameter is important for the exoplanets located close to the star, which are exposed to intense fluxes of stellar radiation in the XUV and soft X-ray ranges. In particular, calculations of the heating of the hot Jupiter HD 209458b by hard UV stellar radiation [109, 110] revealed that the heating efficiency does not exceed 0.25 at thermospheric heights if the effect of suprathermal photoelectrons is taken into account.

Depending on the upper atmosphere composition and heating efficiency, the escape mode may change from hydrostatic (evaporation) to hydrodynamic (outflow). To analyze this problem, a one-dimensional self-consistent model of hot Jupiter atmosphere was constructed,[111] which included three main components: Monte Carlo, chemical kinetics, and gas dynamics modules. The heating rate of the atmosphere, photolytic reaction rates, and the rates of the reactions induced by suprathermal photoelectrons were calculated in the Monte Carlo module by solving the Boltzmann equation.[110] In the chemical kinetics module, the system of chemical kinetics equations was solved based on the photolytic reaction rates obtained in the Monte Carlo module and the concentrations of atmospheric components in each cell were calculated. The profiles of macroscopic atmospheric parameters (density, escape velocity, and temperature) were calculated in the gas dynamics module. The photoelectron contribution was taken into account in the atmosphere heating function. Since the model is one-dimensional, it was necessary to use the approximation of three-dimensional Roche potential, equating it to the gravitational potential along the line connecting the planet and star centres.

The atmosphere of the hot Jupiter HD 209458b was simulated taking into account the simplified Roche potential, and the influence of the reactions with participation of suprathermal photoelectrons on the dynamics, changes in the chemical composition, and outflow rate of the hydrogen – helium atmosphere was investigated.[111] Calculations were performed within two models, taking into account the photoelectrons (model M+) and disregarding them (model M–). The calculation data were compared with the results obtained by other researchers. The calculation showed that the contributions of suprathermal electrons cause significant differences in the density profiles in the M+ and M– models. The gas flow velocities behind the Lagrange point $L1$ (4.5 of the planet radius) are practically the same in both models, whereas the densities differ by several times. This leads to a difference in the atmospheric gas temperatures (Fig. 11) and, correspondingly, its atmospheric loss rates due to the hydrodynamic escape.

The calculated [111] atmospheric loss rates (v_a) were compared with the observational estimates and calculations of other researchers, specifically, with the estimate obtained from the analysis of the Hubble space telescope (HST) observations [100] and the results of gas-dynamic calculations within the models.[104, 106]

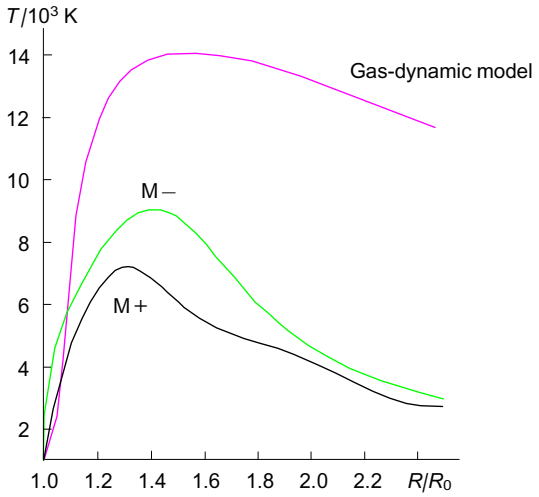


Figure 11. Radial profiles of the atmospheric temperature of hot Jupiter HD 209458b, calculated within the models taking into account (M+) and disregarding (M–) the kinetics and transport of suprathermal photoelectrons; the calculation results obtained within the gas-dynamic model are given for comparison [101] (R is the distance from the planet centre; R_0 is the planet radius).

v_a/g s^{-1}	$\sim 10^{10}$	4×10^{10}	7×10^{10}	4×10^{10} (see §)	8×10^{9} (see ¶)
Ref.	100	104	106	111	111

Despite the difference in the details (physical model completeness, numerical methods of solution, suggested main atmospheric components, and chemical complexity of the medium), both models yield results that are in satisfactory agreement with the observations of the hydrogen cloud around the hot Jupiter HD 209458b. From the evolutionary point of view, the most interesting fact is that the found model values of hydrogen loss rates coincide with an accuracy of a factor of several units.

The found atmospheric parameters can be used as boundary conditions for the three-dimensional gas-dynamic calculations modelling the planet interaction with stellar wind. Estimates of the efficiency of conversion of stellar XUV radiation (which plays an important role in the processes of ionization, photochemistry and thermal dissipation of the upper atmosphere of planets exposed to intense extreme radiation fluxes) into heat energy are especially demanded for. It was established that the heating efficiencies calculated for the solar spectrum can also be applied to stars that are younger than the Sun after scaling the photon flux in the soft X-ray and extreme UV ranges, in correspondence with the observation data on stellar spectra. Thus, one can estimate the atmosphere outflow rates for planets near young stars with spectra differing from the solar spectrum. One would expect future observations to impose additional limitations on the developed models of dissipation of exoplanet atmospheres, which will facilitate progress in planetary aeronomy and provide a deeper insight into the evolution processes, including the formation

¶ Calculation within the M+ model.
§ Calculation within the M– model.

of atmospheres and climate on the terrestrial-group planets in the Solar system.

4.2. Suprathermal atoms and molecules in the gas envelopes of icy moons of Solar system planets

The outer regions of the Solar system are characterized by a large variety of celestial bodies. Examples are icy moons of giant planets, such as Europa (Jupiter's moon) with its bizarre surface; small but geologically active Enceladus (Saturn's moon); Titan, which is the only Saturn's moon with a significant atmosphere; dwarf planet Pluto with nitrogen glaciers; and many others. Spacecraft measurements performed in the last 25 years showed that many of these celestial bodies are ocean worlds with liquid water under icy surfaces. Ocean worlds, forming a new group of celestial bodies, are of interest for researchers because they may serve as habitats.[112] As far as we know, a necessary condition for life existence, along with the energy and nutrition supply and stable environment, is the presence of liquid water. Some of these icy celestial bodies meet these requirements. The main problems to solve are as follows: it is necessary to identify ocean worlds; characterize the oceans; estimate their habitability; and, in the long run, study any form of life that can be found in these potential habitats. This all-inclusive purpose covers, in particular, the problem of determining characteristics and ways of chemical exchange between the subglacial ocean, icy surface, and gaseous envelope of celestial body under consideration.[113 – 116]

During the last two and half decades Jupiter's system has been intensively studied using both orbital and ground-based instruments. The interest in this system is primarily due to the presence of such a unique and interesting icy moon as Ganymede in it. Observations showed that Ganymede is the only moon with intrinsic magnetosphere, it has a significant near-surface oxygen atmosphere and an extended atomic-hydrogen envelope, and there is likely an ocean under its icy surface. Ganymede's magnetosphere is a unique phenomenon: it is the only known example of a magnetosphere formed upon a collision of a sub-Alfvén flow of heavy ions with a strong intrinsic planetary magnetic field.

In the next subsection we discuss the main chemical schemes of the formation of Ganymede's H_2O- and O_2-dominant atmospheres and present a kinetic Monte Carlo model which considers the role of suprathermal atoms and molecules in the formation of a relatively dense near-surface (Knudsen) layer at the icy moon surface.

4.2.1. Physical model of the formation of H_2O- and O_2-dominant atmospheres

The range of values of water-molecule sources on an icy moon surface is generally set based on experimental data on the photolysis and radiolysis yields, as well as NASA's Galileo spacecraft data on the magnetospheric plasma fluxes in the vicinities of orbits of Jupiter's moons Europa and Ganymede.[117] Estimates of the fluxes of H_2O molecules to the atmosphere under sputtering of icy Europa's surface vary from $\sim 2\times 10^8$ to $\sim 2\times 10^{11}$ cm^{-2} s^{-1} (Ref. 118). Measurements with the Energetic Particle Detector (EPD) on board of Galileo spacecraft showed protons to be the main component of high-energy ion flux. The EPD measurements correspond to a flux of H_2O molecules of $\sim 1.8\times 10^8$ cm^{-2} s^{-1} (Ref. 117); specifically this value was used in the simulation. As follows from laboratory measurements, the energy spectra of water molecules under ion sputtering of icy surfaces[119] are characterized mainly by a thermalized core in the region of low kinetic energies (because the sputtering of frozen molecular solids is basically determined by the solid chemistry initiated by a penetrating ion, the so-called ice radiolysis)[118] and a supplemented non-thermal distribution in the region of high kinetic energies. Correspondingly, when bombarding an icy surface, heavy ions knock out O_2 and H_2O molecules from the surface with the following (measured in laboratory) distributions:[120]

$$F_{O_2}^{surface}(E) \sim \frac{U}{(E+U)^2}\,(U = 1.5\,\mathrm{e} - 3\,\mathrm{eV}) \tag{37}$$

$$F_{H_2O}^{surface}(E) \sim \frac{2\,EU}{(E+U)^3}\,(U = 5.5\,\mathrm{e} - 3\,\mathrm{eV}) \tag{38}$$

which approximate the measured energies of knocked-out molecules under ice bombardment by heavy ions with energies on the order of several tens of keV.

Photolysis of an icy moon surface under UV irradiation also leads to ejection of parent molecules. Here, the kinetic energy distributions of ejected molecules are close to Maxwellian at an intermediate temperature of the icy surface.

$$F^{surface}(E) \approx \frac{E}{(kT)^2}\exp\left(-\frac{E}{kT}\right) \tag{39}$$

In other words, the photolysis of an icy surface can be considered as a thermalized surface source of parent molecules. Other thermal sources of parent molecules on Ganymede's surface are evaporation (sublimation), degassing, and micrometeoroid impacts. Moreover, since sputtering, radiolysis, and photolysis occur in porous regolith on moon's surface, the ejected molecules can be subjected to further thermalization under collisions with ice and dust grains in the surface layer.

Thus, thermal degassing and nonthermal radiolysis of water ice on the surface of moons in the systems of giant planets leads to the formation of rarefied gaseous envelopes, whose main (parent) component is H_2O molecules, with an admixture of molecular products of radiolysis: H_2 and O_2. The ionization processes in these rarefied gaseous envelopes occur under the UV irradiation from the Sun and the impact of solar wind plasma and(or) magnetospheric plasma. The chemical complexity of icy moon gaseous envelope is due to the processes initiated by fluxes of UV photons ($h\nu$) and plasma electrons (e_p) in the rarefied gas of H_2O-dominant atmosphere:

$$H_2O + h\nu,(e_p) \rightarrow H_2 + O(^1D) + (e_p) \tag{40}$$

$$OH + H + (e_p) \tag{40a}$$

$$H + H + O + (e_p) \tag{40b}$$

$$H_2O + h\nu,(e_p) \rightarrow H_2O^+ + h\nu,(e_p) \tag{41}$$

$$H + OH^+ + e + (e_p) \tag{41a}$$

$$H_2 + O^+ + e + (e_p) \tag{41b}$$

$$OH + H^+ + e + (e_p) \tag{41c}$$

$$H_2 + h\nu,(e_p) \rightarrow H(1s) + H(1s, 2s, 2p) \tag{42}$$

$$H_2^+ + e + (e_p) \quad (42a)$$

$$H(1s) + H^+ + e + (e_p) \quad (42b)$$

$$O_2 + h\nu,(e_p) \rightarrow O(^3P) + O(^3P, {}^1D, {}^1S) \quad (43)$$

$$O_2^+ + e + (e_p) \quad (43a)$$

$$O(^3P) + O^+ + e + (e_p) \quad (43b)$$

The processes of photolysis and electron impact (40) – (42b) are accompanied by the formation of chemically active radicals with excess kinetic energy (H, O, and OH) and H^+, O^+, OH^+, and H_2O^+ ions in the reactions of dissociation, direct ionization, and dissociative ionization of parent H_2O molecules with admixture of molecular products of radiolysis: H_2 and O_2. Photolysis products are also affected by fluxes of UV photons and plasma electrons in the reactions

$$H, O + h\nu,(e_p) \rightarrow H^+, O^+ + e + (e_p) \quad (44)$$

$$OH + h\nu,(e_p) \rightarrow H, O(^3P, {}^1D, {}^1S) \quad (45)$$

$$OH + e + (e_p) \quad (45a)$$

$$H + O^+ + e + (e_p) \quad (45b)$$

$$O + H^+ + e + (e_p) \quad (45c)$$

Further chemical changes in the composition of rarefied atmosphere are due to the neutral – neutral and ion-molecular reactions and processes of dissociative recombination of molecular ions with thermal electrons.[121]

It is known that high-energy magnetospheric ions, measured by EPD on the board of Galileo spacecraft (see, *e.g.*, Ref. 117), pass through the rarefied atmosphere of icy moon practically without collisions and cause only sputtering of its icy surface, whereas the low-energy plasma interacts with the atmospheric gas *via* collisions. This plasma leads to atmospheric sputtering[122] through collisional processes, which are accompanied by dissociation, ionization, and momentum and charge transfer.

Magnetospheric ions transfer their kinetic energy to parent atmospheric molecules O_2 and H_2O in elastic and dissociative collisions, which leads to the formation of suprathermal H, O, and OH particles. The model under consideration uses the following concept of low-energy-plasma affecting the atmosphere:[123] a flux of $\sim 10^8$ corotation magnetospheric ions O^+, passing through 1 cm^2 per second, having a Maxwellian energy distribution with a characteristic energy $E_0 = 0.75$ keV (*i.e.*, with a mean ion energy of 1.5 keV).

An additional source of formation of hot oxygen and water molecules is thermalization of primary suprathermal atoms in the atmospheric gas. Suprathermal hydrogen and oxygen atoms and OH radicals lose their excess kinetic energy as a result of elastic and inelastic collisions with the main atmospheric components (O_2 and H_2O). However, in the case of primary suprathermal atoms with a high initial energy, their elastic and inelastic collisions with atmospheric thermal oxygen may give rise to the so-called secondary suprathermal oxygen molecules, whose energy often exceeds the escape energy. Thus, the local kinetics of relaxation collisions of suprathermal oxygen atoms plays an important role, determining the balance between the thermalization rates of primary suprathermal atoms and the formation of secondary suprathermal hydrogen and oxygen atoms and molecules.

4.2.2. Numerical model of the formation of H_2O- and O_2-dominant atmospheres

The atmospheric gas flow in the rarefied gaseous envelope of an icy moon is nonequilibrium for the following reasons:

— parent H_2O molecules and molecular products of ice radiolysis, H_2 and O_2, are knocked out from the surface as a result of the action of thermal and non-thermal surface sources: thermal evaporation and non-thermal sputtering of the icy moon surface by high-energy magnetospheric plasma ions;[118]

— products of dissociation of parent molecules are formed with an excess kinetic energy, *i.e.*, they are suprathermal;[113, 114]

— atmospheric gas leaves to the Jupiter's inner magnetosphere due to the so-called atmospheric sputtering processes: momentum transfer and dissociation in collisions with the low-energy magnetospheric plasma.[122] Atmospheric gas is also lost in the charge exchange reactions of the main atmospheric molecules with the ionospheric ions captured and accelerated by the magnetospheric plasma: O_2^+ and H_2O^+ (Ref. 124).

Therefore, the gas flow in the near-surface gaseous envelope of Ganymede, where the Knudsen number is <0.1, should be described by the kinetic Boltzmann equations for all atmospheric components: [113]

$$\boldsymbol{v}\frac{\mathrm{d}}{\mathrm{d}\boldsymbol{r}}f_i + \boldsymbol{g}\frac{\mathrm{d}}{\mathrm{d}\boldsymbol{v}}f_i = Q_i^{(v)} + Q_i^{(e)} + \sum_j \sum_m J_m(f_i, f_j) - L_i^{\mathrm{plasma}} \quad (46)$$

Here, $f_i(\boldsymbol{r},\boldsymbol{v})$ are the distribution functions of the atmospheric components ($i,j = H_2O$, OH, O, O_2, H, H_2) over translational and internal degrees of freedom; $\boldsymbol{g}$ is the acceleration of gravity for Ganymede; and J_m are the collisional terms for elastic, inelastic, dissociative, and ionization processes and charge exchange reactions.[18] The sources of parent H_2O molecules and molecular products of radiolysis (H_2 and O_2), due to the surface sputtering and evaporation, are set by boundary conditions on the icy moon surface. The terms $Q_i^{(v)}$, $Q_i^{(e)}$ are sources of neutral and ionized particles during photolysis and electron impact, which have the form

$$Q_i^{(v)} = \sum_j A_{j\rightarrow i}\, n_j - n_i \sum_j A_{i\rightarrow j} \quad (47)$$

$$Q_i^{(e)} = \left(\sum_j a_{j\rightarrow i}\, n_j - n_i \sum_j a_{i\rightarrow j} \right) n_e \quad (47a)$$

Here, the coefficients $A_{j\rightarrow i}$ and $a_{j\rightarrow i}$ determine the photolysis and electron impact rates; they are calculated [115, 121] using the model flux of UV radiation from the Sun and the energy distribution of magnetospheric electrons.

The last term L_i^{plasma} in Eqn (46) describes the loss of neutral components due to the charge exchange reactions with corotation ions of magnetospheric plasma and captured ionospheric ions. The same term specifies the source of thermal ions generated during charge transfer to the atmospheric components. The neutral atoms and molecules formed as a result of charge exchange have high energies and, correspondingly, escape from the icy moon exosphere into the giant planet system. The steady-state solutions for this system of kinetic Boltzmann equations can be obtained using the kinetic Monte Carlo method.[18]

4.2.3. Suprathermal atoms and molecules in Ganymede's gaseous envelope

Observations have shown that Ganymede is surrounded by a relatively dense near-surface O_2-dominant atmosphere and a rarefied extended corona consisting of atomic hydrogen. There is likely an ocean under its icy surface. The presence of extended H corona, in agreement with the observations,[125] was confirmed [126] based on the observations using the Space Telescope Imaging Spectrograph (STIS) installed on the HST. In addition, several UV emission measurements demonstrated the presence of atomic oxygen in Ganymede's atmosphere. Observations with a high-resolution spectrograph on board of HST revealed [127] excess emissions of atomic oxygen in the 130.4- and 135.6-nm lines in the solar spectrum reflected from Ganymede. These observations were interpreted as the existence of a molecular oxygen atmosphere with a column concentration ranging from 10^{14} to 10^{15} cm^{-2}. The observations confirmed also that the oxygen emission is concentrated near the polar regions. Later investigations, performed with a higher resolution [126] using the STIS not only confirmed that the UV luminescence is observed mainly in latitudes above $\pm 45^\circ$ but also showed that it is concentrated near the cusp separating open and closed lines of force of Ganymede's magnetic field.

Ganymede, which has a high astrobiological potential, is one of the most important objects studied by space missions in Jupiter's system.[112] Calculations of Ganymede's rarefied gaseous envelope were performed for the region extending from the surface (where collisions of neutral particles in the relatively dense near-surface (Knudsen) layer are important) to altitudes of ~ 500 km, at which the atmosphere becomes practically collisionless.[113–116] The size of the calculation cell closest to the surface, determined by the local mean free path, was estimated to be $\sim 1.5 \times 10^5$ cm for the models under consideration. In correspondence with the numerical approach in use, the atmospheric gas parameters within a specified cell were assumed to be constant. Calculations were carried out for the two aforementioned formation sources [116–118] of this gaseous envelope: (i) sputtering (radiolysis) of the icy surface by high-energy magnetospheric ions in moon's polar regions and (ii) evaporation of water ice by solar radiation in the subsolar region. Two characteristic models were considered.

Model A describes the subsolar region (in the latitude range $\lambda = 0^\circ - 15^\circ$), where water ice is evaporated under solar radiation. It was assumed that parent water molecules, as well as H_2 and O_2 molecules (products of water ice photolysis on Ganymede's surface) leave the surface with kinetic energies and directions corresponding to the above-mentioned Maxwellian distribution (39). The local flux of water molecules ejected from the surface was set at the subsolar point $\lambda = 15^\circ$ to be $F(\lambda = 15^\circ) = 1.4 \times 10^{13}$ cm^{-2} s^{-1}. The surface temperature at the subsolar point was $T_s(\lambda = 15^\circ) = 148$ K.

Model B considers moon's polar regions (latitude $\lambda \approx 90^\circ$), in which the main source is water ice radiolysis by magnetospheric ions. The surface temperature on the pole was taken to be $T_s(\lambda = 90^\circ) = 80$ K. The water ice radiolysis near the pole is accompanied by the formation of upward fluxes of molecules and atoms (H_2O, OH, O, and H), whose energy distributions are set by function (38), and the magnitudes are $F_{H_2O}(\lambda = 90^\circ) = 1.8 \times 10^8$ and $F_{H,O,OH} = 1.0 \times 10^7$ cm^{-2} s^{-1}. The upward fluxes of molecular radiolysis products, H_2 and O_2, were assumed to be $F_{H_2}(\lambda = 90^\circ) = 2.8 \times 10^9$ cm^{-2} s^{-1} and $F_{O_2}(\lambda = 90^\circ) = 1.4 \times 10^9$ cm^{-2} s^{-1}. However, their energy spectra were approximated by the Maxwellian distribution, because it was assumed that these radiolysis products have enough time to be thermalized in the subsurface icy layer before leaving the surface.[114, 115]

The microscopic characteristics of atmospheric gas flow for the models A and B are presented in Fig. 12, which shows the energy spectra of upward (moving away from the surface) and downward (moving to the surface) fluxes of water molecules and ice radiolysis product — molecular oxygen — at altitudes of 1.5, 12.5, and 100 km for model A. These altitudes are characteristic of, respectively, the near-surface relatively dense atmosphere (Knudsen layer), the transition region, and the exosphere with dynamic mode of atmospheric particle escape.[113–115]

Calculations showed [115] that the distributions of fluxes of water molecules in the subsolar region of Ganymede's atmosphere have the following properties:

— a thermal core is formed in the energy spectrum of the near-surface layer close by the subsolar region due to the presence of initial thermal source on the surface — evaporation of water ice, as well as the physical processes of absorption and thermal desorption at the icy surface/atmosphere interface;[113]

— insignificant suprathermal tails are formed in the energy range above ~ 0.2 eV (see Figs 12 *a*, *c*) at all altitudes due to the collisions with suprathermal products of water vapour dissociation;[114]

— the transition region and external exosphere are populated mainly by thermal water molecules and products of water photolysis with suprathermal energies; these altitudes are reached by the water molecules that were injected into the atmosphere with initial suprathermal energies as a result of evaporation from the surface or accumulated these energies in collisions with suprathermal photolysis products.

An analysis of the structure of the energy spectra of H_2O fluxes showed [114–116] that the altitude distribution of the main components of Ganymede's atmosphere in the subsolar region at an altitude of 10 km is determined by the interactions occurring at the atmosphere/icy surface interface, whereas the energy distribution of gas particles in the upper layers (at altitudes of 100 km or higher) is determined by suprathermal particles, both those supplied by the surface sources and those formed during photolysis [see Eqns (40) – (45c)].

The calculation results for model B, which describes the Ganymede's near-surface atmosphere in the polar region, are presented in Figs 12 *b*, *d*, which show the energy spectra of upward and downward fluxes of the O_2 molecules formed as a result of water ice radiolysis on moon's surface, calculated for altitudes of 1.5, 12.5, and 100 km.

In correspondence with the calculation results,[115] the main neutral component in the near-surface atmospheric layer in Ganymede's polar regions is molecular oxygen: a stable product of water ice radiolysis under impact of magnetospheric ions. The distributions of upward and downward fluxes of O_2 molecules have the following properties:

— a thermal Maxwell core is formed in the energy spectrum of the near-surface region due to the physical

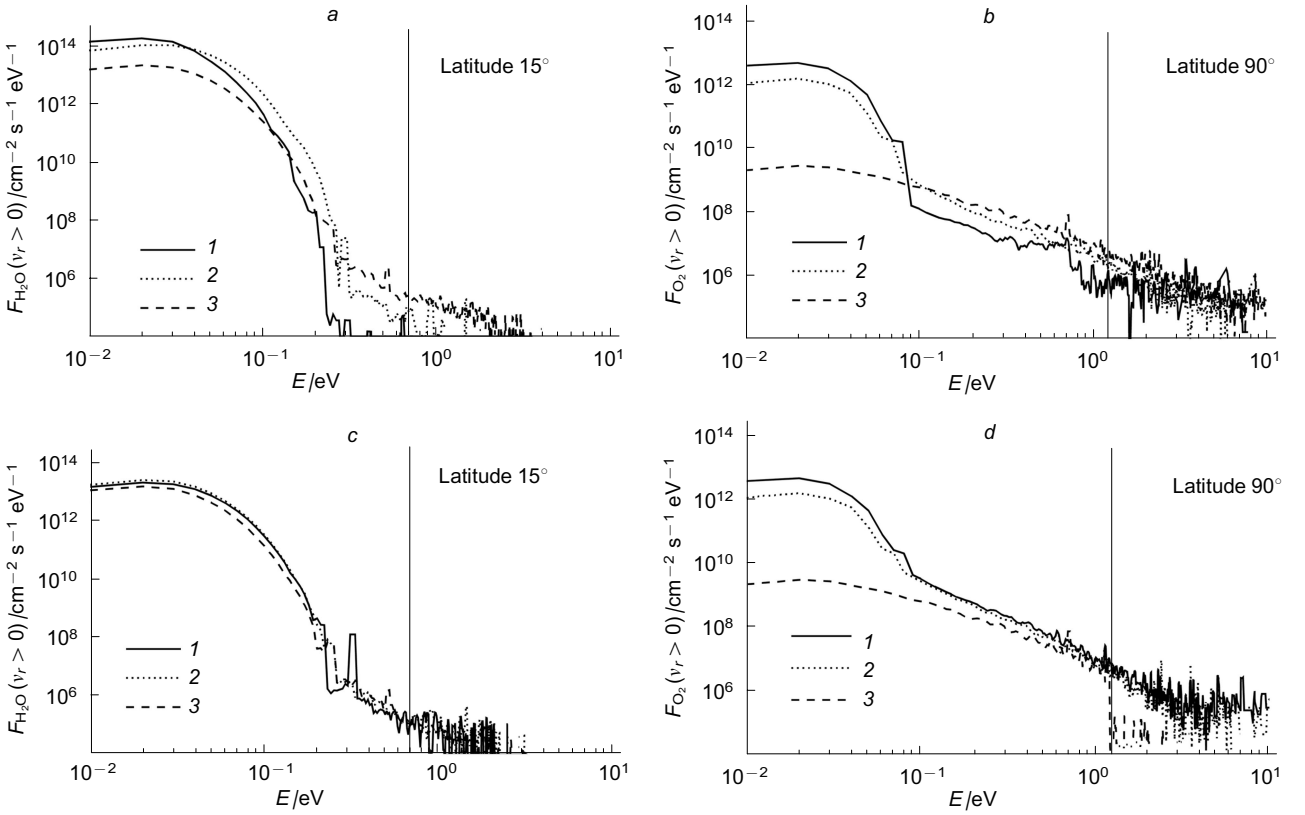


Figure 12. Energy spectra of the (*a*, *b*) upward and (*c*, *d*) downward fluxes of (*a*, *c*) parent H_2O molecules for model A (subsolar region) and (*b*, *d*) O_2 molecules for model B (polar region), calculated for altitudes of (*1*) 1.5, (*2*) 12.5, and (*3*) 100 km.[115] The vertical lines indicate the escape energies of H_2O and O_2 molecules from Ganymede's atmosphere.

processes of exchange at the icy surface/atmosphere interface (*i.e.*, the processes of absorption and thermal desorption of oxygen molecules);

— significant suprathermal tails are formed in the energy range above ~0.1 eV at all altitudes (see Figs 12 *b*, *d*) both due to the surface sputtering [non-thermal source with spectrum (37)] and atmospheric sputtering (20) by the magnetospheric plasma; an important source of oxygen molecules with excess thermal energy is the collisions with suprathermal products of dissociation of H_2O and O_2;

— the transition region and exosphere are populated mainly by suprathermal oxygen molecules; these altitudes are reached by the oxygen molecules injected into atmosphere with initial suprathermal energies during surface sputtering or acquiring these kinetic energies in collisions with suprathermal dissociation products of H_2O and O_2 and with magnetospheric plasma ions; the external exosphere is populated by oxygen molecules with energies close to the escape energy from the atmosphere or exceeding it.

All macroscopic characteristics of the atmospheric gas flow in Ganymede's near-surface atmosphere are estimated by averaging the microscopic characteristics calculated in the simulation: the distribution functions of atmospheric gas particles over kinetic energy. Figure 13 *a* shows high-altitude distributions of the numerical densities of parent H_2O molecules and neutral products of photolysis and chemical evolution of the gaseous envelope (H, O, and OH) for the subsolar point model. The photolysis products of parent molecules are formed in the processes of dissociation and dissociative ionization with excess kinetic energy; therefore, the atoms and radicals moving upwards easily escape from the atmosphere (their average velocities greatly

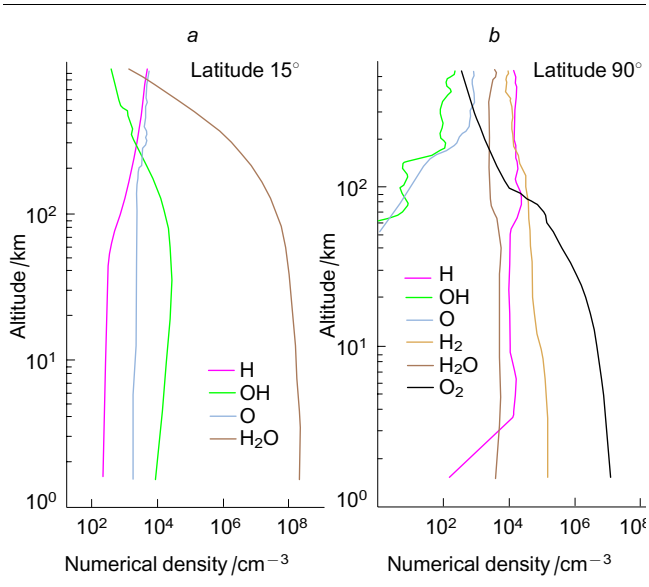


Figure 13. Distributions of the numerical densities of (*a*) water vapour and molecular and atomic products of water photodissociation (model A, subsolar region) and (*b*) atomic products of water ice radiolysis (model B, polar region).[115]

exceed the escape velocity), whereas photolysis products moving downwards are adsorbed on moon's icy surface.

An analysis of the high-altitude profiles presented in Fig. 13 *a* showed that the near-surface atmosphere in Ganymede's subsolar region consists mainly of water vapour, *i.e.*, is H_2O-dominant. At the same time, one can see that the rarefied oxygen atmosphere in Ganymede's polar regions (Fig. 13 *b*) is formed and maintained due to both thermal and non-thermal sources of molecular O_2, which is a stable product of water ice radiolysis by magnetospheric ions. In the region closest to the surface ($\sim$10 km), the distribution of oxygen molecules is determined by joint processes of their thermal desorption from the surface and non-thermal sputtering of the icy surface. The O_2 molecules injected into this region with kinetic energies exceeding the gravitational binding energy with the moon almost immediately escape from the atmosphere. Therefore, the near-surface region of the atmosphere is populated mainly by thermal oxygen molecules. When colliding with the surface, these molecules almost immediately return to the gas phase due to the thermal desorption. Correspondingly, the average kinetic energies of oxygen molecules in this region correspond to the temperature of moon's icy surface.

The transition region between 10 and 100 km is populated mainly by molecules with kinetic energies of $\sim$0.1 eV, which were either injected with such energies under surface sputtering or became suprathermal due to the momentum and energy transfer in collisions with the water molecules knocked-out from the icy surface with non-thermal distribution (37) or with suprathermal dissociation products of H_2O and O_2 molecules and magnetospheric plasma ions. The neutral atmosphere in these near-surface regions is on average dynamically stable. Suprathermal hydrogen and oxygen atoms and H_2 and H_2O molecules are accumulated in the upper ($\geqslant$100 km) atmospheric layers, which leads to the formation of Ganymede's rarefied hot corona. Each of the aforementioned regions of polar atmosphere is characterized by its height scale (Fig. 13 *b*). In other words, the processes of surface and atmospheric sputtering, as well as the charge exchange with participation of magnetospheric plasma ions, play a key role in the structurization of Ganymede's neutral atmosphere in the polar regions.

In this subsection we considered the processes of formation and dynamics of a rarefied gaseous envelope near Ganymede's icy surface, where collisions between parent water molecules and products of water ice photolysis and radiolysis on the surface exposed to UV solar radiation and magnetospheric plasma play an important role. As a result of thermal degassing and non-thermal radiolysis of water ice on moon's surface, a rarefied gaseous envelope is formed, whose main (parent) component is H_2O molecules, with an admixture of molecular radiolysis products of H_2 and O_2.

More massive icy moons allow for the formation of a rarefied exosphere with a relatively dense near-surface layer; examples are Galilean moons Europe and Ganymede in Jupiter's system.[113–116,128] The collisions of parent molecules, H_2O and O_2, both with each other and with the suprathermal products of their photolysis and radiolysis, are important specifically in this relatively dense near-surface (Knudsen) layer. It was shown that a fraction of suprathermal particles, which determines to a great extent the distribution of neutral particles in Ganymede's exosphere, is formed in the near-surface gaseous layer.

Our knowledge of the general radiation-induced physical and chemical processes occurring in the rarefied atmosphere of icy moon and the matter exchange between the moon surface and the magnetosphere of giant planet remains limited. Since the number of *in situ* observations is fairly small, the development of various models based on different scenarios and considerations led to fragmentary understanding of the interaction of magnetospheric ions with the icy moon surface and neutral gaseous envelope. The observations of both the neutral and plasma media around icy moons of giant planet were reviewed.[11,116,117] Currently, active attempts to develop a unified model of a rarefied atmosphere for Jupiter's icy moons have been made.[116] Correspondingly, the above-reported calculation results can be used to calibrate the instruments of the space missions that are currently prepared for studying Jupiter's icy moons, ESA Jupiter Icy Moon Explorer (JUICE) [129] and NASA Europa Clipper,[130] and to interpret the data on the composition and distribution of neutral particles and ions in Ganymede's near-surface gaseous envelope.

4.3. Stochastic kinetics on the surface of interstellar dust grains

In this subsection we consider a numerical method for studying the astrochemical kinetics on the surface of interstellar dust grains; this method is based on the kinetic versions of the Monte Carlo method for chemical kinetics on the solid surface.[131] The proposed approach, first, can be efficiently used to investigate the kinetics of both simple and complex chemical reaction networks on interstellar dust grains; second, due to the application of the splitting method by physical processes, it can be fairly simply combined into hybrid models for studying the chemical exchange between the gas and dust fractions of interstellar medium. The chemical processes occurring on the surface of dust particles — exothermic reactions and non-thermal desorption — serve as a source of suprathermal particles, in particular, for the surrounding gaseous envelope.[26]

4.3.1. Stochastic approach to the astrochemistry on the surface of interstellar dust grains

Recently, the formation of molecules on the surface of interstellar dust grains has been studied using different stochastic approaches: analogue Monte Carlo method, direct solution of the chemical master equation, model of continuous-time random walks, *etc*. However, the computational efficiency of these approaches is generally rather low because of the strict requirements to computational resources.[14] The essence of the kinetic version of the Monte Carlo method, which is based on the splitting method by physical processes, is as follows:[19,20] each of the main physical processes (adsorption of atoms on the surface, thermal diffusion, formation of molecules, and their desorption from the surface) is considered as an independent random process of Markovian type and modelled using stochastic algorithms.

Atoms and molecules on the surface of a solid body [interstellar and(or) interplanetary dust grain] generally vibrate with respect to certain active centres (sites), which correspond to the minimum of free energy and are separated by relatively high energy barriers. In other words, this surface can be approximated by a lattice with a specified number of active sites N_L. The lattice dimensionality can be arbitrary. Atoms and molecules occasionally jump (pass)

from an occupied active site, generally to the nearest site (the so-called vacancy). In most cases the time scale of these jumps greatly exceeds the time scales of thermal vibrations. Correspondingly, it is assumed that, after many thermal vibrations, the system under consideration passes to a state close to equilibrium. Then the translational degrees of freedom of all atoms (molecules) and their thermal vibrations are integrated to calculate the rates of microscopic processes, which are used in the stochastic description of the system. The state of the system under study will be described at the microscopic level by the vector $\boldsymbol{X}$,[17, 22] which depends on the position of active sites and time:

$$\boldsymbol{X} = \{\boldsymbol{X}_1(t), \ldots, \boldsymbol{X}_i(t), \ldots, \boldsymbol{X}_{NL}(t)\}, \quad (48)$$

$$\boldsymbol{X}_i(t) = \{X_1(i,t), \ldots, X_i(i,t), \ldots, X_K(i,t)\}$$

Here, $\boldsymbol{X}_1(i,t)$ is the state vector of the system in the active site i, whose components $\boldsymbol{X}_i(i,t)$ indicate the type of the particle [atom, molecule, and(or) vacancy] occupying this active site. The transition (jump) of atom (molecule) will be referred to as a microscopic process if this transition leads to a change in the state vector of the system. Let N_p be the total number of processes occurring in the active site i. The stochastic description of the kinetics of the astrochemical system on dust grain surface is set as a change in the state vector of the system in the active site i

$$\mathrm{d}\boldsymbol{X}_i = \sum_j \Gamma_{ij}^{+}(\boldsymbol{X})\mathrm{d}t - \sum_j \Gamma_{ij}^{-}(\boldsymbol{X})\mathrm{d}t \quad (49)$$

due to all possible processes j that lead to the occurrence of particles in the active site i (or their removal from this site) with a transition probability $\Gamma_{ij}^{+}(\Gamma_{ij}^{-})$. Equation (49) is referred to as the master equation.[76, 77, 131] Because of the large number of dimensionalities (and, correspondingly, possible states), the master equation cannot be solved directly for many astrochemical systems under study.[22, 76] An efficient way to investigate numerically these systems is to use analogue algorithms of the Monte Carlo method.[17, 18] The kinetic versions of this method imply that each process is an independent Markovian random process.

It was noted above that the transition probability matrix $\{\Gamma_{ij}(\mathbf{X})\}$ can generally have a large dimension; however, only few elements of this matrix are nonzero (a highly sparse matrix), because only particle transitions to neighbouring active sites may occur at the low temperatures considered here. Let us introduce a designation $\{\varepsilon_{ij}\}_{j=1}^{N_p}$ for the so-called participation indices of active site i, which indicate if the process j occurs in a given active site ($\varepsilon_{ij} = 1$) or does not occur ($\varepsilon_{ij} = 0$). Thus, the matrix $\{\varepsilon_{ij}\}_{j=1}^{N_p}$ will consist of zeros and units; the specific values for a given active site depend on the neighbouring interacting sites and change with time. Correspondingly, the transition probabilities $\{\Gamma_{ij}\}_{j=1}^{N_p}$ depend on the participation indices for a site involved in this process and are set by the expressions

$$\Gamma_{ij} = \Gamma_j \varepsilon_{ij}, \quad i = 1, ..., N_L, \quad j = 1, ..., N_p \quad (50)$$

In other words, if an active site i is involved in a microscopic physical or chemical process j, the probability of this transition is $\Gamma_{ij} = \Gamma_j$; in the opposite case, $\Gamma_{ij} = 0$.

The basic steps of all kinetic algorithms of the Monte Carlo method are as follows:

— random choice of process, which is made with allowance for the transition probabilities for all possible processes;

— sampling of the chosen transition and making the corresponding change in the state vector of the system;

— renewal of the time counter time and transition probabilities.

From the mathematical point of view, kinetic algorithms of the Monte Carlo method implement a discrete Markovian model of the evolution of a physical or chemical system under study with a continuous time step, which is determined from the exponential distribution modelling the expectation time of the next transition in the system.[17, 18]

Each of the above-listed algorithmic steps has its specificity. In the case of astrochemical kinetics, it is necessary to use standard and(or) develop new efficient tools within the Monte Carlo method. For example, physical and chemical processes occurring on the surface of a solid can be modelled both within an approximation without a model surface lattice and within an approximation involving a model lattice. In the former case, no spatial coordinates are assigned to particles on the solid surface. This is the so-called mean-field approximation, in which the average positions of particles on the surface are determined either randomly or from estimates of the free energy minimum. Within this approximation the changes in the state of a system studied are modeled applying the classical Metropolis algorithm,[132] and the transition probabilities are estimated using the thermodynamic parameters of the system. This conventional application of the Monte Carlo method takes into account that the displacements of atoms and molecules over the solid surface are generally very small; therefore, the sampling of the configuration space is carried out slowly. Correspondingly, for each successive sampling determining the change in the state vector of the system, a uniformly distributed random number r is compared with the calculated Metropolis transition probability p, and the transition occurs if $r < p$; otherwise, the state of the system does not change (zero event).

Most of astrochemical systems are characterized by significantly different time scales of thermal vibrations and microscopic chemical and physical processes. This separation of time scales in numerical analysis is referred to as the system stiffness. Generally the computational efficiency of molecular dynamics methods and the conventional Monte Carlo method (in the mean-field approximation) decreases significantly in the case of stiff systems due to the presence of high energy barriers: the overwhelming part of the calculation time is spent on sampling fast vibrations rather than calculating transitions induced by chemical reactions in the system. In the terminology of the Monte Carlo method, the transitions of this kind are referred to as rare events. An attempt was made to eliminate the effect of computational system stiffness in the kinetic versions of the Monte Carlo method involving surface lattice models by averaging the contributions of thermal vibrations when calculating the microscopic probabilities (rates) of processes. Within these models, discrete spatial coordinates corresponding to the positions of active sites on the chosen model surface lattice are assigned to particles, and only slow processes (*i.e.*, rare events) are sampled.

In practical applications of the Monte Carlo method, two classes of algorithms are used for spatial modelling of systems: algorithms with zero events and algorithms with

necessary jumps. An example of algorithms with zero events is the aforementioned Metropolis algorithm, where energetically favourable events (reducing the free energy in the system) are chosen with a probability $p = 1$, whereas the events increasing the free energy of the system are chosen with a probability $p < 1$. In the algorithms with necessary transitions all chosen events are sampled. In sum, the above-described general approaches to Monte Carlo simulation of astrochemical systems follow the stochastic dynamics of the master equation; note that the above algorithms use possible parameterization of transition probabilities.[17,22] The Monte Carlo method involving transition probabilities is generally referred to as the kinetic Monte Carlo method.

The best known algorithm is the so-called stochastic simulation algorithm (SSA).[75,77] We should note that the SSA described in subsection 3.6, being a rigorous realization of the kinetic Monte Carlo method, is an analogue solution of the master equation (49) of stochastic chemical kinetics on the solid surface.[131] However, it is known that rigorous stochastic algorithms of this kind impose fairly strict requirements on computational resources.[77] Correspondingly, approximate algorithms are used in the practice of stochastic simulation of chemical kinetics, which approximate the SSA algorithm and have a higher computational efficiency.[16,17,77,131]

4.3.2. Models of hydrogen formation: role of stochastic processes

Since hydrogen is the most widespread element in the Universe, it is no surprise that H_2 is the most abundant molecule. Moreover, reactions involving molecular hydrogen lead to the occurrence H_3^+ ions in interstellar clouds; in turn, more than two hundreds of molecules are formed in the complex astrochemical network of ion-molecular transformations with participation of H_3^+; these molecules were found in interstellar and circumstellar media.[2] However, it is well known that the formation of molecular hydrogen in the gas phase under interstellar medium conditions is hindered; actually, H_2 molecules should be formed on the surface of interstellar dust grains.[133] The true mechanism (or mechanisms) of H_2 formation on the surface of cold dust grains is still discussed. The most popular version[134] is the so-called Langmuir – Hinshelwood mechanism for low temperatures, according to which hydrogen atoms from the gas phase are adsorbed on cold dust grains and are bonded with their surface by weak forces (*i.e.*, physisorption occurs). These bonds arise generally on the so-called active lattice sites, corresponding to the surface free energy minima of the system. Weakly bound hydrogen atoms can move over the surface during thermal diffusion through the potential barriers of active sites. Molecular hydrogen is formed without activation energy, in the case where two hydrogen atoms occupy the same active site.

A mechanism opposite to the above-considered one is the desorption of hydrogen atoms from the dust grain surface either by thermal evaporation or *via* non-thermal processes, such as sputtering by galactic cosmic rays, photoevaporation, *etc*. The formation of molecular hydrogen according to the Langmuir – Hinshelwood mechanism can be efficient in only a limited temperature range. The lower temperature limit is obtained when hydrogen atoms move over the surface so slowly (in view of the exponential dependence of the thermal diffusion rate on the dust grain temperature) that H_2 molecules can barely be formed. The upper limit of the temperature range is reached when the desorption rate exceeds the diffusion rate, and the residence time of hydrogen atoms on the surface becomes short.

At sufficiently low temperatures the thermal diffusion almost ceases on the dust grain surface, and hydrogen can be formed in another process: the so-called Eley – Rideal mechanism. In this case, the hydrogen atoms bound on the surface are directly bombarded by gas-phase atoms. The situation may be even more complex if the adsorbed hydrogen atoms fall into potential wells of different depth (depending on the specificity of surface active sites). A very simple example is a double system of sites on the surface, in which an adsorbed atom can form both weak (physisorption) and strong (chemisorption) bonds with an active site.[135] A possible consequence for this system is efficient hydrogen formation in a wider temperature range.

In the last years the hydrogen formation on many cold surfaces of objects modelling the interstellar medium has been intensively investigated in different astrophysical laboratories.[34] An analysis of these experimental results showed[136] that the H_2 formation on olivine and amorphous carbon can be approximated by the simple Langmuir – Hinshelwood mechanism with identical binding energies of hydrogen atoms for all active surface sites and with ordinary diffusion barriers. In addition, quantum tunnelling was not observed for nearest sites. Further estimations showed that, under conditions of diffuse clouds, molecular hydrogen is efficiently formed in only very limited temperature ranges: at about 8 K for olivine dust grains[43] and at about 13 K for amorphous carbon.

On the assumption that molecular hydrogen is formed as a result of thermal diffusion on the surfaces of interstellar dust grains (such as olivine or amorphous carbon particles) with the same physisorption energy and one value of diffusion barrier for hydrogen atoms, the question of determining the rate of this process on the dust grain surface remains open. In contrast to the surfaces used in laboratory experiments, the interstellar dust grains differ significantly in size, especially in the small-size range; in addition, at a low interstellar gas density, the occupancy of the dust particle surface by hydrogen atoms should also be low.

Indeed, calculations showed that the average number of hydrogen atoms per grain is close to unity or even smaller under characteristic conditions of diffuse interstellar medium and known size distributions of dust grains.[43] In this case, the standard approach using the balance equations of chemical kinetics, which is applied to analyze the astrochemical processes occurring on the surfaces of dust particles,[41,43] is invalid because of the discreteness of the average number of hydrogen atoms on these surfaces and possible large deviations of occupancy from the mean value.[22,43] To solve this problem, it was necessary to apply more rigorous stochastic approaches, such as the Monte Carlo method[21,42] and direct solution of the stochastic master equation.[43,137] A method for simulating the H_2 formation on regular and rough surfaces of different types[138] using the well-known Monte Carlo procedure[139] — continuous-time random-walk method — was proposed. This approach turned out to be fairly efficient for simulating the formation of H_2 molecules on various homogeneous and inhomogeneous surfaces of interstellar dust grains.[138] However, it should be noted that the requirements imposed on computational resources for

implementing this method are excessively strict; in addition, it is poorly matched with the standard stochastic and(or) deterministic methods for calculating the astrochemical processes occurring in the gas phase.[140]

Let us consider the formation of molecular hydrogen under typical conditions of diffuse molecular clouds as an example of very simple astrochemical system.[19, 20] The kinetic energies of hydrogen atoms are below ~ 100 K, and the dust temperature is < 20 K;[135] therefore, the hydrogen atoms adsorbed on the dust particle surface and captured by active sites can barely move over the surface. The energy barriers for thermal (diffuse) displacements ($E_{\rm H}^{\rm diff}$) depend on the surface morphology. It is generally assumed that, in the case of formation of a weak bond with an active site,

$$E_{\rm H}^{\rm diff} \approx (0.2 - 0.3)\, E_{\rm H}^{\rm des} \tag{51}$$

where $E_{\rm H}^{\rm des}$ is the atom desorption energy from the surface. The surface area of a typical spherical interstellar dust grain with a radius of 0.1 μm amounts to $S \approx 10^{-9}$ cm^2, and the number of active sites on it is $(10^{12} - 10^{15})\, S$. Several characteristic time scales can be selected for this astrochemical system:

— time between successive arrivals of hydrogen atoms at the grain surface;

— residence time on the surface;

— time between successive events of absorption of interstellar UV photons, causing fluctuations of dust grain temperature.

The dust grain sizes, surface porosity, and distribution of energy barriers for active sites are also important parameters of the system under consideration. Let us estimate how these time scales are interrelated and affect the formation rate of molecular hydrogen.

The collision rate of hydrogen atoms with a dust grain is $n_{\rm H} v_{\rm H} \sigma$, where $n_{\rm H}$ and $v_{\rm H}$ are, respectively, the density and velocity of thermal hydrogen atoms in the gas phase and σ is the geometric cross section of the dust grain. Let a fraction ξ of hydrogen atoms colliding with a grain be adsorbed on its surface. Then, for $n_{\rm H} = 100$ cm^{-3}, $v \approx 10^5$ cm s^{-1}, and a gas temperature of ~ 100 K, we obtain the collision rate of hydrogen atoms with a typical grain to be on the order of 1 particle per 300 s. The residence time on the dust grain surface is

$$t_{\rm H} = \frac{1}{v} \exp \frac{E_{\rm H}^{\rm des}}{k_{\rm B} T} \tag{52}$$

Here, v is the thermal vibration frequency (generally on the order of $\sim 10^{12} - 10^{13}$ s^{-1}). For the desorption energy $E_H^{\rm des}/k_{\rm B} \approx 500$ K and a dust grain temperature of 10 K, the residence time on the grain surface is $10^8 - 10^9$ s; however, at a grain temperature of 15 K, the $t_{\rm H}$ value decreases to 30 – 300 s, which is comparable with the arrival time of atoms at the surface. The dust grain temperature in a diffuse medium depends strongly on the field of interstellar UV photons. The time scale of photon absorption by a grain can be estimated as

$$t_{h\nu} = (\sigma Q \Phi)^{-1} \tag{53}$$

where Q is the absorption efficiency and Φ is the energy flux of UV photons, which is equal on average to 2.6×10^{-3} erg cm^{-2} s^{-1} for diffuse clouds.[141]

For large dust grains, the interval between UV absorption events is short (several tenths of a second), and their temperature is almost stable in the range of 15 – 20 K. In the case of small dust grains, the temperature fluctuations may reach 10 – 20 K at a grain diameter $a \approx 0.01$ μm, when $t_{h\nu} \approx 750$ s, and 15 – 20 K for $a \approx 0.02$ μm, when $t_{h\nu} \approx 100$ s.[142] For these (and smaller) dust grains, the arrival time of H atoms at the surface is a critical parameter, because the following inequality must be satisfied to maintain the high efficiency of molecular hydrogen formation on the surface:

$$\frac{\xi {\rm d}N}{{\rm d}t} > t_{h\nu}^{-1} \tag{54}$$

In this astrochemical system, the residence time of H atoms on the dust grain surface is very sensitive to the grain temperature, which, in turn, depends on the grain size. Therefore, the reaction of molecular hydrogen formation on the surface is efficient in only a narrow temperature range.[143] These limitations can be reduced taking into account the enhanced surface porosity. In this case, rapid repeated adsorption of hydrogen atoms (that have just left the surface) may occur. The limitations on the surface temperature can also be reduced due to the more complex distribution of active sites on the dust grain surface and, naturally, a wider distribution of particle sizes (especially towards small diameters), which leads to an increase in the effective surface of dust grains and the arrival rate of atoms at these grains.

In this subsection we present the results of calculating the molecular hydrogen formation rate using the above-described approximate algorithm of the kinetic Monte Carlo method and compare the calculation results with the solutions obtained by other researchers (Refs 43, 136, 138). To make the comparison more correct, the below calculations were performed using similar physical models of interstellar dust grains; specifically, the simulation was carried out on two model surfaces: homogeneous olivine and homogeneous amorphous carbon.

In correspondence with the above-described standard procedure of stochastic simulation of chemical reactions, the surface of interstellar dust grains is a model lattice, whose active sites are occupied by H atoms arriving from the gas phase. We will consider only the hydrogen atoms located on the surface, on the assumption that they can move between the nearest active lattice sites and that their thermal energy is sufficiently high to overcome the energy barrier separating the sites. The following microscopic processes occur in this very simple astrochemical system: formation of H_2 molecules and their instantaneous desorption into the gas phase, adsorption of hydrogen atoms from the gas phase onto the grain surface, their diffusion over the surface, and thermal desorption. The adsorption on the surface, thermal diffusion, and desorption are random Markovian processes, for which the time interval Δt between two successive transitions obeys the exponential distribution

$$\psi_j(t) = \Gamma_j \exp(-\Gamma_j t) \tag{55}$$

where Γ_j is the rate of process j and $\Gamma_j t$ is the mean time between successive transitions for this process. The expectation time of a current transition is determined by the standard SSA formula.

An essential feature of the proposed algorithm,[19] in contrast to the above-described rigorous realization of the kinetic Monte Carlo method, is the use of the splitting method by physical processes. The splitting time was taken to be the minimum among the mean desorption, displacement, and adsorption times for one atom. This approximate approach made it possible to accelerate the rigorous algorithm; at this, the splitting time did not exceed the mean expectation time between the fastest process events. The error of the proposed approximate algorithm in comparison with the rigorous KMCM realization does not exceed $O(\Delta t_r)$, where Δt_r is the time of splitting by the microscopic processes considered for the astrochemical system under study. This algorithm, in contrast to the rigorous KMCM realization, is naturally matched with both stochastic (direct simulation of random Markovian processes using analogue Monte Carlo algorithms) and deterministic (solution of the balance equations of chemical kinetics) approaches for studying the astrochemical kinetics in the gas phase.[20]

Let the adsorption of hydrogen atoms be considered as a process with a number $j = 1$; then the adsorption probability (or rate) can be written as

$$\Gamma_1 = n_{\mathrm{H}}\, v_{\mathrm{H}}\, \sigma \xi \tag{56}$$

The probability of process $j = 2$ (thermal diffusion of hydrogen atoms over the surface) can be written as

$$\Gamma_2 = \nu \exp\left(-\frac{E_{\mathrm{H}}^{\mathrm{diff}}}{k_{\mathrm{B}} T} \right) \tag{57}$$

where the frequency of thermal lattice vibrations, accepted in the calculations below, is $\nu = 10^{12}\ \mathrm{s}^{-1}$. In turn, the rate of process $j = 3$ (thermal desorption of hydrogen atoms from the dust grain surface) has the form

$$\Gamma_3 = \nu \exp\left(-\frac{E_{\mathrm{H}}^{\mathrm{des}}}{k_{\mathrm{B}} T} \right) \tag{58}$$

The mean times of the microscopic processes under consideration are determined by the above-specified rates. The splitting time is chosen as the minimum among these mean times. For all H atoms located on the surface, the time of their participation in a microscopic process — displacement over the surface or desorption into the gaseous medium — is determined in accordance with the above-reported distribution (53). The expectation time for the thermal adsorption of hydrogen atoms is found in the same way. Any time when an atom moves to another active site or a new atom arrives at the surface, a new expectation time is calculated for its next motion and is compared with the splitting time. The simulation is performed using periodic boundary conditions, which is acceptable for the model lattice in use, because a hydrogen atom can always return to the arrival place by continuing its motion in the specified direction. After some time, the simulated system comes to 'saturation', at which the number of H atoms simultaneously located on the surface fluctates near a constant value. The settling times, which are necessary for the numerical model to reach a stable stationary state, range from 10^3 to 10^8 s. After reaching the stationary state, the numbers of arriving hydrogen atoms (N_{H}) and newly formed hydrogen molecules (N_{H2}) are continuously counted; the recombination efficiency (η) of hydrogen atoms in the astrochemical system under consideration is determined from the formula

$$\eta = \frac{2\, N_{\mathrm{H}_2}}{N_{\mathrm{H}}} \tag{59}$$

Since the simulation is performed for long time, the number of hydrogen atoms arriving at the surface is sufficiently large, and the stochastic noise is low.

The calculations were performed in very simple versions, using planar lattices with uniform values of energy barriers for the thermal processes of diffusion and desorption. In correspondence with the data,[136] these lattice energy parameters were taken to be 287 and 373 K for olivine and 511 and 658 K for amorphous carbon. Calculations were performed for two models of surface arrangement of active lattice sites: model 1 corresponds to a dust grain where each active site has four nearest neighbors, and model 2 describes a dust grain with six nearest active sites. The sizes of the model lattices approximating dust grains were varied in calculations from 10^2 to 10^6 active sites. Correspondingly, they are related to the sizes of dust grains (on the assumption that the latter are spherical) by the relation

$$S_{\mathrm{a}} = \pi d^2 s \tag{60}$$

where S_{a} is the number of active lattice sites, d is the dust grain diameter, and s is the active site density on a surface of specified physical nature. For example, using the experimental value of active site density for homogeneous olivine, equal to $2 \times 10^{14}\ \mathrm{cm}^{-2}$ (Ref. 43), we find that an olivine dust grain with 10^6 active sites has a diameter of ~ 0.4 μm, whereas the smallest particles containing 10^2 active sites have a diameter of ~ 4 nm. Calculations were performed for the stationary conditions of diffuse interstellar medium, where the atomic hydrogen density in the gas phase varies within $10 - 10^3\ \mathrm{cm}^{-3}$ and the temperature is 100 K.

The calculated dependences of the formation efficiency of molecular hydrogen on interstellar dust olivine grains at a grain temperature of 10 K on the number of surface active sites are presented in Fig. 14.

The calculations showed a strong dependence of the molecular hydrogen formation efficiency on the number of active sites on dust grain surface and a corresponding dependence on the grain size. One can see satisfactory agreement between the results of calculations performed using different methods; note also that all obtained estimates of efficiency almost coincide for small dust grains (olivine particle with 624 active sites). When passing from dust grains containing 10^4 active sites to those with 10^5 sites, the efficiency changes significantly (as compared with the 10^5 to 10^6 transition). The efficiency also increases for model 2 in comparison with model 1, which can be explained by higher activity of hydrogen atoms on the dust grain surface. Note also that the results obtained within model 2 (which characterizes the arrangement of active lattice sites) for a large number of active sites on the dust grain surface, using the proposed approximate algorithm, are closest to the asymptotic estimate of the efficiency $\eta = 0.19$, which follows from direct solution of the master equation.[43]

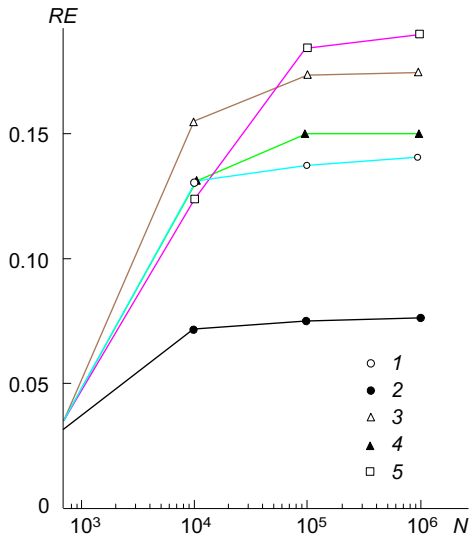


Figure 14. Dependence of the formation efficiency (*RE*) of H_2 molecules on a homogeneous surface of olivine interstellar dust grain at a temperature of 10 K on the number of active sites (*N*). Model 1: (*1*) author's calculations[19] and (*2*) calculations according to the continuous-time random-walk Monte Carlo method.[138] Model 2: (*3*) author's calculations,[19] (*4*) calculations according to the random-walk Monte Carlo method;[138] and (*5*) results of direct solution of the master equation.[43]

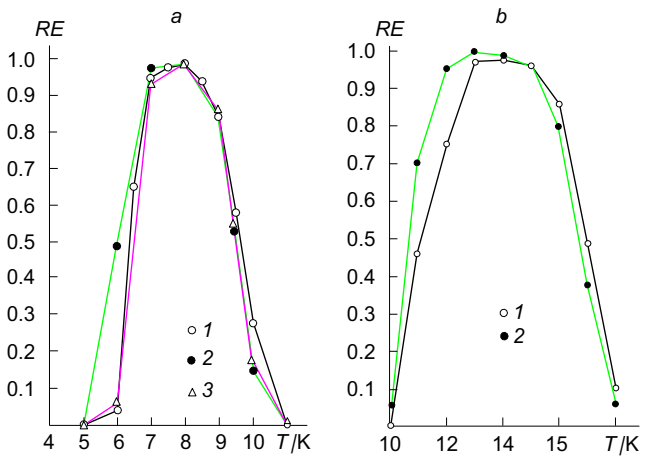


Figure 15. Temperature dependences of the formation efficiency of molecular hydrogen on the surface of interstellar dust grains of (*a*) olivine and (*b*) amorphous carbon, in correspondence with model 2: (*1*) author's calculations,[19] (*2*) calculations according to the random-walk Monte Carlo method,[138] and (*3*) results of direct solution of the master equation.[43]

An analysis of the results of laboratory experiments[34] showed that the molecular hydrogen formation on homogeneous olivine dust grains under conditions of diffuse interstellar medium occurs efficiently in a very limited temperature range. Calculations were performed within model 2 for dust grains with a homogeneous olivine surface containing 10^6 active sites. The results are presented in Fig. 15*a* (curve *1*). The analysis demonstrated fairly good agreement for the calculations performed within different approaches. Moreover, these calculations confirmed the conclusions based on the laboratory experiments[34]; *i.e.*, that the formation of hydrogen molecules on homogeneous olivine dust particles occurs only in a narrow temperature range (6 – 9 K).

Laboratory experiments were also performed for analogues of dust grains of another chemical nature: amorphous carbon grains; the corresponding calculations were also carried out for them. The surfaces of amorphous carbon dust grains are characterized by higher energy barriers for thermal diffusion and desorption.[136] The temperature dependence of the production efficiency of molecular hydrogen is presented in Fig. 15*b* (curve *1*). In correspondence with these laboratory experiments, the temperature range of highly efficient H_2 formation is shifted to higher temperatures (11 – 16 K), which is explained by higher energy thresholds for homogeneous amorphous carbon dust grains. Note also satisfactory agreement between the calculations using different modifications of the kinetic Monte Carlo method.

The investigated simple astrochemical system does not correspond to a full extent to the observational data on the hydrogen formation rate under conditions of diffuse interstellar medium,[144, 145] when the dust grain temperature generally exceeds the values from the above-reported temperature ranges of high production efficiency of H_2 molecules on homogeneous dust grains. Currently, the hydrogen formation under conditions of diffuse interstellar medium is studied using physical models taking into account the chemical inhomogeneity and roughness of dust grain surface.[16, 138, 144, 145]

5. Conclusion

The chemical complexity in the interstellar medium is studied by astrochemistry — a young interdisciplinary science at the junction of astronomy, astrophysics, and chemistry. The last decade is marked by a radical change in the concepts about the evolution of protoplanetary systems and the planet formation processes. This change is mainly due to two observation breakthroughs in the field of studying the gas and dust envelopes of astrophysical objects: the discovery of extrasolar planetary systems and the onset of large-scale observations of protoplanetary disks at young stars. The observations and study of 'primitive building blocks' in the Solar system have proved convincingly the presence of complex organic material in the early Solar nebula.[5, 6] Complex molecules are most likely present in other protoplanetary disks; however, only some of their types were found using modern submillimetre and millimetre interferometers. Astrochemical methods are more and more actively used to interpret observation data on the chemical complexity of interstellar medium.

An important role in the formation and evolution of gas and dust envelopes of astrophysical objects is played by suprathermal particles with kinetic energies greatly exceed the thermal energy of surrounding gas.[9 – 12] These particles are formed in different physicochemical processes, whose products have excess kinetic energy. Observations and theoretical studies revealed the formation of a stable fraction of suprathermal particles, which may perturb significantly the local equilibrium distribution of the thermal energy of gas and dust envelopes around astrophysical objects: prestellar and protostellar cores of molecular clouds, planets, their moons, and comets in the Solar and

extrasolar planetary systems. The main difficulty in studying the formation processes, kinetics, and transport of excited suprathermal atoms and molecules is the necessity of considering these processes at the molecular level. Indeed, suprathermal particles are formed in thermodynamically open systems: gas and dust envelopes subjected to external impacts by radiation and fluxes of high-energy particles from the parent and(or) surrounding stars. Correspondingly, their evolution is determined using the kinetic Boltzmann equations for chemically reacting rarefied gas and dust media. Promising approaches to study the kinetics and transport of suprathermal particles imply the development of discrete mathematical models with probabilistic interpretation of collisions in an ensemble of model particles. The approaches of this class include the kinetic Monte Carlo method and its modifications for studying the nonequilibrium processes in chemically active gas and dust envelopes of astrophysical objects.[10, 11]

We considered the kinetic Monte Carlo method for studying the role of suprathermal particles in astrochemistry at the molecular level. Different KMCM modifications, aimed at studying these particles in the chemical processes occurring in planetary atmospheres and on icy surfaces of astrophysical objects, are discussed. The important role of the fraction of suprathermal particles is demonstrated on several examples of astrochemical applications. The effects caused by the presence of these particles are as follows:

— local changes in the chemical composition, because the rate coefficients of nonequilibrium chemical reactions (especially those occurring with high activation energies) between suprathermal particles and surrounding gas and dust envelope exceed greatly the corresponding coefficients for chemical reactions occurring with thermal energies;

— non-thermal emissions of gas and dust envelope;

— enhancement of chemical exchange between the gas and dust fractions of envelope;

— the formation of extended hot coronae around planets in the Solar and extrasolar systems and an increase in non-thermal atmospheric loss, which determines the evolution of planetary atmosphere on the astronomical time scale;

— additional contribution to the formation of complex molecules in gas and dust envelopes of astrophysical objects.

Since the particles with excess kinetic and internal energies have nonequilibrium properties, the processes of their formation and subsequent evolution must be studied at the microscopic (kinetic) level. The approaches of hot-atom chemistry turned out to be in demand when analyzing the role of suprathermal particles in the physics and chemistry of gas and dust envelopes of astrophysical objects. This is evidenced, in particular, by the significantly increased interest in such studies in the last years; the important role of suprathermal (hot) particles formed in gas and dust envelopes in the chemistry and energetics of these media has been generally recognized.[11, 50] The results of theoretical study of the role and contribution of suprathermal particles to the formation of hot planetary coronae[11, 12, 50] were confirmed by spacecraft observations and measurements. For example, the first *in situ* measurements of the suprathermal fractions of nitrogen and methane molecules in Titan's upper atmosphere were performed with the aid of NASA's Cassini instruments;[63] the possibility of forming these suprathermal fractions was previously predicted theoretically (see, *e.g.*, Refs 11 and 64).

The review section devoted to the astronomical applications of the kinetic Monte Carlo method contains some results of the long-term studies of the contribution of suprathermal hydrogen and oxygen atoms to the coronae and atmospheric dissipation of terrestrial planets, performed by the author and his colleagues. The analysis of the distribution of suprathermal hydrogen, carbon, and oxygen atoms formed in the upper atmospheres of terrestrial planets (and exo-Earths in the planetary systems of other stars) is an important fundamental problem of comparative planetary aeronomy. The studies of the energy transfer in the solar wind – ionosphere – Mars' neutral atmosphere system carried out by the Mars-Express and MAVEN spacecrafts confirmed the simulation results, according to which significant amounts of suprathermal hydrogen, carbon, and oxygen are formed in the upper atmospheres of terrestrial planets. Indeed, the solar forcing on the upper atmospheres of these objects (absorption of UV radiation and atmospheric sputtering by solar plasma) leads to the formation of an extended neutral corona, occupied by suprathermal atoms. In turn, the hot corona changes the flow of solar wind plasma at exospheric altitudes, thus affecting the long-time evolution of the planetary atmosphere. It was shown that suprathermal H, C, and O atoms are important components of extended neutral coronae; these atoms determine the processes of thermal and non-thermal atmospheric dissipation, being a characteristic feature of the space around a planet. Data on the thermal and non-thermal dissipation of the upper atmospheres of Mars and Venus suggest important conclusions about the key processes in the evolution of neighbouring terrestrial planets and, correspondingly, about possible unfavourable trends in Earth' evolution.

An interesting and urgent field of research is the observation-based characterization of the so-called ocean worlds, estimation of their habitability, and search and study of any form of life that can be found in these potential habitats. In terms of this all-inclusive goal, one can select, in particular, the following problem: to determine (using the kinetic Monte Carlo method) the characteristics and ways of chemical exchange between the subglacial ocean, icy surface, and gas envelope of a celestial body under study.[113 – 116] It was shown in the presented KMCM application that a fraction of suprathermal particles is formed in the near-surface gas layer and determines to a great extent the distribution of neutral particles in Ganymede's exosphere. The reported calculation results can be used to calibrate the instruments of the currently developed space missions for studying Jupiter's icy moons (mainly Ganymede and Europa), ESA JUICE[129] and NASA Europa Clipper,[130] and to interpret data on the composition and distribution of neutral particles and ions in Ganymede's near-surface gas envelope.

The kinetic Monte Carlo method is also in demand when considering the astrochemical kinetics on the surface of interstellar dust grains.[131] This approach may be efficient for studying the kinetics of simple and complex chemical reaction networks on interstellar dust grains. In view of the application of the splitting method by physical processes, this approach can fairly easily be combined with the hybrid models applied to study the chemical exchange between the gas and dust fractions of interstellar medium.[146] Actually,

the chemical interactions on the surface of dust grains include exothermic reactions and non-thermal desorption processes; *i.e.*, they serve as a source of suprathermal particles, in particular, for the surrounding gas envelope.[26]

The illustrative material presented in the review was compiled from different sources (the references are indicated in figure captions) and revised. Figure 9 is author's.

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