
Plasmas Involving Molecules

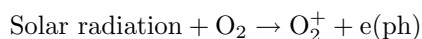
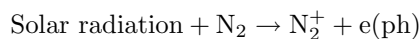
2.1 Ionosphere

A part of the atmosphere of the Earth and other planets is ionized by solar radiation and precipitating particles from outside. The part of rather high density of electrons is called an ionosphere. This is a typical example of molecular plasmas in nature. Here we consider the ionosphere on the Earth. For the ionospheres on the other planets, as well as details of the Earth's ionosphere, see the text book of Schunk and Nagy [144].

The Earth's ionosphere is located at the height of 60–1,000 km. The structure of the ionosphere is different for the day side and night side (more precisely, depending on the local time). It is severely affected by the solar activity. Figure 2.1 shows one example of ionic composition and electron density of the day side ionosphere at the minimum of solar activity [85]. This is a composite picture based on a few rocket and satellite measurements in 1963 and 1964. The absolute value of ion number density is normalized to the electron number density measured separately. Typical value of the electron density is $\sim 10^5 \text{ cm}^{-3}$ at 100 km and $\sim 10^6 \text{ cm}^{-3}$ at 200 km. These values are compared with the density of atmosphere: $\sim 10^{13} \text{ cm}^{-3}$ at 100 km and $\sim 10^{10} \text{ cm}^{-3}$ at 200 km. In the region of ionosphere, the Earth's atmosphere is composed mainly of N_2 , O_2 , and O . Above about 200 km, atomic oxygen dominates over the molecular components.

In the day side region at the height of about 100 km, the ionospheric plasma is maintained in the following manner:

- (1) Ionization by solar radiation, particularly by the radiation of short wavelength



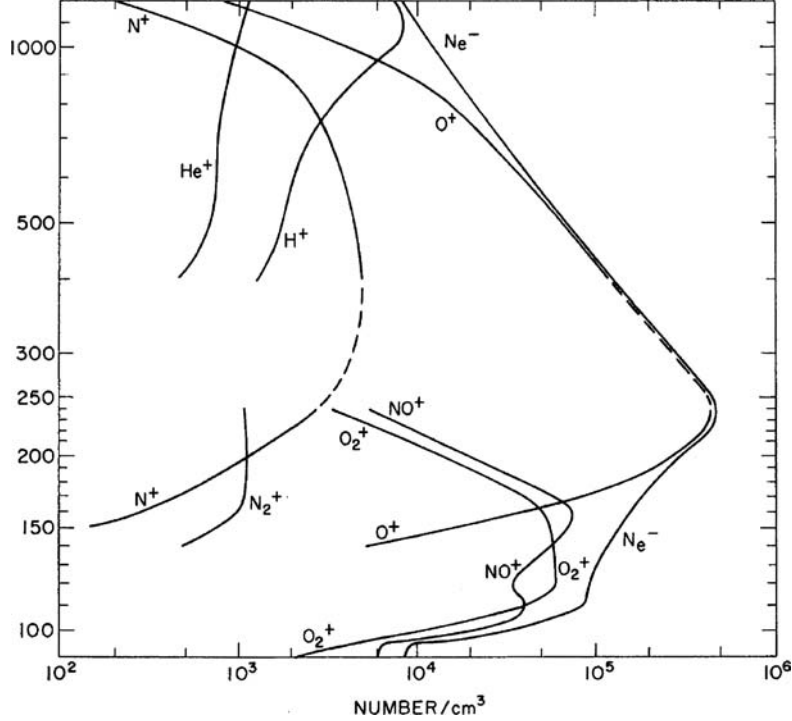
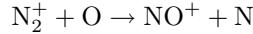


Fig. 2.1. Ion composition and electron density of the day side ionosphere on the Earth, reproduced from [85]. Ordinate is the height in km above the ground

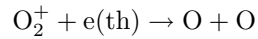
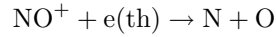
The electrons produced are called photoelectrons (denoted by $e(ph)$). They have a rather high kinetic energy (20–30 eV or more). The N_2^+ is, however, immediately transformed into NO^+ by the reaction



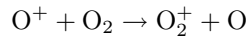
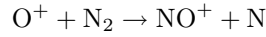
As a result, the most abundant ions at the height around 100 km are O_2^+ and NO^+ as is shown in Fig. 2.1. Above about 150 km, an atomic ion, O^+ , dominates. This ion is produced by the photoionization of atomic oxygen.

(2) Recombination of ions with the thermal electrons.

The photoelectrons lose their energy through the collisions with the atmospheric particles (N_2 , O_2 , O). They eventually join the thermal electrons, whose temperature is around 1,000 K. This slowed-down photoelectron is the source of the thermal electrons in the ionosphere. The energy degradation process of photoelectrons is discussed later in this section. The ions produced in (1) are recombined with the thermal electrons (denoted here by $e(th)$)



Even O^+ disappears through these recombination processes. First it is transformed into molecular ions through the processes:



Then the molecular ions, NO^+ and O_2^+ , recombine with electrons as above.

In the region at around 100 km, these processes (i.e., photoionization, electron energy-degradation, and electron-ion recombination) take place locally. As the height increases, the atmospheric density decreases rapidly and the transport (diffusion) of electrons dominates over those collision processes. In other words, nonlocal effects must be considered for the maintenance of the ionosphere.

Electron-molecule collisions play a significant role in the ionosphere. Examples are the following.

2.1.1 Energy Degradation of Photoelectrons

The photoelectrons lose their energy by the collisions with atmospheric atoms, molecules, ions, and electrons. Because of the large density of the neutral particles, the degradation process is so fast that a steady-state distribution of electron energy is established. The resulting distribution (i.e., the electron energy spectrum) can be observed by rockets or satellites. One example is shown in Fig. 2.2. The figure shows the energy distribution observed with a satellite at the height of 150–282 km by Lee et al. [99]. It corresponds to the daytime ionosphere at the solar minimum condition. Most of the structure in the distributions reflects the structure in the spectrum of solar radiation. To understand the energy degradation, we need information of all the collision processes between the electrons (in the energy range 1–100 eV) and the molecules N_2 and O_2 (and O) (see, for example, [155]). With the use of the information, calculations of the energy distribution of ionospheric electrons have been performed several times (see, for example [8]). Those calculations generally could reproduce the observed spectra of electron energy. For example, the sharp dip at around 2 eV in the energy spectra at the lower altitudes (e.g., at 150 km) was ascribed to the large cross-section of the vibrational excitation of N_2 due to the resonance process (see Sect. 5.5). Once electrons acquire the energy (~ 2 eV) for the resonance to occur, they quickly lose that energy through the resonant vibrational excitation of N_2 .

2.1.2 Optical Emission

Optical emission from the atmosphere (called airglow) is caused by various processes. One of them is the excitation (and excitation following dissociation) of molecules by energetic photoelectrons (see [110]). (Others are resonant

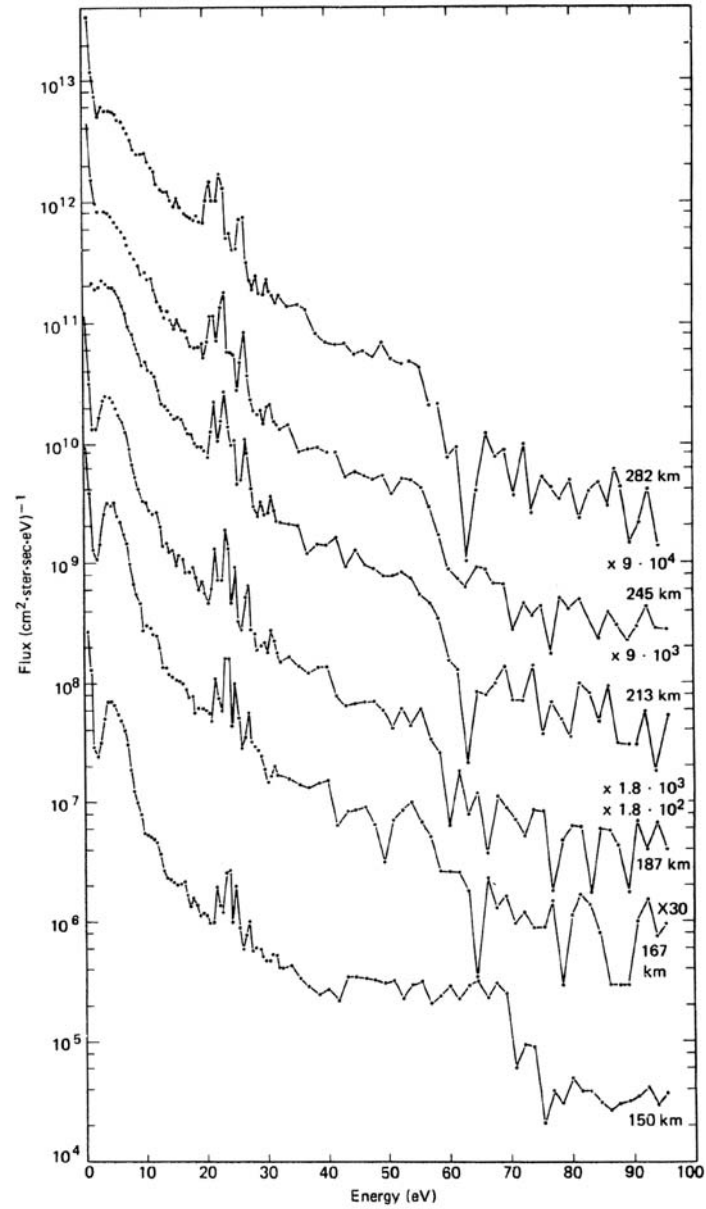


Fig. 2.2. Energy distribution of photoelectrons in the Earth's ionosphere, reproduced from [99]. The photoelectron flux per unit energy, observed by a satellite, is shown for the heights from 150 to 282 km

scattering of sunlight, photoexcitation by solar radiation, chemical reactions of atmospheric atoms and molecules, etc.)

For example, Broadfoot et al. [16] observed the emission in the range 115–900 nm. They identified some part of the spectra as the emission from N_2 induced by electron impact. They were the emissions associated with the transitions:

$$C^3\Pi_u \rightarrow B^3\Pi_g$$

$$B^3\Pi_g \rightarrow A^3\Sigma_u^+$$

$$a^1\Pi_g \rightarrow X^1\Sigma_g^+$$

The emission cross-sections for these transitions are dealt with in Sect. 5.9. If the emission mechanism is known, the observed spectra can be used for the diagnostics of the atmosphere. That is, we can deduce atmospheric composition, density, temperature, etc. from the analysis of the observed spectra of airglow.

Aurora is another example of atmospheric emission (see, for example, [162]). It is caused by high-energy charged particles (usually electrons) precipitating from outside of the atmosphere. Those charged particles (with energies above about 1 keV) are generated in the magnetosphere, transported along the line of magnetic field, and injected into the high-latitude atmosphere. The roles of the electron–molecule collisions in the auroral emission is twofold: energy degradation of fast electrons and emission of radiation. The incoming high-energy electrons quickly reach the lower-range of the ionosphere. Since the atmospheric density increases rapidly with decreasing height, those electrons lose their energies mostly in the lower region (at around 100 km). During the slowing down processes, the electrons collide with molecules to emit radiation. The radiation intensity is proportional to the emission cross-section and the number of emitting molecules. The emission cross-section depends on the electron energy, which, in turn, is determined by the degradation processes.

To understand aurora, modeling calculations have been performed many times. One example is the Monte Carlo simulation by Onda et al. [126]. Starting from the measured energy spectra of the incident high-energy electrons, they simulated the thorough behavior of the electrons until they join the thermal electrons of the ionosphere. They obtained the emission spectra, particularly for the transition:

$$N_2^+(B^2\Sigma_u^+) \rightarrow N_2^+(X^2\Sigma_g^+)$$

This transition is mainly caused by an electron-impact ionization–excitation process:

$$e + N_2 \rightarrow e + N_2^+(B^2\Sigma_u^+) + e$$

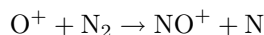
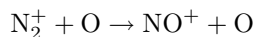
The agreement between the calculated and observed spectra was fairly good. The emission spectra are sensitively dependent on the energy spectra of the

incident high-energy electrons. The notable point of the work of Onda et al. is that the energy spectra of the incident electrons was simultaneously measured with the observation of the auroral spectra and used as an input of the model calculation. By doing so, they could avoid any ambiguity associated with the incident high-energy electrons. Most of other modeling studies assume some model spectra for the incident electrons.

2.1.3 Energy Balance and Transport Phenomena in Thermal Electrons

The thermal electrons in the ionosphere are usually assumed to have a Maxwell distribution of energy. The electron temperature is determined by the balance of heating and cooling. The source of heating is the collision with photoelectrons produced by the solar radiation. Cooling of the thermal electrons is due to the collision with atmospheric molecules. Since the electron temperature is not high ($\sim 1,000$ K), the dominant processes are elastic scattering and rotational and vibrational excitations. In the higher region of ionosphere, electron-ion collisions are the dominant cooling process of electrons. Electric conductivity of the ionosphere is determined by the electron collisions with the atmospheric molecules. More generally, the propagation of radio wave in the ionosphere is governed by the electron-molecule collisions. In these cases, the most important process is a momentum-transfer collision (see Sect. 5.3).

As is already shown, ion-molecule collisions are also important in the ionosphere. The ions produced by the solar radiation are transformed into other ions, through the following processes:



These reactions often result in the products in their excited state. Such reactions, therefore, act as a source of airglow emission. Ions in the ionosphere are heated by the collision with the thermal electrons. The cooling of the ions is mostly due to the collisions between ions and the neutral molecules. The most important process in this case is the momentum-transfer collisions between ions and molecules.

2.2 Interstellar Cloud

Matter in the Universe is mostly in the state of a plasma. On the other hand, molecules are found in many places in the Universe (see [156]). It is natural, therefore, to encounter a molecular plasma in the Universe. One example is the interstellar cloud.

The space between the stars is empty, but not entirely so. It is filled with matter, although very tenuous. Its density is not uniform. Some part of the interstellar space has rather dense matter and is called interstellar cloud. Most of the interstellar clouds are molecular and ionized. They are composed mostly of (atomic and molecular) hydrogen. Its density is 10^2 – 10^4 cm^{-3} . The gas temperature of the cloud is extremely low (10–100 K). The degree of ionization is very low ($\sim 10^{-8}$), but the charged particles still play a significant role.

A wide variety of molecules have been found in the interstellar clouds. Molecular species found are different depending on the cloud and the condition of the observation. For illustration, we present in Table 2.1 a list of abundant molecules. The abundance shown is the result of a model calculation [113], but generally consistent with observation. In the model, the cloud is assumed to have H_2 density of 10^4 cm^{-3} and temperature of 10 K. It should be noted that some of the molecules (e.g., N_2) obtained by the model calculation have not yet been observed. They have no transitions of the energy states suitable for spectroscopic observation.

The formation of the interstellar molecules are thought to follow the scheme described below. Here we consider the so-called molecular cloud, which is of a rather high density ($\sim 10^4$ cm^{-3}) and a low temperature (~ 10 K). Table 2.2 shows the molecular abundance observed in a typical molecular cloud TMC-1 (cited in [113]). In such a cloud, very unsaturated species such as radicals C_nH are dominant. The molecular clouds are important as a source of star formation. Because of the low gaseous density, only two-body collision occurs in the cloud. (In contrast to this, three-body collisions are the main process of molecule formation in laboratories.) Furthermore, only the reactions

Table 2.1. Fractional abundance (with respect to H_2) of interstellar molecules based on a model calculation [113]

Species	Abundance	Species	Abundance	Species	Abundance
H_2	1.0	CO_2	$3.0(-6)^{\text{a}}$	CHOOH	$2.6(-8)$
CO	$1.4(-4)$	H_2O	$2.3(-6)$	H_2CO	$1.4(-8)$
O_2	$8.4(-5)$	SO_2	$3.0(-8)$	C_4H	$7.1(-9)$
N_2	$2.0(-5)$	HNC	$6.8(-9)$	C_3H_2	$5.7(-9)$
NO	$3.3(-6)$	HNO	$4.1(-9)$	C_3H	$2.2(-9)$
OH	$9.6(-7)$	HCN	$4.0(-9)$	HCO^+	$1.3(-8)$
SiO	$5.5(-9)$	NH_2	$3.7(-9)$	H_3^+	$7.1(-9)$
SO	$5.2(-9)$	OCN	$2.4(-9)$	H_3O^+	$2.4(-9)$
PO	$2.9(-9)$	NH_3	$1.4(-7)$	e	$4.4(-8)$
CS	$2.7(-9)$	CH_4	$1.3(-7)$		
HCl	$2.1(-9)$	C_2H_2	$6.2(-8)$		

^a $3.0(-6) = 3.0 \times 10^{-6}$.

Table 2.2. Fractional abundance (with respect to H_2) of interstellar molecules observed in the cloud TMC-1

Species	Abundance	Species	Abundance	Species	Abundance
CO	8(-5) ^a	CH	2(-8)	NH ₃	2(-8)
OH	3(-7)	HCN	2(-8)	CS	1(-8)
C ₂	5(-8)	HNC	2(-8)	C ₃ H ₂	1(-8)
C ₂ H	5(-8)	CCCCH	2(-8)	HCO ⁺	8(-9)
CN	3(-8)	H ₂ CO	2(-8)		

^a 8(-5)= 8×10^{-5} .

with no activation energy are possible in such a cold space. The two-body ion-molecule reaction satisfies this condition (see Sect. 6.4). The possible scheme of molecule formation in the interstellar cloud is as follows [62]:

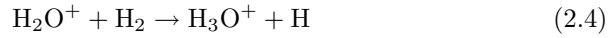
- (1) Ions are produced by collisions of cosmic-rays with interstellar atoms and molecules. Reflecting the abundance, most of the nascent ions are H_2^+ . Because of the rapid reaction



the H_2^+ is immediately transformed into H_3^+ , which is, therefore, the starting point of a series of ion-molecule reactions in the interstellar cloud.

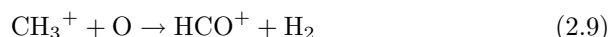
- (2) Through a chain of ion-molecule reactions, larger, as well as complex, molecules are created.
- (3) A part of ions disappear through the collision with electrons (i.e., the electron-ion recombination). The recombination is mostly dissociative, so that some simple molecules are produced as a product of this process.

One simple route to the formation of water molecules is as follows:



In the interstellar clouds, the ion-molecule reactions involving H or H_2 are of primary importance. Such processes as (2.3) and (2.4) above produce new molecules having an additional hydrogen. The electron-ion collisions like (2.5)

are very rare in the interstellar clouds, but still very important, because they produce such small molecules as OH, CO, and H₂O. For example, the formation of CO proceeds through the route:



In the last process (2.10), productions of C + OH and CH + O are also possible, but their probability is known to be very small (see Sect. 7.2).

Finally it should be noted that recent, more refined, models include additional processes: two-body neutral–neutral collisions involving radicals and reactions on a surface of interstellar grains [63,64].

2.3 Gaseous Discharges

Discharge in a molecular gas is a typical example of molecular plasmas. The discharge plasmas are widely used in applications, some of which are:

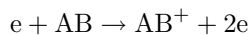
- Production of active molecules (e.g., ozone synthesis)
- Pollution control (destruction of NO_x and SO_x, cleaning of flue gas, etc.)
- Light sources (lightings, gaseous lasers and plasma displays)
- Deposition of materials (production of thin films)
- Etching for semiconductor devices
- Surface modification and treatment
- Plasma sterilization (inactivation of microorganisms)

These applications are possible, because the plasma is in the state of non-equilibrium. That is, the mean energy of electrons much exceeds the gaseous temperature. An applied electromagnetic field supplies energy to keep the nonequilibrium state of the plasma. Thus the plasma serves as a converter of electromagnetic energy into useful materials. Depending on the purposes, different plasmas are produced. It is impossible to fully describe the details of all those plasmas. Here we summarize the roles of molecular processes in those plasmas. More details of the discharge plasmas can be found, for example, in the text book of Lieberman and Lichtenberg [100].

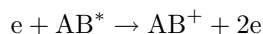
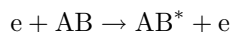
2.3.1 Production and Maintenance of Plasmas

Production of ions needs energy. The energy is supplied from outside mainly through the application of electromagnetic field. Electrons are accelerated

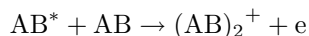
by the field to have enough energy to produce ions. There are two ways of ionization: direct and indirect. Direct ionization is



The incident electron must have an energy above the ionization potential of AB. Indirect process of ionization takes place through an excitation of a molecule followed by an ionization of the excited molecule:



In this case the excited molecule must have a long lifetime. Or more precisely, the lifetime of AB^* should be longer than the mean collision time for the ionization process. In the indirect ionization, the electron energy is not necessarily above the ionization potential. When the gaseous pressure is high, the following process is also possible:



This is called an associative ionization of molecules. It should be noted that, even when the associative ionization dominates, the ionization process is started by the collision of accelerated electrons with the gaseous molecules (for the production of excited molecules).

In a discharge plasma, ions (and electrons also) disappear on the surface of the apparatus. Electron-ion recombinations in a bulk plasma usually play a minor role in the annihilation of ions in a laboratory plasma. But the recombination process may be effective for the production of small radicals, as in the case of the formation of interstellar molecules (see Sect. 2.2).

2.3.2 Determination of Electron Energy Distribution Function

The statistical behavior of electrons in a plasma is governed by the electron energy distribution function (EEDF). Transport properties of electrons are directly dependent on EEDF. Rate coefficients of any electron-molecule collision process are evaluated with the EEDF. In the nonequilibrium plasma used for applications, the EEDF is normally non-Maxwellian. Theoretically EEDF can be obtained by solving the Boltzmann equation. According to the equation, the EEDF is determined by the balance between the acceleration of the electrons by the applied field and the deceleration of them through the collisions with plasma particles (i.e., electrons, ions, and neutral molecules). In a low-temperature, molecular plasma, the electron-molecule collisions play the central role in determining EEDF. Particularly important are the elastic scattering and the rotational and vibrational excitations of molecules. The latter two processes are specific to a molecular gas. To show that, Capitelli

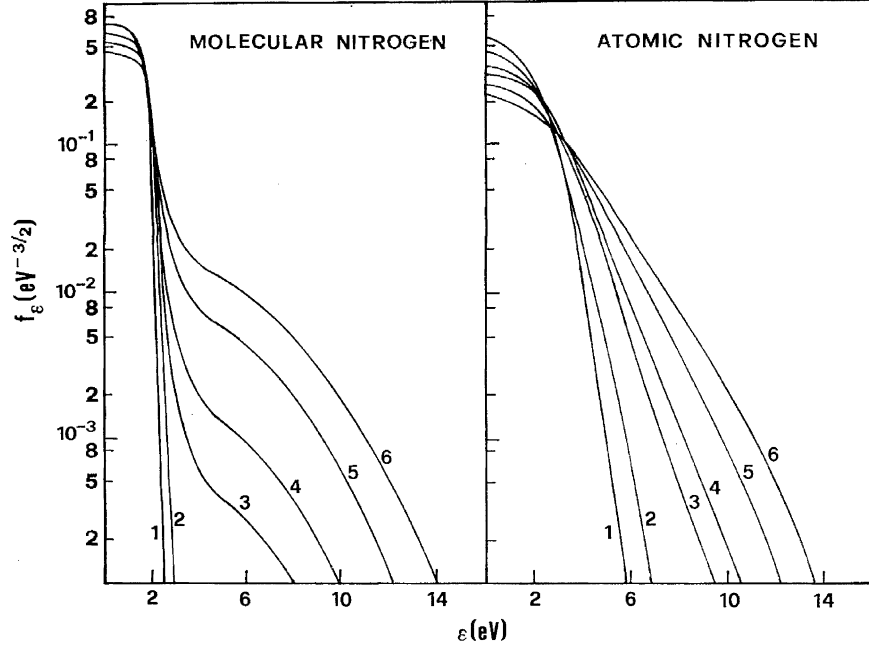


Fig. 2.3. Electron energy distribution functions for N_2 and N plasmas, calculated at different \mathcal{E}/N values (in 10^{-16} V cm^2) (reproduced from [21])

et al. [21] solved the Boltzmann equation separately for molecular nitrogen (N_2) and atomic nitrogen (N). The resulting EEDF is presented in Fig. 2.3.

In the Boltzmann equation, the strength of the applied field \mathcal{E} appears only in the combination with the gas density N in the form \mathcal{E}/N . The EEDF is calculated at a constant value of \mathcal{E}/N . The figure shows EEDF for several different values of \mathcal{E}/N . According to the convention, this EEDF has been normalized as

$$\int_0^\infty \sqrt{\epsilon} f(\epsilon) d\epsilon = 1, \quad (2.11)$$

where ϵ is the electron energy. In both the cases of atomic and molecular nitrogens, the gaseous temperature was assumed to be so low that all the atoms and molecules are in the ground states. The EEDF in the molecular plasma has a peculiar feature compared with the atomic case. In the energy region below about 6 eV, the number of electrons is remarkably reduced. This reflects the significant energy loss of electrons due to the rotational and vibrational excitations of nitrogen molecules. Because of this effect, the mean energy of electrons in the molecular plasma is smaller than the corresponding value in the atomic plasma. (For example, at $\mathcal{E}/N = 3 \times 10^{-16} \text{ V cm}^2$, the mean electron energies for the molecular and atomic plasmas are 1.06 and 1.78 eV, respectively.) In an actual plasma of nitrogen molecules, an accumulation of

vibrationally excited molecules has a significant effect on EEDF. Electrons can gain an energy by the collision with the vibrationally excited molecules (i.e., the super-elastic collision). The behavior of the excited molecules are also affected by their collisions with neutral molecules. In a weakly ionized molecular plasma, therefore, the EEDF and the kinetics of molecules should be treated simultaneously (see, e.g., [21]).

2.3.3 Production of Active Species

Energy supplied from outside through the applied field mainly goes to the electrons. Those electrons (and sometime ions) collide with molecules to produce various active species in the plasma. They are ions, radicals, active atoms, excited atoms and molecules, and high-energy photons. Those active species are utilized for practical applications mentioned above. They collide with other plasma particles to generate secondary products. In this manner, the electron and ion collisions serve as a trigger of a series of chemical reactions.

To show what kinds of active species are produced, we present in Fig. 2.4 the result of a model calculation of CH_4 plasma by Tachibana et al. [153]. This is an RF plasma and the gas pressure is 0.22 Torr. The number density of the species shown was determined by solving a set of rate equations. The rate coefficient of each reaction was evaluated with the EEDF observed by themselves (i.e., not a theoretical one). All possible reactions were taken into account. But some of them have a rate coefficient of large uncertainty, because of a lack of relevant experimental data. The most abundant radical is CH_3 . It is produced mainly by the collision of electrons with CH_4 . The other radicals, CH_2 , CH , and C , are also produced by the electron collision with CH_4 . But, due to the fast radical-molecule reactions, the number density of those radicals is small. The authors investigated the effect of attachment of radicals on the surface. There was no definite information about the sticking probability of CH_3 on a surface. They took two different values for the sticking probability to see the effect. They found that the radical density is very sensitive to the surface condition.

Later a similar modeling calculation of CH_4 plasma was made by Herrebout et al. [65]. They obtained the electron energy distribution function by solving the Boltzmann equation. The result of Herrebout et al. is not necessarily the same as that of Tachibana et al. The most abundant radical in the model of Herrebout et al. is CH_3 as in the model of Tachibana et al. But, in the model of Herrebout et al., higher order hydrocarbons (i.e., C_2H_4 and C_2H_6) are relatively more abundant than the model of Tachibana et al. Herrebout et al. produced even C_3H_8 , which was not included in the calculation of Tachibana et al. Herrebout et al. ascribed the difference to the fact that different reactions were considered in the two models. This confirms the importance of the reliable knowledge of the elementary processes.

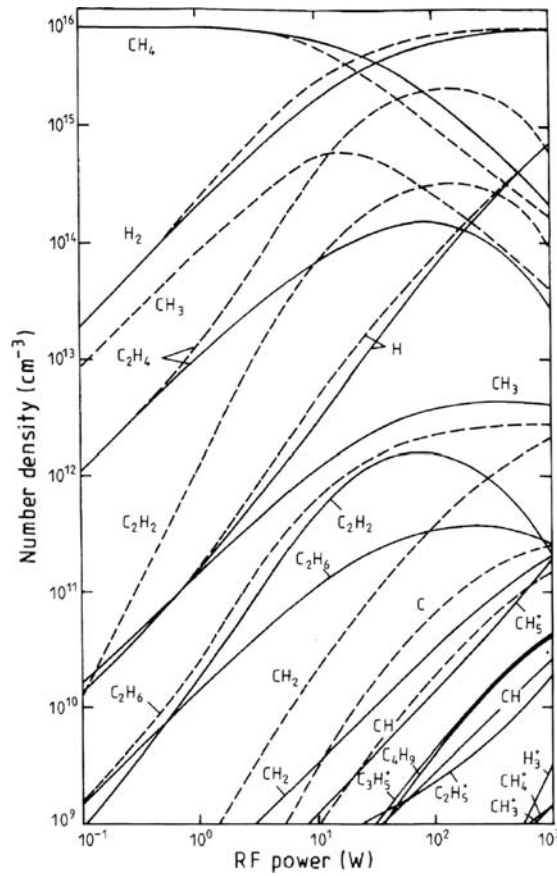


Fig. 2.4. Number densities of radicals and other species produced in a CH_4 plasma. They are plotted as a function of the RF power applied, for two different values of sticking probability of CH_3 on a surface: unity (solid line) and 10^{-3} (dashed line). (Reproduced from [153])

2.4 Fusion Plasma

Fusion plasma is the plasma developed for achieving thermonuclear fusion. The central part of the fusion plasma has a temperature of as high as 10 keV (or 10^8 K) and is fully ionized. The plasma in the boundary region is relatively cool and includes neutral particles. Most of the large fusion devices are now equipped with a divertor, which pulls out the ash of the burnt material and the generated heat from the core plasma. Since contacting special boundary plates (divertor plates), the plasma in the divertor includes molecules originated from the plate. The plasma in the boundary region, including the divertor, is often called the edge plasma. It is a kind of molecular plasma, whose temperature

is normally less than 100 eV. The following two molecular species are involved in the edge plasma:

- (1) H_2 . It is ejected from the wall of the fusion device (or divertor) as a result of an H^+ impact. When a H^+ hits on the wall, it reacts with hydrogen atoms on the wall surface or in the wall materials to produce H_2 . The resulting molecule is ejected from the surface promptly or at the impact of another H^+ .
- (2) C_nH_m . This is generated by a chemical sputtering of H^+ on the carbon coated surface, which is widely used in the current fusion devices.

The study of edge plasma is important (see, e.g., [28]):

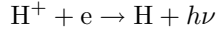
- (1) To establish the boundary condition of the whole fusion plasma. The temperature and density of the bulk plasma are controlled by the boundary condition.
- (2) To investigate the interaction between the plasma and the wall of the device. This is necessary for the protection of the wall materials.
- (3) To understand the behavior of the impurities (e.g., C atoms) in the plasma. They are originated from the bounding surface.

The study of the molecular processes in the edge plasma is different from other cases. Here the plasma itself is given as an extension of the bulk plasma. We investigate the behavior of neutral molecules in such a plasma. The density of molecules is usually smaller than the density of electrons, which is equal to the ion density. To know the behavior of hydrogen molecules (or any other neutral particles) in the plasma, we always resort to spectroscopy. From the analysis of the spectra of the radiation measured, we directly obtain the population of the molecules in particular states. To deduce plasma parameters from the population, we need the knowledge of the mechanism of generating the population. The best way to do so is to solve the equations of the collisional-radiative model of the molecule [58]. It is a set of rate equations for electron-impact and ion-impact excitations (and de-excitations, if necessary) and radiative transitions. We need cross-sections (or rate coefficients) for all possible processes of excitation (and de-excitation) of rotational, vibrational, and electronic states of the relevant molecule. An example of the collisional-radiative model was the study of hydrogen plasma by Sawada and Fujimoto [141].

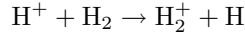
One particular topic of molecular processes in the edge plasma is the behavior of hydrocarbon molecules in a divertor. This study is needed to understand the erosion mechanism of wall materials and the behavior of the C-impurity in the bulk plasma. It is also of significance in the estimate of the loss of hydrogen atoms. Hydrocarbon molecules are ionized in the plasma and eventually return to the wall. Hydrogen atoms are lost as a component of the molecules deposited on the wall. For example, Alman et al. [6] made a model calculation of the behavior of C_nH_m in the edge plasma. They took into account all the possible processes of electron- and proton-collisions

with 16 hydrocarbon molecules (i.e., CH_n with $n = 1-4$, C_2H_m and C_3H_m with $m = 1-6$). They also included the (dissociative) recombination processes between electrons and hydrocarbon ions, leading to the production of small hydrocarbon radicals.

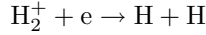
Another special topic of the molecular process in the edge plasma is the molecule assisted recombination. The main component of the fusion plasma, i.e., H^+ , is annihilated through the recombination with the plasma electrons in such a way as



This is a radiative process and very slow. If a molecular hydrogen is present in the plasma, a charge transfer collision can transform H^+ into a molecular ion



Then the molecular ion induces the dissociative recombination

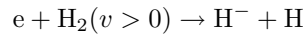


This process is much faster than the radiative recombination of H^+ . Furthermore the last two processes may be enhanced, if the molecules or molecular ions are vibrationally excited. This two-step recombination process of H^+ is called a molecule assisted recombination (MAR). In a real plasma, many other processes compete with MAR. To estimate the effect of MAR, we need a complicated model calculation of hydrogen plasmas. Krasheninnikov [93], for example, carried out one such calculation. He obtained the frequency of the recombination through MAR at the electron temperature $T_e \sim 1-4 \text{ eV}$ and the electron density $N_e = 10^{14} \text{ cm}^{-3}$ to be

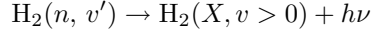
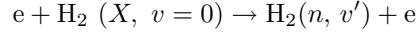
$$\nu_{\text{MAR}} = 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \times N_{\text{H}_2} \text{ (in cm}^{-3}\text{)}$$

When we assume the number density of hydrogen molecules to be of the order of N_e (i.e., $\sim 10^{14} \text{ cm}^{-3}$), the ν_{MAR} has the value by about 100 times larger than the frequency of the radiative recombination. Kubo et al. [94] investigated the behavior of H_2 in the divertor of a large fusion device, JT-60U, with using spectroscopy. They confirmed that the MAR is, at least, as important as the radiative recombination of H^+ .

One of the methods of heating the fusion plasma is an injection of fast neutral (usually atomic hydrogen) beam into the plasma. To produce the fast ($\sim 1 \text{ MeV}$) H beam, a fast H^- beam is used, because an acceleration of ions is easy and H^- has a high neutralization ($\text{H}^- \rightarrow \text{H}$) efficiency even at such a high beam energy. For that purpose, we need an ion source which efficiently generates a large amount of H^- . It is now well known that an electron (dissociative) attachment of H_2 has a large cross-section, once the hydrogen molecule is vibrationally excited (see Sect. 5.13)



If we have any efficient method to produce vibrationally excited H_2 , then we can adopt this process for the H^- source we need. The direct vibrational excitation of H_2 by electron impact is not efficient. One promising process is the two-step process such as



The electronic state, n , is connected with the ground state, X , through a dipole-allowed transition. An H^- source based on this mechanism has been developed and tested (see a review by Bacal et al. [9]). To understand the physics in the ion source and to improve its operation, a modeling of H_2 plasma has been made by a number of authors (e.g., [22]). In the modeling, a knowledge is needed for the collision processes involving H_2 in its vibrationally excited state. One controversial problem is whether the electronically excited molecule can also enhance the production of H^- . To make clear this problem, we need information about the collision processes involving H_2 in its electronically excited state.

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