

CHAPTER 2

Introduction to Plasma and Plasma Diagnostics

Miran Mozetič, Alenka Vesel, Gregor Primc and Rok Zaplotnik

Jozef Stefan Institute, Ljubljana, Slovenia

2.1 NONEQUILIBRIUM STATE OF GAS

Ordinary gas is found in the state of thermal equilibrium. This means that all gaseous particles assume the Boltzmann distribution over kinetic and potential energies. The distribution of gaseous particles over the kinetic energy is calculated as

$$f_E(E) = 2\sqrt{\frac{E}{\pi}} \left(\frac{1}{k_B T}\right)^{3/2} \exp\left(\frac{-E}{k_B T}\right), \quad (2.1)$$

where k_B is the Boltzmann constant ($k_B = 1.38 \times 10^{-23}$ J/K) and T is the so-called “kinetic temperature” of gaseous particles. Other terms also appear in literature such as “neutral gas kinetic temperature” or “translational temperature.” The distribution depends only on the gas kinetic temperature and not on the mass of the gaseous particle. The average kinetic energy of a gaseous particle at room temperature is approximately 0.04 eV. The kinetic energy is defined as $E = \frac{1}{2}m\langle v^2 \rangle$, thus the particles of higher mass will move slower than light particles. A typical random velocity of molecules such as nitrogen and oxygen is close to 500 m/s at room temperature, whereas the velocity of free electrons (if present in equilibrium gas) is much higher, obviously by the factor of $\sqrt{m/m_e}$, where m and m_e are masses of a molecule and an electron, respectively. The dissociation fraction (number of atoms, molecules, and ions) is proportional to different energies:

1. the number of dissociated atoms in a thermal equilibrium is proportional to the dissociation energy E_D ;
2. the ionization fraction is proportional to ionization energy E_i ;
3. the number of molecules excited into a given vibrational state (characterized by vibrational quantum number ν) is proportional to the vibrational energy E_ν ;

4. the number of molecules excited into separate rotational states of the same vibrational level in a given electronic state to rotational energy E_r . Corresponding equations are as follows:

$$N_A \propto e^{-\frac{E_D}{k_B T_D}}, \quad (2.2a)$$

$$N_i \propto e^{-\frac{E_i}{k_B T_i}}, \quad (2.2b)$$

$$N_v \propto e^{-\frac{E_v}{k_B T_v}}, \quad (2.2c)$$

$$N_r \propto e^{-\frac{E_r}{k_B T_r}} \quad (2.2d)$$

The indexes in Eq. (2.2a) correspond to the excited state of molecules. N_A is the number of atoms created by dissociation of the parent molecule, N_i is the number of ions, N_v is the number of molecules in the v -th vibrational state and N_r is the number of molecules in r -th rotational state. The terms T_D , T_i , T_v , and T_r are the dissociation, ionization, vibrational, and rotational temperatures, respectively. The proportional factors are often complex because of the stepwise processes. For a gas in thermal equilibrium all the temperatures in Eqs. (2.1) and (2.2b) are the same, thus, one can calculate the dissociation and ionization fractions as well as distribution of molecules over vibrational and rotational states if the gas temperature is known.

The nonequilibrium states of gases are much more complex. While the relation (1) is often satisfied (at least in a fair approximation) for given types of gaseous particles (neutral molecules and atoms as well as electrons and ions), the electron temperature is usually much larger than the temperature of other gaseous particles. The relations (2) are rarely satisfied. First, there are large differences between T_D , T_i , T_v , and T_r , and eventually the distribution over vibrational states does not assume the Boltzmann relation. In a typical nonequilibrium gas, the rotational temperature will be close to the kinetic temperature of neutral molecules, while the dissociation, ionization, and vibrational temperatures assume almost arbitrary values depending on particular conditions. Therefore, the term “temperature” should not be used in the description of gas in the nonequilibrium state. A more accurate description of the nonequilibrium gas contains the kinetic temperatures, the ionization and dissociation fractions as well as the vibrational temperature of the gaseous molecules if

distribution follows the Boltzmann law (2). Typically, only the first few vibrational states are taken into account when determining the vibrational temperature and they usually follow the Boltzmann law. Population of highly excited vibrational states may differ significantly, though.

One can obtain a nonequilibrium state of a gas by heating only specific gaseous particles. In current praxis the heating of charged particles is chosen. Gas is subjected to an electrical field where charged particles gain kinetic energy while neutral particles remain unaffected. The charged particles then transfer a part of their kinetic energy to the neutral particles causing excitation of ro-vibrational and electronic states, dissociation or/and ionization.

Every nonequilibrium state approaches equilibrium spontaneously. This process is often called “thermalization” and is explained as the equalization of the various temperatures in Eqs. (2.1) and (2.2c). The gaseous particles in various states thermalize either by emitting light quanta (radiation) or by transferring their energy in the excited state to colder particles. The transfer could be through super-elastic collisions (transfer of the internal energy to the kinetic energy of colliding gaseous particles) or by accommodation on surfaces of the gas container. The ratio between gas-phase and surface thermalization depends on the mean free path of gaseous particles which in turn depends on the pressure for a given container. The collision frequency is proportional to the pressure and so is the gas-phase thermalization. Some super-elastic collisions require three-body collisions whose frequency increases with the square of the pressure. A good example is a gas-phase association of two atoms to the parent molecule. Such association requires three-body collisions to satisfy conservation of energy and momentum. Because the collision frequencies increase with increasing pressure the life-time of the nonequilibrium gas state decreases with increasing pressure. In contrast, at pressures where the mean free paths are comparable to the dimension of the gas container the surface accommodation prevails and the life-time increases with increasing pressure. Obviously, there is an optimal pressure for sustaining the nonequilibrium state of gas; in a typical laboratory scale container it is of the order of 100 Pa.

2.2 GASEOUS PLASMA AND AFTERGLOW

A typical example of a nonequilibrium state of a gas is gaseous plasma. Gas in the container is exposed to an electric field. Charged particles (there are always some free electrons in gas) are accelerated in the electric

field, they gain energy and transfer it to neutral molecules causing excitation to ro-vibrational and electronic states as well as dissociation or/and ionization. The new electrons formed at ionization collisions are further accelerated, cause ionization of neutral molecules, and consequently, they multiply. Soon after applying an electrical field of sufficient strength, the breakdown of the gas is observed—originally nonconductive gas becomes conductive and is transformed to the state of plasma. As the density of charged particles increases, the loss probability increases too; therefore, a steady concentration of charged particles appears. At such conditions, the production of charged particles is equal to the loss in the gas phase and/or on surfaces. The steady concentration of charged particles appears soon after applying the electrical field, typically in a microsecond or faster. A longer time is sometimes needed to establish a steady concentration of gaseous particles in various excited states, but typically the steady-state of plasma is obtained in a time scale below a millisecond after applying the electrical field. An exception is dusty plasma where changes are observed over a time scale above one second.

Both negatively and positively charged particles are accelerated in the electric field. Positively charged particles are molecular and atomic ions. In a static electric field, they gain energy equal to the voltage difference between positive and negative electrodes ($e_0(V_+ - V_-) = e_0U$), where e_0 is the elemental charge. Eventually an ion collides with a neutral molecule. The ion and molecular masses are almost identical, thus an elastic collision between a fast ion and a slow molecule causes sharing of the initial ion kinetic energy. A substantial fraction of the ion energy is, therefore, transferred to the kinetic energy of a neutral molecule. Consequently, such collisions contribute to an increase of the kinetic temperature as in Eq. (2.1). Such sharing of the kinetic energy is not possible for collisions between electrons and neutral molecules. The electrons also gain the energy of eU when passing the potential difference of U , but do not lose it upon elastic collision with a molecule because of the difference in masses. At the elastic collision, both the momentum and energy are conserved and only a very small fraction of kinetic energy is exchanged between a fast particle of a low mass (electron) and slow heavy particle (charged or neutral atom or molecule). This is the key reason for discrepancy in kinetic temperature between electrons and any other gaseous particles in the nonequilibrium gaseous plasma: The electrons are heated by acceleration in the electrical field, but do not lose their kinetic energy for heating other particles. Instead, they use their energy for

ionization, dissociation, and excitation events. Obviously, the electron temperature is higher than any of the temperatures in Eqs. (2.1) and (2.2d) in the nonequilibrium gaseous plasma.

The electrons are much faster than the molecular or atomic ions because of their low mass (even if their temperature is not higher than the temperature of the other gaseous particles). In the gas phase, electrons diffuse (move randomly) until they eventually reach the surface of the plasma container. They leave positively charged particles in the gas phase; therefore, plasma becomes positive against the walls (and the walls become negative against plasma). Soon after ignition of the electrical discharge, the plasma becomes positive enough to retard all but the fastest electrons from the surface. The accumulation of the positive charge lasts until the fluxes of ions and electrons onto the surface equalize, which happens in a microsecond if not sooner. A potential difference between plasma and the surface is established and the requirement for a steady state (equal fluxes of positively and negatively charged particles onto the wall) is satisfied. The potential difference occurs in a linear dimension that is of the order of a Debye length, which has been defined as

$$\lambda_D = \sqrt{\frac{\varepsilon_0 k_B T_e}{e_0^2 n_e}} \quad (2.3)$$

where ε_0 is dielectric permeability ($\varepsilon_0 = 8.85 \times 10^{-12}$ F/m), e_0 is the elementary charge (1.6×10^{-19} As), T_e is the electron temperature, and n_e is the electron density. The sheath appears next to the walls of the plasma container as well as next to any object or sample immersed into plasma. The sheath is useful because it prevents draining of electrons from the gaseous plasma. Obviously, the sheath thickness should be smaller than the smallest linear dimension of the plasma container. The Debye length is inversely proportional to the electron density and proportional to the electron temperature. Fig. 2.1 shows the Debye length versus the electron density for a range of densities between 10^{14} and 10^{20} m⁻³ and electron temperatures between 1 and 10 eV.

Apart from electronegative gases that contain a substantial concentration of negatively charged molecules or atoms, the major negatively charged particles are free electrons. As stressed above, they lose their kinetic energy in the sheath next to any object placed into a plasma reactor, thus, their influence on the materials' properties is marginal. The negatively charged ions (if present at all) cannot reach the surface of any

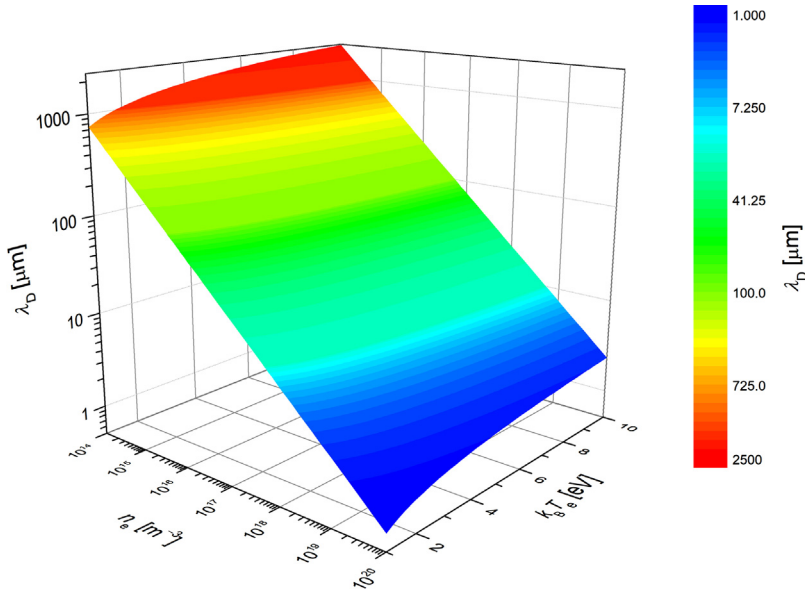


Figure 2.1 The Debye length in gaseous plasma.

material; therefore, their role in modification of surface properties is easily neglected, because the kinetic temperature of massive negative ions is not sufficient to provide negatively charged ions capable of traversing the sheath. In contrast, the positive ions are accelerated across the sheath; therefore, their influence on the materials' modification should always be taken into account. The neutral excited gaseous particles are not affected by the electric field inside the sheath and they reach the surface thermally with a negligible kinetic energy, but with the internal energy corresponding to the energy level of the excited state.

Users of plasma technologies are often concerned about the neutralization of charged particles in the gas phase. Positively and negatively charged particles (ions and electrons) are attracted by the electrostatic force and the collisions between them are frequent. The probability for neutralization, however, is low because of the quantum character and conservation of energy and momentum. The available energy before the collision is a sum of the potential and kinetic energies of colliding particles. The potential energy is equal to the ionization energy if the positively charged ion is in the ground state. The available energy before the collision is, therefore, larger than the ionization energy of the parent atom/molecule. The excessive energy cannot appear as the kinetic energy

of a neutral atom/molecule after collision between a positive ion and electron because of the momentum conservation. Therefore, the neutralization should involve an additional particle. One possibility is a radiative neutralization by emission of a light quantum; however, the probability of such an event is very low because of the rules of quantum mechanics. The other possibility is a three-body collision—usually an electron, ion, and a neutral molecule or atom is involved. The three-body collision frequency increases with a square of the pressure and is regarded marginal at pressures below, say, 100 Pa. The effect is, however, the dominant loss mechanism of charged particles at atmospheric pressure, where the frequency is of the order of MHz. That is the reason why the nonequilibrium plasma at atmospheric pressure can be sustained only in strong electrical fields. Such a field is present at the ionization front of a streamer—a short-duration discharge which is limited to a small volume. Three-dimensional, cold nonequilibrium gaseous plasma is, therefore, unlikely to be sustained in large discharge chambers.

A variety of discharges are suitable for sustaining the nonequilibrium gaseous plasma. A simple DC glow discharge is created by placing two electrodes into a plasma chamber. One electrode can simply be the grounded housing of the chamber. The electrodes could be of the same dimensions (typically in the case of a dielectric reactor made from glass) or they could be asymmetric. The latter case is typically applied in metallic chambers. In such cases, the larger electrode (usually the grounded chamber) should be biased negatively and the smaller electrode positively. Such a coupling prevents too high ion fluxes on the smaller electrode and, thus, problems may arise because of arcing (transformation of a rather high-impedance glow discharge to a low-impedance electric arc). In the case of DC discharge, the sheath next to the cathode is biased few at 100 V below plasma potential; therefore, the positive ions bombard the cathode with substantial kinetic energy causing heating of the cathode and sputtering of the cathode material.

More popular are high frequency discharges. Both radiofrequency (RF) and microwave (MW) discharges are widespread sources of the nonequilibrium plasma. Plasma created with a MW discharge is usually concentrated to the region of a high electrical field, therefore, an asymmetry is often observed. Such an effect is less pronounced in the RF-driven plasma because the penetration depth of the RF field into conductive plasma is larger. Large plasma reactors suitable for treatment of polymer materials are usually driven by RF discharges. Electrodeless RF discharges

are particularly useful. In such discharges, one can take advantage of a resonant electron heating. Such conditions appear where the electron collision frequency is similar to the frequency of the electric field. At the commonly used industrial frequency of 13.56 MHz, such a resonant heating occurs at the pressure of the order of 100 Pa.

All nonequilibrium systems tend to approach equilibrium when selected heating of specific gaseous particles is omitted. Then the electrons quickly cool down and are lost at neutralization either in the gas phase or on the surfaces of the plasma chamber. The typical time is of the order of a microsecond. Other reactive gaseous particles persist in the plasma reactor long after the charged particles have been neutralized and the state of plasma has been lost. A good example are metastables and atoms of molecular gases. They persist in the chamber over a time span of milliseconds, seconds or even minutes (providing they are not simply pumped away from the gas container) as long as the gas pressure is rather low. At atmospheric pressure, all reactive gaseous species thermalize quickly because of the high probability for three-body collisions. The gas that is left after neutralization of charged particles is not plasma but is still in the nonequilibrium state and is called “afterglow” or “postglow.” The afterglow is particularly suitable for modification of the surface properties of polymers. The nonequilibrium gas in the afterglow can be sustained by two mechanisms: either pulsing the discharge or using continuous plasma in a small volume while continuously pumping the gas into a separate chamber—a common expression is “flowing afterglow.” Pulsed systems typically operate at plasma on-time of the order of microseconds (to establish a desired nonequilibrium state of the gas), while the off-time is of a longer magnitude. A recommended configuration of the flowing afterglow is presented in [Fig. 2.2](#). Plasma is limited to a rather small volume inside the discharge chamber. Molecular gas in a thermal equilibrium at room temperature passes the plasma region and enters the afterglow chamber. The orifice between the discharge and the afterglow chambers is preferably small; the conduction for gas flow should be much smaller than the pumping speed of the vacuum pump. A strong pressure gradient appears between the discharge and the afterglow chamber, resulting in drifting gas at subsonic velocity from the discharge to the afterglow chamber, therefore, the loss of reactive particles on the surface of the orifice is minimal. One of the best discharges for sustaining a highly nonequilibrium gaseous plasma in a rather small volume at elevated pressures (around 1000 Pa) is a MW discharge in the surfatron mode.

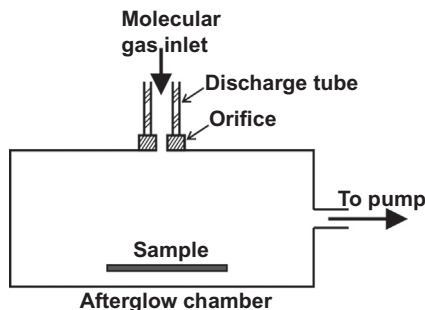


Figure 2.2 A useful configuration for treatment of polymers with neutral reactive particles in the flowing afterglow.

2.3 REACTIVE GASEOUS SPECIES

Nonequilibrium gas, either plasma or its afterglow, is rich in gaseous particles of substantial excitation energy suitable for tailoring surface properties of polymer materials. The particles of substantial affinity for chemical interaction with polymer materials are positively charged ions, neutral atoms in the ground as well as in electronically excited states (if metastable), some types of metastable molecules as well as light quanta that are emitted from gaseous plasma (providing the photon energy is high enough). The light quanta cause bond scission of the surface film of a thickness equal to the penetration depth. For UV radiation the penetration depth in polymers is a fraction of a micrometer. Other particles cause modification of a very thin surface film of the order of nanometer. Surface activation as well as etching is observed as a result of treatment with nonequilibrium gas.

2.3.1 Noble Gases

Pure noble gases are rarely used for tailoring surface properties of polymers. The reason for this is the lack of chemical interaction. Noble gases are characterized by high ionization energies. The electronically excited states are sometimes metastable, which means that the spontaneous relaxation by electrical dipole radiation is forbidden by the rules of quantum mechanics. The radiation life-time is, therefore, long enough that the relaxation frequently appears due to quenching—that is, transfer of internal energy to other particles, usually at super-elastic collisions. [Table 2.1](#) represents the ionization energies for helium, argon, neon krypton, and xenon as well as the energy of the first metastable state and its radiative life-time.

Table 2.1 Ionization and excitation energies for metastable states of the lowest energy and the life-time of the metastable states

Type of particle	Symbol	Excitation energy (eV)	Radiative life-time	References
Ar ground	$^1S_0$	0	Stable ^a	[1]
Ar metastable $1s_5$	$^3P_2$	11.54	56 s	[1,2]
Ar metastable $1s_3$	$^3P_0$	11.72	45 s	[1,2]
Ar ion	$3p^5\ ^2P^{\circ}_{3/2}$	15.76	Stable ^a	[1]
He ground	$1\ ^1S_0$	0	Stable ^a	[1]
He metastable	$2\ ^3S_1$	19.82	~ 7700 s	[1]
He ion	$1\ s\ ^2S_{1/2}$	24.59	Stable ^a	[1]

^aNonradiative state.

The particles likely to be found in nonequilibrium plasma created in noble gases are positively charged ions and electrons as well as metastables. The electron temperature in such a plasma is rather high and increases with the increasing ionization energy; it is the highest for helium and the lowest for xenon. The ions can be accelerated in a sheath next to the powered electrode and inflict radiation damage of the surface film. The surface film's thickness depends on the kinetic energy of the positive ions. The radiation damage often causes structural changes as well as rich morphology. Originally smooth polymer surfaces become rough on the submicrometer scale on treatment with energetic ions. In the case where the polymer is not backed by an electrode with high negative potential powered by a high-frequency generator (samples kept at floating potential) the interaction is marginal. The same applies for metastables.

Gas always contains impurities. The common impurity in a plasma reactor is water vapour. The dissociation energy of water molecules as well as OH radicals is below the energy of metastables, therefore, water is likely to dissociate fully in the plasma of noble gases, especially in helium and argon. The ionization energy of O and H radicals is lower than the energy of some metastables, so the impurities are highly ionized. The plasma of noble gases (in particularly helium and argon) is, therefore, used predominantly as the source of metastables that possess high internal energy.

2.3.2 Oxygen

The nonequilibrium state of oxygen is traditionally used for the activation of polymer surfaces. The activation stands for the formation of

oxygen-rich functional groups on the polymer surface [3,4]. The groups are polar and, therefore, contribute to the polar component of the polymer surface energy and increases its wettability [5]. Oxygen molecules have two metastable electronic states that are worth stressing $O_2(a)$ and $O_2(b)$: the first is at the excitation energy of 0.978 eV and the second one at 1.627 eV. The excitation energies for oxygen molecules are given in Table 2.2.

The dissociation energy of the oxygen molecule is 5.12 eV. The dissociation could appear at the electron impact with a molecule in the ground state, but in plasma of a rather low electron temperature step-wise dissociation prevails: molecules are first excited to metastable states and these are then dissociated. The dissociation by an electron impact rarely leads to the formation of thermal atoms—those with the same kinetic temperature as neutral molecules. A part of the electron energy is spent for kinetic energies of both atoms that are formed upon dissociative collision of an electron with an oxygen molecule. The atoms then effectively thermalize at the elastic collisions with molecules, especially at elevated pressure. The atoms are stable in a vacuum and the major loss mechanism is by three body collisions (at high pressure) or on the walls of the plasma or after-glow chamber. Table 2.3 shows the recombination coefficients for oxygen atoms on selected surfaces. Obviously, the atom density in a reactor will be large if the reactor is made from materials that exhibit low probability for surface recombination.

Table 2.2 Excitation energies of oxygen molecules and atoms

Type of particle	Symbol	Excitation energy (eV)	Radiative life-time	References
O_2 ground state	$X^3 \Sigma_g^-$	0	Stable ^a	[6]
$O_2(a)$	$a^1 \Delta_g$	0.978	~ 55 min	[6,7]
$O_2(b)$	$b^1 \Sigma_g^+$	1.627	~ 10 s	[6,8]
O_2^+	$X^2 \Sigma_g^+$	12.059	Stable ^a	[6,9]
O_3	$X^1 A_1$	0	Stable ^a	[6]
O ground	^3P	0	Stable ^a	[1]
O first metastable	^1D	1.967	100 s	[1]
O second metastable	^1S	4.189	1 s	[1]
O^+	$^4S^{\circ}_{3/2}$	13.618	Stable ^a	[1]

^aNonradiative state.

Table 2.3 Recombination coefficients for oxygen atoms on selected surfaces at room temperature

Material	Recombination probability	References
Al ₂ O ₃	0.0020	[10]
CoO	0.029	[11]
Cu ₂ O	0.025	[12]
NiO	0.27	[13]
Fe	0.01	[14]
Pt	0.0027	[10]
TiO ₂	0.013	[11]
WO ₃	0.012	[11]
Pyrex glass	10 ⁻⁴	[15]
Quartz	10 ⁻⁴	[16]
Stainless steel	0.07	[17]
Teflon	7.5 · 10 ⁻⁵	[10]

One peculiarity of oxygen plasma is a high probability for super-elastic collisions between molecules in vibrational states and atoms in the ground state: $O_2(\nu) + O \rightarrow O_2(\nu - 1) + O$. The excessive energy (difference between the ν -th and $(\nu - 1)$ -th state is shared between the molecule and atom as increased kinetic energy. Such collisions heat the gas rather effectively and lowers the vibrational temperature. Taking into account just two or three lowest vibrational states, the vibrational temperature (Eq. 2.2a) is just above the kinetic temperature (Eq. 2.1) in highly non-equilibrium oxygen plasma. The population of highly excited states may differ substantially from the Boltzmann law.

Oxygen flowing afterglow (Fig. 2.2) is rather cool and its kinetic temperature (which is equal to the rotational or vibrational temperatures) rarely exceeds 40°C as long as the walls of the afterglow chamber are kept at room temperature. The temperature of a polymer placed in the afterglow chamber is somewhat higher because of exothermic surface reactions: heterogeneous surface recombination of atoms and oxidation of polymer. Little knowledge is available on the relaxation of O₂ molecules in both metastable states on polymer materials. The relaxation should cause heating of the solid material, of course, but the probability for such events is unknown. The density of O-atoms in the ground state is always high in the afterglow chamber providing the reactors are made of materials with a low recombination coefficient (Table 2.3) and the plasma system (Fig. 2.2) is properly designed. The dissociation fraction easily exceeds 50% in glowing plasma and 10% in the flowing afterglow [18].

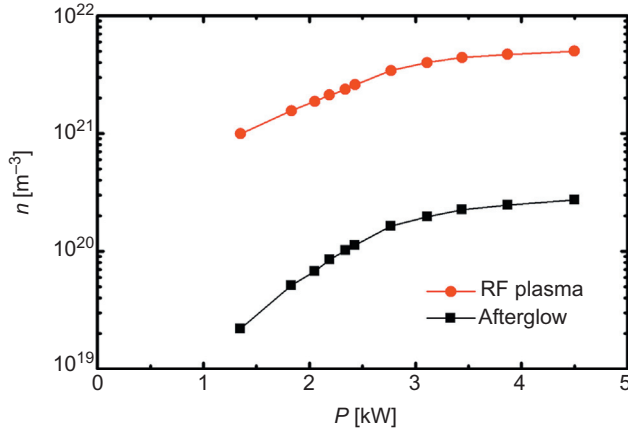


Figure 2.3 The density of O-atoms in RF plasma and its flowing afterglow 2 m away from the plasma source.

Fig. 2.3 represents the O-atom densities in RF plasma and its flowing afterglow 2 m away from the plasma source [19]. The oxygen plasma afterglow is very suitable for functionalization of many polymers because the concentration of polar functional groups is often higher than through the treatment in glowing plasma. Also, in the afterglow the atoms cause negligible etching [20,21].

2.3.3 Hydrogen

Hydrogen afterglow contains only molecules and atoms in the ground electronic state. These gaseous particles are unlikely to interact chemically with most polymers, therefore, the hydrogen afterglow is obsolete and one should rather use glowing plasma for tailoring the surface properties of polymers. Hydrogen molecules or atoms do not have metastable states, therefore, any electronic state of neutral particles is quickly relaxed by radiation. Table 2.4 represents excitation energies of hydrogen molecules and atoms. The dissociation energy of the hydrogen molecule is only 4.5 eV, thus, a dominant mechanism for the formation of neutral H-atoms in the ground state is by electron impact. A peculiarity of hydrogen molecules is the $b^3 \Sigma_u^+$ state which is unstable and dissociates in a short time after formation. Another peculiarity is the existence of the $a^3 \Sigma_g^+$ state with high potential energy. This state relaxes by a photon emission to the dissociative state $b^3 \Sigma_u^+$. The emission appears in the UV range with the maximal photon energy of about 10 eV. Hydrogen plasma is, therefore, an excellent

Table 2.4 Excitation energies of hydrogen molecules and atoms

Type of particle	Symbol	Excitation energy (eV)	Radiative life-time	References
H ₂ ground state	X ¹ Σ _g ⁺	0	Stable ^a	[6]
H ₂ metastable	c ³ Π _u	11.87	1 ms	[22,23]
H ground state	n = 1	0	Stable ^a	[1]
H 1 st excited state	n = 2	10.19	~ 2 ns	[1]
H 2 nd excited state	n = 3	12.08	~ 30 ns	[1]
H 3 rd excited state	n = 4	12.74	~ 100 ns	[1]

^aNonradiative state.**Table 2.5** Recombination coefficients for hydrogen atoms on selected surfaces at room temperature

Material	Recombination probability	References
Al	1.8 10 ⁻³	[24]
Co	0.18	[25]
Cu	0.19	[25]
Ni	0.18	[24]
Fe	0.17	[25]
Pt	0.25	[25]
Ti	0.1	[25]
W	0.06	[25]
Pyrex glass	10 ⁻³	[26]
Quartz	10 ⁻³	[26]
Stainless steel	0.1	[27]
Teflon	4.5 10 ⁻⁴	[28]

source of a continuum radiation in the UV range providing the electron temperature is large enough to excite the a³ Σ_g⁺ state and the dissociation fraction is not too high. These two requirements are contradictory, therefore, a strong continuum radiation does not appear in any hydrogen plasma. One method of stimulating such radiation is the application of a mixture of hydrogen and argon. The excitation energy of the first argon metastable state is just above the excitation energy of H₂ (b³ Σ_u⁺) state and the pumping of energy from argon metastables is efficient. Another method for increasing the continuum radiation from the hydrogen plasma is the construction of a discharge chamber from a material that acts as a catalytic surface for the heterogeneous recombination of H atoms to parent molecules. Table 2.5 shows recombination coefficients for hydrogen atoms on selected surfaces. If the goal is strong UV radiation, one should use metals

such as titanium. On the other hand, if a high dissociation fraction is needed, the best material is quartz glass.

Hydrogen atoms do not have metastable states, therefore, radiation can occur from any excited state directly to the ground state. The radiation is discrete and in the vacuum ultraviolet (VUV) range. In fact, radiation from the first excited state of H-atom to the ground state at 121 nm is defined as the long wavelength boundary of VUV radiation. Both continuum and discrete radiation arising from excited molecules and atoms respectively are suitable for breaking bonds in the surface layer of polymers. The penetration depth of VUV radiation is smaller than for the UV continuum. Synergy between (V)UV radiation and hydrogen atoms leads to the quick removal of oxygen from the surface of polymers, therefore, the treatment is suitable for hydrophobization of moderately hydrophilic polymers rich in oxygen.

Another peculiarity of hydrogen atoms is that the probability for heterogeneous surface recombination of H-atoms to parent molecules on glass surfaces increases significantly with increasing temperatures. Such effects cause the time dependence of the H-atom density in a plasma reactor which is not cooled properly. For example, the H-atom density drops by 30% as the temperature of the plasma reactor made from borosilicate glass increases to 100°C.

2.3.4 Nitrogen and Ammonia

Nitrogen molecules have numerous excited states and some are metastable [29,30]. Table 2.6 represents the excitation energies of selected excited states of nitrogen molecules and atoms. The dissociation energy is much

Table 2.6 Excitation energies of nitrogen molecules and atoms

Type of particle	Symbol	Excitation energy (eV)	Radiative life-time	References
N ₂ ground state	X ¹ Σ _g ⁺	0	Stable ^a	[6]
N ₂ first metastable	A ³ Σ _u ⁺	6.17	0.01 s	[6,23]
N ₂ second metastable	a ¹ Π _g	8.55	0.0001 s	[6,23]
N ₂ ⁺	X ² Σ _g ⁺	15.6	Stable ^a	[6]
N ground	⁴ S ^o	0	Stable ^a	[1]
N first metastable	² D ^o	2.38	~ 10 h	[1]
N second metastable	² P ^o	3.57	~ 10 s	[1]

^aNonradiative state.

higher than for oxygen and hydrogen, thus a step-wise dissociation often prevails. One distinctiveness of nitrogen is its very low probability for super-elastic collisions between vibrationally excited molecules and neutral atoms in the ground state, reaction $N_2(\nu) + N \rightarrow N_2(\nu-1) + N$. The consequence is a high vibrational temperature (taking into account the Boltzmann distribution) in nitrogen plasma. In fact, the vibrational temperature is usually several 1000 K although the kinetic (or rotational) temperature is not much above room temperature. Another peculiarity is the existence of the metastable states of high excitation energy (see Table 2.6). The excitation energy of the A-state is over half of the dissociation energy, therefore, two colliding molecules may produce a positively charged molecular ion and a free electron. Not only does it help ionizing molecules in the glowing plasma, but the charged particles are also formed in the flowing afterglow. Furthermore, unlike afterglows of hydrogen and oxygen, which are dark (except for the weak radiation from metastable oxygen molecules in the “b” state), the nitrogen plasma afterglow emits radiation of pink colour.

Another distinctiveness of nitrogen plasma is its poor emission from excited nitrogen atoms. Unlike oxygen or hydrogen where radiation from atomic species often prevails, atomic lines in nitrogen plasma are usually hardly visible. See Section 4.2 for details.

The richness of various excited states makes the interaction between nitrogen plasma and polymers difficult to understand. Nitrogen plasma definitely causes the formation of nitrogen functional groups on the polymer surface, however, they often appear together with the oxygen functional groups although no oxygen is added intentionally to the plasma chamber. One explanation of this effect which has been observed by most researchers in this field is the excellent dissociation of oxygen (or water vapor) which is present in plasma chambers in small quantities [31]. There are numerous nitrogen species of higher excitation energy than the dissociation energy of oxygen or water molecules.

Treatment of polymers with nitrogen plasma usually leads to the preferential formation of amides rather than amino groups [32]. If amino groups are preferred, it is better to use weakly ionized ammonia plasma. Particularly, such plasma contains NH_x radicals that readily interact with the polymer surface [33]. Some authors reported a substantial concentration of amino groups on polymer surfaces using glowing plasma, but it is usually better to use the afterglow of ammonia plasma if functionalization with amino groups is the goal.

2.3.5 Fluorocarbon Gases

With the increasing number of atoms in a single gaseous molecule, the plasma becomes more complex and parameters are difficult to predict. This is especially true for carbon-containing gaseous molecules of more than five atoms. Molecules are dissociated upon plasma conditions, but the recombination of atoms often does not lead to parent molecules. Atomic clusters may form, especially at elevated pressure, because the rules that prevent simple recombination (as in the case of the recombination of O-atoms) do not prevent recombination of an atom with a cluster. Eventually, the clusters grow in size and “dusty plasma” is formed [34]. Dust particles become negatively charged, therefore, there is an efficient drain of the free electrons and plasma may become unstable.

A carbon-containing gas of particular importance for tailoring the surface properties of polymers is tetrafluoromethane (CF_4). It is chemically perfectly inert but becomes reactive upon the nonequilibrium state, especially in the state of gaseous plasma. Some data about the CF_4 excited states are presented in Table 2.7. A peculiarity of this gas is that positive CF_4^+ ions are rarely observed. The ionization by electron impact rather leads to simultaneous dissociation, therefore, the CF_3^+ ions are formed together with a free fluorine atom. Such atoms are chemically reactive and interact chemically with polymers. The result is the hydrophobization of the polymer surface. The CF_x radicals may or may not deposit on the surface of a material facing plasma, depending on the F/C ratio [36,37]. In the case when hydrocarbon is added into the gas mixture, one usually observes a thin film of hydrogenated carbon with a high fluorine concentration growing on the surface of a material facing plasma. The hydrogen and fluorine atoms recombine to HF in the gas phase (at high pressure) or on surfaces (predominantly at low pressure) and the remaining radicals condense on the surface forming a hydrophobic coating. The fluorine atoms also interact with the walls of the discharge chamber (in particular when the chamber is made from a glass) and cause etching, therefore, the chamber walls should be covered with a foil made from tetrafluoroethylene (or a similar material) to suppress this unwanted effect.

Table 2.7 Excitation energies of CF_4 molecules and F atoms

Type of particle	Symbol	Excitation energy (eV)	Radiative life-time	References
CF_4 ground	X^1T_1	0	Stable ^a	[35]
F ground	$^2\text{P}^\circ$	0	Stable ^a	[1]

^aNonradiative state.

An addition of oxygen or water vapor to a gas mixture causes extensive etching of a polymer exposed to plasma sustained in CF_4 [38,39]. This effect is beneficial when a nanostructured surface finish of a polymer is desirable, but detrimental in the other cases. Because the excitation energy of many excited states of tetrafluoromethane is high, the added oxygen or water molecules are rapidly dissociated. O and OH formed during dissociation interact with the polymer together with fluorine atoms and form volatile molecules composed of carbon, hydrogen, fluorine, and oxygen, therefore, the etching is usually more efficient than using only oxygen plasma.

2.4 BASIC DIAGNOSTIC TOOLS

The surface finish of polymers exposed to gaseous plasma depends on plasma parameters, in particular the fluxes of reactive gaseous species onto the surface of the material facing plasma. Good control of the processing parameters, therefore, requires knowledge of the density and temperatures of such gaseous species. There is no technique for measuring the densities and temperatures of all species, so complementary techniques need be used for a proper characterization. These techniques include electrical probes [40,41], calorimetry, catalytic probes (CP) [42,43], chemical titration [44], mass spectrometry (MS) [45], optical emission spectroscopy (OES) [46,47], actinometry [48], optical absorption spectroscopy including cavity ring down spectroscopy [49], two-photon absorption laser induced fluorescence (TALIF) [50], VUV absorption spectroscopy [51,52], and Fourier-Transform infrared absorption spectroscopy [53]. This section describes the basics of some of the frequently used techniques which are particularly suitable for characterization of plasma used for tailoring the surface properties of polymers.

2.4.1 Electrical Probes

One of the oldest techniques for plasma characterization is using an electrical probe. In the literature these are often called “Langmuir probes.” Both commercial and self-made probes are popular. An electrical probe will give basic information about the electron density and temperature. More sophisticated versions sometimes also allow for the determination of electron energy distribution function.

An electrical probe is a small electrode placed inside the plasma reactor and connected to a DC power supply of an adjustable voltage between

approximately -30 V and $+30$ V. The other connection of the power supply is connected to a large electrode also in contact with the gaseous plasma. The larger electrode is often called the “reference electrode.” The surface of the reference electrode should be at least a few orders of magnitude larger than the probe to assure that the voltage on the probe is the same as that of the power supply. The current flowing from plasma to the probe is measured as shown in Fig. 2.4A. The probe characteristics (current versus voltage) should be as in Fig. 2.4B. When the electron energy distribution function corresponds to the Boltzmann law (Eq. 2.1) the central part of the curve in Fig. 2.4B is exponential and allows for the determination of the electron temperature using the equation [54]:

$$I_e = I_{e0} e^{\left(\frac{eV}{kT_e}\right)} \quad (2.4)$$

In practice, the curve often deviates from exponential. One possible reason is the deviation of the distribution function from Boltzmann law, but more commonly it is because of the plasma’s instabilities or stray effects caused by the high frequency electric field. There should be a knee on the curve when the probe assumes plasma potential (see Fig. 2.4)

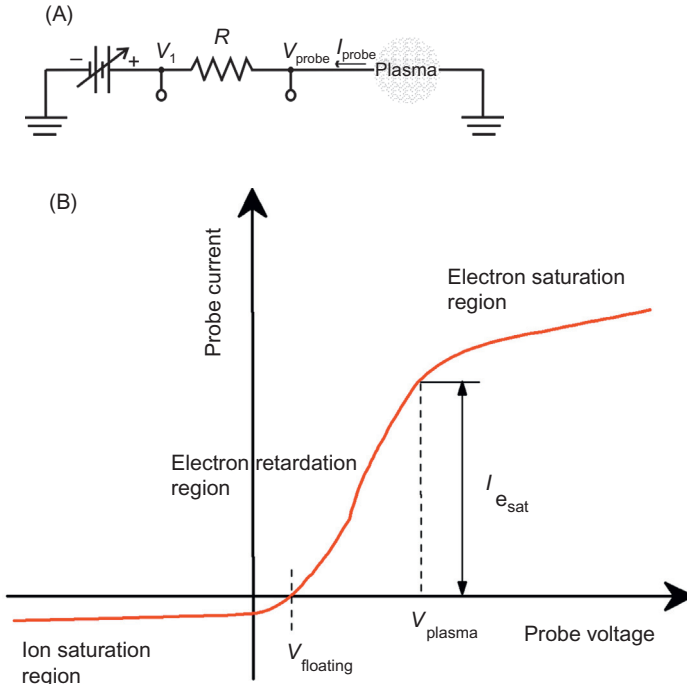


Figure 2.4 Electrical circuit suitable for electrical probes (A) and ideal characteristics (B).

but it is usually not sharp at all. When the probe is above the plasma potential, the electron saturation current (I_{esat}) is observed. In practice, however, the current keeps increasing with the increasing voltage because the thickness of the sheath next to the probe depends on the probe voltage. The electron density is calculated from the saturated current using Eq. (2.5) [55]:

$$n_e = 3.73 \times 10^{13} \frac{I_{\text{esat}}}{A_{\text{probe}} \sqrt{kT_e}}, \quad (2.5)$$

where A_{probe} is the surface of the probe tip. The ion saturation current is observed at large negative biasing of the probe. As in the case of electron saturation, the current keeps increasing with the increasing negative bias; therefore, the density of positively charged ions is difficult to determine. One possibility is extrapolating of the current to the plasma potential but this method is not accurate because the exact behavior of the ion flow versus the probe voltage is unknown. Still, a simple electrical probe allows for the estimation of the ion density in plasma, which is an important parameter. In the case of rather powerful discharges created by RF or MW generators such single probes often fail because of stray effects.

Simple electrical probes perform rather well in metallic chambers, but are impractical in glass chambers powered by electrodeless discharges. In such a case a double probe is a better choice. A probe comprising of two electrodes is immersed in plasma and connected to a DC power supply enabling adjustable voltage between approximately -30 V and $+30$ V as shown in Fig. 2.5A. In this case, both electrodes are floating on the plasma potential, therefore, they are always negatively biased against the plasma. The characteristic of such a double probe is shown in Fig. 2.5B. The ion saturated current (I_{sat}) is observed at both negative and positive biasing and the curve should have the form of hyperbolic tangens [56]:

$$I = I_{\text{sat}} \tanh\left(\frac{eV}{2kT_e}\right) \quad (2.6)$$

The ion density is estimated from the ion saturation currents and the electron temperature from the maximum slope of the characteristics as shown in Fig. 2.5B using the equations [57]:

$$N = \frac{2I_{\text{sat}}}{e_0 A \sqrt{\frac{k_B T_e}{m_+}}} \quad (2.7)$$

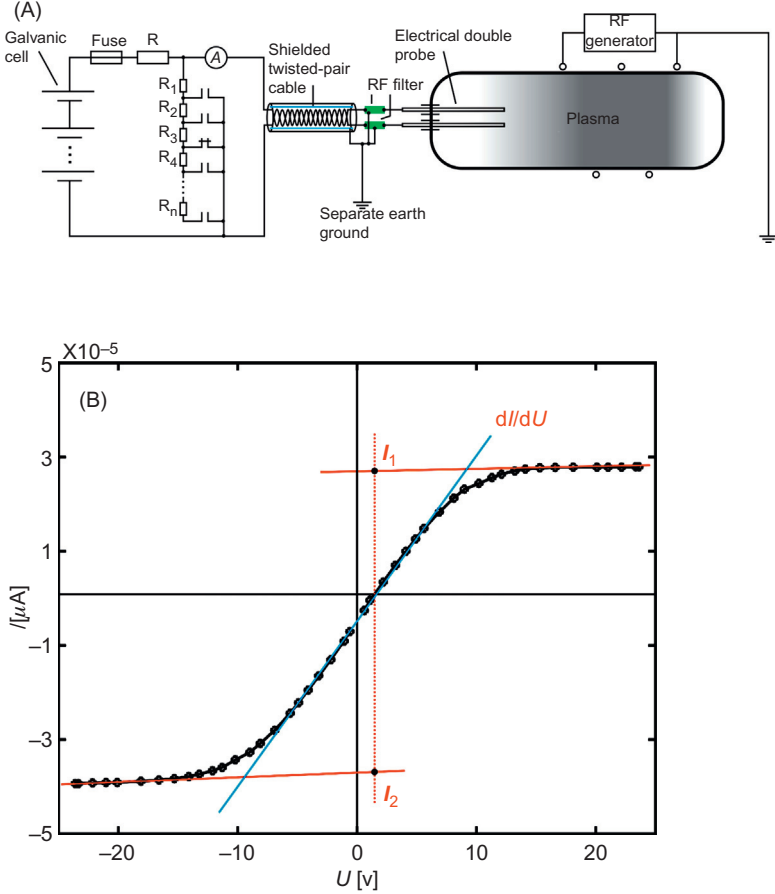


Figure 2.5 Electrical circuit suitable for double electrical probes (A) and ideal characteristics (B).

and

$$kT_e = \frac{e_0 I_1 I_2}{\frac{dI}{dU} (I_1 + I_2)} \quad (2.8)$$

where N is the density of charged particles, A is the probe area, m_+ is the positive ion mass, k is the Boltzmann constant, T_e the electron temperature, e_0 the elementary charge, I_1 the saturated ion current on the first electrode extrapolated to zero net current, I_2 the saturated ion current on the second electrode extrapolated to zero net current, and dI/dU the first derivative of the curve at the inflection point. If electrodes are the same $I_1 = I_2 = I_{\text{sat}}$.

In practice the ion saturation current increases with the voltage, therefore, it is difficult to state the exact ion density. One method of suppressing this effect is the application of electrodes of a rather large diameter, definitely at least of an order of magnitude larger than the Debye length (Eq. 2.3). Double probes are often less sensitive to oscillations or other stray effects than single probes. Electrical probes are only suitable for characterization of nonequilibrium plasma at low pressure. At atmospheric pressure, the probe would disturb plasma too much and any reading may lead to a wrong interpretation.

2.4.2 Optical Emission Techniques

Light emitting volume such as gaseous plasma emits light because of excited atoms or excited molecules. An atom or an ion will emit radiation when radiative transition between two states occur. Below the ionization limit are the discrete energy levels, whereas above this limit there is a continuum of levels. Because of this, three types of radiation can occur:

- Line radiation occurs because of electron transitions between discrete bound levels thus leading to line spectra. An outer shell electron falls from an upper bound level to a lower bound level, when the basic selection rules of spectroscopy are satisfied. This is the most common type of radiation.
- Recombination or free-bound radiation occurs when a free electron recombines with the ion. Because the upper level is continuous, the radiation is also continuous, but with some structure because of the discrete nature of the lower levels. This is a very rare phenomenon in the type of plasmas described here.
- Free-free radiation refers to bremsstrahlung emitted from plasma, that is, the transition between two free energy levels. It occurs when a free electron is decelerated and deflected by another charged particle or when a free-electron collides with a larger particle. In a partially ionized gas, there are competing interactions between electrons and neutral particles, and between electrons and ions. Which type of bremsstrahlung process dominates depends on plasma parameters, especially the degree of ionization. The bremsstrahlung spectrum is continuous, because the initial and final states are continuous.

The schematic presentation of three types of radiation are presented in an energy level diagram in Fig. 2.6A.

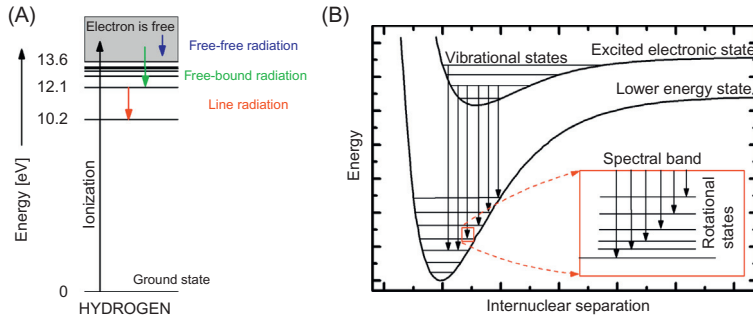


Figure 2.6 Energy level diagram for hydrogen atom with three types of radiation (A). Electronic, vibrational, and rotational states of a molecule with some of the transitions between them (B).

The emission from excited molecules are more complex, because the molecules can occupy not only different electronic states but also vibrational and rotational states (Fig. 2.6B). The ground energy level of a molecule is never null. Each electronic energy level has multiple vibrational levels, and each vibrational energy level consists of multiple rotational levels. All these levels are quantized and, therefore, the molecular spectrum is a line spectrum even though sometimes it may appear as continuous because of the poor resolution of the spectrometer. A group of emission lines that are closely spaced and arranged in a regular sequence are called spectral bands and correspond to a transition between two vibrational levels. Transitions between two electronic states, which consist of multiple bands, is called a system. The schematic presentation of these transitions is presented in Fig. 2.6B.

2.4.2.1 Optical Emission Spectroscopy

Spectra of the light emitted by plasma can be measured with an optical emission spectrometer. The example of the optical path emitted by plasma, collected by collimator with optical fiber and crossing the optical arrangement of a spectrometer is shown in Fig. 2.7.

There are a few things that need to be done before the actual measurements take place. The OES spectrometer needs to be calibrated in two ways. First, wavelengths must be calibrated so there is no shift and second, the OES spectrometer needs to be calibrated for its spectral response. The latter is not necessary, but is recommended. In order to do this, two different light sources are needed: one for a wavelength calibration, such as mercury argon lamp and the other for spectral response

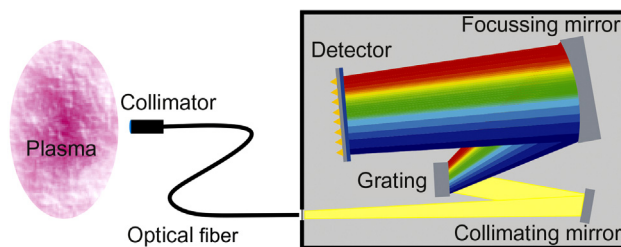


Figure 2.7 The schematics of an optical emission spectrometer and the optical path of the light emitted by plasma.

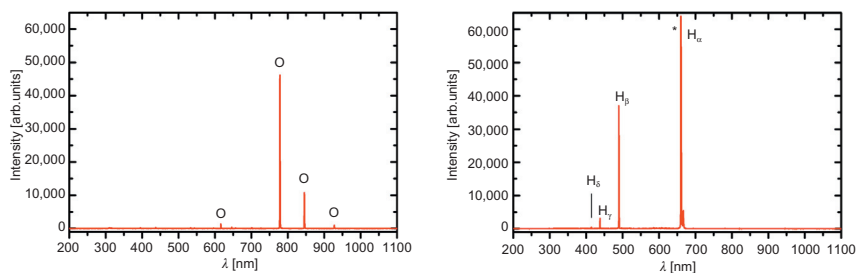


Figure 2.8 OES spectra of an oxygen (left) and hydrogen (right) ICP plasma in H-mode.

calibration, usually a deuterium-halogen lamp. Once the spectrometer is calibrated and positioned, the background needs to be measured at the same integration time as will be used in the actual measurements. This background is then subtracted from the measured spectrum.

Examples of atomic line spectra are presented in Fig. 2.8. It can be seen that the oxygen and hydrogen molecules are totally dissociated in ICP H-mode plasma because only excited atoms emit light.

Examples of an excited diatomic molecule spectra are shown in Fig. 2.9. The OES spectra of nitrogen ICP plasma in E-mode and H-mode are presented. Here four different nitrogen spectral features can be observed. The most prominent are the two N_2 spectral systems: first ($\text{B } ^3\Pi_g - \text{A } ^3\Sigma_u^+$) and second ($\text{C } ^3\Pi_u - \text{B } ^3\Pi_g$) positive systems, which consist of multiple bands (transitions between vibrational states) each marked with a dash. It can be seen, especially in the first positive system, that in E-mode these bands are clearly separated, whereas in H-mode plasma the bands are more fused together. This is because of the fact that the rotational temperature in H-mode is higher than in E-mode plasma and, therefore, the rotational transitions are more pronounced, which

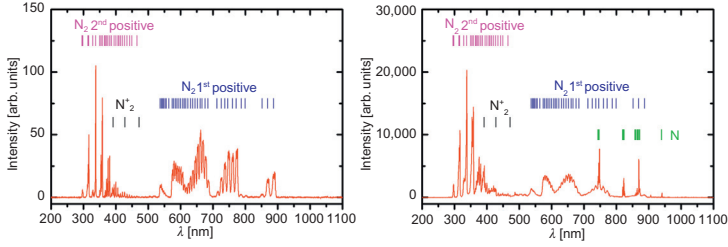


Figure 2.9 OES spectra of nitrogen ICP plasma in E-mode (left) and in H-mode (right).

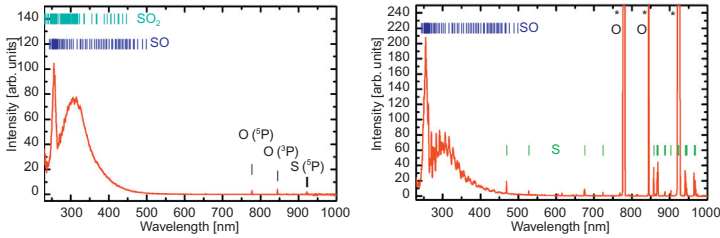


Figure 2.10 OES spectra of SO_2 ICP plasma in E-mode (left) and in H-mode (right).

makes the bands wider. In both E- and H-mode plasma a N_2^+ first negative system ($\text{B } ^2\Sigma_u^+ - \text{X } ^2\Sigma_g^+$) is visible, whereas nitrogen atom lines are only visible in H-mode plasma where more nitrogen molecules are dissociated. Here it should be mentioned that the names negative and positive system simply refers to the occurrence of these bands in the negative glow or the positive column, respectively, of a glow discharge.

The OES spectra of a polyatomic molecules are presented in Figs. 2.10 and 2.11. An SO_2 ICP plasma in E-mode emits light almost only in UV (ultraviolet). Its spectrum is a continuum from approximately 200–400 nm, because of SO and SO_2 bands, and really poor emission atom lines of O and S in the IR (infrared) part of the spectrum. The same gas at higher powers (H-mode) emits light mostly in IR, that is, the S and O atom lines, where the latter are in saturation in Fig. 2.10. The other spectral feature under these conditions is SO system in UV. The lack of SO_2 system suggests that the dissociation of plasma in H-mode is much higher than in E-mode.

One would assume that a molecule with even more atoms, such as ammonia, would emit only a continuum. However, the spectra in Fig. 2.11 shows that this is not the case. The OES spectra of NH_3 in

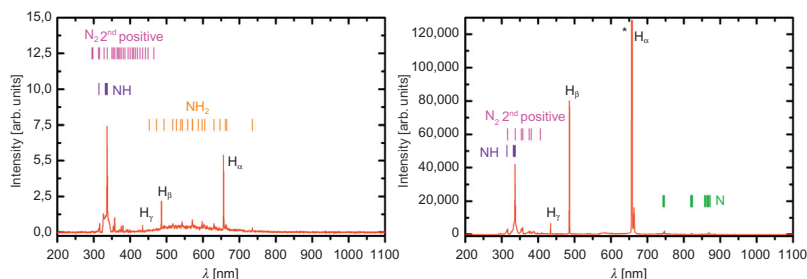


Figure 2.11 OES spectra of NH_3 ICP plasma in E-mode (left) and in H-mode (right).

E-mode clearly shows the NH_2 bands, NH bands, N_2 second positive system, and hydrogen Balmer atom lines. Ammonia dissociation energies are much lower than those of SO_2 , that is, why the ammonia plasma dissociation fraction is higher at the same RF power. The presence of nitrogen molecule emission bands proves the presence of nitrogen atoms, because some nitrogen atoms may recombine on the plasma reactor surface, thus, forming N_2 molecules. In H-mode the dissociation fraction is even higher, therefore, the NH_2 bands are not visible anymore. Furthermore, N atom lines also appear. Here it should be stressed that the integration times in the H-mode plasma were approximately 1000-times lower than in the E-mode, whereas the light emitted by H-mode plasma was much more intense.

In Figs. 2.8–2.11 it can be seen that from OES spectrum one can determine which excited species are present in the plasma, but unfortunately one cannot directly determine its density, because the OES technique is qualitative and not quantitative. However, with some additions and assumptions one can also determine the densities of certain species. This method is called actinometry.

Actinometry was first introduced by J.W. Coburn and M. Chen in 1980 as a method for determining the density of fluorine atoms [58]. This method for determining the density of free atoms in ground state uses OES and an actinometer. The latter is a gas that is leaked into a reactive plasma in small concentrations. Usually it is a noble gas with a radiative transition near the transition of a particle whose density needs to be measured. For example, when neutral oxygen atom densities are measured, the most commonly used actinometer is argon.

The density of neutral oxygen atoms can be determined from the OES line intensity ratios, because the density of an argon atom in a gas mixture is known. The emission lines usually used for this determination

are: oxygen line at 844.6 nm and argon line at 750 nm. The ratio between emission intensities is [59]:

$$\frac{I_O}{I_{Ar}} \propto \frac{n_O}{n_{Ar}} \frac{\int_{\varepsilon_O}^{\infty} \sigma_O(\varepsilon) f(\varepsilon) \sqrt{\varepsilon} d\varepsilon}{\int_{\varepsilon_{Ar}}^{\infty} \sigma_{Ar}(\varepsilon) f(\varepsilon) \sqrt{\varepsilon} d\varepsilon}, \quad (2.9)$$

where I_O and I_{Ar} are peak intensities of emission lines, n_O and n_{Ar} are the number densities of atoms in ground state, σ_O and σ_{Ar} are the energy-dependent electron excitation cross section for excitations of atoms from ground state, $f(\varepsilon)$ is electron energy distribution function and ε is electron energy. This expression does not depend on electron density, but depends on electron energy distribution function. If the integral terms are constant this can be written:

$$\frac{I_O}{I_{Ar}} = \frac{k_O}{k_{Ar}} \frac{n_O}{n_{Ar}} = k'_O \frac{n_O}{n_{Ar}}, \quad (2.10)$$

where k are constants if, σ_O and σ_{Ar} are identical or if $f(\varepsilon)$ remains constant. This term is the basis of actinometry technique. In real systems the cross sections are relatively unimportant while $f(\varepsilon)$ decreases rapidly with increasing energy and, therefore, the density of electrons which exceed the thresholds is what really counts. If the energy thresholds ε_O and ε_{Ar} are similar, then it can be assumed that k'_O is constant.

The biggest flaw of this technique are its two assumptions. Actinometry is based on assumptions that the excited atom is excited only with collision of an electron and an atom in the ground state and that this excited atom loses its energy only with de-excitation by photon emission. The excitation and de-excitation oxygen examples are, $O(2p^4 \ ^3P) + e^- \rightarrow O^*(3p \ ^3P) + e^-$ and $O^*(3p \ ^3P) \rightarrow O(3s \ ^3S) + h\nu$ (844.6 nm), respectively.

However, excited atoms used for actinometry can be obtained not only with excitation from the ground states, but also with multiple stage excitation or with de-excitation of higher energy states or, in some cases, with dissociative oxidation [60]. Besides that, the excited atoms do not lose energy only with de-excitation, but also with atom collisions. These corrections would make the actinometry technique complicated because in determining the densities of atoms in ground states one would need a rather complex kinetic model [61].

Nevertheless, in some cases actinometry gives good results. Fig. 2.12 shows a comparison between catalytic probe measurements and actinometry measurements.

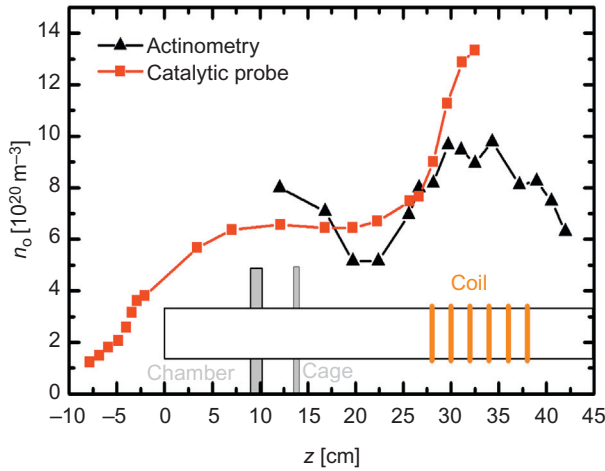
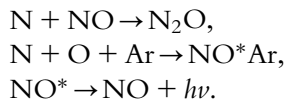


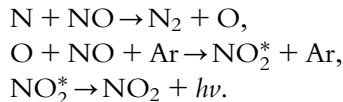
Figure 2.12 O-atom concentration obtained with actinometry compared to the ones obtained with catalytic probe.

NO titration is another way how one can determine the density of atoms with the use of OES. Titration is a quantitative chemical method for determining the unknown concentration of an identified chemical species. In plasma systems the most commonly used titrant is NO and is used to determine the density of O and N atoms. The method is based on reactions between oxygen or nitrogen atoms, generated in plasma, and nitrogen monoxide leaked into flowing afterglow. Because of security reasons usually a mixture of NO and argon is used.

The type of reactions between NO and N atoms depends on the volume flow of the NO. At low flow rates the reactions are [62]:



At higher NO flow rates, reactions are a little different:



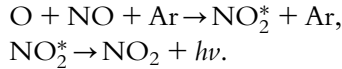
At low volume flow of NO mostly NO* is produced, which emits blue light, and at higher flow NO₂* is produced, which emits green light. The transition between these two regimes is called the extinction point, where the densities of NO and N are the same, and there is no emission

of light. From the extinction point nitrogen density is determined. At higher NO flows the intensity of green light linearly increases with the flow. This can be written as:

$$I(\text{NO}_2^*) = K(\lambda) \cdot n_{\text{N}} \cdot n_{\text{NO}}$$

where the slope of the line is $K(\lambda) \cdot n_{\text{N}}$.

In an afterglow of an oxygen plasma the following reactions are taking place:



In the first reaction a metastable molecule NO_2^* is produced, which at the transition back to the ground state emits green light with a peak intensity around $\lambda = 575$ nm. Intensity of this radiation is measured with OES.

The number of the produced metastable molecules NO_2^* depends on the density of the neutral oxygen atoms from the plasma and on the volume flow of NO. Therefore, the intensity of the emitted light $I(\text{NO}_2^*)$ is proportional to the density of neutral oxygen atoms n_{O} and the density of the nitrogen monoxide n_{NO} . This can be written as:

$$I(\text{NO}_2^*) = K(\lambda) \cdot n_{\text{NO}} \cdot n_{\text{O}}, \quad (2.11)$$

where $K(\lambda)$ is a constant, which depends on the spectral sensitivity of the spectrometer, photon energy, the emission probability, and the rate coefficient of the reactions.

Constant $K(\lambda)$ is similar to the one determined with nitrogen atoms. When the constant is determined, the density of oxygen atoms can be calculated from the line slope where NO flow rates are varied.

This method is not used often because of the toxicity of NO and NO_2 . Also, the method can only be used in the flowing afterglow, whereas in the discharge region the NO would be dissociated because of the electron collisions. The density of the neutral atoms inside the plasma can only be determined with a suitable model and with measurements in the flowing afterglow.

2.4.2.2 Stark Broadening

Besides the wavelength of the emission lines (determining the excited species), and their intensities (in some cases for determining the densities), one can also use the shape of the emission lines in order to determine

some of the plasma parameters. The shape of the emission line is a mixture of instrumental broadening, natural broadening, Doppler broadening, self-absorption broadening, and pressure broadening, which is a combination of van der Waals broadening, resonance broadening, and Stark broadening. Analysis of the Stark broadening of spectral lines emitted by the plasma is the most commonly used method to measure electron density. From a technical point of view, the method is much more affordable than other techniques such as Thomson scattering or IR heterodyne interferometry, and can provide information on electron density with high accuracy. In order to determine the electron density, one must estimate the Stark broadening by fitting the experimental profile of the line with a Voigt function and using deconvolution of Doppler, van der Waals, resonance, and self-absorption broadening.

The optical spectrum can also be used for the determination of electronic, vibrational, and rotational temperature with the use of Boltzmann plot and computer simulation comparison. For example, a vibrational temperature can be determined from the Boltzmann plot, $\ln(I_{\nu'\nu''}/\lambda_{\nu'\nu''}/A_{\nu'\nu''})$ versus $G(\nu')$, where $I_{\nu'\nu''}/\lambda_{\nu'\nu''}/A_{\nu'\nu''}$ and $G(\nu')$ are the integrated band intensities corrected for spectral sensitivity, band origin wavelength and the vibrational energy term, respectively. For a simulation of OES spectra some software, such as Specair [63] and Lifbase [64], etc., are commercially available. A comparison of a simulated spectra of nitrogen plasma and a measured one is presented in Fig. 2.13. Here best fit was achieved with $T_{\text{rot}} = 400\text{K}$ and $T_{\text{vib}} = 8800\text{K}$.

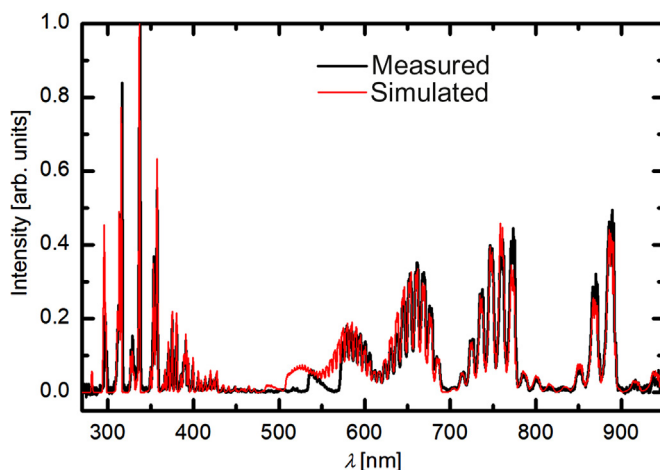


Figure 2.13 Simulated spectra with commercially available Specair software and measured spectra of a nitrogen ICP plasma in E-mode.

2.4.3 Optical Absorption Techniques

Contrary to OES, absorption techniques do not observe emitted light by the plasma, but light absorbed by either the plasma or plasma afterglow. In some cases, these techniques observe light emitted by fluorescence. Nevertheless, for absorption techniques an outer light source is needed and usually a laser is used for this purpose. Here two absorption methods will be presented in more detail.

2.4.3.1 Cavity Ring-Down Spectroscopy

Cavity ring-down spectroscopy is a direct absorption, highly sensitive, versatile technique suitable for the analysis of a wide range of plasma. CRDS belongs to a wide class of cavity-enhanced spectroscopies. A typical experimental setup of the CRDS technique is presented in Fig. 2.14.

In cavity-enhanced absorption spectroscopy, the laser light is guided into an optical cavity with two highly reflective mirrors with a reflectivity greater than 0.999. A light pulse from a tunable pulsed laser enters a cavity and travels back and forth between the mirrors, which increases the absorption length by several orders of magnitude. The signal detected on the other side of a cavity is, therefore, the decaying signal of the subsequent sequence of pulses, each with lower intensity than the previous one, hence the name ring-down. The amplitudes of pulses decay exponentially. When an absorbing medium is introduced into the cavity, the decay time is further reduced. From this an absorption coefficient can be determined. With changing the wavelength of the laser, a spectrum can be obtained.

The absorber density N can be calculated with a simple formula [65]:

$$N = 16\pi^2 \frac{\tau_{21}}{\lambda_{12}^2} \frac{w_1}{w_2} \frac{L}{l} \int \frac{1}{\lambda^2} \left(\frac{1}{\tau(\lambda)} - \frac{1}{\tau_0} \right) d\lambda, \quad (2.12)$$

where τ_{21} is the lifetime of the excited state, λ_{12} is the wavelength of the resonance transition, w_i the statistical weight of state i , L is the cavity

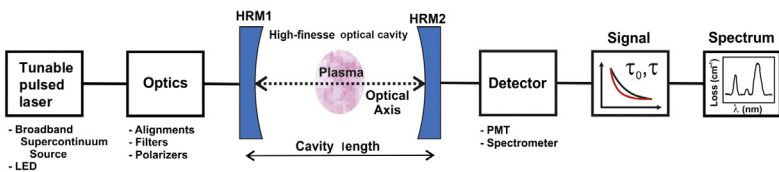


Figure 2.14 Typical experimental setup for CRDS diagnostic of a plasma.

length, l is the length of the absorbing medium, and τ_0 is the laser pulse lifetime of an empty cavity.

2.4.3.2 Two-Photon Absorption Laser-Induced Fluorescence

Laser induced fluorescence (LIF) is a very sensitive technique for the species-selective spatially resolved detection of ground state atoms, which are the most populated state in a low temperature plasma. LIF uses a single photon per excitation of the probed atom or molecule. The use of single-photon transitions limits the available transition energies. The light atoms such as hydrogen, nitrogen, and oxygen have their ground state transition at energies higher than 6.5 eV, which makes the use of VUV laser system necessary. The use of VUV photons has its problems. First, the media is not always transparent enough for VUV photons, which makes the probed volume optically thick. And second, it is experimentally challenging to provide an oxygen free environment for the laser pathway to allow the VUV radiation to reach the plasma. However, problems connected with single-photon excitation can be avoided with the application of a multiphoton excitation scheme. The use of two UV-photons instead of one VUV-photon is, therefore, simpler. In Fig. 2.15 two-photon excitation schemes for hydrogen, nitrogen, and oxygen atoms are presented.

In the oxygen atom example, for a transition from the ground state $2p^4\ ^3P$ to the excited state $3p\ ^3P$ around 11 eV is needed, which corresponds to the energy of two photons with wavelengths of 225.58 nm.

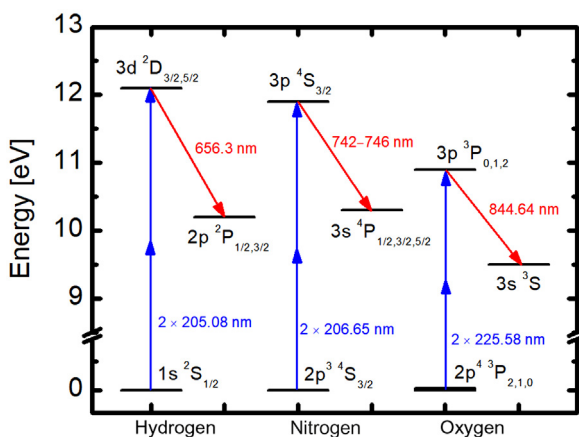


Figure 2.15 A two-photon excitation scheme for hydrogen, nitrogen, and oxygen atoms.

The density of the oxygen atoms in the ground state can then be determined with the use of measurement of the fluorescent light emitted at 844.64 nm (transition from $3p\ ^3P$ state to $3s\ ^3S$ state [66]). In order to get the absolute densities, this method needs to be calibrated for each measured species. For example, for O atoms usually NO titration or calibration with noble gases are used [67].

Even though TALIF is a powerful diagnostic tool for monitoring the ground state atom properties in a plasma environment, it is not used that often because it is a very complex and expensive technique.

2.4.4 Catalytic Probes

Electrical probes enable at least an estimation of the ion density in plasma which is useful information, but major reactive gaseous particles suitable for tailoring surface properties of polymer materials are neutral, especially atoms. Charged particles are almost absent in the afterglow, therefore, an electrical probe is obsolete for characterization of nonequilibrium gas in the afterglow chamber (Fig. 2.3). A similar, but complementary, tool which enables measurements of the neutral reactive particles is a catalytic probe.

The origin of CP is calorimetry. It is definitely the simplest technique for plasma characterization. A piece of metal is mounted into plasma, kept at a floating potential, and the energy flux is determined from the rise of the metal temperature after igniting plasma. Then the density of atoms in the vicinity of the metal is calculated using several assumptions which are usually not correct. These assumptions are: the energy flux comes only from surface association of atoms to parent molecules and the accommodation of energy is complete. The first prediction is obviously wrong for glowing plasma but almost true in the afterglow. The second one is always wrong because the accommodation depends on the surface finish, recombination coefficient (Tables 2.3 and 2.5) as well as temperature of the catalytic material. A sophisticated version of a catalytic probe operates at a constant temperature of the catalytic tip and is protected from other sources of energy fluxes [68]. Such a probe is schematically presented in Fig. 2.16.

CP take advantage of the heterogeneous surface recombination of atoms to parent molecules. The recombination coefficient (Tables 2.3, 2.5, 2.8) depends on the type of atoms and a solid material which is called the catalyzer. The energy flux onto the surface of the catalyzer is [43]:

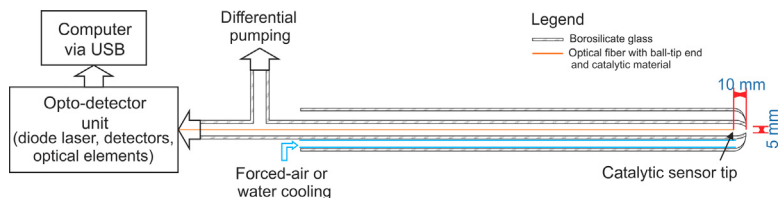


Figure 2.16 A sophisticated version of a catalytic probe.

Table 2.8 Recombination coefficients for nitrogen atoms on selected surfaces at room temperature

Material	Recombination probability	References
Al	$< 10^{-2}$	[69]
Co	0.43	[70]
Cu	0.07	[69]
Fe	0.021	[71]
Pt	0.31	[70]
Pyrex glass	10^{-5}	[72]
Quartz	10^{-4}	[73]
Stainless steel	0.07	[74]
Teflon	$2.9 \cdot 10^{-5}$	[75]

$$P = \frac{1}{4} n v \frac{W_D}{2} \gamma A, \quad (2.13)$$

where n is the atom density in the vicinity of the catalytic tip, v is the average thermal velocity of atoms $v = \sqrt{8k_B T / \pi m}$, W_D is a dissociation energy, γ is a recombination coefficient for atoms, and A is the area of the catalyst. The recombination coefficient (γ) depends also on the surface morphology as well as temperature. Typically, the recombination coefficient increases with the increasing temperature, but the temperature dependence is often complex; therefore, it is preferable to keep the temperature constant during measurements. One method is heating of the catalytic tip by laser radiation. The catalyst is typically heated by laser to approximately 1000K. As long as the gas in the vicinity of the tip is in thermal equilibrium (negligible concentration of atoms) no additional heating occurs. Once molecular gas is dissociated, there is a rather high concentration of atoms and they associate to parent molecules releasing the dissociation energy on the surface of the catalytic tip. The association of atoms on the catalyst surface represents an additional heating thus the temperature starts rising when gas is transformed to the nonequilibrium

state and plasma is ignited. The temperature is measured by fast electronics connected to the laser. As soon as additional heating due to surface association of atoms appears, the heating by laser is suppressed in order to keep the catalyst temperature constant. The power difference is measured and transformed to the atom density using Eq. (2.13). The response time of the probe depends on adjustment of the electronics and is typically well below a second, therefore, almost real-time measurements are possible. Fig. 2.17 represents a measurement of the H-atom density in an empty reactor powered by a RF generator of variable power. The discharge is electrodeless inductively coupled using a helicon coil. The power was chosen in such a way to enable transformation of a discharge mode from E to H. The H-atom density is larger in the H than in the E-mode because of the more efficient heating of electrons using the induced electric field inside the coil.

As shown in Fig. 2.16 the catalytic probe is placed in the cooled housing to suppress other channels for heat dissipation on the surface of the catalytic tip, thus, overcoming the deficiency of a simple calorimetry. Namely, if a tip is placed into the glowing plasma without the housing it is heated also by radiation arising from plasma, bombardment with positive ions, surface neutralization of charged particles, and relaxation of metastables of high excitation energy. The role of the housing is, thus, to allow for neutralization of almost all charged particles (the probability for such a reaction on any surface is almost 100%) screening radiation and allows for the relaxation of metastables of high excitation energy

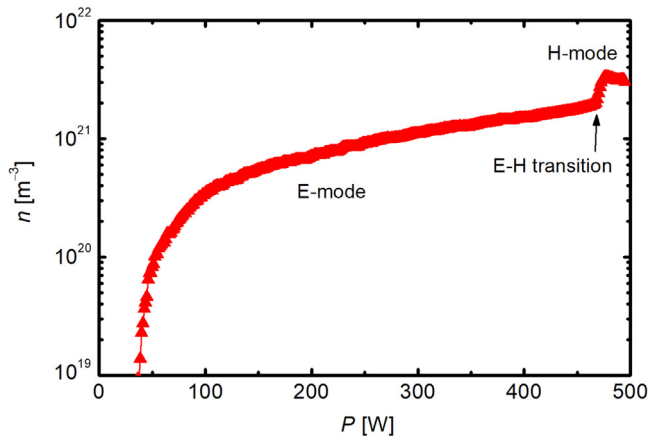


Figure 2.17 The H-atom density in a glass reactor versus the RF power.

(the probability is also very high). The metastables of low excitation energy still persist but they are supposed not to interact extensively with the catalyst. The housing is cooled to suppress any changes in kinetic or rotational gas temperature because after igniting the discharge, the inner walls of plasma reactor warm up in a time scale of seconds and the neutral gas temperature adapts to this temperature. The gas in the vicinity of the catalytic tip, therefore, resembles afterglow conditions. Obviously, the atom density at the tip is somewhat lower than in unperturbed plasma, therefore, calibration in an afterglow (or by any other technique such as TALIF [50]) is necessary. The housing is obviously obsolete if the measurements are performed in the afterglow chamber.

The density of neutral atoms in a plasma reactor depends on the quantity and type of materials immersed into the plasma. The recombination of atoms does not occur only on the catalytic tip or surfaces of plasma or afterglow chambers, but also on the surfaces of materials treated by the nonequilibrium state of gas. Worst cases represent hollow objects made from a material with a high recombination coefficient. Fig. 2.18A represents a schematic of the experimental setup and Fig. 2.18B the O-atom density versus the position of the probe outside and inside a copper tube. Copper has a large recombination coefficient, therefore, it represents a sink for O atoms. Plasma was sustained in a large glass cylinder by an inductively coupled RF plasma. The pressure was 100 Pa. This is the optimal pressure for sustaining extremely nonequilibrium gaseous plasma with high maximal density of neutral atoms. The powers were 500, 700,

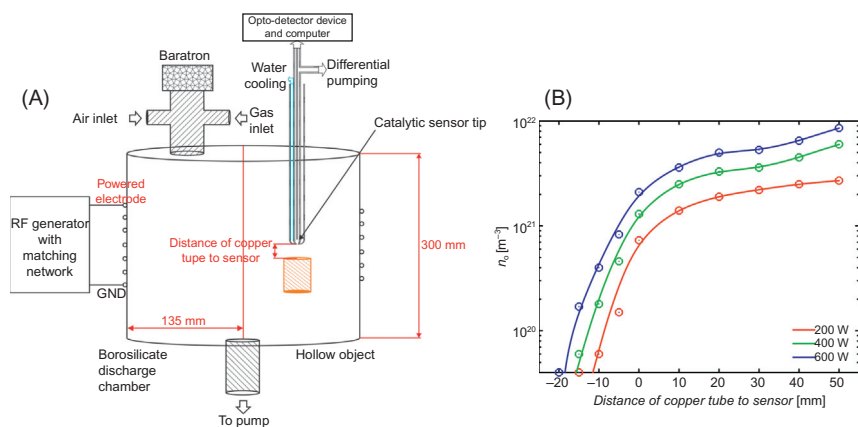


Figure 2.18 The setup for measuring O-atom density inside a hollow object (A) and the O-atoms density versus probe position (B).

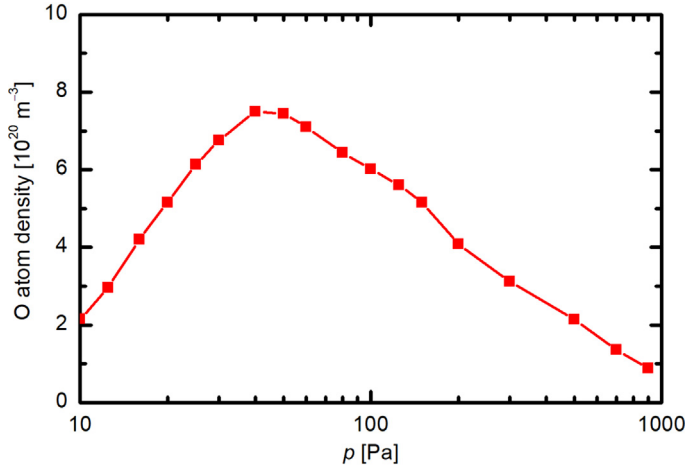


Figure 2.19 The O-atoms density in an afterglow chamber.

and 800 W. The O-atom density 5 cm away from the hollow object is several 10^{21} m^{-3} . As the probe moves toward the object, the O-atoms' density slowly decreases because of heterogeneous surface association to parent molecules. The gradient is rather small until the probe comes 1 cm away from the copper tube. The gradient, however, increases inside the tube (negative values of distance in Fig. 2.18) and eventually the O-atom density becomes immeasurably small approximately 2 cm inside the cylinder. Such effects are rarely addressed in scientific literature but should be taken into account when designing reactors for the treatment of catalytic materials [68,76].

Finally, we schematically present the O-atom density in an afterglow chamber in Fig. 2.2. A MW discharge in the surfatron mode was applied for sustaining plasma in the small chamber (glass tube of inner diameter 6 mm). The behavior of the O-atom density versus the pressure at fixed discharge power of 150 W is presented in Fig. 2.19. There is a well-expressed maximum in the O-atom density that appears at the pressure of 50 Pa inside the afterglow chamber. The pressure in the plasma chamber is larger in order to assure subsonic drift of nonequilibrium gas from the discharge to the afterglow chamber. The maximum is explained by several mechanisms. First, the atom density in plasma increases with the increasing pressure because the density of molecular gas leaked into the system increases. Therefore, there are more molecules available for dissociation. Second, the loss of atoms on surfaces decreases with the increasing pressure, thus, both effects allow for increasing the O-atom density in the

afterglow chamber at rather low pressures. After reaching 80 Pa, the O-atom density decreases with the further increase of pressure for the following reasons: first, the plasma in the discharge tube shrinks to a smaller volume thus dissociation is less efficient, and second, the gas-phase recombination is not negligible anymore because the probability for three-body collisions increases as the square of the pressure. Such maxima always appear, but are shifted to different pressures depending on particular conditions. As a general rule, the maximum shifts to higher pressures as the discharge power is increased.

2.5 CONCLUSIONS

The chemical reactivity of molecular gases is increased significantly by excitation, dissociation, and/or ionization of molecules which occupy the lowest states in a thermal equilibrium gas at room temperature. The reason for excitation of molecules to energetic states while keeping the gas temperature close to room temperature is a negligible transfer of an electron energy to a translation energy of gaseous molecules. Such poor gas heating is the consequence of a huge difference in the mass between an electron and a molecule. Free electrons are heated in an electric field, gain substantial energy, and diffuse in the plasma volume where they cause the formation of chemically reactive species such as radicals and ions. The charged particles neutralize quickly after turning off the electric field due to extensive surface reactions. The neutral reactive particles like atoms in the ground state persist long after the glowing plasma vanishes, because the probability for heterogeneous surface recombination could be as low as 10^{-5} . The flowing afterglow is, therefore, rich in neutral reactants but the concentration of charged particles is negligible. Therefore, it is particularly useful for tailoring surface properties of delicate materials. Nonequilibrium state of gas is usually created in a gaseous plasma where the main parameters are the electron temperature and density. The simplest method for the estimation of these parameters is a floating electrical probe. Density of neutral reactive species should be determined with other techniques. The optical emission and absorption techniques represent almost nondestructive methods for measuring densities of such reactants, whereas a catalytic probe is particularly suitable for determining the density of neutral atoms in the ground state.

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