Current Applied Physics 14 (2014) S162–S166

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Dissociation and excitation coefficients of nitrogen molecules and radical generation in nitrogen plasma

Han S. Uhm*, Young H. Na, Chae-Bok Lee, Eun H. Choi, Guangsup Cho

Department of Electronic and Biological Physics, Kwangwoon University, 447-1 Wolgye-Dong, Nowon-Gu, Seoul 137-701, Republic of Korea

ARTICLE INFO

Article history:
Received 31 July 2013
Received in revised form
12 November 2013
Accepted 16 November 2013
Available online 23 January 2014

Keywords:
Dissociation of nitrogen
Excitation of nitrogen
Hydroxyl
Nitrogen monoxide
Plasma medicine

ABSTRACT

The dissociation and excitation coefficients of nitrogen molecules are investigated by making use of the Boltzmann distribution of the electrons in atmospheric plasma. The excitation and electron-impact dissociation coefficients are analytically expressed in terms of the electron temperature T_e in units of eV. As an application example of these coefficients, hydroxyl generation through nitrogen plasma jet is investigated, showing that the hydroxyl concentration n_{OH} increases, reaches its peak value and then deceases, as the mole fraction χ of water molecules increases from zero to a few percents. The experimental data of the hydroxyl generation agree qualitatively with analytical results obtained from a theoretical model, confirming that a nitrogen plasma jet is one of the best means of hydroxyl production. The other example of the coefficient application is the nitrogen monoxide generation by making use of microwave energy at 2.45 GHz. The nitrogen monoxide concentration can easily be controlled by the nitrogen flow rate, the mole fraction of the oxygen gas, and the microwave power. An experiment involving nitrogen monoxide production was conducted, and the experimental data were found to agree remarkably well with the theoretical results from the analytical expression.

1. Introduction

Hydrogen peroxide initiates signal proteins [1–3], which control living mechanisms in cells. Nitric oxides also participates in various activities in living cells, as it is involved in signaling molecules, related to disease resistance in plants [4,5], and associated with various circulation systems in animals [6,7]. Obviously, reactive oxygen species (ROS) and reactive nitrogen species (RNS) play critical roles in living cells. Particularly, nitric oxide is important for smooth blood circulation in humans, providing various health advantages [8–14]. Plasma is a good candidate as an ROS and RNS provider for living cells. Our recent studies [15–17] indicate that atmospheric plasmas have many uses in various living cells. The key issue in these studies is the proper identification of ROS and RNS when synthesized in plasma. They can be characterized by the plasma density n_p and electron temperature T_e. The most important factors in ROS and RNS synthesis in nitrogen plasma are the excited metastable level $N_2(A_3\sum_u^+)$ of nitrogen molecules and nitrogen atoms. Therefore, it is essential to find the dissociation coefficient α_d of nitrogen molecules in terms of the electron temperature. Moreover, determining the excitation coefficient α_{N2^*} of nitrogen molecules which leads to the metastable state is critical. In Section 2, we therefore derive analytical expressions of the excitation (α_{N2^*}) and electron-impact dissociation (α_d) coefficients of nitrogen molecules, in terms of the electron temperature T_e. As an application example of these coefficients, an estimation of hydroxyl density in a nitrogen plasma jet at the atmospheric pressure will be presented in Section 3. The nitrogen monoxide generation through a microwave torch is also carried out in Section 4 for a development of medical tool.

2. Dissociation and excitation coefficients of nitrogen molecules

Once the electrons gain enough kinetic energy by electric fields, they collide with neutral molecules, producing ions and secondary electrons. In reality, the energy distribution function $f(\varepsilon)$ of the plasma electrons can be a complicated function, but we assume a Maxwellian distribution for simplicity in the subsequent analysis, which is expressed,

$$f(\varepsilon) = \frac{2\sqrt{\varepsilon}}{\sqrt{\pi}T_e\sqrt{T_e}}\exp\left(-\frac{\varepsilon}{T_e}\right), \quad (1)$$

* Corresponding author.
E-mail address: hsuhm@kw.ac.kr (H.S. Uhm).

1567-1739/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cap.2013.11.054

where T_e is the electron temperature. In general, the reaction coefficient $\alpha(T_e)$ of a gas species by plasma electrons can be calculated from,

$$\alpha(T_e) = \int_0^\infty \sigma(\varepsilon) v f(\varepsilon) d\varepsilon, \tag{2}$$

where $\sigma(\varepsilon)$ is the cross-section of a particular reaction by electrons with energy ε and v is the thermal velocity of electrons with energy ε.

The cross-section of a particular reaction by electrons including dissociation and excitation of nitrogen molecules have been measured and presented in various data journals [18,19]. All these cross-sections have the reaction energy ε_{reac}, below which the cross-section is zero and above which $\sigma(\varepsilon)$ has a finite value. Usually, the cross-section of this reaction increases almost linearly from zero at $\varepsilon = \varepsilon_{reac}$, then slowly reaching its peak value at a high electron energy and slowly decreases, as the electron energy ε increases from ε_{reac} to infinity. In general, the electron energy corresponding to the peak cross-section is much larger than the reaction energy ε_{reac}. Also, the electron temperature T_e of the plasma jet at the atmospheric pressure is much less than the reaction energy ε_{reac}. In this regards, the cross-section of a particular reaction by electrons may be approximately expressed as,

$$\sigma_{reac}(\varepsilon) = q_{reac}(\varepsilon - \varepsilon_{reac})\Theta(\varepsilon - \varepsilon_{reac}), \tag{3}$$

when the electron temperature T_e is substantially less than the excitation energy ε_{reac} with $T_e << \varepsilon_{reac}$. The symbol $\Theta(x)$ in Eq. (3) is the Heaviside step function, which is defined by $\Theta(x) = 1$ for $x > 0$ and $= 0$ for $x < 0$, while the symbol q_{reac} is the increase rate of the reaction cross-section in units of cm^2/eV. Substituting Eqs. (1) and (3) into Eq. (2) and carrying out a straightforward algebraic manipulation process, we obtain the reaction coefficient $\alpha(T_e)$ of nitrogen molecules,

$$\alpha(T_e) = \frac{2}{\sqrt{\pi}} q_{reac} v_{th} (\varepsilon_{reac} + 2T_e) \exp\left(-\frac{\varepsilon_{reac}}{T_e}\right), \tag{4}$$

where v_{th} is the electron thermal speed. Eq. (4) is the general expression of reaction coefficient for a broad range of gas kinetics. Any reaction coefficient can be found from Eq. (4) in terms of the electron temperature T_e for known value of the increase rate q_{reac} of the reaction cross-section in units of cm^2/eV and the reaction energy ε_{reac}.

The excitation coefficient $\alpha_{N2^*}(T_e)$ of the nitrogen molecules to the metastable level $N_2(A_3\sum_u^+)$ can be found from Eq. (4) by making use of the excitation energy $\varepsilon_{reac} = \varepsilon^* = 6.8$ eV and the increase rate $q_{reac} = q_{exc} = 1.38 \times 10^{-17}$ cm^2/eV of the excitation cross-section in units of cm^2/eV from Ref. [18]. The excitation coefficient $\alpha_{N2^*}(T_e)$ is eventually expressed as,

$$\alpha_{N2*}(T_e) = 6.53 \times 10^{-10} \sqrt{T_e}(6.8 + 2T_e) \exp\left(-\frac{6.8}{T_e}\right). \tag{5}$$

Similarly, the electron impact-dissociation coefficient $\alpha_d(T_e)$ of nitrogen molecules can be also found by substituting the dissociation energy $\varepsilon_{reac} = \varepsilon_d = 10$ eV and the increase rate $q_{reac} = q_d = 9 \times 10^{-18}$ cm^2/eV of the dissociation cross-section from Ref. [19] into Eq. (4). Therefore, the electron-impact dissociation coefficient $\alpha_d(T_e)$ of nitrogen molecules is expressed as,

$$\alpha_d(T_e) = 4.26 \times 10^{-10} \sqrt{T_e}(10 + 2T_e) \exp\left(-\frac{10}{T_e}\right). \tag{6}$$

The excitation $\alpha_{N2^*}(T_e)$ and electron-impact dissociation $\alpha_d(T_e)$ coefficients in Eqs. (5) and (6) are used for evaluation of various radical concentrations in plasmas at the atmospheric pressure generated from microwave, radio-frequency, medium frequency or low frequency electrical discharges. We can numerically find the excitation $\alpha_{N2^*}(T_e)$ and electron-impact dissociation $\alpha_d(T_e)$ coefficients by submitting the measured excitation cross-section in Ref. [18] and the measured dissociation cross-section in Ref. [19] into Eq. (2) without making any approximation of Eq. (3). However, the excitation coefficient $\alpha_{N2^*}(T_e)$ in Eq. (5) remarkably agrees well with the numerical values for T_e less than 2.5 eV. Similarly, the electron-impact dissociation coefficient $\alpha_d(T_e)$ in Eq. (6) agrees well with its numerical values for T_e less than 10 eV.

3. Generation of hydroxyl in nitrogen plasma jet

One of the best ways to generate the radical oxygen species in the nitrogen plasma jet is the generation of hydroxyl molecules by [20] $N_2(A_3\sum_u^+) + H_2O \rightarrow OH + H + N_2$ with dissociation coefficient of $\alpha_{OH} = 5 \times 10^{-14}$ cm^3/s, returning back to the ground state of N_2 and generating the hydrogen atom, H. For the electron temperature $T_e = 1$ eV, the excitation coefficient in Eq. (5) is calculated to be $\alpha_{N2^*} = 6.4 \times 10^{-13}$ cm^3/s. Hence, the nitrogen plasma jet with a small mole fraction of water vapor may provide a reasonable concentration of hydroxyl molecules, where system configuration is similar to Fig. 1 in Ref. [21]. However, the nitrogen molecules are excited to the metastable level by the plasma electrons, which can be influenced by the content of water molecules. Plasma electrons are attached to water molecules by dissociative attachment to water [22], which is represented by $e + H_2O \rightarrow H^- + OH$ with its maximum attachment cross section of 5×10^{-15} cm^2 at the electron energy of 6.5 eV. Most of the plasma electrons are born at the micro-discharges [21] in pores. The ionization mechanism of nitrogen molecules generates electrons, whereas electron attachment to water molecules eliminates electrons. These two mechanisms compete with each other, depending on the water concentration, applied electric fields and discharge geometry. The detailed investigation of this discharge properties is very complicated and beyond the scope of this article. Nevertheless, the high energy electrons, if there are any, may exist in the limited time during the discharge, participating into the dissociative attachment to water molecules. Therefore, the plasma density n_p in the plasma jet can be modeled as $n_p = n_{p0}(1 - \gamma\chi)$ where $\chi = n_{H2O}/n_{N2}$ is the ratio of water molecular density n_{H2O} to nitrogen density n_{N2} and the factor γ represents the attachment properties of high energy electrons to water molecules, which may strongly depend on the applied electric field.

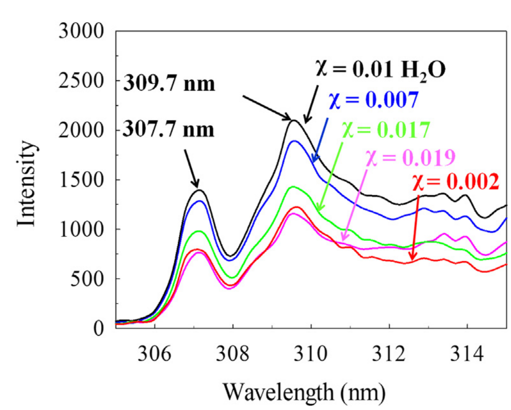

Fig. 1. Plots of emission spectrum from nitrogen plasma jet in the wavelength range of 306 nm–310 nm, are corresponding to the OH radical emission. The vertical scale of this figure is in arbitrary units.