Publ. Astron. Obs. Belgrade No. 102 (2022), 57 - 60 *Contributed Paper*

DISSOCIATION OF N_2 BY ELECTRON IMPACT IN RF ELECTRIC FIELD

V. STANKOVIĆ[1], M. RISTIĆ[2], R. RANKOVIĆ[2], M. AONEAS[3], M. VOJNOVIĆ[1] and G. B. POPARIĆ[1]

[1]*University of Belgrade, Faculty of Physics, Studentski Trg 12, P.O.Box 44, 11000 Belgrade, Serbia*

[2]*University of Belgrade, Faculty of Physical Chemistry, Studentski Trg 12, P.O.Box 47, 11000 Belgrade, Serbia*

[3]*University of Zawia, P.O. Box 16418, Zawia, Libya*

E-mail ristic@ffh.bg.ac.rs

Abstract. Rate coefficients for electron impact dissociation of the N_2 molecule to neutral fragments under the presence of radio-frequency (RF) electric field are calculated for field frequencies of 13.56, 100 and 200 MHz and for root mean square values of the reduced electric field strength of 300 and 500 Td.

1. INTRODUCTION

Dissociation of excited nitrogen molecules is important from many aspects of environmental and industrial chemistry as well as in many technological processes such are RF plasma nitriding, sterilization of medical instruments by nitrogen atoms and many others (see Guiberteau et al. 1997, Villeger et al. 2003).

Dissociation of N_2 to neutral fragments is taking place via electronically excited states of N_2 that subsequently dissociates into atoms:

$$e + N_2 \rightarrow N_2^* \rightarrow N + N + e \quad (1)$$

Threshold energy for reaction (1) is 9.75 eV and most of nitrogen molecules' electronic states lie above this energy. Excess energy during dissociation is transferred to atoms.

Zipf and McLaughlin 1978 were first to recognize the importance of dissociation of the excited N_2 molecules over radiative relaxation across manifold of singlet valence and Rydberg states. They have shown that nitrogen molecules that were excited to various $^1\Pi_u$ and $^1\Sigma_u^+$ states, whether by electron impact or UV photon absorption, mostly follow the predissociation path, although photon relaxations via dipole-allowed transitions to the singlet ground state were expected

to be dominant (see Green and Barth 1967). Dissociation to neutrals occurs in a time interval of 10^{-13} s, while radiative decay lasts 10^{-8} s (Itagaki et al. 2003). Main contribution to N_2 dissociation below 100 eV electron energies originates from family of $^1\Pi_u$ states, which predissociate with almost 100% efficiency. Contributions of $^1\Sigma_u^+$ states to dissociation vary depending on the states' vibrational level. Above 100 eV, the states contributing to dissociative ionization become dominant contributors to dissociation. The cross sections for reaction (1) are measured and reported by several groups (see Itikawa et al. 1986, Itikawa 2006). In the present work, we shall calculate the rate coefficients for dissociation to neutral fragments only, under the presence of RF electric field for frequencies of 13.56, 100 and 200 MHz and for E_R/N values of 300 and 500 Td. For this purpose we will use the cross sections that were measured and recommended by Cosby 1993 and electron energy distribution functions (EEDF) that are obtained by using our Monte Carlo simulation.

2. METHOD

Monte Carlo simulation code has been developed previously to track the electron transport trough the nitrogen atmosphere in the presence of RF electric field (see Popović et al. 2014, Ristić et al. 2017). Electrons are exposed to the action of a time-varying electric field that periodically oscillates at a fixed frequency f as a function of time t:

$$\boldsymbol{E}(t) = \sqrt{2}E_R\boldsymbol{k}cos(2\pi ft) \tag{2}$$

where E_R denotes the root mean square value of the electric field strength and $\boldsymbol{k}$ is the unit vector set in the direction of the electric field. After certain time that electrons have passed in the simulation, quasi-steady state is reached and EEDF is sampled over a period of the field oscillation. Electron's coordinates and velocity components are determined in each small time step of the simulation, dt by solving the differential equation of motion:

$$m\frac{d^2\boldsymbol{r}}{dt^2} = e\boldsymbol{E}(t) \tag{3}$$

where $\boldsymbol{r}$ is the electron radius vector, m is the electron mass and e is its charge. All scattering processes that can happen in interaction of electron and N_2 molecules (elastic, inelastic and ionization) were included in the model by carefully choosing the cross sections for all relevant processes. Dissociation is involved implicitly through the inclusion of all available electronic states that contribute to the dissociation process. For more details of the Monte Carlo code we refer the reader to reference Ristić et al. 2017.

The EEDFs obtained by simulation at a given point in time within one period of field oscillation and for the mean electron energy $\bar{\varepsilon}_t$, were used to calculate the rate

coefficients $K(\bar{\varepsilon}_t, t)$ for the dissociation with the corresponding effective cross section $\sigma(\varepsilon)$, having a threshold energy ε_{th}, using the formula:

$$K(\bar{\varepsilon}_t, t) = \sqrt{\frac{2}{m}} \int_{\varepsilon_{th}}^{\infty} \sigma(\varepsilon) \sqrt{\varepsilon}\, f_\varepsilon(\bar{\varepsilon}_t, \varepsilon, t) d\varepsilon \tag{4}$$

where ε represents the actual kinetic energy of the electron and $f_\varepsilon(\bar{\varepsilon}_t, \varepsilon, t)$ is the EEDF at specific time *t*.

3. RESULTS AND DISSCUSION

The rate coefficients for dissociation of N_2 to neutral fragments vs. phase of the RF electric field for frequencies of 13.56, 100 and 200 MHz are presented in Fig. 1 for E_R/N values of 300 (Fig. 1 a) and 500 Td (Fig. 1 b).

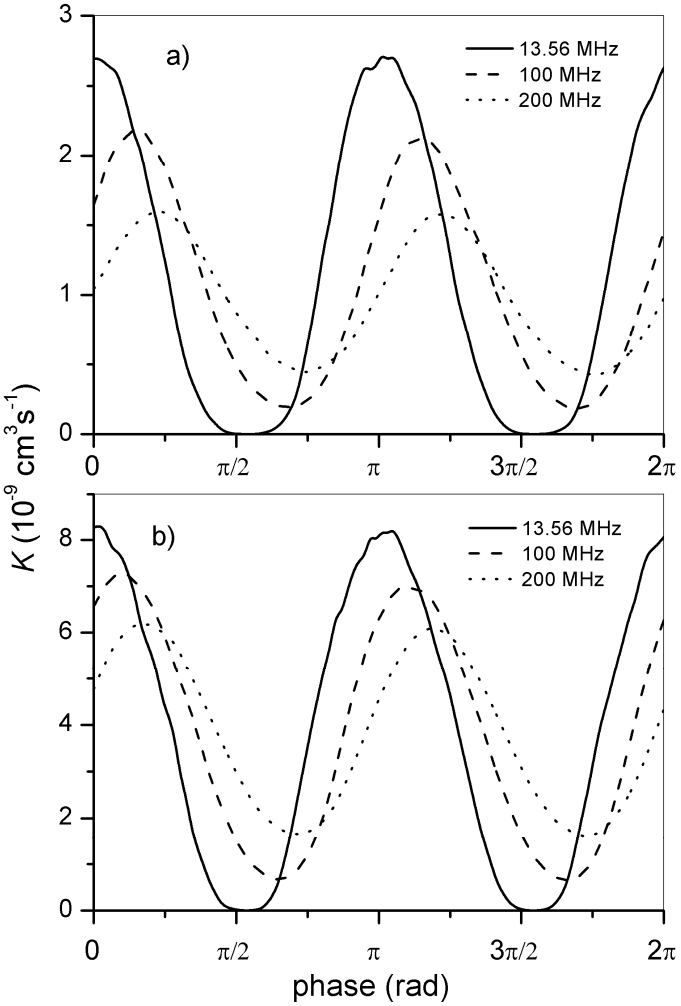

Figure 1: Rate coefficients for dissociation of N_2 to neutral fragments vs. phase of the RF electric field for indicated frequencies and at a) E_R/N=300 Td and b) E_R/N=500 Td.

One can see that the dissociation rates are higher at 500 Td than at 300 Td. This is because the cross section for dissociation is rising steeply from its threshold and at higher E_R/N electrons will have higher energies and overlapping integral between $\sigma(\varepsilon)$ and $f_\varepsilon(\bar{\varepsilon}_t, \varepsilon, t)$ shall have greater value.

At 13.56 MHz, the rates are in phase with the electric field, but with rising the frequency of the field, a phase lag of the dissociation rates is becoming more pronounced. This is caused by electrons' inertia while moving through the nitrogen gas.

Table 1: Period averaged rate coefficients (in 10^{-9} cm^3s^{-1}) for dissociation of N_2 to neutral fragments under considered conditions

	f = 13.56 MHz	f = 100 MHz	f = 200 MHz
E_R/N = 300 Td	1.1590	1.0640	0.9709
E_R/N = 500 Td	3.9337	3.7783	3.7960

For the sake of practical purposes, we have calculated period-averaged dissociation rates to neutral fragments. These values are presented in Table 1. When frequency is raised at E_R/N=300 Td, the period-averaged rate is decreasing. At E_R/N=500 Td, relative changes of the period-averaged dissociation rates are lower and no constant decreasing with rising the f is present. We believe that presented dissociation rates can be useful in many processes that involve capacitively-coupled RF nitrogen plasma.

Acknowledgments

This work was supported in part by the Ministry of Education, Science and Technological Development of the Republic of Serbia under contracts No. 451-03-9/2022-14/200162 and 451-03-68/2022-14/200146.

References

Cosby P. C: 1993, *The Journal of Chemical Physics* **98,** 9544

Green A. E. S. and Barth C. A: 1967, *J. geophys. Res.* **72,** 3975

Guiberteau E, Bonhomme G, Hugon R, and Henrion G: 1997, *Surf. Coat. Technol.* **97**, 552.

Itagaki N, Iwata S, Muta K, Yonesu A, Kawakami S, Ishii N, and Kawai Y: 2003, *Thin Solid Films* **435,** 259

Itikawa Y, Hayashi M, Ichimura A, Onda K, Sakimoto D, Takayanagi K, Nakamura M, Nishimura H. and Takayanagi T: 1986, *J. Phys. Chem. Ref. Data* **15,** 985

Itikawa Y: 2006, *J. Phys. Chem. Ref. Data* **35,** 31

Popović M. P, Vojnović M. M, Aoneas M. M, Ristić M. M, Vićić M. D, and Poparić G. B 2014: *Phys. Plasmas* **21**, 063504

Ristić M. M, Aoneas M. M, Vojnović M. M, and Poparić G. B: 2017, *Plasma Chem. Plasma Process*. **37**, 1431

Villeger S, Cousty S, Ricard A, Sixou M: 2003, *J. Phys. D: Appl. Phys.* **36**, L6.

Zipf E. C. and McLaughlin R. W: 1978, *Planet. Space Sci.* **26,** 449