

# ELECTRONIC AND VIBRATIONAL KINETICS OF MOLECULAR COMPONENTS IN THE MIDDLE ATMOSPHERE DURING SOLAR PROTON EVENTS

*Kirillov Andrey (1), Werner Rolf (2), Guineva Veneta (2)*

(1) Polar Geophysical Institute of Russian Academy of Sciences  
Apatity, Murmansk region, Russia

(2) Space Research and Technology Institute of Bulgarian  
Academy of Sciences Stara Zagora Department, Stara Zagora,  
Bulgaria

**Abstract.** It is known that electronically and vibrationally excited molecules are very active in chemical and radiational balances of the atmosphere. Any correct study of chemical composition of a disturbed atmosphere needs a model of electronic and vibrational kinetics of main and minor atmospheric components. Here we pay special attention to the development of the model of electronically and vibrationally excited molecules in the middle atmosphere during precipitations of fluxes of high-energy solar protons. Quantum-chemical theoretical methods and the results of our calculations for rates of inelastic molecular collisions are taken into account in the consideration of electronic and vibrational kinetics of molecular components in the atmosphere. The calculated quenching rate coefficients of electronically excited molecular nitrogen ( $N_2^*$ ) and molecular oxygen ( $O_2^*$ ) in inelastic collisions with  $N_2$  and  $O_2$  are applied in the simulations of vibrational populations of the molecules  $N_2^*$  and  $O_2^*$  at the altitudes of the middle atmosphere during solar proton events. The influence of electronically excited molecules  $N_2$  and  $O_2$  on vibrational kinetics of the molecules at the altitudes of the middle atmosphere is considered.

## INTRODUCTION

In order to consider correctly the balance of stratospheric and mesospheric components including ozone, it is necessary to calculate the contents of numerous minor atmospheric components produced during solar proton events. It is known the odd-nitrogen compounds ( $\text{NO}_y$ ) and the odd hydrogen compounds (including the hydroxyl radical OH) are important components. Toumi (1993), Siskind et al. (1993) have proposed that the reactions of singlet molecular oxygen  $\text{O}_2(\text{b}^1\Sigma_g^+)$  with either molecular hydrogen  $\text{H}_2$  or nitrous oxide  $\text{N}_2\text{O}$  could be sources of OH and  $\text{NO}_y$ , respectively. Moreover, sometimes the interaction of metastable molecular nitrogen  $\text{N}_2(\text{A}^3\Sigma_u^+)$  with molecular oxygen  $\text{O}_2$  is considered as possible source of nitrous oxide at altitudes of the middle atmosphere [Zipf, 1980; Zipf and Prasad, 1980].

Solar protons precipitating in the middle atmosphere produce effectively secondary electrons in collisions with  $\text{N}_2$  and  $\text{O}_2$  molecules. The electrons take active part in the production of different electronically excited states of main atmospheric components  $\text{N}_2$  and  $\text{O}_2$  [Konovalov and Son, 1987]. Since collisional lifetimes of the states are less or comparable with radiational ones at the altitudes of the middle atmosphere so the collisional processes influence the electronic kinetics of the components. Therefore the energies of electronic excitations are accumulated on energetically lowest states  $\text{N}_2(\text{A}^3\Sigma_u^+)$ ,  $\text{O}_2(\text{b}^1\Sigma_g^+)$ ,  $\text{O}_2(\text{a}^1\Delta_g)$ . The collisions of the metastable molecules with  $\text{N}_2$  and  $\text{O}_2$  lead to the production of vibrationally excited  $\text{N}_2(\text{X}^1\Sigma_g^+, \nu > 0)$ ,  $\text{O}_2(\text{X}^3\Sigma_g^-, \nu > 0)$ .

## MODEL

To calculate the rates of ion-electron pair production by precipitated particles we use the following formula for rates of solar proton energy dissipated in cubic centimeter per second at the altitude  $h$  (Dorman, 1975, chapter 6):

$$w(h) = \rho(h)A \int_{E_{\min}}^{E_{\max}} \int_0^{\frac{\pi}{2}} f(E) \left[ E^{m+1} - A(m+1) \frac{X}{\cos \theta} \right]_{m+1}^m 2\pi \sin \theta dE d\theta . \quad (1)$$

Here  $\rho$  is the density of the atmosphere,  $f(E)$  is the energetic spectrum of solar protons,  $X$  is the respective depth in gram/cm<sup>2</sup>,  $E_{\min} = 1$  MeV,  $E_{\max} = 400$  MeV, parameters  $A$  and  $m$  are equal to 242 and 0.75, respectively. The rate of ion-electron pair production is related with the value  $w(h)$  by the relation

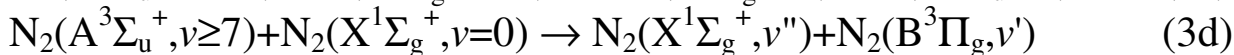
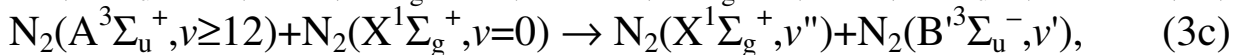
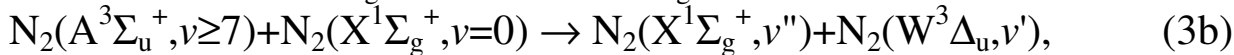
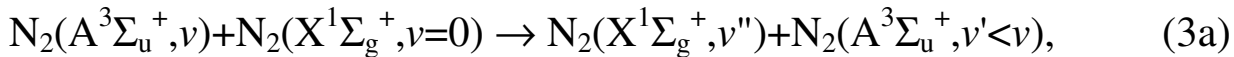
$$q(h) = \frac{w(h)}{Q} , \quad (2)$$

where  $Q$  is equal to 35 eV. Here we suggest the isotropic distribution of solar protons on the pitch angle  $\theta$  in all our calculations. The rates of electronic excitations of N<sub>2</sub> and O<sub>2</sub> molecules can be calculated in the same manner as in (1), (2), but the values  $Q$  have to be taken from [Konovalov and Son, 1987].

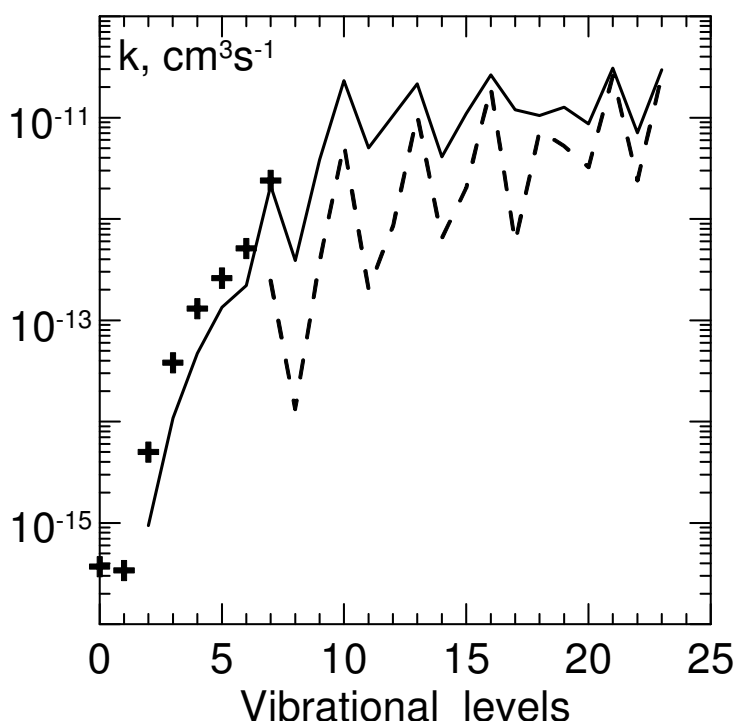
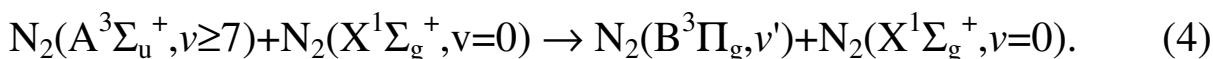
## ELECTRONIC QUENCHING

We use analytical expressions for the rate coefficients of electronic quenching in molecular collisions based on quantum-mechanical Landau-Zener and Rosen-Zener approximations and presented by Kirillov [2004a,b]. Franck-Condon factors for the calculations related with transitions in N<sub>2</sub> molecule are taken from [Gilmore et al., 1992]. Franck-Condon factors for the transitions in O<sub>2</sub> molecule are calculated applying Morse approximation [Kirillov, 2004b].

Here we present the results of our calculations for the quenching constants of the collisions  $N_2(A^3\Sigma_u^+, v=2-23)+N_2$ . The calculations include the consideration of intermolecular electron energy transfer processes



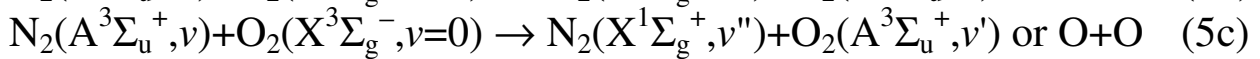
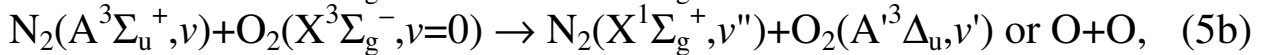
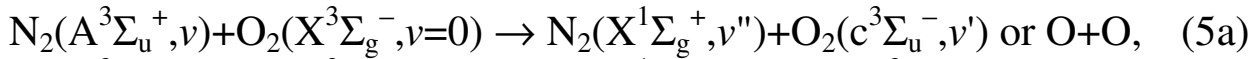
and intramolecular process



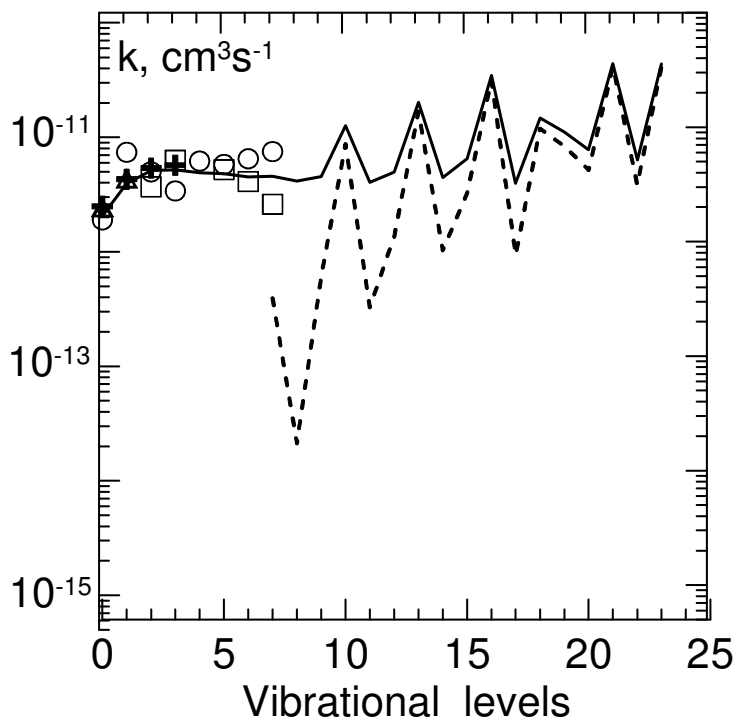
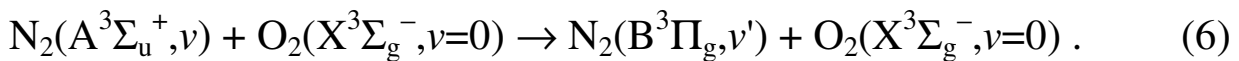
**Fig.1.** The calculated quenching constants for the collisions  $N_2(A^3\Sigma_u^+, v=2-23)+N_2$  (solid line) are compared with experimental data of [Dreyer and Perner, 1973] (crosses); the contribution of intramolecular process (4) – dashed line.

The calculated quenching constants for the collisions  $N_2(A^3\Sigma_u^+, v=2-23)+N_2$  at room temperature are compared with experimental data of [Dreyer and Perner, 1973] in Fig.1. Also we show here the contribution of intramolecular process (4). It is seen good agreement of our results with the data.

Here we present the results of our calculations for the quenching constants of the collisions  $N_2(A^3\Sigma_u^+, v=0-23)+O_2$ . The calculations include the consideration of intermolecular electron energy transfer processes



and intramolecular process

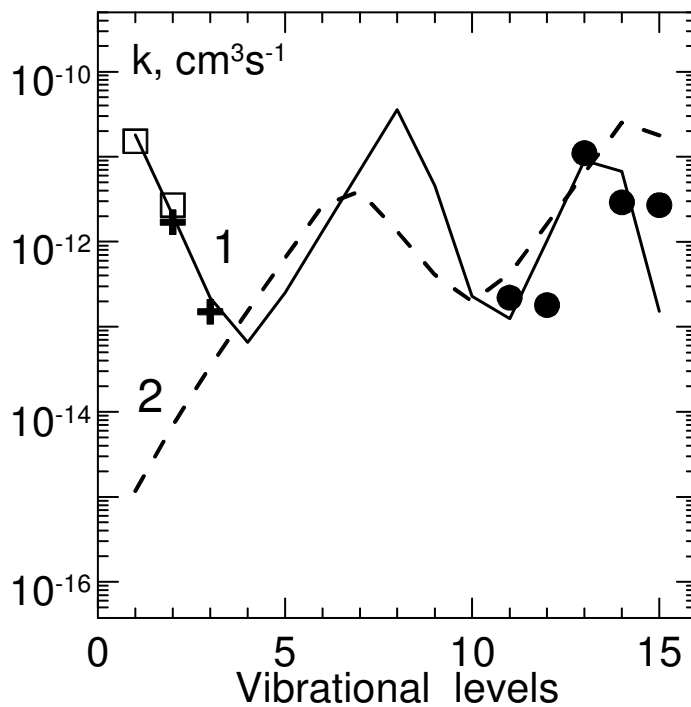
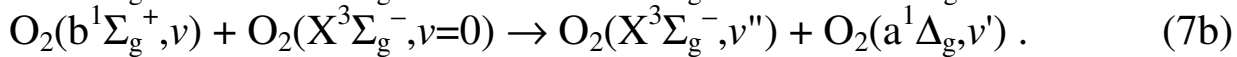
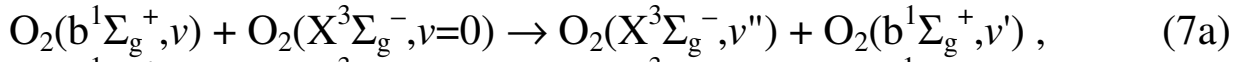


**Fig.2.** The calculated quenching constants for the collisions  $N_2(A^3\Sigma_u^+, v=0-23)+O_2$  (solid line) are compared with experimental data of [Dreyer et al., 1974] (circles), [Piper et al., 1981] (triangles), [Thomas and Kaufman, 1985] (crosses), [De Benedictis and Dilecce, 1997] (squares); contribution of intramolecular process (6) – dashed line.

The calculated quenching constants for the collisions  $N_2(A^3\Sigma_u^+, v=0-23)+O_2$  at room temperature are compared with experimental data of [Dreyer et al., 1974], [Piper et al., 1981], [Thomas and Kaufman, 1985], [De Benedictis and Dilecce, 1997]

in Fig.2. Also we show here the contribution of intramolecular process (6). It is seen good agreement of our results with the data.

Here we present the results of our calculations for the quenching constants of the collisions  $O_2(b^1\Sigma_g^+, v=1-15)+O_2$ . The calculations include the consideration of intermolecular electron energy transfer processes



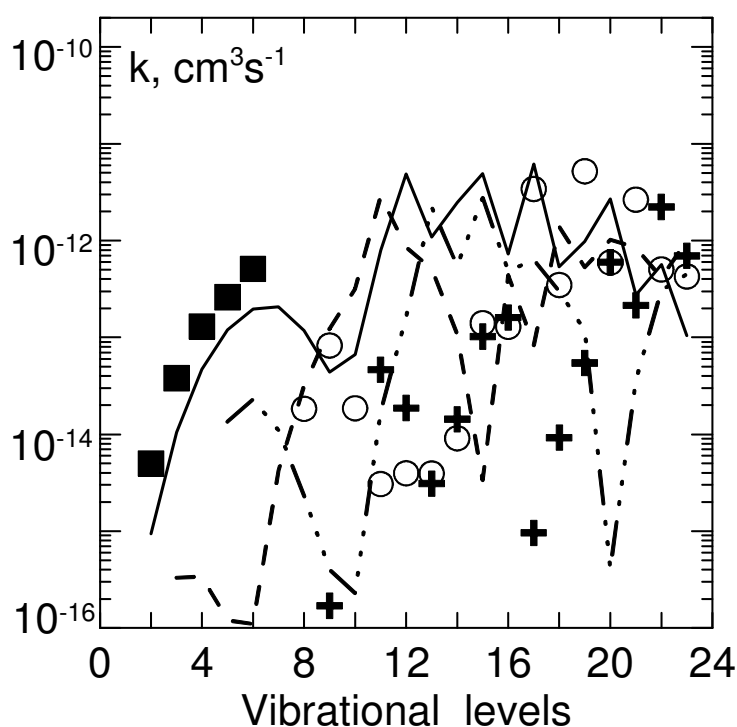
**Fig.3.** The calculated quenching constants for the collisions  $O_2(b^1\Sigma_g^+, v=0-15)+O_2$  (solid and dashed lines for the processes (7a) and (7b), respectively) are compared with experimental data of [Bloemink et al., 1998] (squares), [Kalogerakis et al., 2002] (crosses), [Amaral et al., 2002; Slanger and Copeland, 2003] (circles).

The calculated quenching constants for the collisions  $O_2(b^1\Sigma_g^+, v=0-15)+O_2$  at room temperature are compared with experimental data of [Bloemink et al., 1998], [Kalogerakis et al., 2002], [Amaral et al., 2002], [Slanger and Copeland, 2003] in Fig.3. It is seen good agreement of our results with the data.

## VIBRATIONAL EXCITATION

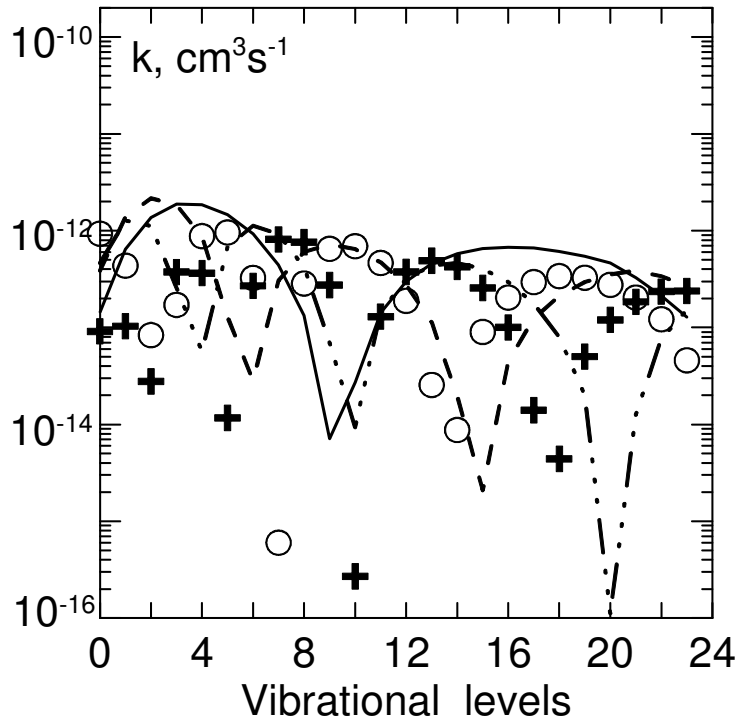
Here we follow to the suggestion of Kirillov (2004a,b) that a process of electronic energy quenching in a molecular collision consists from ones of quasi-resonant intermolecular and intramolecular energy transfers.

Intermolecular electron energy transfers in the collisions lead to both the electronic excitation of target molecule and vibrational excitation in the ground state of primary excited molecule. Intramolecular transfers contribute to the production of vibrationally excited molecule when there are transitions from electronically excited state to the ground state during inelastic collisions. We make our calculation of rates of inelastic molecular collisions paying special attention to vibrational excitation in the processes.



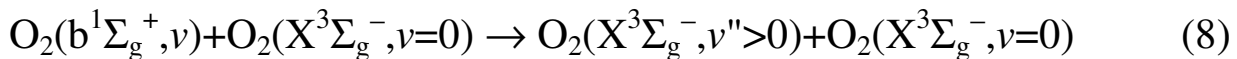
**Fig.4.** The calculated rate coefficients for the  $\text{N}_2(\text{X}^1\Sigma_g^+, v''=1-5)$  production in the process of electronic quenching  $\text{N}_2(\text{A}^3\Sigma_u^+, v=2-23) + \text{N}_2: v''=1$  (solid line),  $v''=2$  (dashed line),  $v''=3$  (dash and three dotted line),  $v''=4$  (circles),  $v''=5$  (crosses) are compared with experimental data of [Dreyer and Perner, 1973] for  $v''=1$  (squares).

The calculation of the rate coefficients for the production of vibrationally excited  $N_2(X^1\Sigma_g^+, v'' > 0)$  molecules in the processes of electronic quenching is made for the collisions of triplet  $N_2(A^3\Sigma_u^+)$  in the processes (3a-d) and (5a-c). The results of the calculations for  $N_2(X^1\Sigma_g^+, v'' = 1-5)$  are presented in Fig.4 and Fig.5. Also we show experimental data of [Dreyer and Perner, 1973] for  $v'' = 1$ .



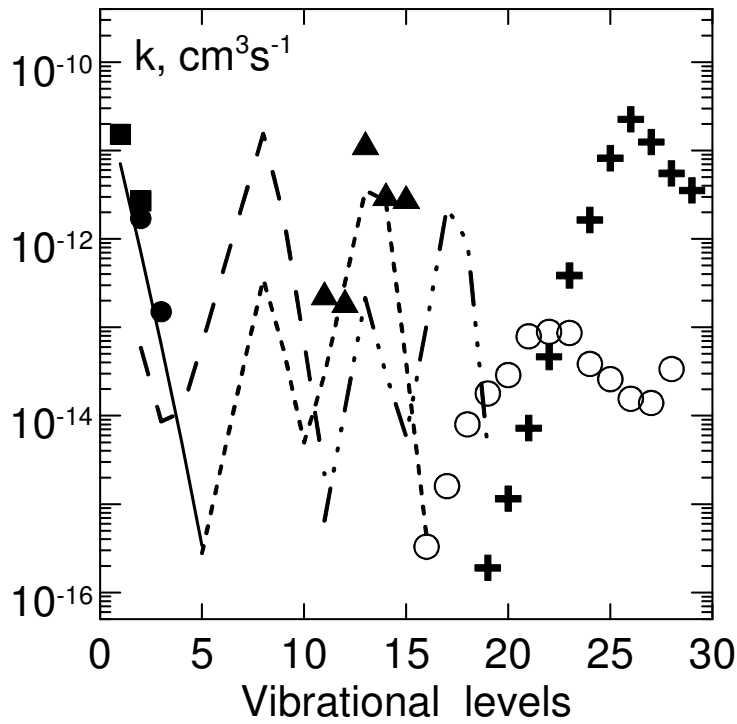
**Fig.5.** The calculated rate coefficients for the  $N_2(X^1\Sigma_g^+, v'' = 1-5)$  production in the process of electronic quenching  $N_2(A^3\Sigma_u^+, v = 0-23) + O_2$ :  $v'' = 1$  (solid line),  $v'' = 2$  (dashed line),  $v'' = 3$  (dash and three dotted line),  $v'' = 4$  (circles),  $v'' = 5$  (crosses).

Similar estimations for the rate coefficients of intermolecular process (7a) with  $v = 1-30$  and  $v'' = v, v-1, v-2, v-3$  and intramolecular process



with  $v'' = v+9, v+8$  are presented in Fig.6. Also we plot in Fig.6 experimental data of  $O_2(b^1\Sigma_g^+, v)$  electronic quenching constants by Bloemink et al. [1998] for  $v = 1, 2$ , by Kalogerakis et al. [2002] for  $v = 2, 3$  and by Amaral et al. [2002], Slanger and Copeland [2003] for  $v = 11-15$ . It is seen there is an agreement of the calculated constants with experimental data.





**Fig.6.** The calculated rate coefficients for the  $O_2(X^3\Sigma_g^-, v'')$  production in the quenching  $O_2(b^1\Sigma_g^+, v=1-30)+O_2$  for the process (7a):  $v''=v$  (solid line),  $v''=v-1$  (long dashed line),  $v''=v-2$  (short dashed line),  $v''=v-3$  (dash and three dotted line) and for the process (8):  $v''=v+9$  (open circles),  $v''=v+8$  (crosses) are compared with experimental data by Bloemink et al. [1998] (squares), by Kalogerakis et al. [2002] (solid circles) and by Amaral et al. [2002], Slanger and Copeland [2003] (triangles).

## CONCLUSIONS

The calculated quenching rate coefficients of electronically excited molecular nitrogen ( $N_2^*$ ) and molecular oxygen ( $O_2^*$ ) in inelastic collisions with  $N_2$  and  $O_2$  are applied in the simulations of vibrational populations of the molecules  $N_2^*$  and  $O_2^*$  at the altitudes of the middle atmosphere during solar proton events. The comparison of our results for metastable nitrogen  $N_2(A^3\Sigma_u^+)$  and metastable oxygen  $O_2(b^1\Sigma_g^+)$  shows good agreement with experimental data in Figs.1-3. It is seen from Figs.4-6 that the influence of electronically excited molecules  $N_2$  and  $O_2$  on vibrational kinetics of the molecules at the altitudes of the middle atmosphere is important.

## REFERENCES

- Amaral G.A., Kalogerakis K.S., Copeland R.A. Temperature dependence of the collisional removal of  $O_2(a^1\Delta_g, b^1\Sigma_g^+, \text{ and } c^1\Sigma_u^-)$  molecules in highly vibrationally excited levels. // EOS, Trans. AGU, 2002, v.83, p.S236.
- Bloemink H.I., Copeland R.A., Slanger T.G. Collisional removal of  $O_2(b^1\Sigma_g^+, v=1,2)$  by  $O_2, N_2,$  and  $CO_2$ . // J. Chem. Phys., 1998, v.109, p.4237-4245.
- De Benedictis S. and Dilecce G. Rate constants for deactivation of  $N_2(A) v=2-7$  by  $O, O_2,$  and  $NO$ . // J. Chem. Phys., 1997, v.107, p.6219-6229.
- Dorman L.I. Experimental and theoretical background of astrophysics of cosmic rays. Nauka, Moscow, 1975 (in russian).
- Dreyer J.W. and Perner D. Deactivation of  $N_2(A^3\Sigma_u^+, v=0-7)$  by ground state nitrogen, ethane, and ethylene measured by kinetic absorption spectroscopy. // J. Chem. Phys., 1973, v.58, p.1195-1201.
- Dreyer J.W., Perner D., Roy C.R. Rate constants for the quenching of  $N_2(A^3\Sigma_u^+, v=0-8)$  by  $CO, CO_2, NH_3, NO,$  and  $O_2$ . // J. Chem. Phys., 1974, v.61, p.3164-3169.
- Gilmore F.R., Laher R.R., Espy P.J. Franck-Condon factors, r-centroids, electronic transition moments, and Einstein coefficients for many nitrogen and oxygen band systems. // J. Phys. Chem. Ref. Data, 1992, v.21, p.1005–1107.
- Kalogerakis K.S., Copeland R.A., Slanger T.G. Collisional removal of  $O_2(b^1\Sigma_g^+, v=2,3)$ . // J. Chem. Phys., 2002, v.116, p.4877-4885.
- Kirillov A.S. Application of Landau-Zener and Rosen-Zener approximations to calculate rates of electron energy transfer processes. // Adv. Space Res., 2004a, v.33, p.993–997.
- Kirillov A.S. Calculation of rate coefficients of electron energy transfer processes for molecular nitrogen and molecular oxygen. // Adv. Space Res., 2004b, v.33, p.998–1004.
- Konovalov V.P. and Son E.E. Degradation spectrum of electrons in gases // Khimiya plasmy, 1987, v.14, p.194–227, in russian.
- Piper L.G., Caledonia G.E., Kennealy J.P. Rate constants for deactivation of  $N_2(A) v'=0,1$  by  $O_2$ . // J. Chem. Phys., 1981, v.74, p.2888-2895.
- Siskind D.E., Summers M.E., Mlynczak M.G. An evaluation of  $O_2(b^1\Sigma_g)$  as a possible source of OH and odd-nitrogen in the stratosphere and mesosphere. // Geophys. Res. Lett., 1993, v.20, p.2047-2050.
- Slanger T.G. and Copeland R.A. Energetic oxygen in the upper atmosphere and the laboratory. // Chem. Rev., 2003, v.103, p.4731-4766.
- Thomas J.M. and Kaufman F. Rate constants of the reactions of metastable  $N_2(A^3\Sigma_u^+)$  in  $v=0,1,2,$  and 3 with ground state  $O_2$  and  $O$ . // J. Chem. Phys., 1985, v.83, p.2900-2903.
- Toumi R. A potential new source of OH and odd-nitrogen in the atmosphere. // Geophys. Res. Lett., 1993, v.20, p.25-28.
- Zipf E.C. A laboratory study on the formation of nitrous oxide by the reaction  $N_2(A^3\Sigma_u^+) + O_2 \rightarrow N_2O + O$ . // Nature, 1980, v.287, p.523-524.
- Zipf E.C. and Prasad E.E. Production of nitrous oxide in the auroral D and E regions. // Nature, 1980, v.287, p.525-526.