Ultraviolet Emission in the Dissociation of N_2 and O_2 by K^+ Impact

M. R. Gochitashvili, B. I. Kikiani, R. V. Kvizhinadze, and N. R. Jaliashvili

Physics Department, Tbilisi State University,
Tbilisi, 380028 Georgia

Ion-impact processes on molecular nitrogen and oxygen, N_2 and O_2, have been studied extensively because of their importance in upper-atmosphere reactions and gas discharges. The excitation function and absolute emission cross section of atomic lines of nitrogen and oxygen have been measured in the vacuum ultraviolet (VUV) spectral region from 50 nm to 130 nm by K^+ ion-impact dissociative excitation of N_2 and O_2 molecules in the K^+ projectile energy range 3-8 KeV. The experimental arrangement and calibration procedures of the light-recording system have been described in more detail previously [1]. The uncertainties in the absolute values of the cross sections given here are estimated to be about 20%. Polarization of the radiation emitted in the investigated processes is assumed to be negligible.

Fig. 1 shows examples of the emission spectrum obtained for the collision of K^+- ions with N_2 and O_2 at a laboratory energy of 4.0 keV for the K^+ ion. Only the atomic lines of nitrogen and oxygen are observed. These results indicate that direct dissociation plays an important role in the formation of N* and O*. There are many dissociative highly excited (Rydberg) molecular states that can produce a contribution to this inelastic channel. It is necessary to mention that the direct excitation of dissociative molecular states by alkali metal ions is favored energetically. For example, the minimum energies which are needed to produce the emission of dissociative products of N I (at λ = 120.0 nm) are ΔE = 20.1 eV, 30.2 eV, 34.6 eV in direct-dissociative, charge-exchange dissociative and ionization-dissociative processes, respectively.

The energy dependence of the emission cross-sections of excited atomic products of N and O is presented in Fig. 2. It seems that the cross sections are independent of the energy of the K^+ ion in the investigated energy range. It appears that the "core" ion model [2] is adequate to interpret the experimental results. This model predicts that dissociation is governed entirely by the core of the ion and strongly depends on the form of the potential curves. Potential curves of the highly excited molecule will be parallel to those of the core ion and lie lower in energy (electron binding energy). The excited molecular states whose cores decay spontaneously in the Frank-Condon region give rise to a major contribution of the formation of excited atomic products. After the decay of the molecular ion core the weakly bound electron is moving to the atomic ions N^+ or O^+ and captured by them in excited states.

In beginning to explain the dissociation mechanism we should remember that the spin conservation rule is valid, because the spin-orbital interaction is ignored in our case. This implies that during K^+-N_2 collisions the intermediate molecular state which is excited is a singlet. Therefore, both fragments of atoms are left in the same state multiplicities. In the case of the excitation of the more intense nitrogen atomic line at λ = 120.0 nm (transition $3s\ ^4P$-$2p^3\ ^4S$) both fragments of the dissociation must be formed in quartet states in the following way:

$$K^+(3p^6\ ^1S)+N_2(X^1\Sigma_g^+) \rightarrow K^+ + N(3s^4P) + N(2p^3\ ^4S).$$
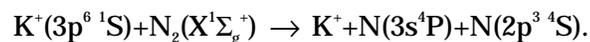
Similarly, the atomic line at λ=124.3 Å (transition 3s' ^{2}D $\to$ 2p^3 ^{2}D) can be emitted as a direct result of the dissociation process of N$_2$ when both fragments are formed in doublet states:

$$K^+ + N_2 \to K^+ + N(3s'\ ^2D) + N(2p^3\ ^2D).$$
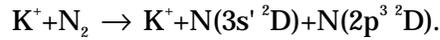
In the framework of the core ion model the emission of the more intense nitrogen atomic line at λ=120.0 nm may be caused by the excitation of an intermediate molecular singlet state of N$_2$* in which the ion core N$_2^+$ is in the states C$^2\Sigma_u^+$ or D$^2\pi_g$ (Fig. 3). The dissociation limit for these cores is N(2p^3 ^{4}S)-N$^+$(2p^2 ^{3}P). For the C$^2\Sigma_u$ state this dissociation limit is reached by predissociation through the $^4\Pi_u$ state. Formation of the nitrogen atomic line at λ=123.4 nm can be due to the decay of an excited intermediate molecular state of N$_2$* with core N$_2^+(^2\Pi_u)$. The dissociation limit for this core is N(2p^3 ^{2}D)+N$^+$(2p^2 ^{3}P). In both cases the excited atomic products are formed when the weakly bonding molecular electron is attached to the N$^+$(2p^2 ^{3}P) ion. A high value of the cross section in the first case may be connected with a comparably small value of energy defects for the inelastic process in this case.
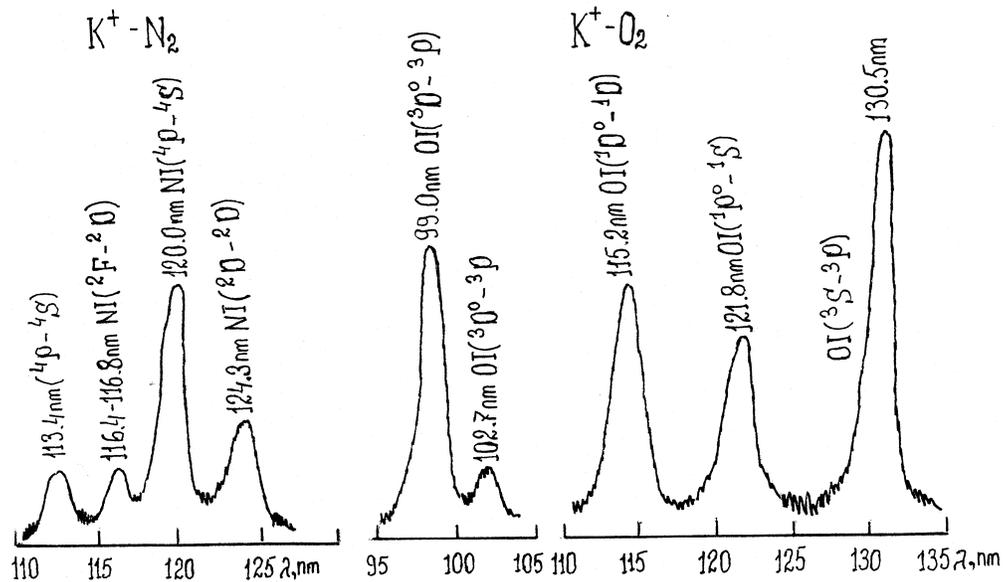

Figure 1

In the K$^+$-O$_2$ collision the intermediate highly excited state of molecular oxygen must be a triplet because the oxygen molecule in the ground state is in the triplet state, too. Following the spin conservation rule the summed spin of the dissociative fragments should be equal to one. In the framework of the core ion model the observation of the more intense oxygen atomic lines at λ=99.0 nm (transition 3s' ^{3}D $\to$ 2p^4 ^{3}P) and at λ=130.5 nm (transition 3s ^{3}S $\to$ 2p^4 ^{3}P) may be due to the excitation of an intermediate molecular triplet state O$_2$* with an ion core O$_2^+$ in the A$^2\Pi_u$ or B$^4\Sigma_g^-$ states. The dissociation limit for these cores is O$^+$(^{4}S)-O(^{3}P). The triplet 3s' ^{3}D and 3s ^{3}S states of the oxygen atom can be formed as a result of the capture of an electron by the O$^+$(^{4}S) ion and hence these dissociative fragments must be correlated with the dissociative fragment O(^{3}P). Similarly, the formation of the oxygen atomic lines at λ=115.2 nm (transition 3s' ^{1}D^0 $\to$ 2p^4 ^{1}D) and at λ=121.8 nm (transition 3s" ^{1}P^0 $\to$ 2p^4 ^{1}S) may be caused by the decay of the intermediate molecular triplet state with the core $^2\Pi_u$(III). The dissociation limit for them is O$^+$(^{2}D)-O(^{3}P) when a weakly bonded electron is attracted by O$^+$(^{2}D) ions and captured by them. The formation of singlet

states 3s' $^1D^0$ or 3s" $^1P^0$ takes place and hence these dissociative fragments should be correlated with the fragment O(^{3}P), too.

In summary, it is necessary to mention that all core states $N_2^+(C^2\Sigma_u^+, D^2\Pi_g, {}^2\Pi_u)$ and $O_2^+(A^2\Pi_u, B^4\Sigma_g^-, {}^2\Pi_u(III))$ decay spontaneously in the Frank-Condon region.
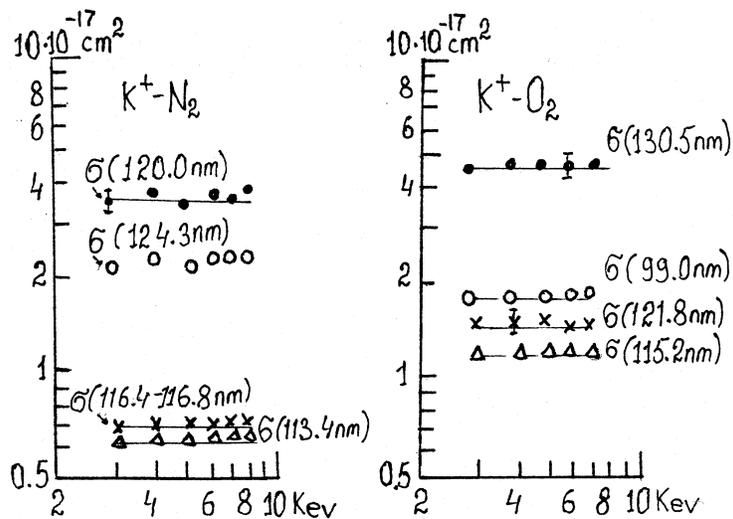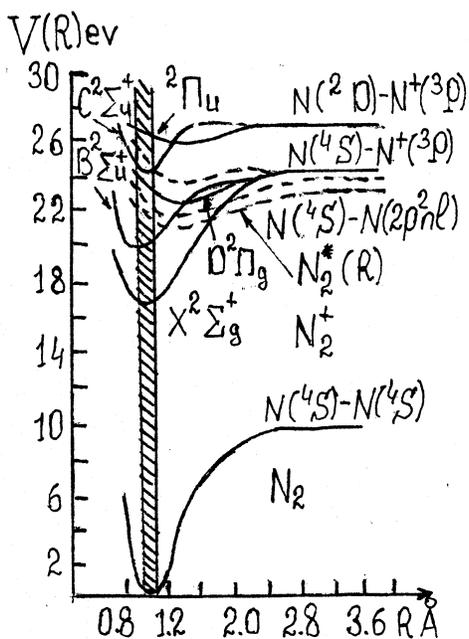

Figure 2

Figure 3

R e f e r e n c e s

[1] M. R. Gochitashvili, R. V. Kvizhinadze, N. R. Jaliashvili, and B. I. Kikiani, *Zh. Tech. Fiz.* **49** 2338-43 (1993); see also the contributed paper by M. R. Gochitashvili, B. I. Kikiani, and R. A. Lomsadze "Measurement of the absolute cross section of inelastic processes in slow atomic collisions", in these proceedings

[2] K. C. Singlet, J. A. Schiavone, and R. S. Freund, *J. Chem. Phys.* **59,** 5225-40 (1973)