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Abstract

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I. P. Zapesochnyi and S. M. Kishko

On the Complex Structure of the Excitation Functions of Bands of the Molecular Ions N_2^+, CO^+, and NO^+

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The excitation functions of the bands of diatomic molecules, giving the dependence of the band intensity on the energy of the exciting electrons, have been little studied. Until recently there were only a few works ([1–4]) in which it was established that the excitation functions of bands have a maximum, but the shape and position of this maximum for one and the same band were found by different authors to be entirely different. Since these experiments were carried out by very imperfect methods, their results cannot be regarded as reliable.

In order to obtain more accurate data on the character of the optical excitation functions of diatomic molecules, we carried out a series of experiments to study the excitation by electron collisions of the band spectra of nitrogen, carbon monoxide, and nitric oxide, emitted both by neutral molecules and by singly charged ions of these molecules. The relative intensities of the bands studied were determined by means of photoelectric registration, previously successfully applied by one of the authors in studying the fine structure of the excitation functions of mercury lines ([5]).

The experiments were carried out with an excitation tube not substantially different from that described earlier in work ([6]). By means of a dosing system the tube was filled with the spectrally pure gas under investigation, the pressure of which was strictly controlled. An ISP-51 spectrograph was used as the monochromator, and the intensities of the selected band regions were measured with an FEU-17 photomultiplier with a direct-current amplifier assembled on an electrometer tube ([7]).

In the visible region of the spectrum we measured the excitation functions of the bands of the second positive system of N_2 (transition $C^3\Pi \to B^3\Pi$) and the bands of the Angström system of CO (transition $B^1\Sigma \to A^1\Pi$).* Especially carefully and comprehensively investigated were the excitation functions of bands emitted by molecular ions, namely: the bands of the negative system of N_2^+, corresponding to the electronic transition $B^2\Sigma \to X^2\Sigma$; the bands of the comet-tail system of CO^+, corresponding to the electronic transition $A^2\Pi \to X^2\Sigma$; and the bands of the NO^+ system, the electronic-vibrational transitions of which are

Figure 1

Figure 1: Figure 1

unknown.**

In our measurements, measures were taken to eliminate the influence of side factors (the pressure of the gas under investigation, the current density of the exciting electrons, the degree of monokineticity of the electron beam, and others) on the shape of the experimental curves. Special measurements established the suitability of the oxide cathode as a source of a stable electron beam in the working range of pressures of the gases studied ([8]).

The final measurements were carried out at a pressure of the gas under investigation of $0.5 \cdot 10^{-3}$—$1 \cdot 10^{-3}$ mm Hg, an electron current density of not more than $1 \cdot 10^{3}$ A/cm^2, and an electron energy spread of less than 1 eV.

* Because of the very weak intensity of the bands emitted by nitric oxide molecules in the visible region, the excitation functions of the bands of neutral NO molecules were not studied.

** The wavelengths corresponding to the quanta of these bands were determined approximately.

The excitation functions of the bands of N_2^+ (9), CO^+, and NO^+ observed by us are shown in Fig. 1, and Table 1 gives the excitation potential of the band system and the number and positions of individual maxima on these curves. Repeated measurements carried out by us in excitation tubes with different geometries of the electron system, in the region of a linear dependence of the band intensity on gas pressure and current density, always gave one and the same form of the experimental curve for a given band.

Fig. 1. Excitation functions of the bands of NO^+
(1 –λ 4880 Å, 2 –λ 4500 Å, 3 –λ 4380 Å);
N_2^+ (1 –λ 4278.1 Å, 2 –λ 3914.4 Å) and CO^+
(1 –λ 4565.8 Å, 2 –4274.3 Å, 3 –λ 4019.7 Å)

Thus, it may be asserted that in our experiments a complex structure (or fine structure) of the excitation functions of the bands emitted by the molecular ions N_2^+, CO^+, and NO^+ has been found.

From the form of the experimental curves one can also formulate the following regularity: the excitation functions of bands belonging to a definite system of a given molecular ion are completely identical*.

Thus, the difference in the electronic-vibrational levels, the transition between which leads to the emission of a band of the given system, is not manifested in the corresponding excitation functions. The determining factor is the electronic state of the excited ion.

In contrast to molecular ions, the excitation functions of bands of neutral diatomic molecules do not have secondary maxima (10, 11), despite the fact that the determination of the band functions both of neutral molecules and of their ions was carried out in the same tubes and under the same experimental conditions. The excitation functions of the bands of the neutral molecules N_2 and CO, as is seen from Fig. 2, have only one maximum**, although for some bands the dependence of band intensity on electron energy was followed up to 200 eV.

The complex structure of the excitation functions of the bands of N_2^+, CO^+, and NO^+ cannot be explained by transitions with different geometry of the electron system,

Table 1

Band systems of molecular ions	Excitation potential of the system, V	Number of maxima	Electron energy corresponding to maxima on the excitation functions of bands, eV
Bands of the negative system N_2^+	18.7	5	29; 49; 56; 67 and 85–88
Bands of the comet-tail system CO^+	16.9	4	24; 44; 72 and 100–105
Bands of the NO^+ system beginning at 6000 Å	$\sim$ 13.0	4	21; 33; 43 and 53

* The excitation potentials of individual bands of the system differ only by tenths of a volt.

** Generally speaking, the possibility of detecting fine structure on the excitation functions of neutral diatomic molecules is not excluded, provided an electron beam of considerably better monoenergeticity than monoenergeticity within 1 eV is used.

from higher electronic levels of the molecular ion to the upper level of the band (cascade transitions), as was the case for the excitation functions of certain lines of mercury atoms ([5,12]). The fact is that band systems corresponding to such cascade transitions in the molecular ions N_2^+, CO^+, and NO^+, so far as we know, have not been observed at all.

Fig. 2. Excitation functions of the bands of N_2 (1—λ3998.4 Å, 2—λ4059.4 Å, 3—λ4200.5 Å) and CO (1—λ4123.6 Å, 2—λ4393.1 Å, 3—λ4510.9 Å)

Figure 2: Fig. 2. Excitation functions of the bands of N_2 (1—λ3998.4 Å, 2—λ4059.4 Å, 3—λ4200.5 Å) and CO (1—λ4123.6 Å, 2—λ4393.1 Å, 3—λ4510.9 Å)

At present the most probable supposition is that the maxima of the fine structure in the excitation functions of the bands are ultimately due to various elementary processes—dissociation and ionization of diatomic molecules—which occur at definite energies of the colliding electrons.

The following facts support such an interpretation:

1. To each maximum of the fine structure of the excitation function of a band of a given ion one can assign a definite elementary process whose appearance potential corresponds to the value of the accelerating potential at which this maximum lies.
2. The comparatively large probabilities of recombination processes ([13]), inverse to the processes of dissociation and ionization of diatomic molecules, may lead to an appreciable contribution to the population of excited states of molecular ions, in addition to the direct excitation of these states by electron impacts.

Fig. 2. Excitation functions of the bands of N_2 (1—λ3998.4 Å, 2—λ4059.4 Å, 3—λ4200.5 Å) and CO (1—λ4123.6 Å, 2—λ4393.1 Å, 3—λ4510.9 Å).

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Uzhgorod State
University

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Note: Figure translations are in progress. See original paper for figures.