EXCITATION OF THE $\lambda = 4278 \text{ Å}$ BAND OF THE FIRST NEGATIVE SYSTEM OF THE N_2^+ ION BY IONS AND ATOMS OF NOBLE GASES

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Submitted August 16, 1968

Zh. Eksp. Teor. Fiz. 56, 161-166 (January, 1969)

We measured the excitation functions of the $\lambda = 4278$ Å band of the first negative system of the N_2^+ ion. The luminescence was excited by collision with ions and atoms of He, Ne, and Ar with energy 1–30 keV and with nitrogen molecules. It is concluded that in the excitation of the $\lambda = 4278$ Å band by ion impact a predominant role is played by the charge-exchange process. The excitation cross sections of the level $B^2\Sigma_u^+$ (v = 0) of the N_2^+ ion is compared with the total cross sections for the production of this ion, obtained with the aid of a mass-spectrometer procedure.

INTRODUCTION

 $W_{\text{HEN singly-charged positive ions pass through nitro$ $gen, N_2^{\star} ions are produced as a result of the processes$ of charge exchange

$$I^+ + N_2 \rightarrow I^0 + N_2^+ \tag{I}$$

and ionization

$$I^+ + N_2 \rightarrow I^+ + N_2^+ + e.$$
 (II)

If atoms that do not form stable negative ions (atoms of noble gases) pass through the nitrogen, the N_2^+ ions can be produced only as a result of ionization processes

$$I + N_2 \rightarrow I + N_2^+ + e. \tag{III}$$

The N_2^+ ions produced in the processes (I)-(III) may be not only in the electronic ground state, but also in excited states. The presence of excited N_2^+ ions (in the region where the beam of fast particles passes through the nitrogen) is revealed by their emission spectrum. By measuring the intensity of the bands of this spectrum pertaining to the same upper vibrational level of the electronic transition, it is possible to determine the effective excitation cross section of this level. Significant conclusions can be drawn also by measuring the intensity of only one band of the system, i.e., by measuring the effective excitation cross section of this band.

In the present investigation, we measured the effective cross sections for the excitation of the band $\lambda = 4278 \text{ Å} (0, 1)$ of the first negative system of the $N_2^{\star} (1 \text{ ns } N_2^{\star})$ (electronic transition $B^2 \Sigma_u^{\star} \rightarrow X^2 \Sigma_g^{\star}$) in the case when beams of He, Ne, and Ar ions and atoms, with energies from 1 to 30 keV, pass through the nitrogen. These measurements were made in order to clarify the characteristic features of the excitation functions of the $\lambda = 4278 \text{ Å}$ band excited by like charged and neutral particles. In addition, by comparing the data of the present work with the result of mass spectrometer measurements of the total effective cross sections for the production of N_2^{\star} ions, we can determine the ratio of the N_2^{\star} ions in the $B^2 \Sigma_u^{\star}$ (v = 0) state to the total number of these ions produced in the same process.

The effective cross section for the production of $N_2^+(B^2\Sigma_u^+)$ ions in collisions between noble-gas ions and

 N_2 molecules were measured also in^[1,2]. Insofar as we know, no such measurements were made with atoms of noble gases.

APPARATUS

The experimental setup used for the measurement is shown in Fig. 1. The ion beam was formed and accelerated by a system consisting of an arc ion source 1 and a three-electrode lens 2. The focused and accelerated ion beam was directed to the neutralizer chamber 3. The electric field of capacitor 4 eliminated the admixture of charged particles from the beam of particles leaving the neutralizer. The pure atomic beam was then directed to the collision chamber 5. Magnet 7, located in this chamber, prevented the electrons knocked out from its walls from penetrating into the region from which the glow of the N_2^+ ($B^2\Sigma_u^+$) ions entered the ISP-51 spectrograph. An achromatic lens 8 was used to focus the glow on the slit of the spectrograph. The intensity of the $\lambda = 4278$ Å band was measured photoelectrically. A description of the photoelectric apparatus used for these measurements is contained in^[3]. The current of the beam passing through the collision chamber was measured with a detector 6, which was constructed in such a way that it served as a Faraday cylinder in the measurements of the current of the ion beam, and the equivalent current of the atomic beam was determined by measuring the temperature rise of a steel plate on which this beam was incident. The signal from the thermocouple secured to this plate was graduated in terms of the charged-particle current.

The intensity of the $\lambda = 4278$ Å band was measured with the nitrogen pressure in the collision chamber not exceeding the upper limit of the region of linear dependence of the band intensity on the nitrogen pressure (the region of single collisions). This limit was of the order of 10^{-3} mm Hg. Channels 9 produced a pressure drop between chambers 3 and 5 and the remaining part of the setup.

MEASUREMENT RESULTS AND DISCUSSION

Relative measurements were made of the effective cross sections σ^* for the excitation of the $\lambda = 4278$ Å



FIG. 1. Diagram of the experimental setup.

band by ions and atoms of He, Ne, and Ar with energy from 1 to 30 keV. To recalculate the relative values into absolute ones, we used the effective excitation cross sections of the $\lambda = 3914$ Å band (1 ns N^{*}₂) by Ar⁺ ions, as obtained by Neff and Carleton^[1], and the intensity ratios I_{42.78}/I₃₉₁₄ taken from the paper by Bates^[4].

The results of the measurements are shown in Fig. 2 in the form of plots of σ^* against the velocity of the exciting particles. For comparison, the same figure shows the $\sigma^*(v)$ plots as given by Neff and Carleton^[1] and by Sheridan and Clark^[2]1]. In the upper part of Fig. 2 are shown plots of $\sigma_i^*(v)$ and $\sigma_a^*(v)$ (σ_i^* and σ_a^* are the total effective cross section for the production of N₂^{*} ions by fast ions and atoms), as obtained from other massspectrometer measurements^[5]2].

From a comparison of the $\sigma^*(v)$ curves for like ions and atoms we can draw the following conclusions:

1) The values of σ_i^* are approximately one order of magnitude larger than σ_a^* (σ_i^* and σ_a^* are the effective cross sections for the excitation of the $\lambda = 4278$ Å band by ions and atoms respectively).

2) The maxima of the $\sigma_a^*(v)$ curves are shifted towards higher velocities compared with the maxima of the $\sigma_i^*(v)$ curves.

As indicated in the introduction, when fast ions pass through nitrogen, the N_2^+ ions are produced as a result of charge exchange and ionization (processes (I) and (II)), whereas in collisions between fast atoms and nitrogen molecules, the N_2^+ ions are produced only as a result of ionization processes (III)). It follows therefore that the values of σ_1^* and σ_2^* can be expressed by means of the following equations:

$$\sigma_i^* = \sigma_I^* + \sigma_{II}^*, \tag{1}$$

$$\sigma_a^{\bullet} = \sigma_{\rm III}^{\bullet}, \qquad (2)$$

where σ_{I}^{*} , σ_{II}^{*} , and σ_{III}^{*} are the effective cross sections for the production of the ions $N_{2}^{*}(B^{2}\Sigma_{u}^{*}, v = 0)$ in the

processes (I), (II), and (III) respectively.

The inequality $\sigma_i^* \gg \sigma_a^*$, which follows from a com-

parison of the $\sigma_i^*(v)$ and $\sigma_a^*(v)$ curves, is realized, in particular, under the following conditions:

$$\sigma_{II}^{*} \approx \sigma_{III}^{*}, \qquad (3)$$

$$\sigma_{\rm I}^* \gg \sigma_{\rm II}^*. \tag{4}$$

From the published data on the measurement of the effective cross sections of ionization of gases by like ions and atoms^[7,8] we can conclude that the approximate equality (3) is valid. As to the inequality (4), arguments presented below will show that it is also satisfied.

The $\sigma_i^*(v)$ curves for He⁺ ions has a maximum at a velocity $v_{max}\approx 10^8~cm/sec.$ As is well known, the maximum value of the effective cross section of an atomic-collision process is reached at a colliding-particle relative velocity v_{max} calculated on the basis of the Massey adiabatic criterion

$$v_{max} = a \left| \Delta E \right| / h, \tag{5}$$

where a is the range of the interaction forces between the colliding particles, ΔE is the resonance defect, and h is Planck's constant.

If we assume that the maximum of the $\sigma_i^*(v)$ curve for the ions is connected with the charge-exchange process (I), then we can calculate a from formula (5), substituting in it the resonance defect of process (I)



FIG. 2. Dependence of the cross sections on the velocity of the exciting particles. Solid curves $-\sigma^*(\mathbf{v})$ for ions and atoms; dashed curves $-\sigma^*(\mathbf{v})$ for ions and atoms; dotted curves $-\sigma^*(\mathbf{v})$ for ions as given by $[^{1,2}]$. $\bigcirc -\mathrm{He^+}$, $\times -\mathrm{Ne^+}$, $\bigcirc -\mathrm{Ar^+}$, $\blacksquare -\mathrm{He^0}$, $\diamondsuit -\mathrm{Ne^0}$, $\blacklozenge -\mathrm{Ar^0}$. $\square -\mathrm{Ar^+}$ [¹], $\bigtriangleup -\mathrm{Ne^+}$ [¹], $\bigstar -\mathrm{He^+}$ [²]

¹⁾To construct the $\sigma^*(v)$ curves, the effective cross sections of the excitation of the $\lambda = 3914$ Å, measured in [¹;²], were multiplied by the intensity ratios I₄₂₇₈/I₃₉₁₄ taken from the paper of Bates [⁴].

²⁾ In [⁵] the cross sections for the production of N₂⁺ and N⁺ ions were measured in relative units. To obtain the values of σ_1^+ and σ_a^+ in absolute units, a graduation was performed against the results of [⁶], where the total cross section for the formation of positive ions in collisions of He⁺ ions with nitrogen molecules was measured in absolute units.

with participation of the He^{\dagger} ions, and the value v_{max} = 10⁸ cm/sec. It turns out to equal 7 Å. Such a value of a is obtained for many single-electron charge-exchange processes^[9].

Assuming that a has the same value 7 Å for processes of type (I) with participation of the Ne⁺ and Ar⁺, we can determine v_{max} of the $\sigma_i^*(v)$ curves for these ions. For the ions Ne⁺ and Ar⁺, the values of v_{max} are 4.7 $\times 10^7$ and 5×10^7 cm/sec, respectively. As follows from the course of the $\sigma_i^*(v)$ curves for these ions, their maxima are in the velocity regions calculated on the basis of formula (5) for the charge-exchange processes.

Were ionization the main process in the formation of the $N_2^*(B^2\Sigma_u^*)$ by ion impact, then, owing to the increase of the resonance defect of the processes, the maxima of the $\sigma_i^*(v)$ curves would be shifted towards larger velocities relative to the maxima due to the charge-exchange processes. Such a shift of the maxima is indeed observed in the case of the $\sigma_a^*(v)$ curves, when the ions $N_2^*(B^2\Sigma_u^*)$ are produced only as a result of ionization processes.

Thus, it can be concluded that $\sigma_{I}^{*} \gg \sigma_{II}^{*}$, i.e., the main contribution to the formation of the $N_2^{\scriptscriptstyle +}(B^2\!\Sigma_1^{\scriptscriptstyle +})$ ions by ion impact is made by charge-exchange processes. This conclusion is valid not only in the case of the production of the N_2^* ions in the $B^2\Sigma_u^+$ state, but also in cases when these ions are produced in the ground state and in other excited states, as follows from a comparison of the $\sigma_i^*(v)$ and $\sigma_a^*(v)$ curves shown in the upper part of Fig. 2. In this case we also have the inequality $\sigma^{\scriptscriptstyle +}_{\mathbf{i}}\gg\sigma^{\scriptscriptstyle +}_{\mathbf{a}},$ which is connected with the fact that the charge-exchange processes make the main contribution to the formation of the N_2^+ ions in all the electronic states. This is seen particularly clearly in a comparison of the $\sigma_i^{\scriptscriptstyle +}(v)$ and $\sigma_a^{\scriptscriptstyle +}(v)$ curves for the $Ar^{\scriptscriptstyle +}$ ions at low velocities. The value of σ_i^* for this velocity region increases rapidly with decreasing velocity, owing to the fact that the $\sigma_i^*(v)$ curve should have a maximum at a velocity 3×10^6 cm/sec, connected with the formation of N_2^{\dagger} ions in the ground state by the charge-exchange process. In the same velocity region, the value of σ_a^+ decreases quite rapidly with decreasing velocity.

The dominating contribution of the charge exchange processes to the formation of the N₂⁺ ions in ion impact affects also the shape of the $\sigma_1^*(v)$ curve for Ne⁺ ions, the inflection on which in the velocity region 4–4.5 $\times 10^7$ cm/sec is obviously connected with the presence of a maximum of the corresponding $\sigma_1^*(v)$ curve in this velocity region.

Having the values of the effective cross sections σ^* and σ^* , we can calculate the ratio $\eta = \sigma^B/\sigma^*$ (σ^B is the effective cross section for the excitation of the zeropoint vibrational level of the $B^2\Sigma_u^*$ state of the N_2^* ion), equal to the ratio of the number of $N_2^*(B^2\Sigma_u^*, v = 0)$ ions to the total number of these ions. The values of σ^B can be calculated by multiplying the values of σ^* by the factor $\Sigma W_{ok}/W_{ol}$, where W_{ol} is the probability of the transition corresponding to the $\lambda = 4278$ Å band, and ΣW_{ok} is the sum of the probabilities of the transition from the zero-point vibrational level of the state $B^2\Sigma_u^*$ to all the low-lying vibrational levels of the ground state $x^2\Sigma_g^*$ of the N_2^* ion.

Using the values of W_{ok} taken from the paper of Bates^[4], the authors calculated the effective cross sec-

E, keV	ni ,%			n _a ,%		
	He+	Ne+	Ar+	Не	Ne	Ar
30 20 10 5	6.5 11 14.5 11.5	42 53 60 29	20.5 25 12.5 1.8	5.1 5.0 2.8 3.1	15.4 12.3 9.2 5.2	21 21 15 9

tions σ^{B} and the values of η . The values of η for several values of the energy of the exciting particles are listed in the table.

It should be noted that if we were to use for the normalization of the effective cross sections σ^* to the absolute values not the data of Neff and Carleton^[1], but the data of Sheridan and Clark^[2], then the values of η listed in the table would have to be doubled. This would lead to unreasonably large values of η_i for the Ne⁺ ions. By virtue of this, we must assume that the results of Sheridan and Clark are overestimated. This is precisely why we used the data of Neff and Carleton for the normalization of σ^* .

The values of η listed in the table are a manifestation of the course of the functions $\sigma^B(v)$ and $\sigma^*(v)$ in the investigated interval of exciting-particle energy. Thus, the fact that η for Ne⁺ ions are much larger than for the other particles is a result of the fact that the energy interval 5–30 keV is located near the maximum of the function $\sigma^B(v)$ for these ions. The steep drop of the value of η with decreasing energy for the Ar⁺ ions is connected with the presence of a maximum of the function $\sigma^+(v)$ in the region of low energies. The decrease of η with decreasing energy of the He, Ne, and Ar atoms is a reflection of the fact that the functions $\sigma^B(v)$ have in that energy region a steeper drop with decreasing energy than the functions $\sigma^*(v)$.

Student M. M. Yarashevskaya of the Khar'kov State University took part in the measurements.

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Translated by J. G. Adashko 23