INVESTIGATION OF THE DISSOCIATIVE IONIZATION OF N_2 MOLECULES, DUE TO EXCITATION OF THE VIBRATIONAL MOTION OF NUCLEI INDUCED BY COLLISIONS WITH FAST IONS AND ATOMS

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Submitted July 5, 1968

Zh. Eksp. Teor. Fiz. 55, 2128–2135 (December, 1968)

The formation of N^+ and N_2^+ ions produced by collision of fast hydrogen, helium, neon, and argon ions and atoms (3–37 keV energy) with nitrogen molecules was investigated by a mass-spectrometer technique. The relative populations of the first vibrational level of the $B^2\Sigma_u^+$ state of the N_2^+ ion are measured simultaneously for the same elementary processes, by means of an optical-spectroscopy technique. It is concluded on the basis of the experiments that the formation of N^+ ions is the result of excitation of the N_2^+-ion vibrational levels lying above the dissociation limit of the electronic states of this ion.

INTRODUCTION

THE measurement of the relative intensities of the spectral bands of the first negative system of the N_2^+ ion (1 ns N_2^+), excited by collision of different ions and slow electrons with N_2 molecules, has shown that the population of the first vibrational level of the $B^2\Sigma_u^+$ state of the N_2^+ ion proceeds with violation of the Franck-Condon principle, the population of this level being much larger than the value calculated in accordance with the Franck-Condon principle[1,2]. It has been previously suggested[1] that the cause of this effect is the additional vibrational excitation of the nuclei of the N_2^+ ion, due to the direct action exerted in the nucleus by the field of the incoming particle. If this suggestion is valid, then an increase of the population is to be expected also for the higher vibrational levels of the N_2^+ ion.

The increase of the population of the higher vibrational levels of the electronic states of the N_2^+ ion may cause the dissociation of this ion to proceed not only as a result of excitation of electronic states with a potential-energy curve of the repulsive type, but also as the result of population of vibrational levels lying above the dissociation limit of the bound states of this ion.

An effect of similar kind was already observed in the number of investigations[3-5] devoted to the formation of fragment N^+ ions upon collision between slow electrons and N_2 molecules. It is obvious that the N^+ ions produced in the dissociation processes as the result of excitation of higher vibrational levels of the N_2^+ ions will have a zero initial kinetic energy. A study of the energy spectrum of the N^+ ions, carried out in the cited investigations, has shown that such ions appear at sufficiently low electron energies. The number of N^+ ions with zero kinetic energy increases with decreasing velocity of the incoming electrons. These facts themselves indicate the existence of a process of dissociation of the N_2^+ ion as a result of its vibrational excitation. A theoretical treatment of this process was presented by Oksyuk[6]. In collisions of heavy particles with molecules, the process of fragment-ion production is a result of vibrational excitation of molecular ions has not been observed by anyone as yet.

We report here investigations aimed at observing the dissociation of the N_2^+ ion, induced by vibrational excitation of its nuclei in collisions of fast ions and atoms with N_2 molecules. To this end, a mass-spectrometer procedure was used to measure the relative values of the effective cross sections for the production of N^+ and N_2^+ ions in collisions of ions and atoms of hydrogen, helium, neon, and argon with N_2 molecules. Simultaneously, we measured the relative population of the first vibrational level of the N_2^+ ion in the $B^2\Sigma_u^+$ state, produced upon collision of He, Ne, and Ar atoms with N_2 molecules. These measurements were made with the setup described in[1,7], which was equipped with a neutralizer to obtain beams of neutral particles.

APPARATUS

The measurements were made with a double mass-spectrometer installation, the injector part of which is described in[8], and whose magnetic mass-spectrometer for the analysis of the slow-ion composition is described in[9]. To carry out the present investigations, we replaced in the experimental setup the collision chamber and the system for forming the secondary-ion beams. A diagram of these units of the experimental setup is shown in Fig. 1.

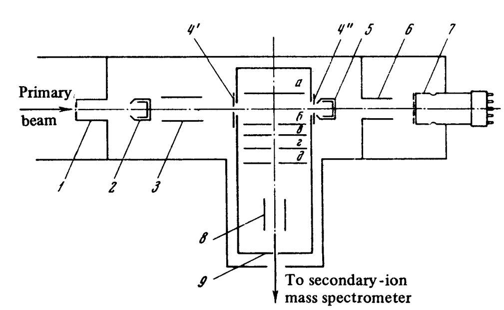

FIG. 1. Collision chamber and system for forming secondary-ion beams.

The collision chamber is separated from the remaining part of the setup by means of input and output channels 1 and 6. The input channel 1 was collimated by a slit measuring 1.5×6 mm. The current of the primary charge beam was measured with removable Faraday cylinders, one located past the input channel (2) and one located past the exit from the secondary-ion beam formation system (5). The equivalent current of the primary atomic beam was measured with a scintillation counter 7. The primary charged beam trajectory was corrected by the electric field of a parallel-plate capacitor 3.

The primary beam entered the region from which the slow ions were drawn out, between plates a and b of the parallel-plate capacitor, through slit 4′ with dimensions 1×4 mm, and left this region through slit 4″ measuring 1.5×7 mm; slit 4′ was insulated from the grounded housing of the draw-off system and was under a potential of +300 V in order to suppress the secondary electrons knocked out by the beam from the edges of the slit 4′.

The secondary ions produced in the ionization region were repelled by a weak electric field through the slit of plate b, accelerated, and focused by a system of three plane parallel plates with slits. All the slits in the plates of the draw-off system measured 1×7 mm. The formed beam of slow ions entered the input slit 9 of the mass spectrometer, with dimensions 0.2×12 mm. The parallel-plate capacitor 8 served as a corrector for the secondary-ion beam trajectory. The secondary-ion beam current past the output slit of the mass spectrometer was measured with the ion counter described in[10]. The counter made it possible to measure currents up to $(1-2) \times 10^{-18}$ A.

The initial energies of the secondary N^+ and N_2^+ ions produced upon passage of the primary beam through nitrogen are not equal; whereas the N_2^+ ions have thermal initial energies, the fragment N^+ ions can be produced with energies on the order of several electron volts. It is known that a draw-off system with a narrow capture solid angle can have an essentially different efficiency for the gathering of ions with different initial energies. As a result, the relative content of the N^+ and N_2^+ ions at the spectrum may not equal the relative concentrations of the N^+ and N_2^+ ions in the region of their formation.

Detailed investigations were made for the purpose of selecting the geometry of the secondary-ion beam formation and the distribution of the potentials on the electrodes of this system, so as to obtain the same ratios of the N^+ and N_2^+ currents as were obtained in other investigations, in which other systems for drawing out the secondary ions were used. As a result of these investigations, which were made with protons and hydrogen atoms, we were able to obtain N^+ and N_2^+ ion-current ratios that coincided, within the limits of the measurement error ($\sim 10\%$), with the results of[9,11], in which the systems used to draw out the slow ions had significantly larger capture angles. The distribution of the electrode potentials of the draw-off system, which ensured equal efficiency of the gathering of the N^+ and N_2^+ ions, was as follows: a positive potential (200 + 140 V) was applied to plate a, and +2000 V to plate b. Plates c and d were grounded, and a focusing voltage $\sim$ + 1400 V was applied to plate e; the distances between the electrodes of the draw-off system were as follows: 8 mm between plates a and b, 3 mm between b and c, and 5 mm each between c and d and d and e.

The mass spectrum of the slow ions produced in nitrogen by the passage of beams of ions and atoms of hydrogen, helium, neon, and argon revealed the presence of N_2^+ and N^+ ions and a very small amount of N^{2+} ions. We measured, in relative units, the effective cross sections for the production of the N_2^+ and N^+ ions. The measurements were made at nitrogen pressures and primary-particle beam currents such that single collisions were produced.

MEASUREMENT RESULTS AND DISCUSSION

Plots of the effective cross sections for the production of N_2^+ and N^+ ions against the velocities of the ions and atoms of hydrogen, helium, neon, and argon are shown in Figs. 2 and 3 respectively. Figure 3 shows, besides the $\sigma_{N^+}(v)$ curves also plots of N_1/N_0 against v (N_1 and N_0 are the populations of the first and zeroth vibrational levels of the $B^2\Sigma_u^+$ of the N_2^+ ion) for He^+, Ne^+, and Ar^+ ions, taken from[1], and for He, Ne, and Ar atoms, as obtained in the present investigation.

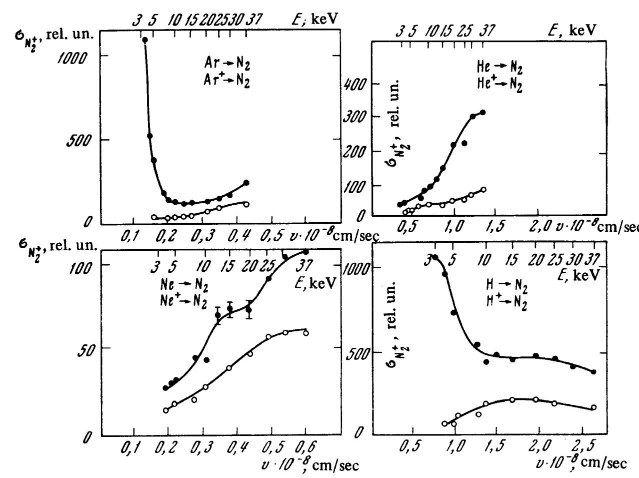

FIG. 2. Plots of the effective cross sections for the production of N_2^+ ions against the velocity of the ions and atoms of hydrogen, helium, neon, and argon. ● – positive ions, ○ – neutral atoms.

In collisions between ions and N_2 molecules, the N_2^+ ions are produced as a result of the following processes:

$$I^+ + N_2 \rightarrow I^0 + N_2^+ \quad \text{charge exchange}, \qquad (I)$$

$$I^+ + N_2 \rightarrow I^+ + N_2^+ + e \quad \text{ionization}. \qquad (II)$$

In the case of collision of atoms with N_2 molecules, the N_2^+ ions are produced only as a result of the ionization process[1])

$$I^0 + N_2 \rightarrow I^0 + N_2^+ + e. \qquad (III)$$

An examination of Fig. 2 shows that the $\sigma_{N_2^+}(v)$ plots

1)In collisions of H atoms with the N_2 molecule, charge exchange $H^0 + N_2 \rightarrow H^- + N_2^+$ does occur, but the cross section of this process is small [8] and this process can therefore be disregarded.

Table I

State of the N_2^+ ion	Potential, eV	H^+		He^+		Ne^+		Ar^+	
		$\lvert\Delta E\rvert$, eV	v_{max}, cm/sec	$\lvert\Delta E\rvert$, eV	v_{max}, cm/sec	$\lvert\Delta E\rvert$, eV	v_{max}, cm/sec	$\lvert\Delta E\rvert$, eV	v_{max}, cm/sec
$X^2\Sigma_g^+$	15.58	1.98	$3.82\cdot10^7$	9	$1.74\cdot10^8$	5.98	$1.15\cdot10^8$	0.18	$3.48\cdot10^6$
$A^2\Pi_u$	16.7	3.1	$6\cdot10^7$	7.88	$1.52\cdot10^8$	4.86	$9.35\cdot10^7$	0.94	$1.81\cdot10^7$
$B^2\Sigma_u^+$	18.75	5.15	$1\cdot10^8$	5.93	$1.14\cdot10^8$	2.81	$5.42\cdot10^7$	2.99	$5.8\cdot10^7$
$C^2\Sigma_u^+$	23.5	9.9	$1.91\cdot10^8$	1.08	$2.1\cdot10^7$	1.94	$3.74\cdot10^7$	7.74	$1.49\cdot10^8$

have a structureless form in the case of N_2^+-ion production by atomic collisions; this form is characteristic of ionization processes. Certain features observed on the $\sigma_{N_2^+}(v)$ curves, corresponding to the formation of N_2^+ ions by ion collisions, can be explained by taking into account the fact that these ions are produced not only as a result of the ionization processes (process II), but also as a result of charge exchange (process I).

It is possible to apply to the charge exchange process the Massey adiabatic criterion, which determines the value of the velocity v_{max} at which the maximum of the effective cross section of a certain charge exchange process is obtained, by the condition

$$v_{max} = a\,|\Delta E|\,/\,h, \tag{1}$$

where a is the distance over which the interaction forces act between the colliding particles, ΔE is the resonance defect of the process, and h is Planck's constant. In the case of single-electron charge-exchange processes the value of a is 7–8 Å [12].

Table I lists the values of v_{max} calculated by means of formula (1) at a = 8 Å. In the calculation we took into account the fact that the N_2^+ ion can be produced as a result of charge exchange both in the ground state $X^2\Sigma_g^+$ and in the excited electron states $A^2\Pi_u$, $B^2\Sigma_u^+$, and $C^2\Sigma_u^+$.

Comparing the values of v_{max}, given in Table I, with the shape of the $\sigma_{N_2^+}(v)$ curves in Fig. 2, we can explain in general outline the shape of these curves. Thus, for example, in the case of the H^+-N_2 pair, the growth of the cross section $\sigma_{N_2^+}$ with decreasing proton velocity is due to the fact that maxima connected with charge-exchange processes are located in the velocity region 3.8×10^7–1×10^8 cm/sec.

There are no singularities on the $\sigma_{N_2^+}(v)$ curve for the He^+-N_2 pair. Apparently the charge-exchange processes in which N_2^+ ions are produced in the excited states $B^2\Sigma_u^+$ and $C^2\Sigma_u$ have a low probability, and the maxima of the cross sections of the charge exchange processes in the ground state $X^2\Sigma_g^+$ and in the first excited state $A^2\Pi_u$ are located outside the velocity interval investigated in the present paper.

The structure on the $\sigma_{N_2^+}(v)$ curve for the Ne^+-N_2 pair is apparently connected with charge exchange processes in which the N_2^+ ion is produced in excited electron states.

Finally, in the case of the Ar^+-N_2 pair, the rise of the $\sigma_{N_2^+}(v)$ curve in the direction of low velocities is due to charge exchange with production of the N_2^+ ion in the ground state, and the rise of this curve in the direction of high velocities is due to charge exchange with formation of the N_2^+ ion in excited electronic states[2)].

In collisions between ions with N_2 molecules, the N^+ ions result from the processes

$$I^+ + N_2 \to I^0 + (N^+_2)^* \to I^0 + N^+ + N \quad \text{dissociative charge exchange,} \tag{IV}$$

$$I^+ + N_2 \to I^+ + (N^+_2)^* + e \to I^+ + N^+ + N + e \quad \text{dissociative ionization.} \tag{V}$$

In the case of atomic impact, the N^+ ions are produced only as a result of dissociative ionization

$$I^0 + N_2 \to I^0 + (N^+_2)^* + e \to I^0 + N^+ + N + e. \tag{VI}$$

As seen from Fig. 3, the $\sigma_{N^+}(v)$ curves corresponding to the formation of N^+ ions in collisions between He, Ne, or Ar atoms with N_2 molecules have a singularity which is not observed in the case of production of N_2^+ ions by collision with the same atoms (see the curves of Fig. 2). This singularity consists in the fact that in the region of velocities $v < 1.5\times10^7$ cm/sec for Ar, $v < 2.2\times10^7$ cm/sec for Ne, and $v < 5\times10^7$ cm/sec for He, an increase in the cross section σ_{N^+} is observed with decreasing velocity of the atom. Usually for all the ionization processes that are endothermal, one observes in this velocity region a decrease of the cross section of

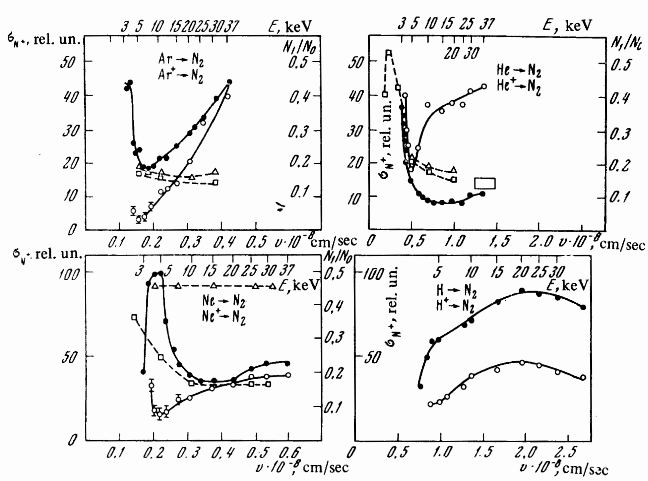

FIG. 3. Solid lines—plots of the effective cross sections for the production of N^+ ions against the velocity of the ions and atoms of hydrogen, helium, neon, and argon. ● – positive ions, ○ – neutral atoms. Dashed lines—plots of the ratio N_1/N_0 against the velocity of the ions and atoms of helium, neon, and argon. □ – positive ions, △ – neutral atoms.

[2)] The rise of the $\sigma_{N_2^+}(v)$ curve on the high-velocity side is partially due to the fact that the N_2^+ ions are produced also as a result of an ionization process, whose effective cross section in the investigated velocity region increases with increasing velocity, as can be seen from the $\sigma_{N_2^+}(v)$ curve for the Ar^0-N_2 pair.

the process with decreasing velocity, as is the case, for example, for the process of production of N_2^+ ions by atomic collision.

This raises the question of how to interpret the rising branch of the $\sigma_{N^+}(v)$ curve in processes of dissociative ionization of the N_2 molecule by atomic collision. We think that the only way to explain the increase of the cross section σ_{N^+} in the region of low velocities is to assume that in this region the production of the N^+ ions occurs principally as a result of excitation of the vibrational motion of the nuclei of the N_2^+ ion produced in the ionization process.

If the foregoing assumption is true, then in the case of dissociative ionization of the N_2 molecule by ionic collision there should be observed, at low velocities, the production of N^+ ions as a result of excitation of the vibrational motion of the nuclei of the N_2^+ ion. An examination of the $\sigma_{N^+}(v)$ curves for the ion-molecule pair shows that in this case in the region of low velocities there is observed on the $\sigma_{N^+}(v)$ curve either a rising branch (He^+ or Ar^+ ions), or else a maximum (Ne^+ ion). Only for the H^+-N_2 pair is a decrease of σ_{N^+} observed with decreasing velocity.

In a discussion of the form of the $\sigma_{N^+}(v)$ curves in the case of ion collisions it is necessary to bear in mind that the N^+ ions are produced not only in the dissociative ionization processes (IV), but also in dissociative charge exchange processes (V). As a result, maxima connected with the charge exchange processes should appear on the $\sigma_{N^+}(v)$ curves. The positions of these maxima can be determined by using the Massey adiabatic criterion (formula (1)). It is appropriate to assume here, just as in the discussion of the shape of the $\sigma_{N_2^+}(v)$ curves, that a is equal to 8 Å. Table II lists the values of v_{max} calculated from formula (1).

As seen from the data of Table II, the rising branch of the $\sigma_{N^+}(v)$ curve for the He^+-N_2 pair in the velocity region $v < 7 \times 10^7$ cm/sec can be connected not only with the process of vibrational excitation of the N_2^+ ion, but also with the presence of a maximum in the charge-exchange process at a velocity $v_{max} = 5.4 \times 10^6$ cm/sec. The maximum on the $\sigma_{N^+}(v)$ curve for the Ne^+ ion at $v \approx 2 \times 10^7$ cm/sec is apparently connected with the dissociation of the ion as a result of excitation of the vibrational motion of its nuclei, inasmuch as the maxima connected with the processes of dissociative charge exchange are located at larger collision velocities (see Table II). Finally, the growing branch on the $\sigma_{N^+}(v)$ curve for the Ar^+ ion, in the region $v \leq 2 \times 10^7$ cm/sec, can be attributed only to vibrational excitation of the N_2^+ ion, inasmuch as the maximum connected with the charge exchange is shifted far away in the direction of larger velocities.

Thus, in the case of production of N^+ ions by ion collisions, the process whereby these ions are produced by vibrational excitation of the N_2^+ ion determines the behavior of several $\sigma_{N^+}(v)$ curves in the region of small v.

The assumption that the predominant contribution is made to the dissociation cross section of the N_2^+ ion in the region of small velocities by processes wherein higher vibrational states of this ion are excited implies the conclusion that the corresponding vibrational levels have an anomalously high population, as can occur only if the Franck-Condon principle is violated. The fact that the population of the vibrational levels of the N_2^+ ion in the processes investigated in the present paper proceeds with violation of the Franck-Condon principle in the low-velocity region follows from the data on the population of the first vibrational level of the $B^2\Sigma_u^+$ of the N_2^+ ion. All the plots of N_1/N_0 against v, shown in Fig. 3, lie above the level $N_1/N_0 = 0.1$ corresponding to population of the level under consideration in accordance with the Franck-Condon principle. In addition, for all the pairs of colliding particles, with the exception of the Ne^0-N_2 pair, an increase of the relative population of the first vibrational level with decreasing vector is observed in the investigated velocity region. The same tendency is observed also in $\sigma_{N^+}(v)$.

It was emphasized in [1] that excitation of the first vibrational level of the $B^2\Sigma_u^+$ state of the N_2^+ ion has a resonant character (see the maximum on the $N_1/N_0 = f(v)$ curve for the He^+-N_2) pair, i.e., the maximum of N_1/N_0 should occur under the condition t = T (t—collision time, T—period of the vibrations of the N_2^+ ion). As seen from Fig. 3, a similar resonant character is possessed also by the excitation of the higher vibrational levels, inasmuch as the $\sigma_{N^+}(v)$ curves have branches that increase towards lower velocities, and in one case (the Ne^+ ion) a maximum is observed. Since the period of the oscillations decreases with increasing energy of the vibrational motion, the maxima of the $\sigma_{N^+}(v)$ curves should be shifted towards larger velocities relative to the maximum of the $N_1/N_0 = f(v)$ curve. This is clearly seen for the Ne^+-N_2 pair, and similar tendencies are observed also for all the remaining pairs with the exception of Ne^0-N_2.

Thus, the results of the present measurements, which were made with the aid of mass-spectrometer and spectroscopic techniques, lead to the conclusion that at sufficiently slow collisions of the ions and atoms with the N_2 molecules there are produced N_2^+ ions with anomalously high population of both the high-lying and low-lying vibrational levels. This effect of vibrational excitation of the N_2^+ ion during the course of its formation has two consequences: 1) formation of N^+ ions as a

Table II

State $N^+ + N$	Appearance potential, eV	H^+		He^+		Ne^+		Ar^+	
		$\lvert\Delta E\rvert$, eV	v_{max}, cm/sec	$\lvert\Delta E\rvert$, eV	v_{max}, cm/sec	$\lvert\Delta E\rvert$, eV	v_{max}, cm/sec	$\lvert\Delta E\rvert$, eV	v_{max}, cm/sec
$N(^4S^0) + N^+(^3P)$	24.3	10.7	$2.08 \cdot 10^8$	0,28	$5.4 \cdot 10^6$	2.74	$5.3 \cdot 10^7$	8.54	$1.65 \cdot 10^8$
$N(^2D^0) + N^+(^3P)$	26.7	13.1	$2.52 \cdot 10^8$	2.4	$4.65 \cdot 10^7$	5.14	$9.9 \cdot 10^7$	10,95	$2.12 \cdot 10^8$
$N(^4S^0) + N^+(SP^{35}S^0)$	28.0	14.4	$2.78 \cdot 10^8$	3.7	$7.15 \cdot 10^7$	6.44	$1.24 \cdot 10^8$	12.24	$2.38 \cdot 10^8$

result of dissociation of the N_2^+ ion and 2) redistribution of the intensities of the bands in the (1 ns N_2^+) spectrum compared with the corresponding distribution at larger relative velocities of the colliding particles.

It is of interest to investigate further the effect of vibrational excitation of the molecules by the field of the incoming particle. To this end it is necessary, first of all, to perform experiments at collision velocities that are lower than in the present investigation[3)]. It is desirable to study the formation of the fragment ions of other molecules, particularly H_2, since the H_2^+ ion has excited electronic states of only the repulsive type, and consequently H^+ ions will be produced upon vibrational excitation of the H_2^+ ion only in the electronic ground state.

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[3)] Thus, for example, in collisions between protons or hydrogen atoms with N_2 molecules the effect of excitation of the higher vibrational levels is not observed at all (see the $\sigma_{N^+}(v)$ curves of Fig.3), because the velocities of the incoming particles were not low enough.

Translated by J. G. Adashko
235