Vibrational excitation of N_2^+ ions in collisions of protons and electrons with N_2 molecules

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We measured the excitation cross sections of the bands of the first negative system of the N_2^+ ion (transitions $B^2\Sigma_u^+ - X^2\Sigma_g^+$) in excitation of N_2 molecules by protons of energy 0.2–10 keV and electrons of energy 0.8 keV. The measurements have shown that the population of the vibrational levels with $v' = 1, 2$ of the state $B^2\Sigma_u^+$ increases with decreasing energy relative to the level with $v' = 0$ of this state. Anomalous population of the highly excited levels $v' = 2, 3$ of the state $B^2\Sigma_u^+$ was observed when N_2 molecules were excited by fast ($v \gtrsim 10^8$ cm/sec) protons. Even at a proton energy 10 keV, at which according to earlier investigations, the experimental results should agree with a calculation that follows from the Franck-Condon theory, the $v' = 2$ level and the $v' = 3$ level populations are higher than the calculated values by 5 and 150–170 times, respectively. It is also observed that the relative populations of the vibrational levels of the $B^2\Sigma_u^+$ state, upon excitation by 10 keV protons and by electrons, agree within the limits of the experimental error. The observed singularities are explained within the framework of an introduced model representation introduced that takes into account the quasimolecular behavior of the system of particles in the course of the collision process as well as the multichannel character of the processes of the excitation of the states. At low proton energies, $E_p < 5$ keV, the excess population of the vibrational levels of the final electronic state is attributed to transition via quasimolecular intermediate states of the system of particles. At high proton energies, $E_p \gtrsim 10$ keV, the excess level population is attributed to virtual transitions, taken into account in second-order perturbation theory, through the intermediate state of the system of particles when the molecules are excited by electrons (virtual transitions through intermediate states of an isolated molecule).

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1. INTRODUCTION

Collisions of electrons and protons with N_2 molecules, which lead to formation of N_2^+ ions in excited states, were investigated in a number of studies (see, e. g., Refs. 1–7). Most attention was paid in these studies to excitations of the bands of the first negative system (NS) of the N_2^+ ion (the transition $B^2\Sigma_u^+ - X^2\Sigma_g^+$). The interest in this system is due to the fact that measurements of the absolute cross sections for the excitation of the bands of the system, and the determination of the relative probabilities of the population of the vibrational levels of the electronic state $B^2\Sigma_u^+$, permit a deeper study of elementary processes in the upper layer of the atmosphere, and particularly an explanation of the mechanism of auroras.

The available experimental data on the cross sections for band excitation by protons are not systematic or complete. At low proton energies, only the cross section for the excitation of the (0,0) λ3914 Å band was measured. The lowest energy at which the measurements were made was 1.0–1.5 keV.[8-11] One of the purposes of the present paper is to obtain the cross sections for the excitation of the bands of the first NS at lower proton energies.

Besides being of practical importance, measurements of the excitation cross section yield data needed for the development of a theory of ion-molecular collisions. A pressing problem is the experimental investigation of the applicability of the Franck–Condon (FC) principle (theory) to processes of population of vibrational levels in transitions between electronic states. It was shown in a number of studies that the population of the vibrational levels of the state $B^2\Sigma_u^+$ of the N_2^+ ions when an N_2 molecule is excited by protons of energy $E_p \lesssim 5$ keV (Refs. 10, 12, 13) and by electrons of energy $E_e \lesssim 100$ eV (Ref. 5) differs from the population that follows from the FC model, and with decreasing collision velocity the population of the excited vibrational levels increases relative to the ground level ($v' = 0$).

For a long time, practically up to the publication of Birely's paper,[10] the deviation of the population of the vibrational levels from the population that follows from the FC model was explained within the framework of the concept of long-range polarization interaction, and was correspondingly connected with the distortion of the vibrational wave function of the molecule by the field of the incident ion.[12-14] Measurements of the level populations following excitation of molecules by atoms have shown[10] that this model representation does not agree with the experimental data.

At the present time there is no unified point of view concerning the mechanism of the vibrational excitation and concerning the causes of the deviation of the level populations from the FC model in slow collisions. To a certain degree this is connected with contradictions in the presently available experimental data. Thus, the relative population of the vibrational levels depends according to the data of Fogel' *et al.*[15] on the kind of incident particles, while according to Moore and Doering[13] it is determined only by the charge of the particles and is practically independent of electronic structure.

To obtain additional information of the mechanisms of the excitation of the vibrational levels and to develop on this basis model representations of the vibrational excitation, we have measured the excitation cross sections of the beams of the first NS of the N_2^+ following

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excitation of N_2 molecules by protons in the energy range 0.2–10 keV and by electrons of energy 0.8 keV.

2. EXPERIMENTAL SETUP AND MEASUREMENT PROCEDURE

In the experimental setup, an ion beam from a high-frequency source was focused and accelerated by an ion-optical system, mass-analyzed by a magnetic mass spectrometer, passed through collimating slits, additionally focused by an electrostatic quadrupole doublet, and fed to the collision chamber. The emission produced in the collision chamber as a result of the collisions of the ions with the gas molecules focused by a single lens on the input of an optical spectrometer. The light was gathered at an angle 90° to the direction of the ion beam.

The emission spectrum was investigated with an ISP-51 spectrometer. The light was recorded photoelectrically with a cooled FÉU-79 photomultiplier operating in the current regime.

The errors in the measurements of the energy dependences of the spectral-line emission cross sections are connected, as shown by an analysis of the experimental studies, principally with errors in the measurement of the beam current in the region where the light is gathered in the collision chamber. In the present study we used a current-receiver design that made it possible to decrease the current-measurement error to several percent. The current receiver was a deep hollow cylinder with two openings. The entrance opening (6 × 8 mm) was in the immediate vicinity of the entrance slit of the collision chamber (4 × 5 mm). The second and lateral opening (10 mm diameter) was located 10 mm from the entrance in the direction of beam propagation and was used to extract the light from the cylinder. The recorded current was determined by the ions that entered the cylinder and was independent of the subsequent change of their charge state. The attenuation of the beam on the path from the entrance region to the light-gathering region did not exceed 3%.

The absolute calibration of the sensitivity of the installation was carried out by comparing the cross section for the excitation of the band (0,0), λ3914 Å with the area of the corresponding structure in the initial spectrum. It was assumed that at a proton energy 10 keV the cross section for the excitation of the (0,0) band is 8×10^{-17} cm^2. This value agrees with the data of Refs. 10 and 16 and corresponds approximately to the average value of the results of the measurements in Refs. 3 and 9. The systematic error due to the indicated calibration procedure is estimated by us at 10%.

The relative spectral sensitivity of the installation was measured with a standard SI-8 tungsten lamp. The relative error in the determination of the spectral sensitivity in the wavelength region 4200–7200 Å does not exceed 5%. It increases somewhat when the wavelength is decreased from 4200 to 3850 Å (to 10%).

As follows from the tables of Refs. 17 and 18, the wavelengths of some of the investigated molecular bands and of a number of lines of the N^+ ions and N atoms overlap. The spectral resolution of the spectrometer (2–10 Å in the wavelength region 3900–4200 Å) was not always sufficient to resolve them. In such cases the intensity of the atomic line and accordingly the ensuing error in the measurement of the bands were estimated by comparison with the intensities of the lines emitted in transitions from the same upper levels of the ions and atoms as of the lines that introduce the errors. The resultant error of the output measurements of the cross sections is estimated by us (depending on the collision energy) at 15–25%.

All the measurements were made at an ion current in the collision chamber 1–10 μA and at a pressure not exceeding $(5-9) \cdot 10^{-4}$ Torr, thus ensuring the production of single collisions.

3. MEASUREMENT RESULTS

The results of the measurements of the cross sections for the excitation of the bands of the first NS of the N_2^+ ion are given in Figs. 1 and 2 and in the Table. The band (0,0), λ3914 Å can be used, as proposed by Hoffman, Lockwood, and Miller,[16] for absolute calibration of the sensitivity of the experimental setups. Since this band is furthermore included among the intense bands in the aurora spectra, the interest in the measurement of the cross section for its excitation is understandable.

The data of Refs. 8–10 are shown in Fig. 1 in a form normalized to the measurement results of De Heer and Aarts,[9] as was done by Birely in Ref. 10. At ion energies ≥1 keV, at which the comparison is possible, our data on the form of the dependence agree well with the most accurate, in our opinion, data of Refs. 9 and 11, and differ from them by 2–7% in the energy interval 2–8 keV. The difference may be due to failure to take into account in Ref. 9 the beam attenuation as a result of the charge exchange process when the ions travel from the light-gathering region to the region where they

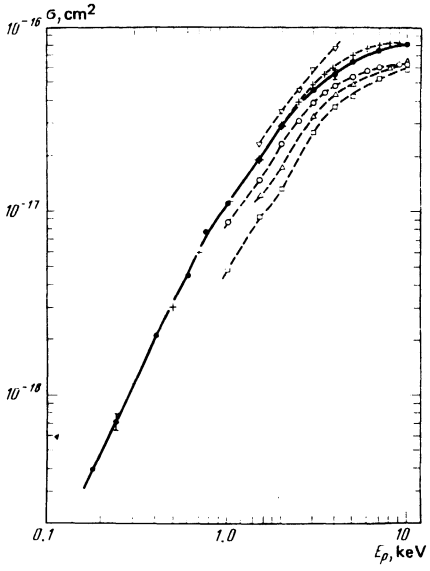

FIG. 1. Dependence of the cross section for the emission of the band (0, 0) = 3914 Å of the first negative system of the N_2^+ ion on the proton energy: ●—our data, +—from Ref. 11, ○—,[9] Δ—,[10] □—,[8] ▽—[2].

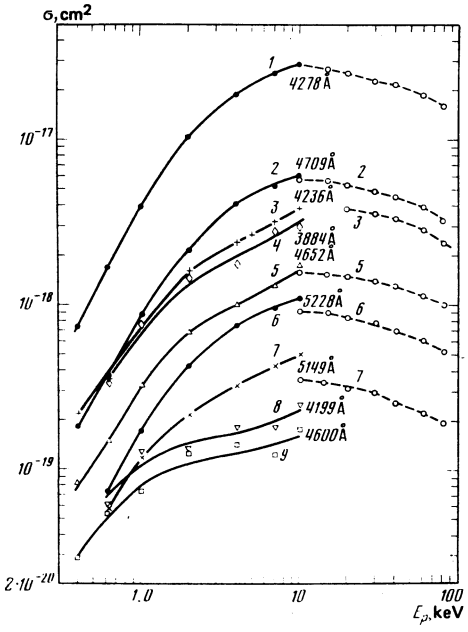

FIG. 2. Dependence of the emission cross sections of the bands of the first NS of the N_2^+ ion on the proton energy: 1—$\sigma[(0.1)$, λ4278 Å], 2—$\sigma[(0.2)$, λ4709 Å], 3—$\sigma[(1.2)$, λ4236 Å], 4—$\sigma[(1.1)$, λ3884 Å], 5—$\sigma[(1.3)$, λ4652 Å], 6—$\sigma[(0.3)$, λ5228 Å], 7—$\sigma[(1.4)$, λ5149 Å], 8—$\sigma[(2.3)$, λ4199 Å], 9—$\sigma[(2.4)$, λ4600 Å]; ○—data of Ref. 3.

TABLE I.

v''	$\sigma(v',v'')/\sigma(0,1)$			
	$v'=0$	1	2	3
0	λ3914 Å 2.77 * 2.88 ** 2.9±0.3 *** 3.1 **** 2.8±0.3 *****			
1	λ4278 1.00 1.00 1.00 1.00 1.00	λ3884 0.106 0.113 0.12±0.01 0.16 0.10±0.01		
2	λ4709 0.222 0.203 0.21±0.01 0.21 0.22±0.01	λ4236 0.133 0.128 0.14±0.01 0.15 0.14±0.01		
3	λ5228 $3.90\cdot10^{-2}$ $3.9\cdot10^{-2}$ $(3.9\pm0.2)\cdot10^{-2}$ $3.3\cdot10^{-2}$ $(4.0\pm0.2)\cdot10^{-2}$	λ4652 $5.27\cdot10^{-2}$ $5.0\cdot10^{-2}$ $(5.4\pm1.0)\cdot10^{-2}$ $6.4\cdot10^{-2}$ $(6.0\pm1.0)\cdot10^{-2}$	λ4199 $1.71\cdot10^{-3}$ $(8.3\pm1.4)\cdot10^{-3}$ $(9.0\pm3.0)\cdot10^{-3}$ – $(8.4\pm2.0)\cdot10^{-3}$	
4	λ5865 $5.70\cdot10^{-3}$ – – – $(6.5\pm1.0)\cdot10^{-3}$	λ5149 $1.35\cdot10^{-2}$ $1.2\cdot10^{-2}$ $(1.5\pm0.3)\cdot10^{-2}$ $1.3\cdot10^{-2}$ $(1.7\pm0.3)\cdot10^{-2}$	λ4600 $1.09\cdot10^{-3}$ $(4.7\pm0.9)\cdot10^{-3}$ $(5.0\pm2)\cdot10^{-3}$ – $(6.0\pm2.0)\cdot10^{-3}$	
5			λ5077 $3.83\cdot10^{-4}$ – – – $(1.5\pm0.5)\cdot10^{-3}$	λ4554 $1.73\cdot10^{-5}$ $(3.0\pm0.6)\cdot10^{-3}$ – – $(2.5\pm1.0)\cdot10^{-3}$

*Calculation.[28]
**Experiment.[6,28] Excitation by electrons.
***Our data, excitation by electrons.
****Experiment.[3] Excitation by protons.
*****Our data, excitation by protons.

are registered. An indication of this causes the fact that the data of Refs. 9 and 11 are too high, and precisely in the energy region where the charge-exchange cross section is maximal.

We have measured also the polarization of the λ3914 Å line. The measurements have shown that the polarization is small and amounts to +4% at an ion energy 0.5–1.0 keV and does not exceed ±1% at 7 keV. These values agree with measurements at higher energies,[16,19] according to which the polarization is <2% at an ion energy 10 keV.

Figure 2 shows the cross sections for the excitation of the remaining lines of the first NS of the bands measured by us. A comparison of the results of our measurements with those of Philpot and Hughes,[3] performed at proton energies $E_p > 10$ keV, shows that the dependences of the cross sections complement each other, being in agreement in form, and for the intense line also in magnitude.

The ratio $\sigma(v',v'')/\sigma(0,1)$ of the cross sections of the emission of the bands of the first NS of the N_2^+ ion upon excitation of the molecule by electrons of energy $E_e = 0.9$ keV are given in the Table. To determine the relative probabilities of the excitation of the various bands and for convenience of their comparison, the Table gives also data obtained by others on the excitation of bands by electrons of energy 1.5 keV,[6,20] our data on the excitation of the bands by protons of energy 10 keV, the data of Ref. 3 on the excitation by protons of energy 20 keV, and the results of theoretical calculations of the ratios of the cross sections for the band emission.[20]

Figures 3 and 4 show the plots of the ratios of the band-emission cross sections against the proton energy in transitions from the vibrational levels $v' = 1$ and $v' = 2$,

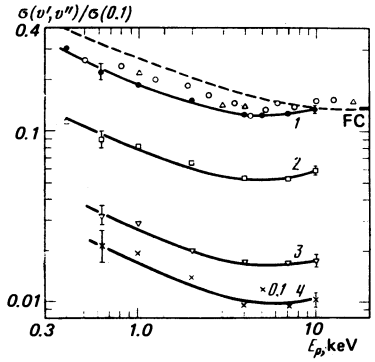

FIG. 3. Dependence of the ratios of the cross sections of the emission of the bands of the first NS of the N_2^+ ion on the proton energy for transitions from the level $v' = 1$:

$$1 - \frac{\sigma((1,2),\lambda\,4236\text{ Å})}{\sigma((0,1),\lambda\,4278\text{ Å})},$$

$$2 - \frac{\sigma((1,3),\lambda\,4652\text{ Å})}{\sigma((0,1),\lambda\,4278\text{ Å})},$$

$$3 - \frac{\sigma((1,4),\lambda\,5149\text{ Å})}{\sigma((0,1),\lambda\,4278\text{ Å})},$$

$$4 - \frac{\sigma((1,1),\lambda\,3884\text{ Å})}{\sigma((0,1),\lambda\,4278\text{ Å})};$$

The points ○ and △ show the data of Ref. 10, the dashed curve shows the data of Ref. 13 for the ratio $\sigma(1.2)/\sigma(0.1)$; FC—calculation[20] of the ratio $\sigma(1.2)/\sigma(0.1)$.

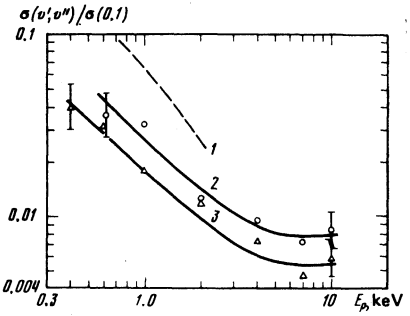

FIG. 4. Dependence of the ratios of the cross sections of the emission of the bands of the first NS of the N_2^+ ion on the proton energy for transitions from the level $v'=2$; curve 1—the ratio σ[(2.3), λ4200 Å]/σ[(0.1), λ4278 Å] according to Ref. 13, curves 2, 3—σ[(2.3), λ4200 Å]/σ[(0.1), 4278 Å] and σ[2.4), λ4600 Å]/σ[(0.1), λ4278 Å]. The calculated values of these ratios are respectively 1.71×10^{-3} and 1.09×10^{-3} (see Ref. 20).

respectively. The data are given in a form normalized to the emission cross section of the (0,1) band, for the purpose of demonstrating the effect of the increase of the probability of population of the excited vibrational levels in comparison with the ground level when the collision energy is decreased.

4. DISCUSSION OF RESULTS AND MODEL REPRESENTATIONS

1. A comparison of the obtained experimental data with the results of a calculation within the framework of the FC model (Figs. 3 and 4, Table) shows that in the case of excitation by protons the experimental ratios of the intensities of the spectral lines differ from the calculated values in practically the entire investigated collision-energy region, particularly for transitions from highly excited vibrational levels.

In the calculations of the probabilities of both the population of the vibrational levels and of their decay, the first born approximation[21] is used. In this approximation, when the assumption that the electron and nuclear motions are independent and that the moments $G^2(\bar{r})$ of the electronic transitions have a weak dependence on the internuclear distance r, the probabilities of the corresponding process are proportional to the product of the FC factors $q_{v'v''}$ by the moments $G^2(\bar{r})$. When one speaks of the deviation of the measured populations of the vibrational level from calculations that follow from the FC principle, or even of "violation" of this principle, it is precisely calculations in accordance with the indicated scheme that are meant.

The discrepancy between the experimental data and the the calculation, which reaches a factor 150–170 in transitions from the level $v'=3$ of the $B^2\Sigma_u^+$ state (see the Table), raises the question of the reliability of primarily the calculated data. We shall show that this discrepancy cannot be attributed to errors in the calculations of the decay probabilities of the excited states, and consequently it is due to their anomalous population. To this end, we discuss the reliability with which the corresponding FC factors and the moments of the electronic transitions are determined for the decay process.

In the concrete case of the first NS of bands, the FC factors were calculated both with Morse potentials,[22] and with Rydberg-Klein-Rees (RKR) potentials.[20] The difference between the results of these calculations is small, so that we are assured that the errors in the calculated FC factors does not lead to the indicated discrepancies. It follows from our measurements that there are no grounds likewise for assuming that the dependence of G^2 on the internuclear distance is substantially stronger than would follow, for example, from the results of Brown and Fandshoff.[23] It is thus seen from the Table that the relative values of the emission cross sections of the bands of the progression with $v'=0$, which are equal to the corresponding relative decay probabilities, agree well with the calculated cross sections. We thus arrive at the conclusion that the discussed deviation is connected with processes of excitation (population) of vibrational levels. This conclusion is confirmed also by the experimentally observed fact that the intensities of the bands (2,3) and (2,4), which have a common upper level, differ from the calculated values by the same number of times.

When attributing the considered deviations primarily to the inadequacy of the theory, we started from the premise that the experimental results are reliable. Two circumstances, besides control experiments, point in our opinion to the reliability of the observed anomalous population of the highly excited states in the case of excitation by protons: 1) the anomalous population observed in excitation by fast ($v\gtrsim10^8$ cm/sec) protons is observed also in the case of excitation by electrons, 2) the deviation from the calculations observed for all bands whose upper levels are highly excited ($v'=2,3$). It should be noted that the first to point out the anomalous population of the highly excited vibration levels of the state $B^2\Sigma_u^+$ were Pendleton and O'Neil[20] in excitation of N_2 molecules by fast ($E=1.5$ keV) electrons. As seen from the Table, our data on electron impact agree with their results.

2. Inasmuch as the deviations of the relative intensities of the spectral lines in electron-vibrational transitions from the calculated values are connected with inaccuracies of the theoretical analyses of the processes of population of the vibrational levels in the collisions, we turn to consider the results and call attention to singularities connected with level-population processes.

a) The populations of the excited vibrational levels of the state $N_2^+(B^2\Sigma_u^+)$ are as a rule higher than the calculated values and increase with decreasing collision energy. Our measurements of the population of the level with $v'=1$ agree with the data of Birely[10] and point to a definite overestimate in the results of Moore and Doering[13] (Fig. 3). A comparison of the population of the $v'=2$ level with the data of Ref. 13 (Fig. 4) shows that in this case, too, the results in Ref. 13 are too high, and quite appreciably. The measurements of the population of the $v'=3$ level were made for the first time ever.

b) The plots of the populations of the levels with $v'=1$, 2 relative to the $v'=0$ level against energy reveal a

minimum (Figs. 3 and 4). An important circumstance is that in the region of the minimum the relative populations of the levels turn out to be lower than the calculated values.

c) Likewise unexpected is the observation of the anomalously large population of the highly excited states ($v'=2,3$; Fig. 4; Table). Even at the proton energy 10 keV ($v \sim 1.4 \cdot 10^8$ cm/sec), at which one should expect according to Moore and Doering[13] agreement between experiment and calculation, the population of the $v'=2$ level exceeds the calculated value by approximately five times, and that of the $v'=3$ level by approximately 150–170 times.

d) With increasing vibrational quantum number v', the deviation of the populations of the levels from the calculation increases. The slope of the plot of the deviation against energy also increases (Figs. 3 and 4). The plot of the population of the $v'=2$ level shows in the energy region 1–3 keV a singularity which is missing from the plots of the populations of the levels with $v'=0$ and 1.

e) The deviations from the calculated values of the relative populations of the vibrational levels, practically coincide for states excited by 10-keV protons and by electrons (see the Table).

3. Proceeding now to a discussion of the results, we turn first to the electron-vibrational transitions in ion-molecular collisions; the transitions following electron impact will be considered later.

In the latest studies the mechanism of additional population of the vibrational levels in ion-molecule collisions is attributed to transfer of momenta to the molecule atoms by the incident particle.[24-28] A model-based analysis of this mechanism at collision energies much higher than thermal is presented in Ref. 29. Within the framework of this model, no quasimolecular analysis of the process of vibrational excitation is in fact carried out. The relative variation of the potential-energy surface of the system with changing internuclear distance, and the nonadiabatic interactions of the initial and final states of the system with other states, are not considered. It is assumed that the population of the vibrational levels in the case of an electronic transition in the region of the pseudointersection of the potential-energy surfaces proceeds in accord with the FC principle and is determined by the factors for the isolated molecule. It is assumed that the additional population of the vibrational levels takes place only in the process of the adiabatic development of the electronic state of the system.

In the present paper we wish to call attention to the possible existence of other mechanisms of vibrational excitation, determined by the quasimolecular character of the motion in the system of the colliding particles and associated with the nonadiabatic transitions between the potential surfaces.

First, inasmuch as in the regions of the pseudo-intersection of the surfaces the electronic transitions take place between quasimolecular states that differ from states of the isolated molecule, the relative population of the vibrational levels in these transitions will differ from the population determined by the FC factors for the isolated molecule.

In the case when the electronic transitions take place between nonintersecting potential surfaces that interact nonadiabatically (the Rosen-Zener-Demkov mechanism[30,31]) there appears one other possibility of additionally populating the vibrational levels of the final state, connected with the exchange interaction of the colliding particles, as a result of which the population of the vibrational levels of the initial and final states changes. Since the additional population of the vibrational levels via exchange interaction can take place in interaction of the initial and final states also with other states of the system, it is obviously necessary to take into account the interactions between all the states that participate in the transitions.

Cases are also possible when the system finds itself in the final electronic state as a result of several consecutive transitions, both between nonintersecting surfaces and in the case of pseudo-intersection. In these cases, the resultant population of the final state will differ from the calculated population determined by the FC factors for a direct transition from the initial to the final state, even if no deviation from the calculated population is observed in any of the transitions.

4. Quantitative estimates of the role of the considered mechanism in the excitation of the vibrational levels are difficult. We confine ourselves therefore to a qualitative discussion and to a comparison with the experimental data. We turn first to consideration of the relative variation of the quasimolecular terms of the system $(H-N_2)^+$ (Fig. 5). It is seen from the figure that the system can reach the final state $H^0-N_2^+(B^2\Sigma_u^+)$ either as a result of direct electronic transitions from the initial state $H^+-N_2(X^1\Sigma_g^+)$ or as a result of transitions via the intermediate quasimolecular state $H^0-N_2^+(X^2\Sigma_g^+)$.

Proceeding to the analysis of the mechanism of the direct transitions and of their influence on the populations of the vibrational levels, we note that the excitation functions of the ground and excited vibration levels of the state $B^2\Sigma_u^+$ of the N_2^+ ion are different (Figs. 1 and 2). The measured energy dependence of the cross section for the excitation of the zeroth vibrational level of the state $B^2\Sigma_u^+$ was compared by us with the theoretical dependence obtained by Olson[32] for the charge-exchange cross section in the case of nonintersecting terms:

$$\sigma = {}^1/_2 \pi R_c^2 \sigma^*, \qquad (1)$$

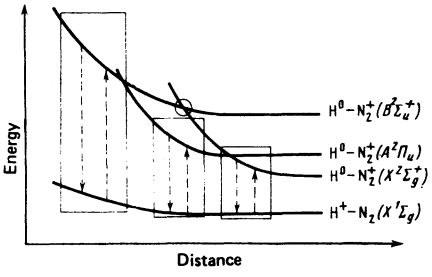

FIG. 5.

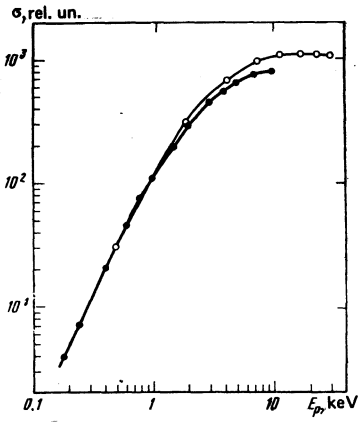

FIG. 6. Experimental (●) and calculated (○) dependences of the excitation cross sections of the state $B^2\Sigma_u^+(v'=0)$ of the N_2^+ ion on the proton energy.

where σ^* is a tabulated[32] function of the parameter $\delta^{-1} = \hbar\lambda v_0/\pi H_{12}(R_c)$, $H_{12}(R_c)$ is the off-diagonal matrix element of the exchange interaction in the region of the non-adiabatic transitions R_c, v_0 is the collision velocity and λ is a parameter determined by the binding energies of the electron in the atom and in the molecule. In the derivation of expression (1) for the transition probability we used Demkov's formula.[31] Within the limits of the applicability of (1), the energy dependence of the cross section of the process is determined completely by the function $\sigma^*(\delta^{-1})$. After determining the parameter λ from the relation[33] $\lambda = \frac{1}{2}(\sqrt{2I_A} + \sqrt{2I_M})$ (where I_A and I_M are the energies of the ionization of the atom and of the ionization with excitation of the molecule), we obtain, by selecting the scale parameter R_c, an energy dependence that agrees in the region of low collision energies with the experimental dependence (Fig. 6). Despite the discrepancy between the calculation and the experiment in the region of the maximum of the cross section, due to the imperfection of the theory in this energy region, the behavior of the cross section is on the whole correctly described by expression (1). This allows us to conclude that the mechanisms of populating the zeroth vibrational level of the $B^2\Sigma_u^+$ state in slow collisions is determined by the non-adiabatic transition between the non-intersecting potential surfaces.

More complicated is the mechanism of population of the excited vibrational levels of the state $B^2\Sigma_u^+$. In this case an important role can be played by transitions via the intermediate quasimolecular state, as a result of exchange in direction, into the intermediate state $H^0 - N_2^+(X^2\Sigma_g^+)$ and then, owing to pseudo-intersection, to the final state. The assumption that this mechanism makes a contribution is based on the fact that, as follows from Refs. 21 and 22, the products of the FC factors of the transitions from the initial level to the levels of the intermediate electronic state $H^0 - N_2^+(X^2\Sigma_g^+)$ and of the transitions from these levels to the excited levels of the final state are larger than those of the corresponding FC factors of the direct transitions. The probability of the electronic transitions to the state $H^0 - N_2^+(X^2\Sigma_g^+)$ is also large, as follows from the fact that the transitions to this state determine the cross section of the charge-exchange process. If we subtract from the total charge-exchange cross section,[2,34,35] which amounts to $\sim 10^{-15}$ cm^2 in the 1–10 keV region, the contributions of the cross sections for the population of the state $H^0 - N_2^+(B^2\Sigma_u^+)$ and of the state $H^0 - N_2^+(A^2\Pi_u)$, which according to our special measurements of the intensities of the bands of the Meinel system [the transitions $N_2^+(A^2\Pi_u) - N_2^+(X^2\Sigma_g^+)$] has a maximum in the region 4–6 keV, then we find that the state $H^0 - N_2^+(X^2\Sigma_g^+)$ is populated with the maximum probability at proton energies 1–3 keV. The position of this maximum coincides with the position of the singularity observed in the excitation function of the vibration level with $v' = 2$ of the state $B^2\Sigma_u^+$ (Fig. 2). This agreement can be regarded as a confirmation of the role of transitions via the intermediate quasimolecular state in the population of excited vibrational levels. The presence of a singularity on the excitation curve of the level with $v' = 2$, and its absence from the excitation curve of the levels with $v' = 0$, 1 is explained by the fact that the contribution of the transitions via an intermediate quasimolecular state in the population of the levels is significant predominantly in the cases when the direct transitions are unlikely because of the smallness of the FC factors.

For the confirmation of the role of multichannel mechanism in the population of the vibration levels, an important factor is the singularities observed in the present paper in the populations of the levels; these singularities cannot be explained within the framework of the momentum-transfer model. They include the fact that the deviations of the relative populations of the vibration levels from the calculated values are close in value when the $B^2\Sigma_u^+$ state of the N_2^+ ion is excited by 10-keV protons and by electrons. We note also that the relative populations of the highly excited levels ($v' = 2, 3$) upon excitation by both protons and electrons cannot be close to each other, but are anomalously high compared with calculation.

Proceeding now to discuss the effect, we recognize that in the case of charge exchange in ion-molecular collisions, the probability of transition to the final state in the region of the maximum of the cross section is large even in the approximation wherein two states interact with each other non-adiabatically (it amounts to ~0.5).[31] Within the framework of perturbation theory the large probability of the transition is due, besides that of the first order to the contribution of higher orders of the theory, and in particular (when only two states interact) to the contribution of the third and other orders. In the case of transitions from the state $H^+ - N_2$ $(X^1\Sigma_g^+)$ to the state $H^0 - N_2^+(B^2\Sigma_u^+)$ in the region of the maximum of the cross section the probability of the transitions is determined by the interaction of not two states but of a larger number of states, in view of the close values of their energy. In this case, besides the population of the final state, the exchange interaction gives rise also to a possibility of its population via virtual intermediate states.[36] Such states are $H^0 - N_2^+(X^2\Sigma_g^+)$, $H^0 - N_2^+(A^2\Pi_u)$, $H_0 - N_2^+(C^2\Sigma_u^+)$ and $H^+ - N_2(C^1\Pi_u)$. The contribution of the transitions via virtual states, taking into account in second order of perturbation theory, can be larger than the contribution of multiple transitions in exchange interaction of two states. It is precisely with

transitions via virtual intermediate states that we connect the anomalous population of the highly excited levels at high collision energies (in the region of the maximum of the cross section we have $E \sim 10$ keV). Since the probabilities of direct population of the levels of the state $B^2\Sigma_u^+$, determined by the FC factors $q_{v'',v'}$, decrease drastically with increasing vibrational quantum number v' (thus, when the level with $v'=1$ is populated we have $q_{01}=1.07\cdot10^{-1}$, while for the level with $v'=3$ we have[21] $q_{03}=2.7\cdot10^{-5}$), the deviation of the level populations from the calculated values as a result of transitions via virtual states will be larger for the more excited states.

When the molecule is excited by electrons, the anomalously high population of the highly excited states can be explained if it is assumed that, just as in the excitation by protons in the region of the maximum of the cross section, the cross section is determined by transitions via virtual states, in this case via the states $N_2^+(X^2\Sigma_g^+)$, $N_2^+(A^2\Pi_u)$, $N_2^+(C^2\Sigma_u^+)$, $N_2(C^1\Pi_u)$, and $N_2(C^3\Pi_u)$.

The proximity of the relative populations of the levels and their deviation from the calculated values when excited by electrons and protons with energy 10 keV is in this case not unexpected, since we assume in essence an identical level-population mechanism. A more detailed analysis shows that in order for the deviations to be close it is necessary that the virtual transitions determine the population of not only the highly excited states, but also the population of the "zeroth" vibrational level. In this case, if we confine ourselves to the second-order approximation of perturbation theory, the relative populations of the levels do not depend on the collision velocity, but are determined by the properties of the molecule. Obviously, when the levels are excited by protons this condition is satisfied only in the region of energies close to the energy E_m corresponding to the maximum of the cross section. Thus, the indicated agreement should not be observed in slow collisions (as is confirmed by experiment) or at energies somewhat larger than E_m, an assumption worthy of verification. With further increase of the energies of the protons and electrons, the populations of the levels will approach the calculated values that follow from the FC theory.

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