the photon momentum $\mathbf{k}_{ef}^{(e)}=\mathbf{k}$. In fact, as shown above, the value of $\mathbf{k}_{ef}^{(e)}$ has an additional numerical factor of 8/5. Clearly, this factor (~1) does not affect the qualitative estimate given in Ref. 3. On the other hand, an accurate quantitative determination of the distribution of the photon momentum between electrons and ions in a laser plasma is hardly possible because of many secondary phenomena. It is likely that the optical pressure forces exerted on particles in the stimulated inverse bremsstrahlung can be determined more easily in the case of a semiconductor plasma, in which case the current j can be measured with a high accuracy. The drag of particles in the process of stimulated inverse bremsstrahlung may also be manifested in astrophysical phenomena.

In conclusion, we should point out that in addition to any practical applications of the above results, the distribution of the photon momentum between charged particles is undoubtedly of intrinsic interest because it is related to such classical phenomena as stimulated direct and inverse bremsstrahlung of light.

[1] F. V. Bunkin, A. E. Kazakov, and M. V. Fedorov, Usp. Fiz. Nauk **107**, 559 (1972) [Sov. Phys. Usp. **15**, 416 (1973)].

[2] A. I. Akhiezer and V. B. Berestetskiĭ, Kvantovaya élektrodinamika, Fizmatgiz, M., 1959 (Quantum Electrodynamics, Interscience, New York, 1965), Chap. V, § 29.

[3] P. P. Pashinin and A. M. Prokhorov, Pis'ma Zh. Eksp. Teor. Fiz. **26**, 687 (1977) [JETP Lett. **26**, 526 (1977)].

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Nonequilibrium distribution of $N_2(C_3\Pi)$ molecules over the rotational levels in a gas discharge

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The distributions of the intensities in the rotational structure of the 2^+ bands of the N_2 system in a dc discharge and in strong-current discharge were investigated. The causes of the appearance of a "hot" group of $N_2(C\,^3\Pi_u)$ molecules with a high rotational excitation level are discussed. It is shown that this group is the result of impact de-excitation of the $N_2(E\,^3\Sigma_g^+)$ molecules. The effect of alternation of the intensities in the emission spectrum of the hot group is considered and found to be connected with the existence of selection rules for the transfer of electron excitations in collisions of heavy particles.

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1. INTRODUCTION

We have previously established[1] that under conditions of a low temperature glow-discharge plasma at reduced pressure, when the lifetime of $N_2(C^3\Pi)$ is shorter than the time between the gaskinetic collisions, the rotational-level distribution of the $N_2(C^3\Pi)$ molecules deviates from Boltzmann's law. The deviations consist in the fact that a so-called "hot" group of molecules is produced, with a high (~2100 K) population temperature. If we subtract the hot part from the total distribution, then the remaining "cold" group has a Boltzmann distribution described by the temperature of the translational motion of the neutral gas. This must be taken into account when attempts are made to determine the gas temperature by measuring the spectrum of the 2^+ system of N_2. The errors that can appear in the determined temperature because of failure to take the hot group into account depends both on the experimental conditions and on the spectral interval in which the measurements are made. These deviations from equilibrium appear in the electron-vibrational-rotational spectrum in discharges in pure nitrogen as well as in mixtures with other atomic and molecular gases.

We note that similar anomalous rotational distributions in discharges in N_2-Ar mixtures were pointed out earlier in a number of papers,[2-5] although no clearcut separation into cold and hot groups was made. It was established in those molecules that N_2^* molecules with fast rotation are produced in the reaction

$$N_2(X^1\Sigma^+)+Ar(3p^54s)\rightarrow N_2^*(C^3\Pi_u)+Ar(3p^6\,^1S_0). \qquad (1)$$

Many details, however, remained unexplained in this frequently described case, particularly the unique alternation of the intensities in the rotational structure of the spectrum of the 2^+ system of the N_2.1)

We have therefore verified experimentally[1] the possibility of the appearance of hot N_2 molecules when no argon was specially added to the initial gases, but residual impurities could be present. Measurements of the densities of the $Ar(2p^54S)$ metastable states have shown that the observed anomalies cannot be ascribed to the influence of the impurities.

In many reports of the study of the mechanisms of

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the population of the $N_2(C^3\Pi)$ state in a gas discharge it is stated that the main channel is direct electronic excitation from the ground state.[7-10] It is not very likely, however, that the formation of the hot group is connected with such a process, for this requires that the electron transfer to the molecule an angular momentum ~(30–40)$\hbar$. It must therefore be assumed that the formation of molecules with high rotational-excitation level proceeds with participation of heavy particles.

The purpose of the present paper is to establish the causes of formation of hot N_2 molecules in a gas-discharge plasma and to explain in this connection the singularities of the spectrum of the 2^+ system of nitrogen.

2. EXPERIMENT

The experimental setup for the investigation for the emission and line absorption spectra in a gas-discharge plasma is described in detail in Ref. 1. Two discharge tubes were used, with discharge gap $l = 60$ cm long and with inside diameter $d = 19$ mm. The gas pressure range was $p = 0.5$–5 Torr. Most measurements were performed with a continuous discharge. The current was varied in the range 5–50 mA. Separate measurements were made in a strong-current (~1 kA) pulsed discharge. In the latter case, and integrator PAR-160 was used in the recording system and made it possible to analyze in detail the waveforms of the current and radiation pulses, as well as to register the emission spectrum at any phase of the pulse with a high temporal resolution (~50 nsec). The influence of the reabsorption was monitored in the pulse measurements with the aid of a mirror.[11]

3. CONTINUOUS CURRENT DISCHARGE

A. Density of metastable states $N_2(A^3\Sigma_u^+)$

In the analysis of the possible channels of populating the $C^3\Pi_u$ state in a glow-discharge plasma, it was suggested in Refs. 12 and 13 that besides the direct electronic excitation, the population process can be

$$2N_2(A^3\Sigma_u{}^+) \to N_2(C^3\Pi_u) + N_2(X^1\Sigma_g{}^+) + \Delta E. \tag{2}$$

The reaction (2) can in principle be resorted to when it comes to explain the observed anomalies, since the energy defect ~1.3 eV can lead to rotational excitation. It follows from (2) that

$$[N_2(A^3\Sigma_u{}^+)]^2\langle v\sigma_2\rangle = A[N_2^{hot}(C^3\Pi_u)], \tag{3}$$

where $[N_2(A^3\Sigma_u^+)]$ is the density of $N_2(A^3\Sigma_u^+)$, $[N_2^{hot}(C^3\Pi_u)]$ is the density of the hot group $N_2^{hot}(C^3\Pi_u)$, $\langle v\sigma_2\rangle$ is the rate constant of reaction (2), and A is the probability of the radiative decay of $N_2(C^3\Pi)$.

By measuring simultaneously the concentrations of $[N_2(A^3\Sigma_u^+)]$ and $[N_2(C^3\Pi_u)]$ under different conditions in the discharge, we can verify whether relation (3) holds. Assume that σ_2 does not depend on the gas temperature T, and consequently $\langle v\sigma_2\rangle = \text{const}\cdot\sqrt{T}$. Figure 1 shows plots of the concentration $[N_2^{hot}(C^3\Pi_u)]$, of the quantity $D = [N_2(A^3\Sigma_u^+)]^2A^{-1}\sqrt{T}$, and of the gas temperature against the pressure of the mixture CO–N_2–He (1:2, 5:10) at a discharge current 30 mA. The concentration of $[N_2(A^3\Sigma_u^+)]$ was determined by the method of line absorption, and that of $[N_2^{hot}(C^3\Pi_u)]$ from the absolute intensity of the emission.

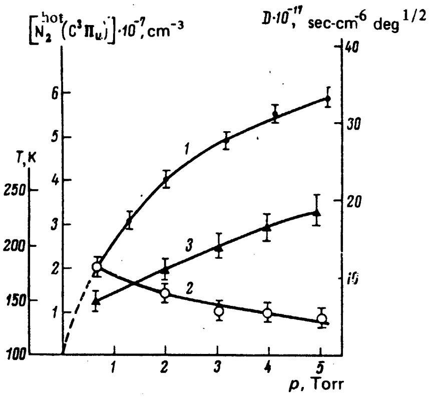

FIG. 1. Plots of the concentration of the molecules of the hot group $[N_2^{hot}(C^3\Pi_u, v=0)]$ (curve 1), of the quantity $D = [N_2(A^3\Sigma_u^+, v=0)]^2\cdot A^{-1}\sqrt{T}$ (curve 2), and of the gas temperature (curve 3) against the pressure of the gas mixture CO – N_2 – He (1:2.5:10). Discharge current $J = 30$ mA, tube cooled with liquid nitrogen.

It is seen that no satisfactory correlation is observed between D and $[N_2^{hot}(C^3\Pi_u)]$ in accord with formula (3). This can be attributed to the fact that σ_2 increases with the gas temperature, rather than remaining constant as had been assumed.

Figure 2 shows plots of D, $[N_2^{hot}(C^3\Pi_u)]$, and T against the discharge current in the same mixture at a total pressure $p = 0.5$ Torr; $[N_2^{hot}(C^3\Pi_u)]$ increases more slowly than D, so that in this case it must be assumed that σ_2 decreases with increasing T, thus contradicting the earlier assumption.

This contradiction indicates that the process (2) cannot be responsible for the formation of the hot molecules under our conditions.

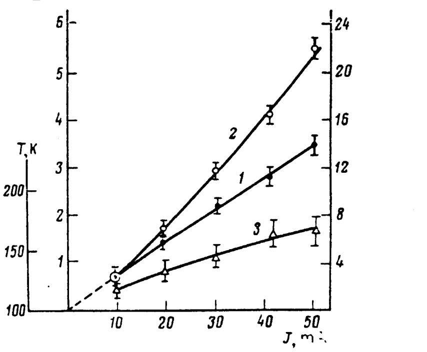

FIG. 2. Plots of the concentration of the hot-group molecules $[N_2^{hot}(C^3\Pi_u, v=0)]$ (curve 1), of the quantity $D = [N_2(A^3\Sigma_u^+, v=0)]^2\cdot A^{-1}\sqrt{T}$ (curve 2) and of the gas temperature (curve 3). Pressure of mixture CO – N_2 – He (1:2.5:10) Torr, tube cooled with liquid nitrogen.

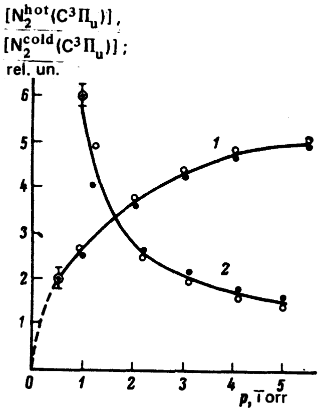

FIG. 3. Plots of the densities of the hot and cold molecules $N_2(C^3\Pi_u)$ against pressure at a current $J=20$ mA in a tube cooled with liquid nitrogen. Curve 1—discharge in mixture $CO-N_2-He$ (1:2.5:10); 2—discharge in high-purity nitrogen; ●—density $[N_2^{hot}(C^3\Pi_u, v=0)]$; ○—density $[N_2^{cold}(C^3\Pi_u, v=0)]$.

B. Hypothesis that quenching process can contribute to the population of N_2 $(C^3\Pi)$

Figure 3 shows plots of the densities of the hot and cold molecules $N_2(C^3\Pi)$ against the pressure for a discharge in a $CO-N_2$-He mixture (curve 1) and in pure nitrogen (2). It is seen that despite the qualitative difference between the corresponding plots in Fig. 3, the concentrations of the cold and hot molecules behave in like fashion in both cases. Since the cold molecules are the result of direct electronic excitation from the ground state $X^1\Sigma_g^+$ (Ref. 1), we can explain this similarity by assuming that the hot group is produced in the course of impact de-excitation of a certain nitrogen state that is itself populated by direct electric impact from the ground state.

Such a state must satisfy the following conditions.

1. The state must have a radiative lifetime long for the quenching process to be noticeably effective.

2. The energy of this state should not greatly exceed the energy of the $C^3\Pi$ state. Otherwise the changes in the form of the electron energy distribution function will lead to a proportional change in the conditions of the excitation of this state and of the $C^3\Pi$ state. To explain the observed value of the rotational temperature of the hot group (~2100 K for $C^3\Pi$, $v=0$), the proposed state must have an energy $\gtrsim 0.7$ eV higher than $C^3\Pi$, $v=0$.

3. Since the quenching in the state $C^3\Pi$ takes place, naturally, mainly in collisions with molecules in singlet ground states, it follows from Wigner's rule that the assumed state should be triplet.

The foregoing requirements are satisfied for the $N_2(E^3\Sigma_g^+)$ state. That the state $E^3\Sigma^+$ can participate in the population of the $C^3\Pi$ state is attested also by experiments with electron beams.[14,15]

4. PULSED DISCHARGE

Since the states $C^3\Pi$ and $E^3\Sigma^+$ are relatively close in energy, it follows that if our assumptions are valid then the presence of hot molecules that are connected with the quenching of the $E^3\Sigma^+$ state should manifest itself in a wider interval of experimental conditions. To verify this assumptions, we performed experiments in a strong-current (~1 kA) pulsed discharge. Despite the strong difference between the physical processes in the pulsed-discharge and continuous-discharge plasmas at low currents, we still expected to observe a superposition of hot and cold molecules in the rotational distribution of $N_2(C^3\Pi)$. In addition, it was natural to expect the kinetics of the development of the cold and hot groups to be different. The measurements have confirmed all this.

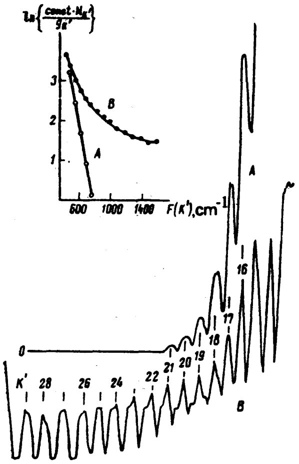

FIG. 4. Spectrograms of the 0–0 part of the 2⁺ band of the N_2 system and their reduction (plot of ln (const$\cdot N_{K'}/g_{K'}$) against the energy of the rotational terms $F(K')$) for the gas mixture $CO-N_2-He$ (0.1:1:10). Pressure $p=0.5$ Torr, tube cooled with liquid nitrogen. A—300 nsec after the start of the current pulse, B—7.5 μsec after the start of the current pulse.

Figure 4 shows sections of the emission spectrograms of the 0–0 band of the 2^+ system of N_3 in different phases of the pulse. The spectrum labeled A was obtained 300 nsec after the start of the current pulse, and the spectrum labeled B after 7.5 μsec. It is seen that only the cold group is present in case A, but both cold and hot molecules appear in case B. The upper part of the figure shows the results of the reduction of the spectrum, namely semilog plots of the relative intensities against the energy of the rotational term $C^3\Pi$, $v=0$. The spectra were obtained in a discharge in a mixture N_2–CO–He at a pressure 0.5 Torr in a tube cooled with liquid nitrogen.

Since the high rotational levels are populated mainly by hot molecules, an investigation of the radiation due to the transitions of the molecules from these levels can yield the dependence of the concentration of the hot molecules on the time. It suffices here to have an oscillogram for only one rotational transition, since the temperature of the hot distribution does not change in the course of the pulse and, just as for a continuous discharge, amounts to ~2100 K.

Figure 5 shows oscillograms for a discharge in the mixture N_2–CO–He (1:0, 01:100) at a pressure 1 Torr: curve 1 shows the total radiation of the 0–0 band (obtained with the monochromator slits fully open in the

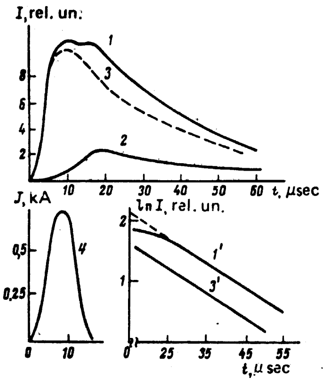

FIG. 5. Oscillograms of the intensities of the 0–0 emission of the 2^+ band of the N_2 system (curve 1), of the molecules of the hot group (2), of the molecules of the cold group (3); oscillogram of the current pulse (4); *s* emilog time plots of the intensities of the 0–0 emission of the band (1′) and of the molecules of the cold group (3′) vs. the time of termination of the current pulse. The characteristic glow damping time is $\tau = 25$ μsec. Gas mixture $CO - N_2 - He$ (0.1:1:100), total pressure 1 Torr, tube cooled with liquid nitrogen.

region of the edge); 2—radiation of hot molecules; 4—discharge current. If we subtract oscillogram 2 from oscillogram 2, then the resultant curve describes the kinetics of only the cold group 3. The oscillograms obtained for the bands of the Angstrom system of CO under the same conditions²⁾ are quite identical to the oscillogram 3 for the 0–0 band of N_2. The emission maxima coincide with the maximum of the current pulse. The characteristic afterglow-damping time of the cold N_2 molecules and of the CO molecules is ~25 μsec (see Fig. 5, curve 3′), and is apparently determined by the plasma decay time.

Oscillograms analogous to those given in Fig. 5 were obtained by us for the transition bands starting with the levels $v = 0$, 1, 2 and 3 of the $C^3\Pi$ state. On the other hand, the oscillograms starting with the level $v = 4$ are identical with the oscillogram on Fig. 5, curve 3, and the spectrum of these bands contains no hot group in any phase of the pulse. This confirms once more the correctness of our assumption that the $E^3\Sigma^+$ state participates in the population of the $C^3\Pi$ state with hot molecules ($\varepsilon(C^3\Pi,\ v = 0,\ 1,\ 2,\ 3) < \varepsilon(E^3\Sigma^+,\ v = 0) < \varepsilon(C^3\Pi,\ v = 4)$) in the process

$$N_2(E^3\Sigma^+) + N_2(X^1\Sigma) \rightarrow N_2(C^3\Pi_u) + N_2(X^1\Sigma_g^+) + \Delta E. \tag{4}$$

5. ALTERNATION OF THE INTENSITIES IN THE 2^+ SPECTRUM OF THE N_2 SYSTEM

An attention-attracting characteristic feature of the spectrum of the hot group is that the triplet groups corresponding to transitions from odd rotational levels K' have a somewhat higher intensity than the triplet groups of transitions with even K' (see Fig. 6). This phenomenon was observed earlier in a discharge in an N_2–Ar mixture and a number of attempts at an explanation[6,16,17] ended in failure. In experiments with high spectral resolution it was established that the relative intensities in the Λ components of the transitions do not correspond to a Boltzmann population when account is taken of the statistical weights $(g_s/g_a) = (i+1)/i = 2$, where g_s and g_a are the statistical weights of the symmetric and antisymmetric Λ components, and i is the nuclear spin.[6,17]

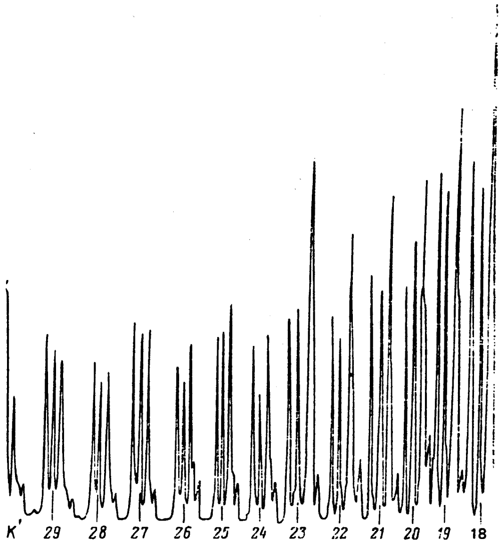

FIG. 6. Spectrogram of part of 0–0 band of 2^+ system of N_2. Discharge in high-purity nitrogen at a current $J = 20$ mA, tube cooled with liquid nitrogen, $p = 0.5$ Torr.

Setzer and Stedman[17] have made in this connection an important remark, emphasizing that the observed disequilibrium is between states described by different electronic wave functions³⁾ (Π^+ and Π^-).

We shall attempt to explain the observed alternation within the framework of the quenching, assumed by us, of the state $N_2(E^3\Sigma)$ in collisions with nitrogen in the ground state $N_2(X^1\Sigma)$.

A. Symmetry of the electronic wave functions of the N_2–N_2 pair

Since the electron motion is characterized by much shorter times than the motion of heavy nuclei, the $E \rightarrow C$ process can be treated in the adiabatic approximation. We note that the plane passing through the axis of one of the colliding molecules and the mass center of the other is a symmetry plane of the system in two limiting cases: a) the second molecule lies in this plane, b) the second molecule is perpendicular to this plane. The symmetry properties of the common wave function of the electron wave function of the colliding molecules relative to the plane in question should be preserved in this case. Prior to the interaction the common electron wave function of the system is $\Psi^0_{\text{com}} = \Psi(X^1\Sigma_g^+)\Psi(E^3\Sigma_g^+)$. Since the states $X^1\Sigma_g^+$ and $E^3\Sigma_g^+$ are positive, Ψ^0_{com} does not reverse sign on reflection in the drawn plane in either of the limiting cases.[18] After the interaction we have $\Psi_{\text{com}} = \Psi(X^1\Sigma_g^+)\Psi(C^3\Pi_u)$ and this function, by virtue of the foregoing, is also positive. The state $C^3\Pi$ corresponds to two functions⁴⁾ $\Psi(C^3\Pi_u^\pm)$, which in fact determine the sign of Ψ_{com}. It is clear from our analysis that a transition to the state

$C^3\Pi_u^-$ is forbidden. Naturally, the molecules collide when they are differently oriented relative to each other. In all the cases intermediate between those considered here the population of the state $C^3\Pi_u^-$ is not strictly forbidden. However, the obtained conclusions and the general premise that the probability of the transition to the $C^3\Pi_u$ state is a smooth function of the relative orientation of the molecule point to a predominant population of the $C^3\Pi_u^+$ state in multiple processes of the quenching of the $E^3\Sigma_g^+$ state.

B. Symmetry of the electron wave functions of the N_2-Ar pair

The proposed explanation of the alternation of the intensities of the Λ-doublet components can be used also in the case when $C^3\Pi$ is excited by collision of N_2 with the atoms $Ar(3p^54s)$. A plane drawn through the internuclear axis N_2 and the Ar atom will always be a symmetry plane of the system. This enables us to account even quantitatively for the alternation of the intensities. The common electron wave functions prior to the collision are $\Psi^0_{com}=\Psi^i_{Ar}\Psi_{N_2}(X^1\Sigma_g^+)$, where Ψ^i_{Ar} is the aggregate of the functions that describe $Ar(3p^54s)$, and can be either positive or negative. After the interaction we have $\Psi_{com}=\Psi_{Ar}(^1S_0)\Psi_{N_2}(C^3\Pi_u)$, $\Psi_{Ar}(^1S_0)$ is positive, so that the symmetry of $\Psi(C^3\Pi_u)$ is determined by the functions Ψ^i_{Ar} and the problem is to count the number of positive and negative states of Ar that are described by Ψ^i_{Ar}.

We use the $L-S$ coupling approximation, which is still meaningful in the case of Ar (Ref. 18). The configuration $3p^54s$ corresponds to the states $^1P_1^0$ and $^3P^0_{1,2,3}$. The population of the $^1P_1^0$ level, which is depleted by the radiative decay, is much less[5)] than the population of $^3P^0_{1,2,3}$, and its contribution to the population of $N_2(C^3\Pi_u)$ can be neglected. Consider, for example, the case $^3P_2^0$. In accord with the rules for the addition of the angular momenta,[19] the wave functions of this state can be written in the form

$$\Psi_1=\Psi_{1,1}\chi_{1,1},\quad \Psi_2=\Psi_{1,-1}\chi_{1,-1},\quad \Psi_3=2^{-1/2}(\Psi_{1,0}\chi_{1,1}+\Psi_{1,1}\chi_{1,0}),$$

$$\Psi_4=2^{-1/2}(\Psi_{1,0}\chi_{1,-1}+\Psi_{1,-1}\chi_{1,0}),$$

$$\Psi_5=\frac{2}{6^{1/2}}\Psi_{1,0}\chi_{1,0}+\frac{1}{6^{1/2}}(\Psi_{1,1}\chi_{1,-1}+\Psi_{1,-1}\chi_{1,1}),$$

where $\Psi_{l,m}$ is the wave function of a state with orbital angular momentum l and its projection m on the z axis (the z axis is perpendicular to the symmetry plane), χ_{S,m_S} is the wave function corresponding to a state with spin S and its projection m_S on the z axis. Since the spin state of the system remains unchanged by virtue of the Wigner rule, we consider only the symmetry of the coordinate part of the wave function. Reflection in the plane is equivalent to inversion in the center of the atom and rotation through 180° about the z axis. Inversion reverses the signs of $\Psi_{1,1}$, $\Psi_{1,0}$ and $\Psi_{1,-1}$ (the term $^3P_2^0$ is odd), and rotation transforms them like spherical harmonics,[19] i.e.,

$$\Psi_{1,0}\to\Psi_{1,0},\ \Psi_{1,1}\to-\Psi_{1,1},\ \Psi_{1,-1}\to-\Psi_{1,-1}.$$

Consequently, $\Psi_{1,1}$ and $\Psi_{1,-1}$ do not reverse sign upon reflection in the plane, while $\Psi_{1,0}$ does. It is now easy to determine the number of $Ar(^3P_2^0)$ states with different symmetry. The results are given in the table.

TABLE I. Probabilities of positive and negative states of $Ar(^3P_2^0)$.

sign Ψ	$\Psi^i_{Ar}(^3P_2^0)$				
	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5
+	1	1	1/2	1/2	1/3
−	0	0	1/2	1/2	2/3

The ratio of the total number of the positive states $Ar(^3P_2^0)$ to the total number of negative ones is obviously 2:1. For the $Ar(^3P^0_{1,3})$ states we obtain the same result. By virtue of conservation of the total symmetry of the wave function of the system in process (1), the states $C^3\Pi_u^+$ and $C^3\Pi_u^-$ will be populated in a ratio 2:1. A similar analysis of the states corresponding to the terms $^3P_1^0$ and $^3P_2^0$ leads to the same result. Taking into account the statistical weights of the symmetric and antisymmetric levels (relative to permutation of the nuclei), we find that for the odd rotational levels the intensity ratio in the Λ doublet is 4:1 and for the even ones the ratio is 2:2 (in the same units), while the ratio of the total intensities of the triplet groups of the emission spectrum of the hot molecules is 5:4, in agreement with our experiments as well as with the experiments of Ref. 17.

It is of interest to analyze the case of excitation of the isotope $^{15}N_5$ in the process (1). In this case, as found in Ref. 16, the alternation of the intensities is inverted–the lines with even K' become more intense. This follows also from our analysis. For odd K', the symmetrical component corresponds to the state $C^3\Pi_u^+$, and the antisymmetric one to the state $C^3\Pi_u^-$, with the converse for the even K'. Since the spin of the nuclei is in this case $i=\frac{1}{2}$, it follows that $g_s/g_a=\frac{1}{3}$. Thus, the states $C^3\Pi_u^+$ and $C^3\Pi_u^-$ are populated as before in a ratio 2:1, but allowance for the statistical weights leads to a higher intensity for the lines with even K'. The assumed intensity ratio in this case is 7:5.

6. CONCLUSION

An investigation of the character and of the causes of the anomalous distribution of the intensities in the rotational structure of the spectrum of the 2^+ system of nitrogen provides physical grounds for a correct application of the method of relative intensities for the purpose of measuring the temperature of a neutral gas in a nonequilibrium plasma. Allowance for the hot molecules shows that the remaining part of the cold molecules has a Boltzmann distribution over the rotational levels. This, assuming a short lifetime of the radiating states, attests to the "copying" properties of the electron impact.[20,21] We note that by "copying" we have in mind here only equality of the rotational temperatures in the ground and excited electronic states (with close rotational constants), and not excitation with a selection rule $\Delta K=0$.[20] In fact, if the rule $\Delta K=0$ were to hold in electron-impact excitation from the state $X^1\Sigma_g^+$ into the state $C^3\Pi_u$, then the N_2-system 2^+ spectrum connected with the transitions of the cold molecules would reveal a characteristic intensity alternation wherein triplets with even K' would be more intense than triplets with odd K', owing to the influence of the nuclear spin. We, however, did not observe such an alternation. This question deserves a special investigation.

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1) This phenomenon was pointed out in the report,[6] and while the experimental conditions in that reference are not quite clear, it can be assumed that disequilibrium was observed there not only in the RF discharge in the N_2–Ar mixture, but also in pure N_2.

2) The radiating state $B^1\Sigma^+$ for the Angstron band system is populated in the discharge by direct electron impact from the state CO ($X^1\Sigma^+$).

3) The wave function is positive if it remains unchanged upon reflection in a plane passing through the axis joining the nuclei, and negative if its sign is reversed by this reflection.

4) We note that when one speaks of the symmetry of an electron wave function relative to reflection in a plane passing through an internuclear axis the reference is to symmetry of its coordinate part.[19]

5) This was verified by experiment.

[1] V. N. Ochkin, S. Yu. Savinov, and N. N. Sobolev, Preprint Fiz. Inst. Akad. Nauk No. 150, 1977.
[2] E. S. Fishburne, J. Chem. Phys. 47, 58 (1967).
[3] D. W. Setser and D. H. Stedman, J. Chem. Phys. 53, 1004 (1970).
[4] O. P. Bochkova and N. V. Chernyshova, Opt. Spektrosk. 31, 677 (1971).
[5] J. Dechamps and A. Ricard, J. Phys. (Paris) 34, C2, 123 (1973).
[6] G. H. Dieke and D. F. Heath, Johns Hopkins Spectroscope Report, No. 17, Baltimore, Md., 1959.
[7] J. R. Howorth, J. Phys. B 5, 402 (1972).
[8] O. V. Ravodina, Candidate's Dissertation, Sov. Phys. Tech. Inst. at Tomsk University, Tomsk, 1974.
[9] I. P. Zapesochnyĭ and V. V. Skubenich, Opt. Spektrosk. 21, 140 (1966) [Opt. Spectrosc. (USSR)].
[10] V. M. Kaslin and G. G. Petrash, Tr. Fiz. Inst. Akad. Nauk 81, 88 (1975).
[11] S. É. Frish, in: Spektroskopiya gazorazryadnoĭ plazmy (Spectroscopy of Gas-Discharge Plasma), ed. S. É. Frish, Nauka, Leningrad, 1970, p. 7.
[12] G. N. Hays, C. J. Tracy, A. R. Demonchy, and H. J. Oskam, Chem. Phys. Lett. 14, 352 (1972); G. N. Hays and H. J. Oskam, J. Chem. Phys. 59, 6088 (1973).
[13] A. S. Sokolov, Candidate's Dissertation, Inst. of Inorganic Chemical Compounds, Akad. Nauk SSSR, Moscow, 1976.
[14] D. E. Golden, D. J. Burns, and V. C. Sutcliffe, Jr. Phys. Rev. A 40, 2123 (1974).
[15] D. E. Golden, D. J. Burns, and D. W. Galliardt, J. Chem. Phys. 65, 2616 (1976).
[16] P. Bleeckrode, Physica (Utrecht) 41, 24 (1969).
[17] D. W. Setser and D. H. Stedman, J. Chem. Phys. 53, 1004 (1970).
[18] M. A. El'yashevich, Atomnaya i molekulyarnaya spektroskopiya (Atomic and Molecular Spectroscopy), Fizmatgiz, 1962.
[19] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika. Nerelyativistskaya teoriya (Quantum Mechanics. Nonrelativistic Part), Nauka, Moscow, 1974. [Pergamon, 1976].
[20] G. Herzberg, Molecular spectra and molecular structure. I. Spectra of diatomic molecules, 2nd ed. D. van Nostrand, N. Y., 1951, p. 207.
[21] A. D. Sakharov, Izv. Akad. Nauk SSSR Ser. Fiz. 12, 372 (1948).

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Highly excited states of the hydrogen atom in an electric field

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We discuss the levels E and their widths Γ of hydrogen atom in the quasiclassical approximation in the presence of a uniform electric field E (all quantities are in atomic units). The effective quantum number $\nu=(-2E)^{-1/2}$ depends on E and on the parabolic quantum numbers n_1, n_2, and $|m|$. For $|m| \ll n_{1,2}$ the ratio ν/n (n is the principal quantum number) with accuracy to quantities of order $(m/n)^2$ is a universal function of two parameters: $S=(n_1-n_2)/n$ and $T=4n^4$ E. The value of ν/n is determined by Eqs. (3.4)–(3.6) and the value of Γ by Eq. (5.8). The values obtained with these relations are close to the results obtained by numerical integration of the Schrödinger equation.

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1. INTRODUCTION

The hydrogen atom in the presence of a uniform electric field is described in parabolic coordinates by well known equations.[1]

We shall designate the energy of the atom by E, $\mathscr{E}$ is the field strength, ξ and η are parabolic coordinates in the atomic system of units, and we introduce the effective quantum number

$$\nu=(-2E)^{-1/2}, \tag{1.1}$$

the reduced field strength

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