On spectral line widths in a nonequilibrium molecular plasma

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An anomalous broadening of the spectral lines has been found in the rotational structure of the 2^+ system of nitrogen, due to spectral excitation during the nonresonant interaction of heavy particles.

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It has been shown[1] that the presence of parallel channels for populating molecular electron-excited states in a reduced-pressure nonequilibrium plasma leads to severe distortions of the shape of the rotational level distribution of the molecules compared with the Boltzmann thermal distribution. If the nonresonant interaction of heavy particles is the elementary excitation event, then so-called "hot" groups of molecules arise for which the average energy of rotational motion exceeds the thermal energy. One such example is that of the "hot" groups of N_2 molecules ($C\,^3\Pi_u$), appearing in the spectrum of the widely known 2^+ system of nitrogen. In this case molecules with fast rotation can be formed as a result of an interaction of the nitrogen molecules themselves or through collisions of $N_2(X\,^1\Sigma_g^+)$ with argon atoms in metastable states.[1-3] It follows from the laws of energy and momentum conservation that as a result of these

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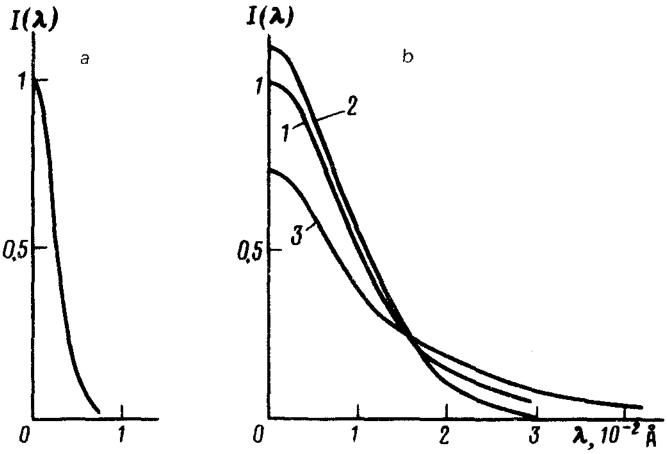

FIG. 1. Contours of the $R_1(3)$ and $R_1(26)$ lines of the (0, 0) band of the N_2 2^+ system: a—contour of $R_1(3)$ line; b—contour of $R_1(26)$ line (1). The calculated Doppler (2) and Lorentz (3) contours are shown for comparison; all three contours have been normalized to one area and to one width.

interactions electron-excited molecules are formed with an initial velocity distribution that is nonthermal. If the radiating state has a short lifetime and collisions play no role, then we must consider the possibility of anomalous broadening of the spectral lines. The fact that the broadening should depend on the number of the vibrational and rotational levels of the radiating state is significant.

A pressure-scanned Fabry-Perot etalon, mated with a DFS-8 monochromator, was used to record the line contours. The radiation of the 2^+ system of N_2 was recorded in a glow discharge in a 20-mm diameter tube at a discharge current of 20 mA in N_2-He (1:10) and N_2-Ar (1:9) mixtures. The wall temperature of the tube was 77 K. The gas temperature at the center of the tube was measured independently with a thermocouple, from the relative intensities in the rotational structure of the spectrum of the "cold" molecule group of the 2^+ system[1] of N_2 and from the Doppler broadening of the helium lines. The results of the measurements agree satisfactorily with one another.

Figure 1 shows the contours of the $R_1(3)$ and $R_1(26)$ lines of the (0, 0) band of the N_2 2^+ system. The discharge was in the N_2-He (1:10) at a pressure of 0.5 Torr. The $K' = 3$ level, from which the $R_1(3)$ transition starts, is primarily populated with molecules of the "cold" rotational group, excited by direct electron impact from the ground state of $N_2(X\,^1\Sigma_g^+)$, while the $K' = 26$ level is populated by molecules of the "hot" group.[1] It is seen that the lines have considerably different widths. The $R_1(3)$ line has a Doppler contour, corresponding to a Maxwellian velocity distribution of the radiators at a gas temperature of $T_g = 150$ K. The broadening of the $R_1(26)$ line does not correspond to the normal Doppler broadening (the calculated Doppler and Lorentz contours are shown in Fig. 1b for comparison; all three contours have been normalized to one area and to one width). A similar broadening for lines with large K' also occurs in N_2-Ar. Nevertheless, if the effective temperature, corresponding to the Doppler

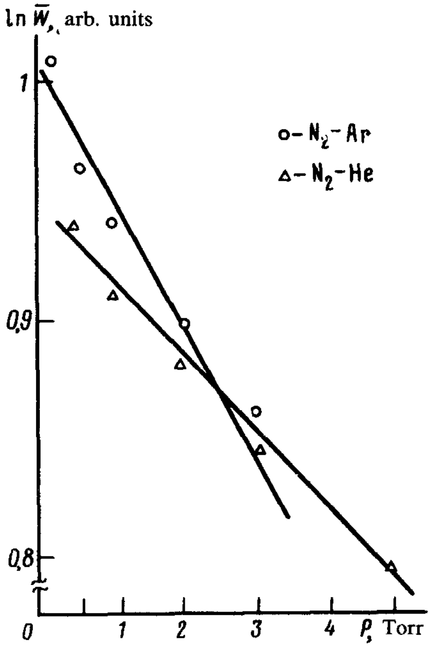

FIG. 2. Dependence of the logarithm of the most probable energy of the translational motion of $N_2(C\,^3\Pi_u, v'=0, K'=26)$ on the pressure of the N_2-He (1:10) and N_2-Ar (1:9) mixtures.

broadening width of $R_1(26)$ is introduced, it is equal to ≈ 2000 K. The value of the most probable energy, which can be found from the maximum of the derivative of the contour with respect to frequency, has greater significance in this case.

Figure 2 shows the dependence of the logarithm of the most probable energy of the translational motion of $N_2(C\,^3\Pi_u, v'=0, K'=26)$ on the pressure of the N_2-He and N_2-Ar mixtures. Despite the short radiation lifetime of the radiator ($\tau \approx 4\times 10^{-8}$ sec) collisional relaxation of the translational motion is already noticeable at pressures of a few tens of Torrs.

The availability of complete information about the molecular distributions in terms of all degrees of freedom can be useful, for example, for identifying the channels of exothermal reactions in a plasma with radiation excitation. Thus, one can consider the reactions

$$N_2(X^1\Sigma_g^+) + Ar(3p^5 4s) \rightarrow N_2(C^3\Pi_u) + Ar(3p^6\,{}^1S_0) + \Delta E_1 \quad \text{in mixture } N_2-Ar\ (1:9), \qquad (1)$$

$$N_2(E^3\Sigma_g^+) + N_2(X^1\Sigma_g^+) \rightarrow N_2(C^3\Pi_u) + N_2(X^1\Sigma_g^+) + \Delta E_2, \qquad (2)$$

$$2N_2(A^3\Sigma_u^+) \rightarrow N_2(C^3\Pi_u) + N_2(X^1\Sigma_g^+) + \Delta E_3, \quad \text{in mixture } N_2-He\ (1:10). \qquad (3)$$

By using the results obtained together with the results of measurements of the relative intensities in the vibrational and rotational structure of the spectrum it can be proved that the formation of the "hot" molecule groups in the N_2-Ar mixture occurs in process (1). In the N_2-He mixture the energy balance condition for the molecules of the "hot" group satisfies reaction (2). At the very least reaction (3) is not very efficient.

In summary, we can state that:

1. Anomalous spectral line broadening effects have been found in a reduced-pressure nonresonance molecular plasma for the case of N_2 molecules. The character of the broadening is different for different rotational components even within the limits of one electron-rotational band.

2. A velocity "sorting" of the electron-excited N_2 molecules occurs as a function of the bound state energy.

3. The phenomena described must be taken into consideration when using classical pyrometric methods and in calculations of the gain coefficients of lasers employing molecular electronic transitions; they can be used to study relaxation processes and to identify excitation mechanisms.

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