Beitr. Plasmaphys. 23 (1983) 2, 145—151

On the Rotational Distribution of N_2 in the Ar—N_2-Discharge The O—O-Band of the Second Positive System

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Abstract

The rotational distribution of the O—O-band of the second positive system of N_2 was determined by the Ornstein method in the glow discharge of an argon-nitrogen mixture at medium pressure. Evidently, for the rotational *R*- and *P*-lines some straight lines can be fitted for rotational quantum numbers between 2 and 60 according to usual representation. The slopes of the curves indicate that the Boltzmann distribution does not exist for all the levels. For each of these straight lines can be declared a value of rotational temperature. The dependence of the several rotational temperatures on the discharge current is essential lower than the corresponding dependence of the gas temperature, which is calculated by means of the energy balance. The influence of the energy transfer from metastable argon atoms to ground-state nitrogen molecules on the rotational distribution seems to be insignificant. Comparisons with rotational distributions in pure nitrogen plasmas point at the influence of interactions between nitrogen species.

1. Introduction

Usually, in non-isothermal plasmas the gas temperature is determined from the rotational structure of molecular spectra [1]. In the last years some authors doubt that it is permitted to make statements about the translational temperature of heavy particles by the Ornstein method, because they found in non-isothermal plasmas differences between translational and rotational temperatures by reason of simultaneous temperature measurements by means of various methods. In the same way as for the system argon-nitrogen deviations are observed both between the rotational and the gas temperature [2—4] and from a general Boltzmann distribution [5—10]. For these phenomena the selective energy transfer from metastable argon atoms to ground-state nitrogen molecules was mostly held responsible.

The method of determination of gas temperature on the rotational structure is based on the assumption that the excitation of the upper electronic levels occurs by direct electron collisions with ground-state molecules, at which the population of rotational levels of the ground-state molecules is resulted from collisions with the neutral particles. In this paper the population of rotational levels is investigated in the positive column of an argon-nitrogen discharge at low currents. In distinction to the investigations of the most other authors a nitrogen portion of more than 10% was chosen. An essential difference between gas temperature and electron temperature at small concentrations of electron was aspired.

2. Experimental arrangement

For the investigation a quartz tube with an interior diameter of 1,4 cm was used. The electrodes were in sideward gussets in order to investigate the radiation of positive column end-on. The discharge was filled with 0.87 kPa nitrogen and 2.61 kPa argon and was carried on with alternating voltage by a high-tension transformer with a maximum voltage of 16 kV. The adjustment of current took place at the primary side. The discharge current was varied from 10 to 50 mA. The distance of electrodes was 17 cm. The voltage of the discharge was in these cases smaller than 2 kV.

The light coming from the positive column was imaged by an objective on the slit of the Zeiss PGS 2 spectrograph. We used the end-on image in order to obtain higher intensity and to evade additional inaccuracies by the Abel-inversion. To get a high spectral resolution the spectra were taken on Orwo UV 1 plates, employing second order double pass of the spectrograph. The dispersion was 0.09 nm/mm and the slit width 20 μm. The calibration values of intensity were determined by a tungsten strip lamp.

The lines were measured by a comparator and coordinated suitably to the rotational quantum numbers according [11]. The intensity of these lines were measured by a micro densitometer.

Furthermore the discharge was photographed side-on with interference filters in order to find out the radial distribution of radiation. The wall temperature was measured by a thermocouple.

3. Results

The intensities of rotational lines of the R- and P-branch were measured without consideration of the fine structure of these lines. Then in the usual way the results of the log ratio of the measured line intensities and transition probability are plotted against the energy of upper level. In this procedure at first the rotational energy of the upper level was supposed to be proportional to $J(J+1)$. In Fig. 1 the dependence of the log ratio on the rotational energy is presented for the R_2-lines at discharge current of 20 mA. Significantly it can be shown that the totality of points does not be placed on a straight line. The run of the curve indicates that the Boltzmann distribution does not exist for all the levels, as would be expected in the case of thermal equilibrium with the translational energy of heavy particles. Therefore it is difficult to declare the rotational temperature. We will try to approximate parts of the run of the curve with a straight line and for these ranges of rotational levels rotational temperatures were determined according to the slopes of these straight lines. The rotational temperatures obtained in this matter are regarded as substitution for a single characteristic parameter of the curve.

For the various discharge currents the typical run is shown in Fig. 2. For the R_1-lines the important results are noticed in this figure. The run of the curve can be approximate by three straight lines. It can be established that the straight lines with similar slope were in the same range of rotational energy. Besides there are two weak maxima at $J = 14$ and $J = 43$. This behaviour is typical for three of four of investigated currents. Only at the lowest current two different straight lines were noticed, because the intensity of lines with $J > 30$ could not be measured. The same representation can be given for the R_{0a}-, R_{0b}- and R_2-lines, too. The P-branch shows a different behaviour. The measurable range of rotational quantum numbers is smaller for the P-branch than for the R-branch by means of which the deviation from a straight line is not marked so distinctly. Further on the slopes of the straight lines are smaller for the P-branch than

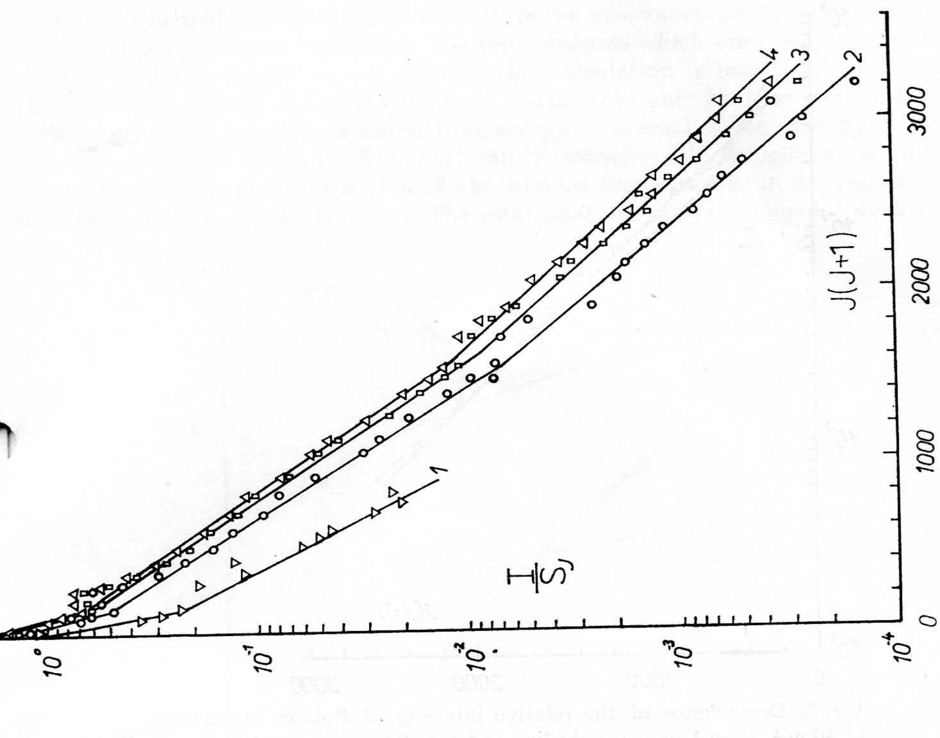

Fig. 2. Representation of the various Boltzmann-straight lines of R_1-branch at 10 mA (1), 20 mA (2), 40 mA (3), and 50 mA (4)

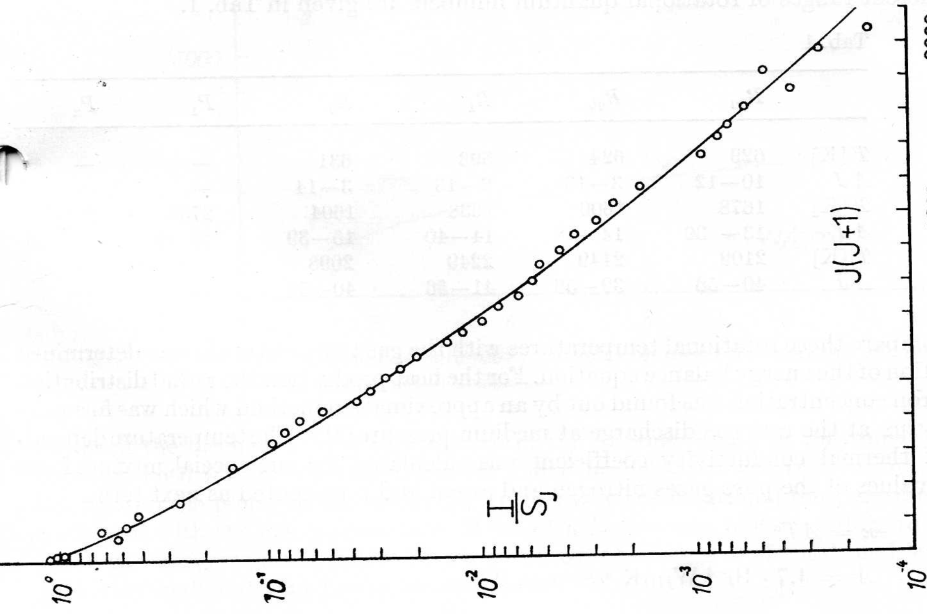

Fig. 1. Dependence of the relative intensity of R_2-lines on the rotational energy

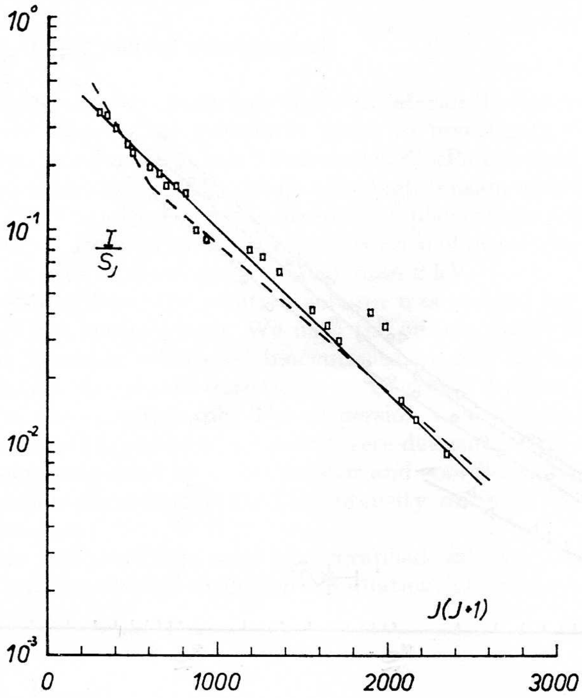

Fig. 3. Dependence of the relative intensity of P_2-lines on the rotational energy at 40 mA. Case 1 one straight line and case 2 two straight lines as possible approximations

for the R-branch. In Fig. 3 for the P_2 -lines the plot log intensity versus rotational energy is represented for a discharge current of 40 mA. The rotational temperatures for the different ranges of rotational quantum numbers are given in Tab. 1.

Tab. 1

	R_{0a}	R_{0b}	R_1	R_2	P_1	P_2
T [K]	629	624	593	631	—	—
ΔJ	10—12	3—13	2—13	3—14	—	—
T [K]	1678	1600	1638	1604	2733	2686
ΔJ	13— 39	14—38	14—40	15—39	18—55	17—59
T [K]	2109	2149	2249	2098	—	—
ΔJ	40—56	39—56	41—56	40—56	—	—

To compare these rotational temperatures with the gas temperature it was determined by solution of the energy balance equation. For the heat production the radial distribution of electron concentration was found out by an approximation method which was formerly used by us at the rare gas discharge at medium pressure [12]. The temperature dependence of thermal conductivity coefficient was calculated for our special mixture from known values of the pure gases nitrogen and argon and represented as next term.

$$\varkappa = AT^{\alpha} \tag{1}$$

$A = 4.7 \cdot 10^{-4}$ W/mK $^{5/3}$ $\alpha = 2/3$

With the help of measured wall temperature the axis value and the radial distribution of gas temperature were calculated. The temperatures which are calculated in this way are regarded as maxima values, because this calculation is based on the assumption that the energy changed in the column is transported only by heat conduction to the wall. However it must be expected that energy also reaches the wall by diffusion of vibrational excited molecules. This part can be considered by a higher value of thermal conductivity [13]. The comparison of the various temperatures in dependence on the discharge current is given in Fig. 4. The rotational temperatures depend weakly on the power of the discharge. This concerns all of the various ranges of rotational quantum numbers both for the R-branch and for the P-branch. The gas temperature depends stronger on the power of the discharge. In this way the rotational temperatures are not correlated with the gas temperature. If we fit a Boltzmann plot according to the measured gas temperature it can be observed an over-population of rotational levels both with very high and very low quantum numbers.

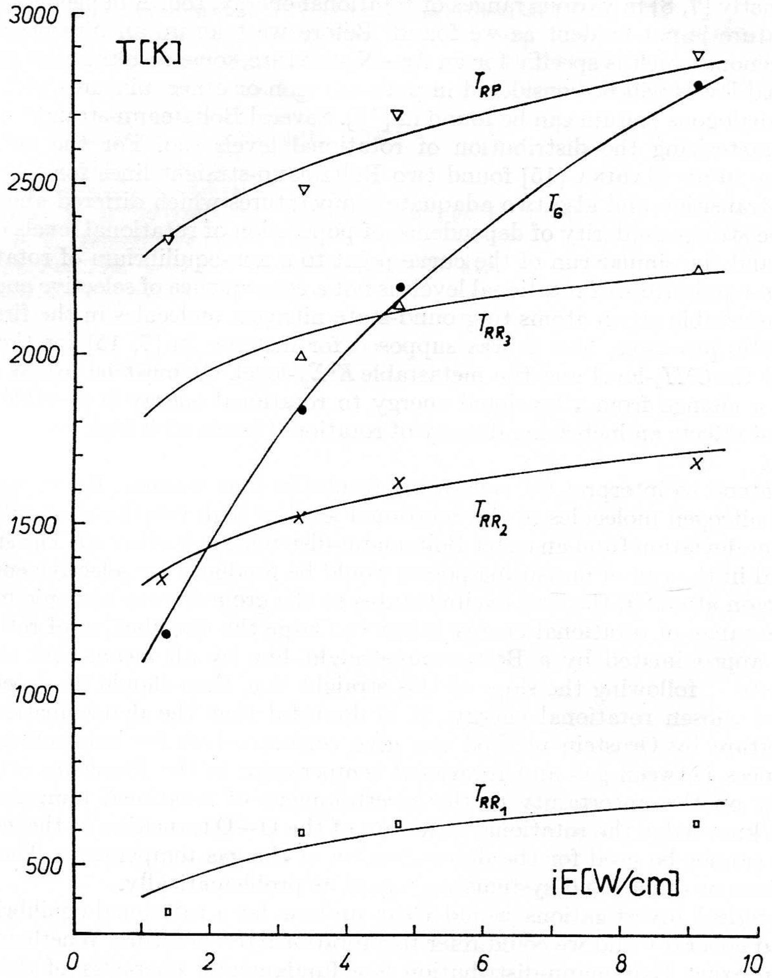

Fig. 4. The variation of different rotational temperatures and the gas temperature (T_G) with the power of the discharge

4. Discussion

For the tested range of the Ar—N_2-discharge a distinct deviation of population of rotational levels is observed from an exact Boltzmann-distribution. The approximation of measuring data by adaquate straight lines in partial ranges of rotational energy does not represent surely the right physical interpretation, but it is possible to compare our results with other investigations. Different rotational temperatures were observed not so distinctly [7, 8] in various ranges of rotational energy, too. A dependence on electron temperature is not evident as we found. Before we take up an interpretation of this phenomenon, which is specific for an Ar—N_2-mixture, some results about populations of rotational levels will be considered in pure nitrogen or other mixtures with nitrogen. A nearly analogous picture can be found in [14]. Several Boltzmann-straight lines are used for characterizing the distribution of rotational levels too. For the hollow cathode discharge in air Madina [15] found two Boltzmann-straight lines for the R-branch of the 0-0-transition and also two adaquate temperatures which differed about the factor two. The strong similarity of dependence of population of rotational levels on rotational energy and the similar run of the curve point to a non-equilibrium of rotational levels. This non-equilibrium of rotational levels is not a consequence of selective energy transfer from metastable argon atoms to ground-state nitrogen molecules in the first place, but of inelastic processes, how it was supposed for instance in [7, 15] for the interaction between the $C^3\Pi_u$-level and the metastable $E^3\Sigma_g^+$-level. It must be tested still in what respect a change from vibrational energy to rotational energy is possible in selective form and effects an increasing density of rotational levels with high rotational quantum number.

We intend to interpret the measuring results in that manner. By energy transfer of excited nitrogen molecules in the rotational level of high rotational quantum numbers a distinct deviation from an exact Boltzmann-distribution is effected. The small maxima observed in the run of measuring points would be produced by selective energy transfer from argon atoms in the first excited states to the ground-state nitrogen molecule.

If the range of rotational energy is not too large the distribution of rotational levels can be approximated by a Boltzmann-straight line by all means, but the rotational temperature, following the slope of this straight line, then should be dependend on the range of chosen rotational energy. It is doubtful that the determination of the gas temperature by Ornstein method can give correct values for non-isothermal plasma. Differences between gas and rotational temperature in the literature can be reduced partially on the uncertainty of the ascertainment of rotational temperature. At the present knowledge the rotational structure of the 0—0 transition of the second positive system cannot be used for the determination of the gas temperature. The use of other transitions or other band systems we regard as problematically.

Theoretical investigations would clear up how far a rotational equilibrium could be assumed generally and we could refer to a rotational temperature. Whether the deviation from an exact Boltzmann-distribution is a fundamental character of these molecular plasmas or it comes by formation of rotational levels with high energy (hot molecules) in consequence of selective energy transfer, this question has to investigate still. Therewith as in [15] the distribution of rotational levels can be considered as superposition of two Boltzmann-distributions with very different temperatures. The observation by Slovetskii [16] that the rotational temperature is about 2000 K for the higher rotational levels independent from discharge conditions can be confirmed by us.

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Received December 29, 1981