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NON-EQUILIBRIUM IN THE HELIUM MOLECULE ROTATIONAL LEVELS OF $3d^3\Sigma^+_u$ (v = 0). ROTATIONAL TEMPERATURE

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Кузман Паскалев, Оля Джилянова. НЕРАВНОВЕСЕН ХАРАКТЕР НА РАЗПРЕДЕЛЕНИЕТО НА ХЕЛИЕВА МОЛЕКУЛА ПО РОТАЦИОННИТЕ НИВА НА СЪСТОЯНИЕТО $3d^3\Sigma^+_u$ (v = 0). РОТАЦИОННА ТЕМПЕРАТУРА

Изследвано е разпределението на молекулите на димера He_2 по ротационните нива на състоянието на $3d^3\Sigma^+_u$ (v = 0). Измерванията са проведени за положителния стълб на тлеещ разряд в чист хелий за широк обхват от условия: стойности на налягането от 2,6 до 70 Torr и на тока – от 10 до 100 mA. Установено е, че в стационарната плазма от централната област на положителния стълб на разряда за налягане под 40 Torr разпределението е неравновесно и понятието T_{rot} няма физически смисъл. При по-високо налягане разпределението на молекулите добре се апроксимира с болцманово разпределение с температура, близка до температурата на газа в разряда. Показано е, че по налягане (за различни стойности на тока) разпределенията на молекулите по ниските ротационни нива са идентични, докато заселеностите по високите нива са подобни при определен ток и различно налягане.

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The rotational level population of the helium dimmer state $3d^3\Sigma^+_u$ (v = 0) has been investigated. The measurements were performed for a wide range of discharge currents and gas pressure values. A non-Boltzman distribution has been found to exist in the central region on axis of the positive column of steady state glow discharge when the pressure is less then 40 Torr, therefore, the parameter T_{rot} appears to be unacceptable. A reasonable equilibrium within the rotation levels of the molecules can occur if the pressure is high enough, with a corresponding temperature close to the gas temperature value too. There is a similarity in the distribution of the low-lying levels when the current values are identical.

Keywords: helium dimmer, stationary glow discharge, non-equilibrium, population of rotational levels

PAKS numbers: 52.25.Rv, 33.70.Fd

1. INTRODUCTION

Emission bands with well-resolved rotational structure are common feature of the spectra of some light molecules like N_2, CO, CN, when they are components of low-temperature plasmas. The energy spacing between the rotational levels of these molecules are close to the mean kinetic energy of the neutrals, hence an effective thermalization in the system is expected to occur, i.e., Boltzmann distribution of the excited molecules along the rotational levels. Anticipating that, the intensity distribution of the rotational lines is in position to reveal the temperature of the gas, as was suggested and successfully applied by Ornstein and Brinkman in 1928 to violet CN-band in carbon arc [1]. Lochte-Holtgreven and Oldenberg were the first to found out that in the case of C_2 the temperature, measured by rotational lines differ from the temperature of the flame [2] and a deviation in the population of rotation level of NO [3] from the Boltzmann low. Similar results were obtained later in many experiments for other diatomic molecules [4].

A common feature of this results is the fact that rotational lines intensities point to a non-equilibrium distribution of the excited molecules through the higher rotational levels, where, as a rule, one observes anomalous strong radiation from upper-lied lines compare to the predicted. The prediction is based on the assumption of Boltzmann distribution with parameters, determined from first few lines in the band. The reasons for this unequilibrium remain unclear thou a number of mechanisms were suggested for the existence of these so called “hot” molecules in the exited electronic states. They could be summarized as: i) slow rotational relaxation; ii) vibrational relaxation; iii) due to electron impacts [5].

The rotational lines intensities of the He_2 eximer were also used for determination of the temperature in different type of electric discharge in helium [6]–[10]. The 4680 $3p\pi b^3\Pi g–2s\sigma a^3\Sigma^+_u$ (v = 0) band was used in all of the cases. For most of them, the emission of transient plasma (impulse discharge [6],[7], afterglow [9],[10], etc) was investigated. The measurements were performed without space resolution either. Nevertheless, the values of rotational temperature (the temperature as an equilibrium parameter) obtained in all these experiments were considered higher than it has been expected for gas-kinetic temperature T_g. This fact leads to the notion “hot distribution” with “rotational temperature” T_{rot} [8]. Are these high rotational temperatures a consequence of processes in the discharge, as been suggested by Deloche et al [9], or are due of temporal and space inhomogeneous remained unclear? The problems with such type of uniformity were eliminated using the wel1-defined plasma in the positive column of steady-stage glow discharge in helium [11]. In this reference the plasma is viewed on-axis and it is confirmed, that the measured by $3p\pi b^3\Pi g$ (v = 0)–$2s\sigma a^3\Sigma^+_u$ (v = 0) band rotational temperatures are in excess of gas temperature and also revealed that the growth of gas pressure and discharge current leads toward equalization of the rotational temperature with that of the gas. Therefore, the “hot” rotational temperatures are connected with the processes in the plasma and pronounce (are expressing) complexity the formation of the exited molecular states.

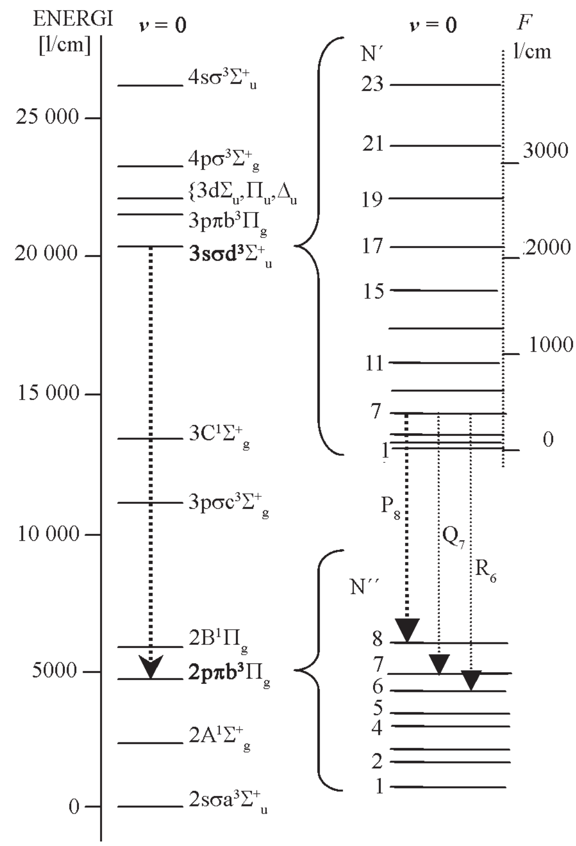

Fig. 1. A scheme of the levels of the He_2 molecule. It is shown the rotational structure of the upper and the down-lied levels of the researched transition

The idea of this investigation was to obtain and analyze the dependences of rotational level population of He_2 from the parameters of well-defined plasma source, namely the positive column of stationary glow discharge. When viewed on-axis it posses a good homogeneity due to the flat plateau of the typical for this discharge Bessel type of radial distribution. In addition to this, it could be operated over a variety of gas pressure and discharge current, influencing in this way the neutral and electron density and temperature. The $3s\sigma d^3\Sigma^+_u$ (v = 0)–$2bp\pi^3\Pi_g$ (v = 0) transition (Fig.1) was choused for two reasons. This band posses a very long and well-resolved P-branch (Fig.2), so that the density of rotational levels with N ~21–23 can be measured.

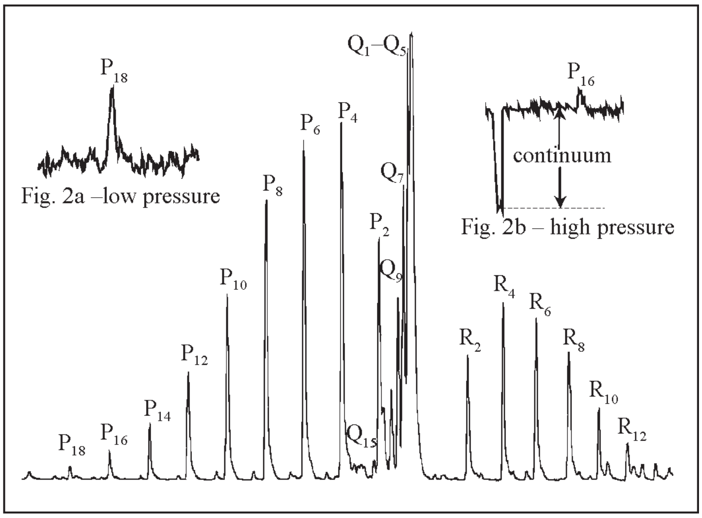

Fig. 2. A common view of the spectrum of the transition
$3s\sigma d^3\Sigma^+_u(v = 0) \rightarrow 2p\pi e^3\Pi_g(v = 0)$ by the conditions: p = 40 Torr; i = 50 mA.
Fig.2a and Fig.2b show the limits, which depend by the types of the noise

In addition to this, the even levels in this electronic state are missing due to their asymmetry, which leads to larger energy spacing and hinders rotational relaxation. In addition to this, the two states, involved in this transition, are in a pure “b” case, so one should not expect problems with the values of Hőnl-London factors [12].

2. EXPERIMENT

The scheme of the experiment is shown on Fig. 3. The positive column length has been 500 mm and the water-cooled glass discharge tube had 19 mm in diameter. The gas used was spectrally pure helium, cleared additionally by a prolonged cataphoresis. The radiation was collected on-axis from the central region on the positive column through a narrow collimated objective, restricting the view to 0.1 of the cross-section. The spectra were obtained by a 0.4 m Czerny-Turner monochromator and a photomultiplier in analogous mode. The signals, due to the collimation are weak and required long scanning times, so special measures were taken to insure temporal stability of the system. The high-voltage power supply insures better than 0.5% stability of the discharge current and the registration drift was less than 0.1 mV/h.

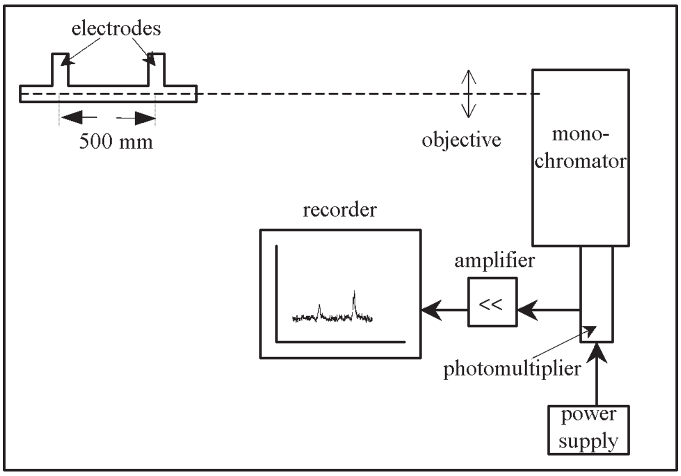

Fig. 3. Scheme of the experiment

The detecting system sensibility has allowed us to measure P branch components up to P_{24}. Though the intensities of rotational lines vary inside the band and with discharge parameters within more than two orders of magnitudes, the recording system, with checked linearity of 10^5, allowed measurements of the intense lines with 2% of accuracy. For the weakest lines the restriction in the accurate detection (less than 20%) are consequence of two different reasons—the noise of the registration system for low pressure and discharge current and the fluctuation of continuum for the pressure above 40 Torr, as shown on Fig.2a,b.The measurements have been performed over currents p = 2.6–70 Torr, i = 10–100 mA.

3. RESULTS AND DISCUSSION

The intensity $I_{n''v''N''}^{n'v'N'}$ of a rotational line, written in the usual way [7] is

$$I_{n''v''N''}^{n'v'N'} = M_{N'} hc \nu_{N'N''}^{*} A_{n''v''N''}^{n'v'N'}, \tag{1}$$

where $M_{N'}$ is the population of the upper level (n', v' , N') , $\nu_{N'N''}^{*}$ is wave frequency and $A_{n''v''N''}^{n'v'N'}$ is the probability for the transition, which in the Born-Oppenheimer approximation can be expressed as

$$A_{n''v''N''}^{n'v'N'} = a \frac{(\nu_{N'N''}^{*})^3}{2N'+1} S_{N'N''} \ .$$

Here a is a constant, characterizing the electron-vibration transition, and $S_{N'N''}$ is the Hőnl-London factor of the particular rotation line. The He_2 S-state is accepted to be in pure "b" Hund`s case, so the calculation of for the transition $3s\sigma d^3\Sigma^+_u(v = 0) \rightarrow 2p\pi e^3\Pi_g(v = 0)$ is reliable[7]. Therefore, the ratio $I_{NN'}/S_{NN}$ is characterizing, in relative units, the distribution of the exited molecules of given electron-vibration state along the rotation levels with different energy and, for the case of Boltzmann distribution the relation

$$\ln\left(\frac{I_{N'N''}}{S_{N'N''}}\right) = \frac{A - F_{N'}}{kT} \tag{2}$$

should hold. Here $F_{N'}=B_v N(N+1)$ is rotational term of the upper electron-vibration level, N is the rotational quantum number, T – the so called "rotational temperature". The constant $B_v = B_e - \acute{a}_e(v+1/2)$, where for the state $3s\sigma d^3\Sigma^+_u$ B_e = 7,34 cm^{-1} and $\acute{a}_e$ = 0,224 cm^{-1}[13].

Our results reviled, that linearly of $\ln\left(\frac{I_{N'N''}}{S_{N'N''}}\right)$ from the rotation energy $F_{N'}$ do not realize for the whole range of current (2–100 mA) and pressure (2.6–70 Torr) values. In most cases there is a given energy F_{N_0} such that, for $F_{N'} > F_{N_0}$ $\ln\left(\frac{I_{N'N''}}{S_{N'N''}}\right)$ decrease much slower than linear dependence (2). This means that the intensities of rotational lines, emitted from the upper levels are stronger than expected; therefore, the assumption for Boltzmann distribution is not entirely correct. This phenomena is most prominent when the pressure is low (small densities of neutrals) and small current. The difference between Boltzmann distribution and the observed one decrease with pressure and current growth (Fig.4) and almost disappears for i = 80–100 mA and p = 70

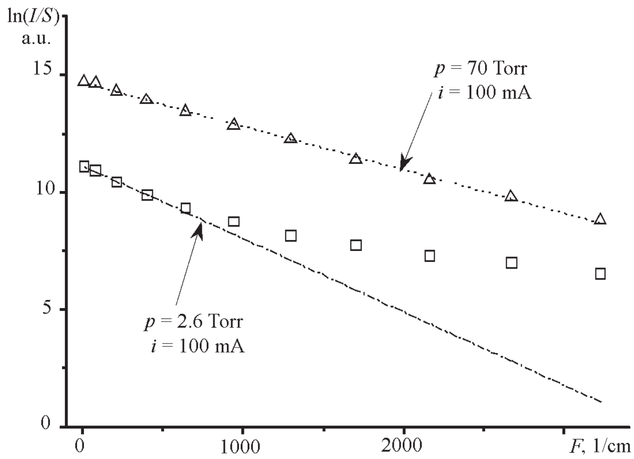

Fig. 4. A comparison of the experimental data by different conditions and a Boltzmann distribution (the broken lines) with T_{rot}, defined from the linear part of the experimental dependence (all 11 points by p = 70 Torr and only 4 points by p = 2.6 Torr)

Torr. In all of the cases, there is an initial linear part in $\ln\left(\frac{I_{N'N''}}{S_{N'N''}}\right)(F_{N'})$ dependence (first 4 points for p = 2.6 Torr and 9 points for p = 70 Torr). Therefore, when the pressure is high enough ($p \geq 60$ Torr) the rotational temperature T_{rot} does not depend on how many points are used for its calculation and Boltzmann distribution with such T_{rot} is a good fit of the experimental data. On the other hand, for the positive column of glow discharge of He_2 is possible to estimate the gas-kinetic temperature T_g through the heat transfer equation [6]. The comparison between T_g and T_{rot}, determined in our experiment shows a coincidence for $p \geq 60$ Torr and $i \geq 60$ mA. Hence, the rotation relaxation is effective for observed lines for these conditions. On the other hand, it appears useless to speak about Boltzmann distribution for $p <$ 40 Torr and $i < 40$ mA. Furthermore, there is a considerable difference between both temperatures for $p \leq 40$ Torr ($T_{rot} > T_g$) and this difference increases when p and i go down, so it is possible to claim as incorrect determination of T_g on the base of rotational lines intensities for $p < 60$ Torr.

The population of a rotational level can be expressed from the measured intensities as follows:

$$M_{N'} = b\frac{I_{N'N''}}{S_{N'N''}}\frac{(2N'+1)}{(\nu^*_{N'N''})^4}. \quad (3)$$

The observed populations might been result of embarrassed thermalization of the levels with energy gaps sufficiently larger than mean neutral component energy. The other explanation might been eventual presence of high temperature source. It is hard to believe the strikes with neutral particles are not dominant process in the population forming especially for down-lied levels. This assertion becomes transparent when one looks on Fig.5, where depending is shown for different *p* and *i*.

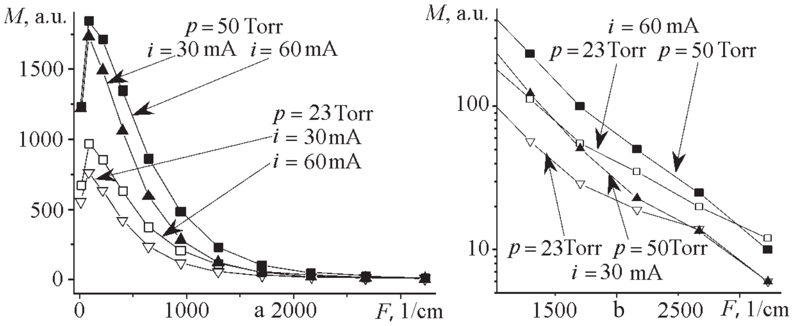

Fig. 5. The distribution of exited molecules of electron-vibration state $3s\sigma d^3\Sigma^+_u(v = 0)$ along the rotation levels *F*. On Fig.5 b) is shown the end of the same dependence, but *M* is in log scale in order to see clearly the similarity between *M* for $N > 11$ when the pressure is different but the current is the same

There is similarity between initial *M* values for different currents but equal pressures and also between $M_{N'}$ for $N > 11$ when the pressure is different but the current is the same. According to our point of view, the population of down-lied levels is achieved through processes depending on the pressure factor (and, hence, the mediator is the neutral component) and the one of the upper-lied–through charged particles.

The population of the low-energy rotational levels in state $3s\sigma d^3\Sigma^+_u(v = 0)$ has been formed dominantly by processes connected with plasma neutral component. The corresponding temperature T_g of this component has appeared to be a natural but not sufficient parameter for molecules distribution description within rotational band. It is necessary, however, to take into account other process also when one considers population of the high-energy levels, especially when the rotational relaxation is embarrassed (low pressure). The investigations on this field are in progress.

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