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PLASMA INVESTIGATIONS =

# Spectra, Line Intensities of the $C^1\Sigma_g^+ \Rightarrow A^1\Sigma_u^+$ and $c^3\Sigma_g^+ \Rightarrow a^3\Sigma_u^+$ Transitions in Liquid Normal He, and Rotational Level Populations of the $C^1\Sigma_g^+$ and the $c^3\Sigma_g^+$ Terms

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Abstract—We observed the rotational spectral lines of the He<sup>\*</sup><sub>2</sub> excimer within the range of 910–930 nm in the corona discharge in normal liquid He at the temperature of 4.2 K and the pressure of 1 atm. The spectral range is filled with the rotational lines of the  $C^{1}\Sigma_{g}^{+} \Rightarrow A^{1}\Sigma_{u}^{+}$  singlet and the  $c^{3}\Sigma_{g}^{+} \Rightarrow a^{3}\Sigma_{u}^{+}$  triplet transitions. These transitions end at the rotational levels of the lowest metastable terms,  $A^{1}\Sigma_{u}^{+}$  and  $a^{3}\Sigma_{u}^{+}$  of the He<sup>\*</sup><sub>2</sub> excimer. Then, the population of the rotational levels with the K' number of the upper  $C^{1}\Sigma_{u}^{+}$  and  $c^{3}\Sigma_{u}^{+}$  terms (the quantity of the molecules with the rotational moment of K' in the excited molecule ensemble in the discharge) is proportional to the intensity of the rotational lines marked K' of the  $C^{1}\Sigma_{g}^{+} \Rightarrow A^{1}\Sigma_{u}^{+}$  singlet and the  $c^{3}\Sigma_{g}^{+} \Rightarrow a^{3}\Sigma_{u}^{+}$  triplet. The populations might be calculated according to the experimental intensities of the rotational spectral lines. The emitting corona plasma in the liquid He is nonequilibrium and the rotational level populations do not correspond to the Boltzmann distribution. The efficient rotational temperature exceeds the liquid He temperature, 4.2 K.

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#### **INTRODUCTION**

The liquid helium luminescence spectra were first observed in [1]; authors created the helium ionization by the fast particles emitted from the radioactive substance grains. These spectra were qualified as the vibro-rotational emission bands of the  $He_2^*$  excimer molecules. Then, similar spectra were observed in the liquid helium irradiated by the fast electron beam [2, 3]. Later on, the investigations moved into the domain where the liquid helium resided in the microdroplet form and was irradiated by the fixed frequency synchrotron emission [4].

In [5, 6], we focused on the atomic and the molecular spectra of the liquid helium. We analyzed the molecular bands emitted by the corona discharge in the normal liquid helium at the temperature of 4.2 K. The liquid helium luminescence is produced by the corona discharge near the 2  $\mu$ m tip electrode at the voltage of several kV. We analyzed the radiation spectrum within the wavelength range of 910–930 nm

filled with the rotational lines of the upper terms,  $C^1 \Sigma_g^+$ and  $c^3 \Sigma_g^+$ . The radiation transitions from those terms

end at the rotational levels of the lowest metastable terms,  $A^{1}\Sigma_{u}^{+}$  and  $a^{3}\Sigma_{u}^{+}$  of the He<sup>\*</sup><sub>2</sub> excimer. The population of the rotational levels with the *K* number belonging to the upper  $C^{1}\Sigma_{g}^{+}$  and  $c^{3}\Sigma_{g}^{+}$  terms (the quantity of the molecules with the rotational moment of *K* in the excited molecule ensemble in the discharge) is proportional to the rotational line intensities with *K* number. This population might be calculated from the experimental intensity values. The performed analysis shows that the corona plasma emission in the liquid helium is nonequilibrium and the distribution of the rotational level with the number of *K* is not the Boltzmann distribution. Herewith, the efficient rotational temperature of the obtained nonequilibrium distribution exceeds 4.2 K—the liquid helium temperature.

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#### **EXPERIMENT**

To investigate the spectra of the liquid helium luminescence at the different pressures up to 50 atm, we established an unique facility. In this paper, we present the results of the experiments in the liquid helium at the temperature of 4.2 K and the pressure of 1 atm. We give the main attention to the spectra observed within the wavelength range of about 920 nm corresponding to the

radiation transitions  $C^1\Sigma_g^+ \Rightarrow A^1\Sigma_u^+$  and  $c^3\Sigma_g^+ \Rightarrow a^3\Sigma_u^+$  in the liquid helium.

We excited helium at the temperature of 4.2 K and the pressure of 1–50 atm by the negative and the positive polarity corona discharge [5, 6]. The intensity of the visible light emitted from the zone near the tip electrode was enough for spectroscopic analysis. We gathered the light emitted from that zone onto the input slit of the SpectraPro-300i spectrograph (300-mm focal length, f/4.0 aperture) equipped with three diffraction gratings (150 grooves/mm and two of 1200 gr./mm, applied in the 750-nm and 300-nm ranges, respectively). The 2D-CCDTKB-UV/AR sensor is located directly on the output spectrograph plane. Its dimensions are  $12.3 \times 12.3$  mm, with 512 × 512 pixels and each pixel,  $24 \times 24 \mu m$ .

To reduce the parasitic current, we cooled the sensor to 153 K (the parasitic current less than 1e/pixel/hour at 153 K). We measured the slit broadening of the spectral lines on the base of the profile of the argon lines emitted by low pressure discharge; it equalled  $\Delta \lambda =$ 0.098 nm for the 1200 gr./mm grating. We gathered the light emitted by the corona and investigated its spectrum within the different domain of the 500-1080 nm range. We identified the atomic lines corresponding to the radiation transitions between the excited states of the He\* atom states and the molecular spectra of the  $He_2^*$  excimer. At the low pressure, the lines are narrow and their position corresponds to the atomic lines and to the molecular spectra in the rarified gaseous helium. Strong spectral continuum within the whole investigated wavelength range occurs in the spectra at the pressures above P = 50 atm. Besides, the line width increases with the pressure increase and their intensity decreases. Above 60 atm, we observed neither atomic lines nor radiation transitions of the  $He_2^*$  excimer. The atomic spectral lines demonstrate the blue shift and the broadening, increasing with the pressure increase.

At the present facility, we obtain a number of results. For the wavelength of 660 nm and 640 nm corresponding to the transitions between the  $d^{3}\Sigma_{u}^{+}$ ,  $D^{1}\Sigma_{u}^{+}$  and the  $b^{3}\Pi_{g}$ ,  $B^{1}\Pi_{g}$  terms, we trace the spectra shape metamorphose (the line shift and width) with the pressure increase [6]. When using the 1200 gr./mm grating, we obtained the spectra resolving the rotation lines of those molecular transitions. The rotational structure is resolved at the pressures of 1–2 atm. The nonresolved electron-vibrational-rotational structure

registered at 6 atm is similar to the spectrum obtained in [2] where the superfluid HeII was excited by an electron beam. The measured shift of the rotational lines is in good agreement with the experimental data [3] obtained in the superfluid HeII at 1.7 K. Note that the rotational structure of the  $D^1\Sigma_u^+ \Rightarrow B^1\Pi_g$  singlet and of the  $d^3\Sigma_u^+ \Rightarrow b^3\Pi_g$  triplet bands resolved for the pressures below 2 atm [6] is similar to the spectrum observed at luminescence of the liquid He drops excited by the synchrotron emission [4]. The shortwave shift of the 706.5 nm atomic line amounts to 8 nm at the high pressures and its value is comparable to the line broadening.

#### STRUCTURE OF THE ROTATIONAL LEVELS OF THE *C* AND *A* SINGLET AND THE *c* AND *a* TRIPLET TERMS

We recall the designations of the excited states of

the He<sub>2</sub><sup>\*</sup> molecule (excimer). The electron state corresponds to a particular term. The term is the molecule energy as the function of the distance between the atoms, *R*. Figure 1 shows the examples of the term designations. In the present work, we consider the  $C^{1}\Sigma_{g}^{+}$ and  $c^{3}\Sigma_{g}^{+}$  terms (the upper terms with higher energy) and the  $A^{1}\Sigma_{u}^{+}$ , and  $a^{3}\Sigma_{u}^{+}$  terms (lower terms with lower energy). Each term has a minimum at  $R \approx 1$  Å; near that minimum, the atoms vibrate with the different quantum number v = 0, 1, 2, etc. Here, we consider the transitions between the v' = 0 vibrational states of the upper terms and the v'' = 0 of the lower terms. Then, the molecule rotates; each rotation is characterized by the quantum numbers *K* and *J* (see below).

The wave function of the vibrational-rotational state of the term  $\Sigma$  is symmetric against the nuclei



**Fig. 1.** Terms of the excited states of the He<sub>2</sub><sup>\*</sup> excimer: the upper terms,  $C^{1}\Sigma_{g}^{+}$ , and  $c^{3}\Sigma_{g}^{+}$ , and the lower terms,  $A^{1}\Sigma_{u}^{+}$ , and  $a^{3}\Sigma_{u}^{+}$ , are marked by the arrows.

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transposition if the term is even and has the positive sign or it is odd and has the negative sign [7]. The upper terms,  $C^1\Sigma_g^+$ , and  $c^3\Sigma_g^+$ , are even (with the *g* index) and, for the symmetric state, they should have the positive sign. The sign of the rotational state of the  $\Sigma_g^+$  term is  $(-1)^K$ , where the quantum number of the rota-

 $\Sigma_g^+$  term is  $(-1)^K$ , where the quantum number of the rotational state,  $K = \Lambda$  (the electron orbital moment) + N (the rotational moment of the nuclei), is the total rotational moment of the molecule without the spin. So,

the *K* quantum numbers of the  $C^{1}\Sigma_{g}^{+}$  term (the *b* Hund case) are even:  $K = \Lambda, \Lambda + 2, \Lambda + 4 = 0, 2, 4...$ 

The lower terms,  $A^{1}\Sigma_{u}^{+}$  and  $a^{3}\Sigma_{u}^{+}$ , are odd (the *u* index) and their rotational states should have the negative sign. Thus, the *K*<sup>n</sup> quantum numbers of the rotational levels of the  $A^{1}\Sigma_{u}^{+}$  and the  $a^{3}\Sigma_{u}^{+}$  terms (the *b* Hund case) are odd and have  $K^{n} = \Lambda + 1, \Lambda + 3, ... = 1, 3...$ 

## TRANSITIONS BETWEEN THE ROTATIONAL LEVELS OF THE $C^{1}\Sigma_{g}^{+}$ , $A^{1}\Sigma_{u}^{+}$ AND THE $c^{3}\Sigma_{g}^{+}$ , $a^{3}\Sigma_{u}^{+}$ TERMS

Each spectral line corresponds to the radiation transition between the rotational levels of the upper and the lower terms. The levels are characterized by the quantum numbers, K, of the rotation moment of the molecule.

Variation of the *K* quantum number of the radiation transition between the rotational levels corresponds to  $\Delta K = K - K'$ , where *K* and *K''* are the rotational numbers of the upper and the lower levels [7]. Figure 2 shows these levels and the transitions between them. The differences are combined into the groups (the branches), such as

*P*-branch:  $\Delta K = K - K'' = -1$  and K'' = K + 1, *R*-branch:  $\Delta K = K - K'' = +1$  and K'' = K - 1.

Usually, the transitions between the rotational levels are designated by the number K'' – the number of the lower level of the transition. To calculate the population of the upper level with the number K, we need the line intensities and the Hönl-London factors as the functions of the upper level number, K. These parameters are usually presented as the functions of the total rotational moment, J'', of the lower transition level. The K connection with J'' differs for the different branches and the calculations of this connection should be performed separately for each branch. The transitions between the rotational levels of the  $C^{1}\Sigma_{\mu}^{+}$ and the  $A^{1}\Sigma_{u}^{+}$  singlet terms are schematically presented in Fig. 2. Actually, the levels are not equidistant and the transition wavelengths are different. Hereafter, we will consider the lines of the particular P or R branch with the K number. Here, K is the torque of the molecule without the spin. The K numbers for the upper



**Fig. 2.** Rotational levels of the singlet terms,  $C^{1}\Sigma_{g}^{+}$  and  $A^{1}\Sigma_{u}^{+}$ , and the transitions between them.

term,  $C^{1}\Sigma_{g}^{+}$ , levels are even and the *K*" numbers for the lower term,  $A^{1}\Sigma_{u}^{+}$ , are odd. The quantum numbers of the torques of the upper levels, *K*', are taken as the transition designation.

The structure of the rotational levels of the triplet upper,  $c^{3}\Sigma_{g}^{+}$ , and lower,  $a^{3}\Sigma_{u}^{+}$ ,—terms is more complicated. The triplet terms have the spin equal to unity. The upper triplet term,  $c^{3}\Sigma_{g}^{+}$ , has the electron orbital moment equal to zero and the spin equal to unity:  $\Lambda = 0$ , S = 1 ( ${}^{3}\Sigma$ -state); the 2S + 1 = 3 value is the multiplicity of the term. The eigenfunction of the He<sup>2</sup><sub>2</sub> molecule state should be "symmetric" against the nuclei transposition [7], According to the above stated rule, the term is "symmetric" if it is even and has the positive sign or it is odd and has the negative sign. The  $c^{3}\Sigma_{g}^{+}$ term is even (the *g* index) and its state is symmetric at the positive sign. The term  $\Sigma^{+}$  sign equals  $(-1)^{K}$  where *K* is the total moment of the molecule without the spin. The *K* quantum numbers of the  $c^{3}\Sigma_{g}^{+}$  term rotational levels (the *b* Hund case) are even and equal  $K = \Lambda$ ,  $\Lambda + 2$ ,  $\Lambda + 4 = 0$ , 2, 4....

The lower term,  $a^{3}\Sigma_{u}^{+}$ , differs from the upper term,  $c^{3}\Sigma_{g}^{+}$ , in the evenness (the *u* index instead of the *g* index). The  $a^{3}\Sigma_{u}^{+}$  term is odd and its state is symmetric if the sign is negative. The sign of the rotational states of the  $\Sigma^{+}$  term equals  $(-1)^{K}$ , so the quantum numbers K'' of the  $a^{3}\Sigma_{u}^{+}$  term levels (the *b* Hund case) are odd:  $K'' = \Lambda + 1, \Lambda + 3, 5...$ 

Each *K*-level of the triplet term is degenerate and includes three levels with the different *J* number: J = K - 1, J = K, and J = K + 1, where *J* is the quantum number of the total moment of the molecule with account for the spin. The energy separating those three levels is negligible and those levels combine into the single level with the number of *K*. Thus, the spectral



Fig. 3. Layout of the rotational levels and the transitions

between the triplet terms,  $c^{3}\Sigma_{g}^{+}$ ,  $a^{3}\Sigma_{u}^{+}$ : the main transitions are marked by the vertical arrows; the transition (spectral line) indication is given for the *P*- and the *R*-branches; the transition (spectral line) number is the number, *K*', of the upper transition level.

line with the K number consists of three lines with the different J numbers (Fig. 3).

Fig. 3 shows the transitions between the rotational levels of the  $c^{3}\Sigma_{g}^{+}$  and the  $a^{3}\Sigma_{u}^{+}$  triplet terms. Take  $\Delta J = J' - J''$  to equal the change of the total molecule moment, *J*; here, *J* and *J''* are the total moments of the upper and the lower levels [8]. The selection rules for the radiation transitions are as follows:  $\Delta J = +1$  for the *R*-branch and  $\Delta J = -1$  for the *P*-branch.

The selection rules for the *K* quantum numbers are similar:  $\Delta K = +1$  for the *R*-branch and  $\Delta K = -1$  for the *P*-branch. If  $\Delta K = \Delta J$ , then the transitions are the principal. Six principal transitions exist: *P*1, *P*2, *P*3, *R*1, *R*2, and *R*3. The transition designated *K* includes three transitions (the multiplet) with the different *J*. The digit "1" (e.g. *P*1) means the *P*-branch transition from the level with the maximal *J* in the multiplet, the digit "3" (e.g. *P*3) – from the level with the minimal *J* in the multiplet. Each of these lines corresponds to the transition from the *J*-th multiplet level of the *K*"-th upper term to the *J*"-th multiplet level of the *K*"-th term. The *R*-brunch transitions are J'' = J' - 1. The principal transitions

sitions of the *R*-branch are  $K \Rightarrow K' = K - 1$  and J' = J - 1). The *P*-branch transitions-J' = J + 1 (Fig. 3).

#### CALCULATION OF THE ROTATIONAL LINE WAVELENGTH

To calculate the wavelengths of the transitions between the  $C^1\Sigma$  and the  $A^1\Sigma$  singlet terms, we took the spectral constants,  $B_e$ ,  $\alpha$ , and  $D_v$  from [8–11]. Consider the rotational structure of the transitions between the vibrational levels (v' = 0, v'' = 0). The energy of that transition equals 10945.5 cm<sup>-1</sup> [8] – it is the "head" of the 913.62 nm wavelength band. The K' = 0 level is the "zero energy" level of the upper term,  $C^1\Sigma$ , and the K'' = 1 level, the "zero energy" level of the lower term,  $A^1\Sigma$ .

The spectral parameters are

$$B_{\nu}(C^{1}\Sigma) = B_{e} - \alpha(\nu + 1/2) = 6.945 \text{ cm}^{-1},$$
$$B_{\nu}(A^{1}\Sigma) = 7.672 \text{ cm}^{-1},$$
$$D_{\nu}(^{1}\Sigma) = 5.24 \times 10^{-4} \text{ cm}^{-1}.$$

The energy of the  $K \Rightarrow K'$  transition between the rotational levels of the  $C^{1}\Sigma$  and the  $A^{1}\Sigma$  terms is

$$E_{K}(C^{1}\Sigma) - E_{K''}(A^{1}\Sigma)$$
  
=  $B_{v}(C^{1}\Sigma)K'(K+1) - D_{v}(C^{1}\Sigma)$   
×  $[K'(K+1)]^{2} - B_{v}(A^{1}\Sigma)K''(K''+1)$   
+  $D_{v}(A^{1}\Sigma)[K''(K''+1)]^{2} + E_{0},$ 

where  $D_v$  is the parameter characterizing the term anharmonicity.

The *P*-branch: K'' = K + 1. The energy,  $E_{K'K''}$ , between the rotational levels, K and K'', as the function of the number, K', of the upper level of the *P*-transition is

$$E_{K'K''} = 6.945 [\text{cm}^{-1}]K'(K'+1) - D_{v}[K'(K'+1)]^{2}$$
  
- 7.672 [cm<sup>-1</sup>](K'+1)(K'+2)  
+ D\_{v}[(K'+1)(K'+2)]^{2}.

The wavelengths for the P-branch lines with the different K are calculated as

$$\lambda_{P}(K') = \frac{913.62 \text{ [nm]}}{\left(1 + \frac{E_{KK'+1}}{E_{0}}\right)} = \frac{913.62 \text{ [nm]}}{\left(1 + \frac{6.945K'(K'+1) - 7.672(K'+1)(K'+2) + 21 \times 10^{-4}(K'+1)^{3}}{10945.5}\right)}$$

As the  $E_{KK'}$  value for the *P*-branch is negative, then the *P*-branch lines are located at the red side as against the center of the 913.62 nm band and their wavelengths for K = 0, 2, 4, 6... equal  $\lambda_P(0) =$  914.9 nm,  $\lambda_P(2) = 917.8$  nm,  $\lambda_P(4) = 921.28$  nm,  $\lambda_P(6) = 925.22$  nm, etc.

The *R*-branch: K'' = K - 1. The energy between the rotational lines of the *K* and *K''* levels of the  $C^{1}\Sigma$  and

the  $A^{1}\Sigma$  singlet terms as the function of the K upper level number corresponds to

$$E_{KK''} = 6.945 \,[\mathrm{cm}^{-1}]K'(K'+1) - D_{\mathrm{v}}[K'(K'+1)]^2 - 7.672 \,[\mathrm{cm}^{-1}](K'-1)K' + D_{\mathrm{v}}[(K'-1)K']^2.$$

The wavelength of the R-branch lines with the different K numbers is determined as

$$\lambda_{P}(K) = \frac{913.62 \text{ [nm]}}{\left(1 + \frac{E_{KK'-1}}{E_{0}}\right)}$$
$$= \frac{913.62 \text{ [nm]}}{\left(1 + \frac{6.945K'(K'+1) - 7.672(K'-1)K' - 21 \times 10^{-4}K'^{3}}{10945.5}\right)}.$$

The *R*-branch lines are located at the violet side as against the 913.62 nm band center because the  $E_{KK}$  is positive for the *R*-branch. The wavelengths with the different *K* are  $\lambda_{K=2} = 911.4$  nm,  $\lambda_{K=4} = 909.7$  nm,  $\lambda_{K=6} = 908.6$  nm, and  $\lambda_{K=8} = 907.9$  nm.

The line wavelengths for the *P*- and the *R*-branches of the singlet  $C^{1}\Sigma \Rightarrow A^{1}\Sigma$  transitions coincide with the data [9].

Similarly, the wavelengths of the rotational lines of the rotational transitions between the triplet  $c^{3}\Sigma$  and  $a^{3}\Sigma$  terms are calculated. The spectral constants for the triplet transition calculations differ from those for the singlet transitions and are taken from [4, 7, 8]:

$$B_{\nu}(c^{3}\Sigma) = B_{e} - \alpha(\nu + 1/2) = 6.855 \text{ cm}^{-1},$$
  

$$B_{\nu}(a^{3}\Sigma) = 7.586 \text{ cm}^{-1},$$
  

$$D_{\nu}(a^{3}\Sigma) = 5.62 \times 10^{-4} \text{ cm}^{-1},$$
  

$$D_{\nu}(c^{3}\Sigma) = 5.58 \times 10^{-4} \text{ cm}^{-1}.$$

The K = 0 level is the "zero energy" level for the upper term,  $c^{3}\Sigma$ , and the K'' = 1, the "zero energy" level for the lower term,  $a^{3}\Sigma$ . The energy between those levels  $E_{0} = 10889.48 \text{ cm}^{-1}$  [7] is the "center" of the 918.32 band. The energy of the  $K \Rightarrow K''$  transition is

$$E_{K'} - E_{K''} = 6.855 \,[\text{cm}^{-1}] \, K'(K'+1)$$
  
- 7.586 [cm<sup>-1</sup>] K''(K''+1) + D<sub>v</sub>[K''(K''+1)]<sup>3</sup>  
- D<sub>v</sub>[K'(K'+1)]<sup>3</sup> + E<sub>0</sub>.

Using the relations between the K' and the K'' for the different branches, we obtain the wavelengths for the different lines of those branches.

The *P*-branch: K'' = K' + 1. The energy between the rotational lines of the transition between the *K* and the *K*'' levels is

$$E_{KK''} = 6.855[\text{cm}^{-1}]K(K+1) - D_{v}[K(K+1)]^{2}$$
  
- 7.586[cm]^{-1}(K+1)(K+2)  
+ D\_{v}[(K+1)(K+2)]^{2}.

The wavelength of the P(K)-branch lines with the K number is calculated according to the formula

$$\lambda_{P}(K') = \frac{918.32 \text{ [nm]}}{\left(1 + \frac{E_{KK'+1}}{E_{0}}\right)} = \frac{918.32 \text{ [nm]}}{\left(1 + \frac{6.855K'(K'+1) - 7.586(K'+1)(K'+2) + 22.4 \times 10^{-4}(K'+1)^{3}}{10889.48}\right)}$$

The *P*-branch lines are on the red side as against the center of the 918.32 nm group as the  $E_{K'K'}$  for the *P*-branch is negative. Their positions for the different *K* correspond to  $\lambda_P(0) = 919.6$  nm,  $\lambda_P(2) = 922.54$  nm,  $\lambda_P(4) = 926$  nm,  $\lambda_P(6) = 930$  nm, etc.

The *R*-branch: K'' = K - 1. The energy between the rotational lines of the K' and K'' level transition is

 $E_{KK'} = 6.945 \,[\mathrm{cm}^{-1}]K'(K+1) - 7.672 \,[\mathrm{cm}^{-1}] \\ \times (K'-1)K' - D_{\mathrm{v}}[K'(K+1)]^2 + D_{\mathrm{v}}[(K'-1)K']^2.$ 

The *R*-branch wavelength with the K number is calculated according to the formula

$$\lambda_{R}(K') = \frac{918.32 \text{ [nm]}}{\left(1 + \frac{E_{KK'-1}}{E_{0}}\right)} = \frac{918.32 \text{ [nm]}}{\left(1 + \frac{6.855K'(K'+1) - 7.586(K'-1)K' - 22.4 \times 10^{-4}K'^{3}}{10889.48}\right)}$$

For the *R*-branch, the  $E_{KK}$  is positive and the wavelengths of the lines with the different *K* are  $\lambda_R(2) = 916$  nm,  $\lambda_R(4) = 914.5$  nm,  $\lambda_R(6) = 913.3$  nm,  $\lambda_R(8) = 912.7$  nm, etc.

The wavelengths for the *P*- and the *R*-branch of the singlet and the triplet transitions coincide with the data [9].

Figure 4 shows the wavelength,  $\lambda_{K}$ , values and the numbers, *K*, of the *P*- and the *R*-branch lines. Each

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**Fig. 4.** Wavelengths,  $\lambda$ , and numbers, K, of the upper levels of the *P*- and the *R*-branch lines of the triplet and the singlet transitions,  $c \Rightarrow a$  and  $C \Rightarrow A$ : 1 - singlet, R; 2 - triplet, R; 3 - singlet, P; 4 - triplet, P.

symbol means the line wavelength (abscissa) and the number, K, of the upper level of the transition (ordinate). A lot of the *R*-singlet and the *R*-triplet lines concentrate in the vicinity of the 910 nm wavelength.

The line wavelength increases with the increase of the line number, K', for *P*-brunch singlet and the triplet. For the *R*-branch lines, this dependence is ambiguous. The wavelength interval from 908 nm to 915 nm is filled with a lot of the *R*-lines of both branches.

#### THE HÖNL–LONDON FACTORS OF THE SINGLET AND THE TRIPLET TRANSITIONS

The intensity of the rotational spectral line equals the product of the population of the upper rotational level, p(K), and the Hönl–London factor, S(K), of the  $K \Rightarrow K''$  transition. The Hönl–London factors, S(K), of the transitions between the rotational levels of the  $C^{1}\Sigma_{g}^{+}$  and the  $A^{1}\Sigma_{u}^{+}$  singlets are presented in Table 1 [8]. These factors differ for the different branches.

Consider the Hönl–London factors of the triplet transitions [8]. Each transition,  $K \Rightarrow K''$ , includes three transitions between the multiplet levels. The Hönl–London factors for the *Q*-branch transitions equal zero as there is no *Q*-transitions between the rotational levels of the terms,  $c^3\Sigma_g^+ \Rightarrow a^3\Sigma_u^+$ . The

**Table 1.** The Hönl–London factors for the singlet transitions as the function of the upper rotational level number, K

Hönl–London factors, $S(K)$	Branch
$S_P(K=0, 2, 4) = K + 1$	Р
$S_R(K = 2, 4, 6) = K$	R

Hönl–London factors for the P- and the R-branches are given in Table 2 as the functions of the total moment, J'', of the lower level (the second and the sixth columns.

To calculate the rotational line intensities, the Hönl–London are needed as the functions of the upper level number, K. The relations between the J'' and the K' numbers differ for the P- and the R-branches; they are given in Table 2 (the fourth and the eighth columns).

The *P*-line intensity with the K number equals the sum of intensities of the three triplet lines; so, the Hönl–London factor of the K multiplet is

$$S_P(K') = \frac{(K'+1)(2K'+5)}{(2K'+3)} + \frac{(K'+2)K'}{(K'+1)} + \frac{(K'+1)(2K'-1)}{(2K'+1)} \approx 3.115K' + 1.667.$$

On the basis of the same argumentation, with correction for the different relations between the J'' and the K numbers (Table 2, the seventh column), we obtain, for the Hönl-London factors of the *R*-transitions as the functions of the upper level number, K,

$$S_R(K) = \frac{(2K+3)K}{(2K+1)} + \frac{(K+1)(K-1)}{K} + \frac{(2K-3)K}{(2K-1)} \approx 3.125K - 1.25.$$

The Hönl–London factors for the *P*- and the *R*-branches and their approximation are engaged in the calculations below.

#### ANALYSIS OF THE *C*–*A* SINGLET AND THE *c*–*a* TRIPLET LINES OF THE EXPERIMENTAL SPECTRA IN THE LIQUID HE AT 4.2 K

We analyzed the experimental data shown in Figure 5 with account for the wavelengths calculated according to above-presented formulas. Each intensity maximum has the wavelength close to that in vacuum [8]. The large intensity peak at  $\lambda \approx 919$  nm belongs to the P(K = 0) line of the *P*-branch transmittance of the  $c^{3}\Sigma_{g}^{+} \Rightarrow a^{3}\Sigma_{u}^{+}$  triplet (Figs. 5 and 6). The two lines on the larger wavelength side from the 919 nm maximum are the triplet lines, p(2) and p(4).

Interpretation of the spectral lines on the shorter wavelength side from the maximum is more difficult. The *R*-branch lines of the  $c^{3}\Sigma_{g}^{+} \Rightarrow a^{3}\Sigma_{u}^{+}$  triplet lay in the range of the shorter wavelengths than 915 nm (Figure 6). The *P*(0) line of the  $C^{1}\Sigma_{g}^{+} \Rightarrow A^{1}\Sigma_{u}^{+}$  singlet gives the evident intensity peak to the left from the main maximum, *p*(0) (Fig. 6).

Modeling of the experimental spectrum from Fig. 6 is performed as the superposition of the rotational lines with the Lorentz profile. We took the line width to

<i>P</i> <sub>1</sub> ( <i>J</i> ")	$\frac{(2J''+1)(J''-1)}{(2J''-1)}$	J'' = K + 2	$\frac{(K+1)(2K+5)}{(2K+3)}$	$R_1(J'')$	$\frac{(2J''+3)J''}{(2J''+1)}$	J'' = K	$\frac{(2K+3)K}{(2K+1)}$
<i>P</i> <sub>2</sub> ( <i>J</i> ")	$\frac{(J''+1)(J''-1)}{J''}$	J'' = K + 1	$\frac{(K+2)K}{(K+1)}$	$R_2(J'')$	$\frac{(J''+2)J''}{(J''+1)}$	J'' = K - 1	$\frac{(K+1)(K-1)}{K}$
$P_{3}(J'')$	$\frac{(2J''-1)(J''+1)}{(2J''+1)}$	J'' = K	$\frac{(K+1)(2K-1)}{(2K+1)}$	$R_{3}(J'')$	$\frac{(2J''+1)(J''+2)}{(2J''+3)}$	J'' = K - 2	$\frac{(2K-3)K}{(2K-1)}$

**Table 2.** The Hönl–London factors as the function of the quantum number, J", of the lower level [8] and the number, K, of the upper level

equal 0.58 nm and shifted the lines by 0.45 nm to the blue spectrum side. Thus, we state that the experimental lines are shifted by 0.45 nm to the blue side from their vacuum position. The shift of 0.45 nm and the line width of 0.58 nm are the functions of the pressure in the liquid [12]. This is the general argument in favor of the model where the excited He\* atom in the liquid is surrounded by an empty bubble. The bubble is the consequence of the long-ranging repulsion of the excited He\* atom and the He atom in the ground state.

The three *P*-branch lines of the p(0), p(2), p(4) triplet transmission (Fig. 6) have the wavelengths within the range of 920–927 nm and their intensity is sufficient for further calculation of the population of the upper rotational levels. A the *R*-branch lines, r(2) and r(4), of the triplet transmissions, the wavelengths are within the range of 914–916 nm. Their intensity is low and non-resolved. The R(0) line from the *R*-branch of the singlet transition is distinctly seen within the spectral range of 912–914 nm. The P(0) line from the singlet *P*-branch located nearby increases its intensity and prevents from its application the calculation of the population of the K = 0 singlet level.



**Fig. 5.** Experimental spectrum within the wavelength range of 907–928 nm measured in the corona discharge in the liquid helium at the temperature of 4.2 K and the pressure of 0.1 MPa.

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### POPULATIONS OF THE ROTATIONAL LEVELS OF THE $C^{1}\Sigma_{g}^{+}$ AND THE $c^{3}\Sigma_{g}^{+}$ , TERMS CALCULATED FROM THE ROTATIONAL LINE INTENSITIES

The intensity of the rotational line with the K number equals the product of the upper level population, p(K), and the Hönl–London factor, S(K), of the transition. The Hönl–London factors differ for the singlet and the triplet transitions and for the lines from the different branches. The intensity, I(K), and the population, p(K), of the upper term level are related by the expressions

$$\begin{split} I_{P}(K) &\propto \left(3.12K + 1.67\right) p(K), \quad K = 0, 2, 4 \dots; \\ I_{R}(K) &\propto \left(3.13K - 1.27\right) p(K), \quad K = 2, 4 \dots \end{split}$$

for the triplet rotational lines and by the expressions

$$I_{P}(K) \propto (K+1) p(K), \quad K = 0, 2, 4...;$$
  
 $I_{R}(K) \propto K p(K), \quad K = 2, 4...$ 

for the singlet lines. These expressions are applied to calculate the populations of the rotational levels of the upper terms as the function of the level number, K. For the equilibrium conditions, the populations



**Fig. 6.** Modeling of the spectrum observed in the corona discharge in the liquid helium within the wavelength range of 910–930 nm: near the maximums, the branch and the line number are given.



Fig. 7. Population distribution of the rotational levels of the upper triplet term,  $c^{3}\Sigma$ , calculated on the base of the experimental data obtained in the corona discharge in the liquid helium at the temperature of 4.2 K and the pressure of 0.1 MPa (*I*) and respective Boltzmann distribution (2).



**Fig. 8.** Spectral lines of the  $C^1 \Sigma_g^+ \Rightarrow A^1 \Sigma_u^+$  and the

 $c^{3}\Sigma_{g}^{+} \Rightarrow a^{3}\Sigma_{u}^{+}$  transitions in He at the pressure of 150 Torr and the temperature of 4.2 K (cryogenic gas at the saturation line) [13]: the lines are designated by the number of the lower transition level.

correspond to the Boltzmann distribution,  $p(K) \sim \exp(-B_e(K+1)K/T_r)$ , where  $T_r$  is the rotational temperature. Here, the  $\ln[p(K)]$  dependence on (K+1)K appears as the straight line in the chart. The sharper its slope, the lower the  $T_r$ .

We engaged the experimental spectrum to calculate the populations of the rotational levels of the upper terms,  $C^{1}\Sigma_{g}^{+}$  and  $c^{3}\Sigma_{g}^{+}$ . Preliminary analysis shows that the 910–920 nm spectral range (Fig. 6) is hardly applicable in that purpose. This spectral interval is filled with the singlet and the triplet lines of the different branches located close to each other, so that their profiles overlap. Thus, several close-lying lines contribute to the intensity maximums. We obtained reliable results when using the intensities of the three nonoverlapping *P*-lines belonging to the p(0), p(2), p(4) triplet and located within the wavelength range of 920–930 nm.

Figure 7 shows the calculation results. We see that the obtained distribution differs from the Boltzmann distribution with the temperature of 4.2 K. Low quantity of the spectral lines suitable for the analysis, due to the overlapping of the neighboring strongly broadened lines, is the main disadvantage of the technique proposed to calculate the population distributions of the upper rotational levels. The broadening is known to increase with the medium density increase; thus, hereafter, we analyze the spectrum obtained in the rarified cryogenic gas [13].

#### ANALYSIS OF THE *c*–*a* AND THE *C*–*A* TRANSITIONS OBSERVED IN THE CRYOGENIC GASEOUS HELIUM AT 4.2 K

Authors [13] initiated the luminescence by the proton beam hitting the gaseous helium at 4.2 K at the saturated vapor pressure of 150 Torr. That thermal state is at the gaseous branch of the saturation curve where the gas has low density. Figure 8 shows the spectrum of the c-a and the C-A transitions observed in [13]. In the present work, we interpret and model this spectrum. Figure 9 shows the results. The wavelength of the A-Csinglet and the a-c triplet rotational lines coincides with that of the insulated molecule lines. The line shift equals zero. The broadening of the lines is  $\Delta k = 9 \text{ cm}^{-1}$ corresponding to  $\Delta \lambda = 0.75 \text{ nm}$ . The Gauss profile better corresponds to the experimental line shapes



**Fig. 9.** Modeling of the spectrum observed in the proton irradiated gaseous He at 4.2 K on the saturation line (150 Torr,  $3.6 \times 10^{20}$  cm<sup>-3</sup>): the line width  $\Delta k = 9$  cm<sup>-1</sup> at the Lorentz (1) or the Gauss (2) profile; the *P*, *R* singlet and the *p*, *r* triplet branches.

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Rotational level population, arb. units



Fig. 10. Populations of the rotational K-levels of the upper

terms of the  $c^{3}\Sigma_{g}^{+}$  triplet (1, 2) and the  $C^{1}\Sigma_{g}^{+}$  singlet (3, 4) calculated from the experimental line intensities in the gas [13] and of the spectrum observed in the liquid helium in the present experiments (5) at 4.2 K: branches of the triplet 1, 5-p and 2-r; of the singlet 3-P and 4-R; 6-the Boltzmann distribution.

than the Lorentz profile – the last gives the larger line overlapping than in the observed spectrum. The spectral line shape distortion takes place due to the collisional interaction of the  $He_2^*$  excimer with the surrounding atoms; thus, the shift/width quotient is low: 0.15 for the collisional interaction; it gives the shift of  $9 \times 0.15 = 1.35$  cm<sup>-1</sup>—insignificant in Fig. 8.

Authors in [13] observed and identified sufficiently larger line quantity. They apply the line intensities obtained in the spectrum modeling to calculate the populations of the rotational levels of the singlet and the triplet terms. Figure 10 shows the calculation results. In the gas, they observed the lines with the same numbers, K, belonging to the same term but to the different branches, P and R. As those lines belong to the transitions from the same level, K, so the populations obtained from the P- and the R-line intensities should be equal (see Fig. 10). The population of the singlet levels is higher than that of the triplet levels, that is, in the ensemble, the quantity of the excited molecules in the singlet state with the zero spin is larger than that of the molecules with the spin equal to unity. This fact might give information on the mechanisms of formation of the molecules in one or another state.

The population of the levels in the cryogenic gas equals that obtained from the analysis of the spectrum in the liquid helium. It is a strange result because in the rarified gas, the emitting molecules or atoms are subjected to collisions by the surrounding atoms whereas in the liquid, are surrounded by the bubbles. In the last case, it is difficult to imagine the mechanism of the excited state formation and of the radiation transitions between them. Yet, the results of the first modeling of the atomic spectra [14] are in satisfactory agreement with the experiment.

Analysis of the data obtained in the cryogenic gas [13] gives the same results as the analysis of the present 173

is nonequilibrium, see the broken line in Fig. 10. For several rotational levels, K = 2, 4, 6, the line slope corresponds to the rotational temperature of 140 K, that is, above the medium temperature of 4.2 K. The populations of the rotational levels with the larger Kexceed essentially the Boltzmann populations [15].

#### **CONCLUSIONS**

The excited molecules form in the ionization zone of the corona discharge due to the interaction of the excited atoms in the  $2^{1}S$  and the  $2^{3}S$  states with the He atoms in the ground state. At short distances, that interaction is attractive. In the liquid, the excited He\* atoms are surrounded by the hollow bubbles. Such bubbles also surround the excited  $He_2^*$  molecules. Thus, the kinetics of the excited molecule formation is complicated. In the present experiment, we fixed the emission occurring at the transitions from the upper term levels to the lower term levels. The shape of the spectral lines of that emission is governed by the density distribution of the medium surrounding the emitting atom [13, 14, 16].

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