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A procedure for the determination of excitation temperatures of vibrational and rotational molecular levels in an atmospheric-pressure gas-discharge plasma with the use of the SPECAIR computer code has been proposed. To simplify and accelerate the processing of radiation spectra, calibration curves for the determination of vibrational and rotational temperatures by analyzing the emission bands of molecules OH(A-X), $N_2(C-B)$, $N_2^+(B-X)$, CN(B-X), and C_2 (d–a Swan transitions) were plotted. The method developed was tested by evaluating the plasma parameters of a discharge in the gas channel with a liquid wall.

1. Introduction

Optical emission spectroscopy is traditionally used for the diagnostics of atmospheric-pressure plasmas. Spectrometers with a high resolution and a small time of spectrum registration are very expensive, so they cannot be applied for monitoring the plasma parameters of technological objects. Therefore, a new approach in optical diagnostics has been intensively developed recently. It is based on the usage of spectrometers with a low resolution in a combination with computer simulation methods. The population temperatures (the electronic, T_e^* , vibrational, T_v^* , and rotational, T_r^* , ones) for corresponding excited levels in atoms and molecules in the plasma concerned are determined by comparing experimental spectra with the results of simulation carried out with regard for the instrument function of a real spectrometer that was used for the registration of emission spectra.

The most known computer codes for the simulation of emission spectra are LIFBASE [1] and SPECAIR [2] ones. The latter is more widespread, because it allows the absolute intensities of spectral radiation emission by gases and plasma with various compositions to be simulated, by considering not only the trapezoidal instrument function (the triangular function being its specific case), but also other functions with an arbitrary shape given by the user. The SPECAIR code simulates the radiation emission by such components as C, N, O, C_2 , CN, CO, N_2 , N_2^+ , NH, NO, O_2 , and OH in a wide range of temperatures and pressures under the assumption of local thermodynamic equilibrium (LTE). For the SPECAIR or an alternative code could be used to simulate an emission spectrum, four parameters (translational or gas-kinetic, electronic, vibrational, and rotational temperatures) must be given, the values of which substantially affect the shape of a calculated spectrum. A lot of time is taken by the fitting of simulation parameters carried on in order to obtain a good accordance between calculated and experimental spectra. For the sake of simplification and acceleration of the spectrum processing procedure, there exists an approach known from the literature [3, 4] and consisting in constructing the calibration curves which are functions of the temperature.

For instance, the review by Kitaeva and Alyamovskii [3] is devoted to the determination of the temperature of heated gases by analyzing the intensity of bands radiated by CN and C_2 with an unresolved rotational structure. The cited authors considered the case of thermodynamic equilibrium in the gas (hence, the gas temperature was assumed to be uniform) and presented curves for the determination of this temperature, which were plotted, by using the integral and maximal band intensities for the relevant molecules. The main shortcoming of the approach proposed is a complicated determination of integral intensities as the areas under corresponding curves. Moreover, the curves were constructed for spectrographs with a rectangular instrument function, which considerably restricted their usage in the case where the spectra are registered by spectrometers with more complicated shapes of instrument contours.

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In work [4], the authors proposed that the widths of band (0,2) N₂ (C–B) at the heights of 20 and 40% of the peak height (intensity) be used as functions of the rotational temperature. The calculations were carried out using the SPECAIR code with regard for the trapezoidal instrument function with a bottom base of 0.66 nm and a top base of 0.22 nm. However, since the band (0,2) overlaps with the band (1,3), it is very difficult to resolve them and determine the half-width at a fixed height, because the half-width changes, as the temperature varies, due to the influence of the neighbor band tail.

Therefore, the technique of linkage of the consideration to maximal intensities at fixed wavelengths is not very convenient as well, because, in the case of noise pollution of experimental spectra and neighbor band overlapping, it may result in substantial errors. Proceeding from this reasoning, we have proposed an approach to constructing curves which is based on a choice of characteristic maxima and minima (the characteristic heights at hump and dip points) in the vicinity of molecular band heads. We have examined general tendencies observed in the shape variation of electronic-vibrationalrotational emission bands, which depends on the corresponding population temperatures for vibrational and rotational molecular levels of molecules, and revealed spectral sections sensitive to a change of only one of the parameters (the vibrational or rotational temperature). The calibration curves for the determination of corresponding population temperatures from the emission spectra of OH (A–X), $N_2(C-B)$, N_2^+ (B–X), CN (B-X), and C_2 (d-a) molecules have been plotted in a wide range of temperatures ($T_v^\ast~=~2000~-~15000~{\rm K}$ and $T_v^* = 2000 - 15000$ K) with the help of SPECAIR code. Simulation was carried out, by taking the instrument function of a spectrometer into account, whose shape is close to the Gaussian. The developed technique was tested by evaluating the plasma parameters of a discharge in the gas channel with a liquid wall (DG-CLW) [5, 6].

2. Simulation Procedures

Radiation spectra of plasma-liquid systems demonstrate the intense and well-studied bands of hydroxyl OH. Therefore, the latter are effectively used for monitoring the rotational temperature (the gas-kinetic temperature) [7]. In work [4], a curve was proposed for the determination of the rotational temperature from the ratio between the intensities of R- and P-branches of (A–X) (0,0) band which is absolutely independent of the vibrational temperature T_v^* . The curve was con-

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structed for a trapezoidal instrument function with a bottom base of 0.66 nm and a top base of 0.22 nm. From the analysis of the curve, it becomes clear that the ratio between the intensities of R- and P-branches of (0,0) band (transition A–X) is sensitive to rotational temperature variations only at $T_r^* \leq 9000$ K. The authors of work [4] indicate that T_r^* should be determined carefully following this routine, because a growth of the plasma optical density could result in the reabsorption of those peaks. As a rule, the peak in the *P*-branch is more absorbed than that in the R-branch. Therefore, the rotational temperature, when being determined from the intensity ratio P/R, can be overestimated in comparison with its actual value. The cited authors also marked that the optical thickness of plasma depends on the plasma length, the OH concentration, and the temperature. For instance, absorption effects in a 1cm plasma at T = 2000 K can be neglected, if the molar fraction of water vapors is less than 1%. Certainly, in plasma-liquid systems, the concentration of water vapors can be higher. Therefore, the self-absorption in the intensive OH (A–X) (0,0) band cannot be neglected.

To exclude errors associated with reabsorption, we propose here that the less intense (1,0) and (2,1) bands of hydroxyl OH (A-X), which lie in the 280–290-nm interval–almost free from the overlapping with the bands from other molecules,– should be used to determine the population temperatures. In order to find the spectral range, which is sensitive to the variation of only the rotational or vibrational temperature, the SPECAIR-assisted simulations of hydroxyl OH (A–X) was done in a spectral interval of 275–301 nm for various vibrational temperatures at a fixed T_r^* , and for various rotational temperatures at a fixed T_v^* . The main simulation results are depicted in Fig. 1.

Figure 1,*a* demonstrates that the slope angle of (1,0) band at $\lambda = 283.1$ nm-the "red shadowing" (a spectral interval of 283.1–286.9 nm)–depends only on the rotational temperature and does not depend on T_v^* . That is why, at the first stage, we calculated the array of rotational temperatures at a fixed equidistant T_v^* 's, the constant increment being equal in this case to the accuracy of T_r^* -measurements (Fig. 1,*b*). The calculated spectra were normalized by the intensity of (1,0) band at $\lambda = 283.1$ nm. The characteristic heights A, B, C, and D were chosen at fixed humps and dips in the vicinity of bandheads. We also checked that the background D near the wavelength $\lambda \approx 273.8$ nm depended neither on the vibrational temperature T_v^* nor on T_r^* in a wide range of temperatures.



Fig. 1. Simulation results for hydroxyl OH (A–X) bands in the spectral interval of 275–301 nm. A and B are the maxima near the heads of bands (1,0) at $\lambda = 283.1$ nm and (2,1) at $\lambda = 288.35$ nm, respectively. C and D are the minima at about $\lambda = 286.87$ and 273.8 nm, respectively



Fig. 2. Curves for the determination of population temperatures T_r^* (a) and T_v^* (b) from the radiation bands (1,0) and (2,1) of hydroxyl OH (A–X) constructed taking the spectrometer instrument function into account, whose shape is close to the Gaussian with the FWHM = 0.6 nm

To simplify the T_r^* determination procedure, we plotted the dependences of the ratio (C - D)/(A - D) on the rotational temperature T_r^* (Fig. 2,a). At the next stage, to construct the calibration curve for determining T_v^* , we calculated the array of vibrational temperatures at a fixed T_r^* , which was found earlier (Fig. 1,a). The vibrational temperature can be determined from the curve exhibited in Fig. 2,b.

From Fig. 2, it is evident that the dependences obtained are functions of only one temperature (vibrational or rotational) in the range of parameters under consideration. Therefore, the temperature determination order has no meaning in this case.

In the case of the air plasma research or using nitrogen as a working gas, an effective diagnostic means is the analysis of the spectrum radiated by the second positive system of nitrogen $(C^3\Pi_u-B^3\Pi_g)$. Having simulated the spectra of the major components of a atmosphericpressure plasma-liquid system (N_2, N_2^+, NH, OH, NO) with the help of SPECAIR code, we determined the spectral intervals of 360–380 and 392–400 nm in the radiated spectrum of N₂ (C–B), where the overlapping with other spectral lines and bands is absent or minimal. Since (C-B) (0,3) and (1,4) bands of N₂ are weakly intense, it is better to use (0,2) and (1,3) bands in a spectral interval of 360–380 nm. Since the intensity of N₂⁺ (B–X) (0,0) band is low (approximately 2.7 times lower than the intensity of N₂ (0,2) band), its "violet shadowing" does not substantially affect the heads of (0,2) and (1,3) bands of N₂ (C–B) molecule. For those reasons, the interval of



Fig. 3. Simulation results for the radiation spectrum of N₂ (C–B) in a spectral interval of 360–380 nm. A and B are the maxima near the heads of bands (0,2) at $\lambda = 380.12$ nm and (1,3) at $\lambda = 375.1$ nm, respectively. C and D are the minima at about $\lambda = 376.19$ and 381.4 nm, respectively



Fig. 4. Curves for the determination of population temperatures T_v^* (a) and T_r^* (b) from radiation bands (0,2) and (1,3) of N₂ (C–B) constructed with regard for the spectrometer instrument function, the shape of which is close to the Gaussian with the FWHM = 0.6 nm

360–380 nm was selected to make diagnostics of population temperatures for vibrational and rotational levels of nitrogen molecules.

We simulated the radiation spectrum of N₂ (C–B) molecule in the interval of 360–380 nm for various vibrational temperatures at a fixed T_r^* and for various rotational temperatures at a fixed T_v^* , and determined spectral intervals that are sensitive to the variation of only one of the temperatures (Fig. 3).

Analogous curves for the determination of population temperatures for the vibrational and rotational levels of nitrogen molecule are shown in Fig. 4.

Figure 4,b testifies that the calibration curves for the determination of T_r^* at different T_v^* do not coincide with one another. This occurs because the height D depends

on both the rotational and vibrational temperatures. That is why it is necessary, first, to determine T_v^* from the curve (B-C)/(A-D) and, then, T_r^* using the collection of curves (C-D)/(A-D).

A similar approach was used, while considering the radiation spectrum of N_2^+ molecular ion, determining the sections of (0,0) and (1,1) bands, which are sensitive to the variation of corresponding population temperatures, and selecting the relevant characteristic heights A, B, C, and D to construct analogous curves (Fig. 5).

As is seen from Fig. 5,c, the curves for the determination of rotational temperatures coincide in the wide range $T_v^* = 3000 - 10000$ K. At the same time, we have a collection of curves for the determination of vibrational temperatures in the range $T_r^* = 3000 - 10000$ K



Fig. 5. (a and b) Simulation results for the radiation spectrum of N_2^+ (C–B) in the spectral interval of 360–380 nm. A and B are the maxima near the heads of bands (0,0) at $\lambda = 394.1$ nm and (1,1) at $\lambda = 388.4$ nm, respectively. C and D are the minima at about $\lambda = 388.9$ and 392.7 nm, respectively. (c and d) Curves for the determination of population temperatures T_r^* (c) and T_v^* (d) constructed taking the spectrometer instrument function into account, the shape of which is close to the Gaussian with the FWHM = 0.6 nm

(Fig. 5,d). Proceeding from this fact, we recommend to determine the rotational temperature firstly and the vibrational one afterwards.

A similar approach was used while considering (0,1)and (1,2) radiation bands of CN (B–X) and C₂ (d³IIa³II) molecules, determining the sections sensitive to a variation of the corresponding population temperatures, and selecting the characteristic heights A, B, C, and D (Fig. 6). The curves for the determination of vibrational and rotational population temperatures from (0,1) and (1,2) radiation bands of CN (B–X) and C₂ (d–a) molecules taking the spectrometer instrument function into account, which is close to the Gaussian with a full width at half minimum (FWHM) of 0.6 nm, are depicted in Fig. 7.

As is seen from Figs. 7,*a* and *b*, for a molecule CN (B–X), we have a family of curves for the determination of both temperatures. At the same time, for a molecule C_2 (d-a), the curves obtained (Figs. 7,*c* and *d*) are func-

tions of only one temperature, so that the order of determination of rotational and vibrational temperatures is insignificant.

3. Results Obtained

The developed procedures were applied to determine the plasma parameters for a discharge in the gas channel with a liquid wall (DGCLW) in two regimes of discharge burning (either both two electrodes are solid or the positive electrode is "liquid") and using various working liquids (distilled water or pure ethanol). The plasma radiation spectra were registered on a "Plasma_spec" spectrometer with the help of CCD elements in the range of 200–760 nm with a spectral resolution of about 0.6 nm.

The electronic population temperatures, T_e^* , were determined from the relative intensities of emission lines of Cu I (the electrode substance) ($\lambda = 465.1, 510.5, 515.3, 521.8, \text{ and } 578.2 \text{ nm}$) and hydrogen H I ($\lambda = 486.1$ and

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Fig. 6. (a and b) Simulation results for the radiation spectrum of CN (B–X) in a spectral interval of 410–422 nm. A and B are the maxima near the heads of bands (0,1) at $\lambda = 421.45$ nm and (1,2) at $\lambda = 419.56$ nm, respectively. C and D are the minima at about $\lambda = 420.50$ and 422.60 nm, respectively. (c and d) Simulation results for the radiation spectrum of C₂ (d-a) in a spectral interval of 530–566 nm. A and B are the maxima near the heads of bands (0,1) at $\lambda = 563.42$ nm and (1,2) at $\lambda = 558.30$ nm, respectively. C and D are the minima at about $\lambda = 559.37$ and 564.54 nm, respectively

656.6 nm) using the method of Boltzmann diagrams. The electronic temperatures $T_e^*(\mathrm{H}) = 4300$ K and $T_e^*(\mathrm{Cu}) = 7200$ K were obtained for the DGCLW regime with a "liquid" anode, at the air flux G = 55 cm³/s, and the discharge current $I_d = 200$ mA.

After the characteristic heights A, B, C, and D for bands (1,0) and (2,1) of a hydroxyl molecule OH (A– X) and bands (0,2) and (1,3) of a molecule N₂ (C–B) had been determined, we estimated, using the curves presented in Figs. 2 and 4, the corresponding vibrational and rotational temperatures. A comparison between the experimental spectrum and the calculated ones is made in Fig. 8.

From Fig. 8, one can see that the best coincidence between the experimental (curve 4) and calculated (curves 2) data was achieved for the temperatures determined from the curves $T_v^*(OH) = 3800$ K, $T_r^*(OH) = 3200$ K, $T_v^*(N_2) = 4000$ K, and $T_r^*(N_2) = 2000$ K. The difference between the experimental and simulated spectra in Fig. 7,*a* can be explained by the fact that, during the OH (A–X) radiation emission stimulation, the radiation spectrum of N₂ (C–B) was not taken into account, although it was also observed in this spectral range. The results of comparison between the experimental and calculated spectra are exhibited in Fig. 9.

The results of comparison between the experimental and calculated DGCLW spectra are depicted in Fig. 10. From this figure, one can see that the best coincidence between the experimental (curve 4) and calculated (curves 2) spectra is attained for the temperatures



Fig. 7. Curves for the determination of population temperatures T_r^* (a and c) and T_v^* (b and d) from radiation bands (0,1) and (1,2) of CN (B–X) (a and b) and C₂ (d–a) (c and d) molecules constructed taking the spectrometer instrument function into account, the shape of which is close to the Gaussian with the FWHM = 0.6 nm



Fig. 8. Comparison between calculated and experimental spectra (the "liquid"-anode regime, the air flux $G = 55 \text{ cm}^3/\text{s}$, $I_d = 200 \text{ mA}$, the working liquid is distilled water): (a) OH (A–X) spectra in an interval of 275–304 nm, (b) N₂ (C–B) spectra in an interval of 360–385 nm



Fig. 9. Comparison between calculated and experimental DGCLW spectra (the "liquid"-anode regime, $G = 55 \text{ cm}^3/\text{s}$, $I_d = 200 \text{ mA}$, the working liquid is distilled water): (a) spectra in the interval of 275–405 nm, (b) scaled-up section of the spectrum. Simulation was carried out for the temperatures $T_v^*(\text{OH}) = 3800 \text{ K}$, $T_r^*(\text{OH}) = 3200 \text{ K}$, $T_v^*(\text{N}_2, \text{N}_2^+) = 4000 \text{ K}$, $T_r^*(\text{N}_2, \text{N}_2^+) = 2000 \text{ K}$ which were determined from the corresponding constructed curves



Fig. 10. Comparison between calculated and experimental DGCLW spectra (the regime with two solid electrodes, the air flux $G = 55 \text{ cm}^3/\text{s}$, $I_d = 60 \text{ mA}$, the working liquid is ethanol): (a) CN(B-X) spectra in the interval of 406–423 nm, (b) C₂ (d-a) spectra in the interval of 528–565 nm

determined from the curves (Fig. 7) $T_v^*(CN) = 4750$ K, $T_r^*(CN) = 3500$ K, $T_v^*(C_2) = 5000$ K, and $T_r^*(C_2) = 4000$ K.

4. Conclusions

A procedure for the determination of population temperatures of molecular vibrational and rotational levels in atmospheric-pressure discharge plasmas has been proposed. The calibration curves for the determination of vibrational and rotational temperatures from the radiation emission bands of molecules OH (A–X), N₂ (C–B), N₂⁺ (B–X), CN (B–X), and C₂ (d–a) have been constructed taking the spectrometer instrument function into account, the shape of which is close to the Gaussian. It was demonstrated that the methodological approach with engaging the SPECAIR computer code can effectively be used for the determination of vibrational and rotational temperatures of other molecules in plasma in the state of local thermodynamic equilibrium.

The developed procedure was tested by determining the parameters of DGCLW plasma. This discharge was shown to generate a nonequilibrium plasma in the operating modes under investigation. The T_r^* -value determined from OH (A–X) band was demonstrated to be a little higher than its counterparts obtained for N₂ (C–B). The last result obtained testifies that the further studies on this issue are needed.

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МЕТОДИКА ВИЗНАЧЕННЯ ТЕМПЕРАТУР ЗАСЕЛЕННЯ КОЛИВАЛЬНИХ ТА ОБЕРТАЛЬНИХ РІВНІВ МОЛЕКУЛ В ПЛАЗМІ ГАЗОВИХ РОЗРЯДІВ АТМОСФЕРНОГО ТИСКУ

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Резюме

Запропоновано методику визначення температур заселення збуджених коливальних та обертальних рівнів молекул в плазмі газових розрядів атмосферного тиску з використанням програми SPECAIR. Для спрощення та пришвидшення обробки емісійних спектрів побудовано робочі криві для визначення коливальних та обертальних температур за емісійними смугами молекул OH(A–X), N₂(C–B), N₂⁺(B–X), CN(B–X) та C₂(d–а система переходів Свана). Розроблену методику апробовано для визначення параметрів плазми розряду в газовому каналі з рідкою стінкою.