SIMPLEST SPECTROSCOPY OF COLD NONEQUILIBRIUM PLASMA

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This paper presents a detailed description of a technique for handling spectra of a gas discharge under conditions of varying air humidity. Some parameters of a cold nonequilibrium plasma measured under different experimental conditions are also presented in the paper.

INTRODUCTION

Investigations of the high frequency (HF) discharge in humid air carried out in early seventieths[1–3] showed that there can occur such conditions when a strong cooling of charged and neutral particles in the discharge is observed that, in turn, results in formation of a cold nonequilibrium plasma possessing a long lifetime. Further investigations into the optical breakdown of air[4] confirmed correctness of these experiments as well as of the conclusions drawn. At present it can be stated that the process of decay of the plasma formations formed due to optical breakdown or HF electric discharge in air can result in a residual ionization of air that has anomalously long lifetime, or, following the terminology from Ref. 5, the effect of plasma conservation takes place. Since this effect plays an important role in ionization of a humid air and can be practicable in studies of the atmosphere it seems reasonable to consider diagnostics of the gas discharge in humid air in a more detail. This paper has been prepared based on data of spectroscopic studies of the HF discharge in humid air and in certain sense it completes the investigations carried out earlier (see Refs. 1–3).

The main goal of this article is to present a detailed discussion of a technique for processing spectral lines aimed at subsequent determination of most important characteristics of plasma. It should be noted here that despite of seeming simplicity of the problem it is very laborious since the electric discharge in humid air is a complicated nonequilibrium system poorly studied as yet. As a result, there are a lot of difficulties in the interpretation of experimental data because of uncertainties in the plasmochemical processes occurring in the discharge.

The spectroscopic techniques of the discharge diagnostics are contactless and therefore they do not intervene the processes in a discharge. Besides, their use enables one to measure parameters of thermodynamically equilibrium or nonequilibrium plasma, as well. The spectroscopic measurement techniques make it possible to extract information about temperature and number density of electrons in the discharge, as well as to measure electric fields in plasma, and to calculate the velocity distribution of emitting hydrogen atoms, and so on.

EXPERIMENTAL CONDITIONS FOR RECORDING SPECTRAL LINES

To excite the emission spectra we used two types of HF electric discharge in air, that is, the capacitive and the induction ones.[2,6] Both types of the discharge are shown in Fig. 1. However, we preferred the capacitive HF discharge because of easier matching of the generator output with the load. For more details of the HF discharge generator, see Ref. 6. Some characteristics of the discharge volumes are given in Table I. Investigations have been carried out with low and high output powers of the generator. In the former case the discharge has been initiated with a continuous HF generator (f = 27.12 MHz and P about 150 W) while in the latter case we used a generator with an independent excitation (f = 36 to 37 MHz, P = 40 to 60 kW, τ = 10 to 75 ms, and F = 1 to 5 Hz). Air pressure in the discharge volume has been chosen taking into account the breakdown threshold for humid air and corresponds to the atmospheric conditions at 40 to 60 km heights above the Earth's surface.

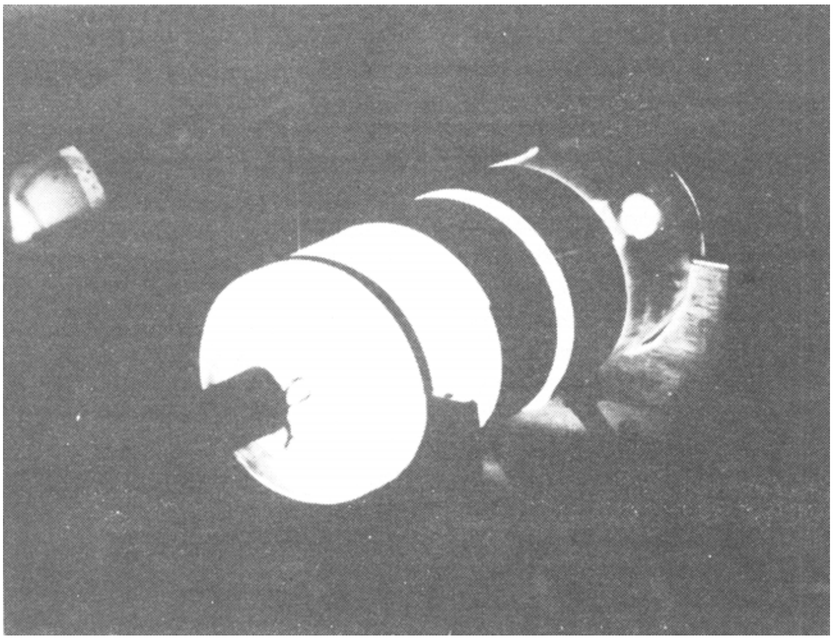
TABLE I. Specifications of the discharge volumes.

Configuration of the discharge volume f, MHz	36.5	27.12
Cylinder d, cm	2.4; 7.2	2.4 (0.6)*
l, cm	35	35
Sphere d, cm	20	–
Total pressure p, kPa	0.1–1	0.01–0.07

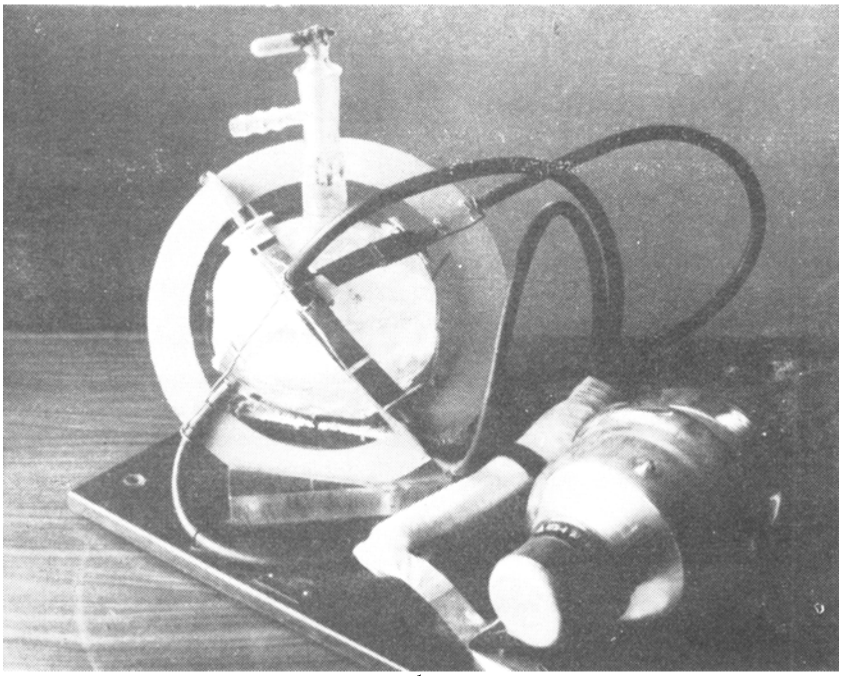
* In order to provide stable discharge glow and improve measurement accuracy the diameter of the discharge tube was reduced to 0.6 cm (Refs. 1 and 14).

The excitation and vibrational temperatures T_{exc} and T_v were determined from spectra recorded with spectrographs DFS–8, ISP–22, and QU–24 on the ORWO WU3 photographic plates. The width of entrance slit was chosen empirically in each case and, for example, for the QU–24 spectrograph it was about 0.1 mm. In the case of high power excitation the excitation temperature was calculated from the ratio of intensities of the hydrogen emission spectral lines of Balmer series recorded with an ICP–51 spectrograph equipped with a camera of 120 mm focal length. The width of the entrance slit in this case was about 0.3 mm. Photometric measurements of spectra recorded on a film were performed with a microphotometer IFO–451. Calibration of the whole recording system was performed using a mercury–vapor lamp.

Recording of isolated spectral lines has been performed using a Fabry and Perot interferometer of Ziess firm and an IT–51 interferometer, the former being the basic spectroscopic device used for this purpose. Plates of this interferometer were coated with silver film and the spacing between the plates could be chosen to be 0.5, 0.8, 1.0, and 4.0 mm. Diameter of the input diaphragm could be varied[7] from 2 to 20 mm. The observed spectra were mainly recorded photoelectrically on a screen of a storage oscilloscope or with a X–Y recorder. In the first case the recording time was about 20 ms, while in the second one it took about 360 s to record the H_β line of hydrogen. The use of X–Y recorder was recognized to be impossible because of strong fluctuations of a signal under conditions of enhanced air humidity.



a



b

FIG. 1. Views of the discharge volumes where cold nonequilibrium plasma was obtained: (a) a unit providing for obtaining capacitive HF discharge, shift of the discharge to the left is due to pumping out of the discharge volume and (b) octahedral excitation winding, HF voltage is applied to the apexes of the octahedron.

The instrumental contour of the Fabry and Perot interferometer was determined either experimentally or from calculations. The experimentally determined contour was more accurate and therefore it was preferred since this allowed an improvement of the accuracy of measuring actual contour of a spectral line to be reached. To experimentally determine the instrumental contour we used an electric discharge tube with a cold hollow cathode emitting distinct lines of Cd at 479.97 and 508.5 nm wavelengths. The wavelengths of spectral lines used for measuring instrumental contours were normally chosen so that they were close to the spectral lines under study. To check up the validity of measurements and avoid occasional superposition of different orders of the interference the measurements have been carried out using different spacings between the interferometer plates. The criterion of the measurement validity was the coincidence of thus obtained results. Of course the instrumental contours were excluded from the measured ones prior to making a comparison since the former contour depended on the interferometer spacing.

ANALYSIS OF SPECTRA OF THE DISCHARGE IN HUMID AIR AND DETERMINATION OF RELEVANT PLASMA CHARACTERISTICS FROM THESE SPECTRA

Emission spectra of a HF–discharge strongly depend on the number density of H_2O molecules in the discharge volume as well as on the total pressure of nonionized mixture (air + water vapor). As to the discharge in dry air its spectrum is mainly composed of emission bands of molecular nitrogen. Then, with the addition of water vapor into the discharge volume, the process of H_2O molecules dissociation becomes prevailing over the vibrational excitation of nitrogen molecules what results in appearance of hydrogen in the discharge. As a consequence, the band spectrum of the discharge transforms into a line spectrum mainly composed of hydrogen spectral lines of Balmer series. The number and intensity of these lines strongly depend on the value of the parameter N/p. Band and line spectrum of the radical OH centered at $\lambda = 306.4$ nm also contributes to this spectrum.

Figure 3 shows an example of spectrum of HF discharge in humid air obtained by microphotometric handling of the spectrum photographic image with a microphotometer IFO–51. In principle, such a spectrum is already acceptable for determination of the discharge characteristics and in particular, of the excitation temperature T_{exc}. It should be noted that the excitation temperature determined using atomic spectral lines refers to the electron temperature in plasma while the temperature calculated from the intensity distribution over a molecular band corresponds to the temperature of the discharge. At present we have developed new, more correct, techniques for temperature measurements but their discussion is out of range of this article.

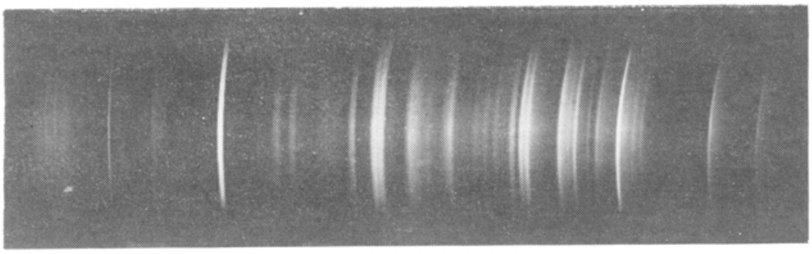


FIG. 2. Spectrum of HF discharge in humid air: $f = 37$ MHz, $\tau = 10$ ms, $F = 5$ Hz, *and* $P = 40$ kW.

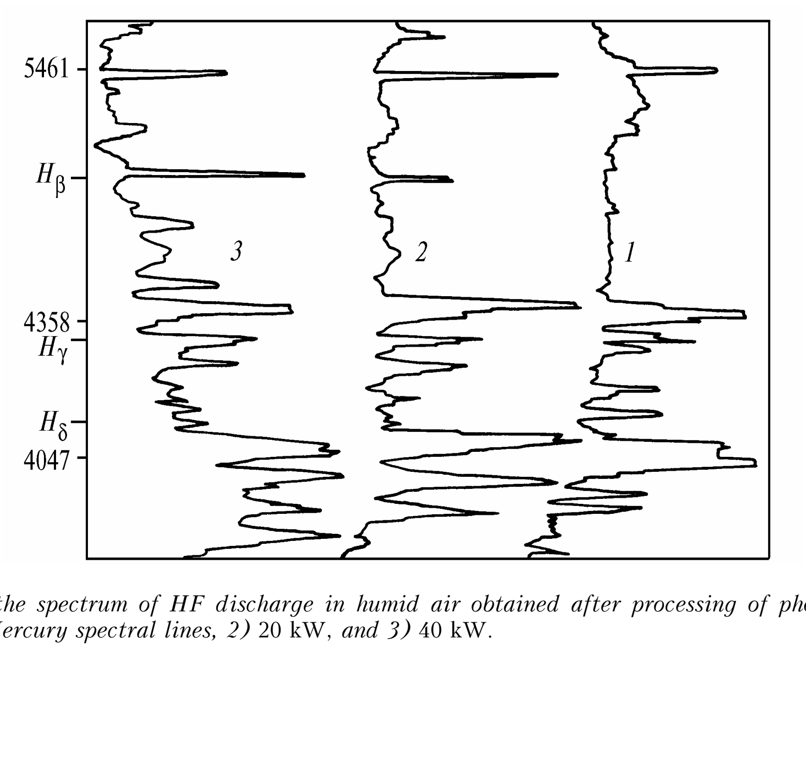


FIG. 3. A portion of the spectrum of HF discharge in humid air obtained after processing of photographic film with a microphotometer: 1) Mercury spectral lines, 2) 20 kW, *and 3)* 40 kW.

After examination of the validity of the Boltzmann law for the energy levels population[8] one can find the excitation temperature from the ratio of total intensities of two spectral lines (J and J') by the following formula[9]

$$T_{\text{exc}} = \frac{E_2 - E_2'}{\ln J\, \lambda^3 f_{12}'\, q' - \ln J'\, \lambda'^3 f_{12}\, q_1}\,, \qquad (1)$$

where E_2 and E_2' are the energies of the upper levels, λ is the wavelength in microns, f_{12} is the oscillator strength and q and q_1' are the statistical weights of the low levels.

As is well seen from Fig. 3 the H_β line is isolated in the spectrum best of all so that its wings do not overlap with other lines what makes it very convenient for plasma diagnostics. An increase of power pumped into the discharge results in an increase of the intensity of H_β and H_δ lines. Besides, additional broadening of H_γ and H_δ lines occurs in this case. The latter fact is indicative of efficient decomposition of water vapor molecules in the discharge resulting in an increase of number density of emitting hydrogen atoms and heating of electrons.[10] The shape and intensity of the H_β line (λ = 486.1372 nm) are strongly affected by electric fields, including those existing inside the plasma. For example, Fig. 4 shows a curve that characterizes the depth of a dip in the H_β line profile depending on the air parameters and in Fig. 5 *b* one can see the line profile with such a dip. For these reasons the lines H_γ (λ = 437.047 nm) and H_δ (λ = 410.174 nm) better suit the calculations of T_{exc}.

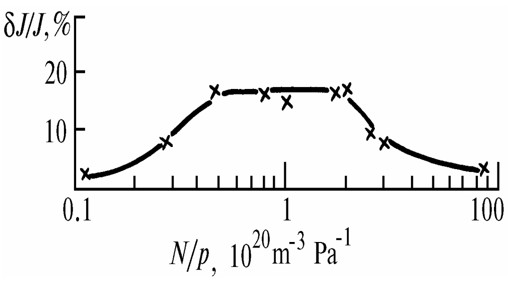


FIG. 4. Dependence of the dip in H_β line profile on the number density N of water vapor molecules in the discharge and on the total pressure of humid air.

Consider now the line H_β in more detail. Figure 5 shows its profiles as a function of water vapor content and total pressure of nonionized mixture of air plus water vapor. The profiles *a* and *c* in this figure can surely be considered of the Doppler type, that is, their shapes are described by a Gaussian curve, while the profile δ is of typically Stark shape. The depth of the dip in the profile and the spectral shift of H_β line bear the information about the strength of the electric fields inside plasma (see Ref. 11) and about the number density of charged particles (see Ref. 12). Nevertheless, to judge at certain on the causes of the dip one needs for additional investigations, since both the electrons and ions (charged clusters) can be responsible for it. Just for this reason the depth of the dip is shown in Fig. 4 as a function of the medium parameters N and p. However other profiles of H_β line, like those presented in Figs. 5 *a* and *c*, can be used for determining the translational temperature of hydrogen atoms (the gas temperature).

In the general case the temperature T and the width of spectral line H_β are related to each other by the following formula[13]

$$T = 8.26{\cdot}10^6 (\Delta\lambda_D)^2\,, \qquad (2)$$

where $\Delta\lambda_D$ is the Doppler broadening of the true profile of H_β line but not of those presented in Fig. 5.

The dependence of H_β line broadening $\Delta\lambda$ on the experimental conditions is shown in Fig. 6 (results of these measurements have been partially used in Refs. 1 and 13).

It is distinctly seen from Fig. 6 that $\Delta\lambda$ increases with increasing pressure that means, according to formula (2), that plasma should become heated. However, it is impossible to say something definite about the changes in temperature of hydrogen atoms until preliminary analysis of the discharge conditions is made. There are two reasons for such a situation.

First of all it is unclear, without an additional study, whether does the cold nonequilibrium plasma obey Maxwell and Boltzmann laws or not. As a result, the use of equation (2) for determining temperature is doubtful. Moreover, in the case of a strong deviation of the velocity distribution of emitting atoms of hydrogen $F(v)$ from the Maxwellian one the term of temperature itself loses any sense.

Second, the measured broadenings of spectral lines (see Figs. 5 and 6) by no means are purely Doppler ones since they involve other types of broadening, for example, the instrumental contour of the Fabry and Perot etalon.

Let us now consider in more detail the handling of measurement data on H_β line profile. It is obvious that in the case of hotter plasma (dry air) the instrumental contour can be neglected while in the case of humid air, where $\Delta\lambda$ is about 0.1 nm, it cannot be neglected since its value amounts about a half of the measured width of the H_β line contour. In other words, the error in temperature measured without the account of the instrumental contour (Fig. 6) can reach 100% what, in turn, mislead understanding of the chemical and physical processes occurring at ionization of humid air. Similarly, the accuracy of measuring other plasma parameters (number density of electrons, velocity distribution of emitting hydrogen atoms, and so on) also depends on correctness of determining true contour of this spectral line. The problem on determining true contour of a spectral line is too complicated and therefore needs for use of a computer. For this reason some peculiarities of its solution are considered below.

Recovering of an actual shape of a spectral line $\varphi(v)$ from a measured contour $f(v)$ (see Fig. 5) is normally reduced to solution of the Fredholm equation of the first kind[14]

$$\int_{-\infty}^{\infty} K(v - v')\, \varphi(v')\, d(v') = f(v)\,, \qquad (3)$$

where $K(v - v')$ is the instrumental function of the Fabry and Perot etalon.

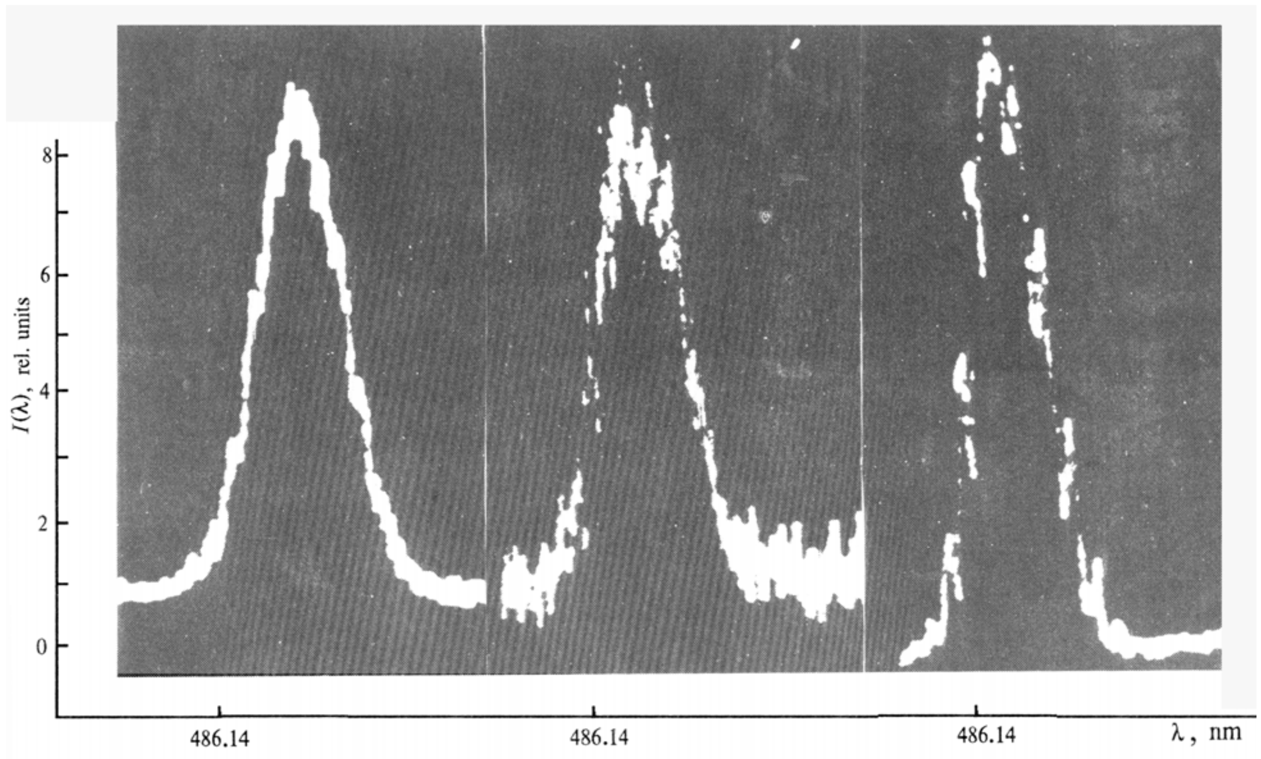


FIG. 5. Typical profiles of the H_β *line (*P = 100 W, p = 100 *to* 700 Pa*) for different values of N/p ratio: (a)* $0.14{\cdot}10^{20}$, *(b)* $0.48{\cdot}10^{20}$, *and, (c)* $9.28{\cdot}10^{20}$ $m^{-3}{\cdot}Pa^{-1}$.

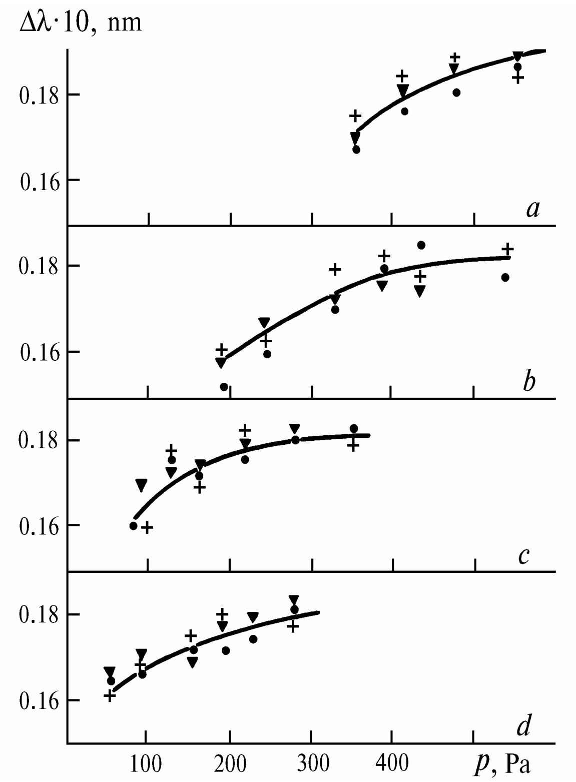


FIG. 6. Values of the H_β *line broadening at different pressures inside the discharge tube and different content of water vapor molecules in air (*$f = 27.12$ MHz *and* $P = 100$ W*): (a)* $8.5\cdot10^{22}$, *(b)* $4.7\cdot10^{22}$, *(c)* $2.1\cdot10^{22}$, *and (d)* $1.3\cdot10^{22}$ m^{-3}.

A description of such a procedure for the case of plasma experiments with humid air can be found in Refs. 2 and 16. Note here that preliminary estimates of the reconstruction errors obtained in these works are $\delta K \simeq 0.01\ K_{max}$ and $\delta f = 0.04\ f_{max}$. The solution of integral equation (3) has been carried out in these references using a regularization method based on generalized discrepancy technique. Such an approach allows for errors in the measured line contour and in the instrumental function.

Thus obtained actual shape of H_β spectral line was considered to be of the Voigt profile that, in turn, is a convolution of the Doppler and Lorentz contours.[17] The parameters of spectral lines can vary due to variations in the experimental conditions and physicochemical processes in the discharge.[18] By varying parameters of the contours one can achieve better than 1% coincidence between the Voigt and actual line shape of a spectral line $\varphi(\nu')$. Then the Doppler line width $\Delta\lambda_D$ obtained from this fitting procedure can be used for estimating, by Eq. (2), the temperature of the hydrogen atoms. Using this technique we have shown[1] that cells of cold nonequilibrium plasma can occur in humid air at temperature 300 to 400 K provided that the condition

$$0.5\cdot10^{20}\ \text{m}^{-3}\cdot\text{Pa}^{-1} < N/p < 3.5\cdot10^{20}\ \text{m}^{-3}\cdot\text{Pa}^{-1} \qquad (4)$$

is fulfilled.

From the comparison of data presented in Figs. 5 *a* and *b* one can see that wings of the H_β line observed under different experimental conditions are strongly different. Thus the line profile in the first case is closer to a Gaussian shape while in the second one it is rather of delta function shape. This, in turn, is indicative of difference between the velocity distributions of particles occurring in these cases. A technique of calculating velocity distribution of hydrogen atoms from the Doppler profile of H_β line is discussed in detail in Refs. 16 and 19 for the case of HF electric discharge in humid air. An example of such calculational results that well illustrates the above considerations is shown in Fig. 7.

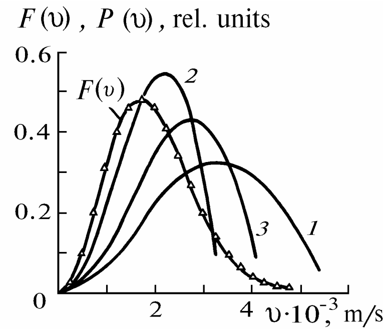


FIG. 7. Distortions of the velocity distribution functions (normalized by a unit area) of excited hydrogen atoms for different N/p values: 1) $0.82\cdot10^{20}$, *2)* $2.47\cdot10^{20}$, *and 3)* $3.25\cdot10^{20}$ m$^{-3}\cdot$Pa^{-1}, $F(\nu)$ *is the Maxwellian distribution.*

In addition to the above said, we should like to point out two very important circumstances that must be taken into account when making spectroscopic analysis of a gas discharge in humid air.

The instrumental function of an interferometer can be either measured using a hollow cathode discharge tube (Cd1) or calculated using a technique described in Ref. 20. However, the accuracy of its reconstruction in the first case (10 to 20 per cent) is higher than that achievable by using the calculational approach. For this reason the use of the former approach to handling of experimentally measured profiles of spectral lines enabled us to find optimal conditions, that involve the characteristics of air medium and the parameters of ionizing radiation, under which cold nonequilibrium plasma can be obtained. Using this approach we have also managed to reveal a direct correlation between the processes of plasma cooling and the increase of the plasma decay time in humid air.

And finally, one can see from Fig. 5 that the measured line profile has a quasiperiodical structure superimposed on its smooth regular basic shape with the period of fluctuating component of 0.01 nm that does not depend on air humidity. Moreover, different operations with the parameters of the interferometer (change of spaces, diaphragms, and/or use of mirrors with different reflectivity) as well as change of humid air for Neon or Argon show that these oscillations in the line profile are not accidental since they are observed only in humid air with their amplitude depending on the number density of water vapor molecules and plasma concentration in the discharge. It is characteristic that the amplitude of the oscillations sharply increases with transformation of the H_β line profile from the Doppler shape to the Stark one, as it is seen from Fig. 5 *b*. It is quite realistic that the nature of these oscillations is closely related to the processes that cause a decrease of the plasma decay rate in humid air. Let us first assume that the periodic structure of the line profile is due to the Stark splitting of the H_β line in an external electric field and compare the widths of a measured line profile and instrumental function of the Fabry and Perot etalon with the width of peaks of the periodic structure. In doing so we readily see that the instrumental function of the interferometer used is about one half of the measured profile width $f(\nu) \approx 1.8 \cdot 10^{-2}$ nm while the width of the periodic peaks on the profile envelope is only 0.1 of its value. In other words, these peaks are much more sharp than the instrumental function of the interferometer even though the Doppler broadening is neglected. This fact can hardly be explained within this approach since even in a limiting case of an infinitely narrow emission line (i.e., the profile $J(\Delta\lambda) = J_0\delta(\Delta\lambda)$, where $\delta(\Delta\lambda)$ is the delta function) its profile of the H_β line recorded instrumentally should be exactly coincident with the instrumental function or be wider because of the Doppler broadening. At the same time we see that the widths of the peaks recorded in this experiment are about five times narrower than the instrumental function of the interferometer. This fact clearly demonstrates that the observed periodic structure of H_β line profile cannot be caused by the Stark effect.

Two circumstances are to be mentioned for better understanding of the origin of these oscillations in the H_β line profile. First of all we should like to note that instrumentally the line profile was recorded on a screen of a storage oscilloscope, therefore time variations of the intensity of a hydrogen emission line, caused, for example, by time variations of the hydrogen atoms concentration, can deform the line profile. Second, it is quite probable that alternating electric fields of the type $\mathbf{E}_0 \cos \omega t$ can occur in the plasma, for example, due to the Langmuir oscillations. In this case $\omega = \omega_{pe}$ and ($f_{pe} \simeq 10^4 \sqrt{n_e}$, Hz). As a result, the emission spectrum will consist, in this case, of a series of satellites spaced from the unshifted line center by spectral distances $\pm \kappa\omega$, where $\kappa = 0, \pm 1, \pm 2, \ldots$.

In this case the expression describing the spectrum is as follows

$$S(\Delta\omega) = \sum_{\alpha,\,\beta} \sum_{\kappa=-\infty}^{+\infty} J_\kappa^2(x) \left[\frac{(d_{\alpha\alpha} - d_{\beta\beta})E_0}{\hbar\,\omega}\right] \varepsilon(\Delta\omega - \kappa\omega), \qquad (5)$$

where $J_\kappa(x)$ is the Bessel function, α and β are the Stark sublevels of the upper ($n = 4$) and low ($n = 2$) energy states and $\Delta\omega$ is the frequency shift from the normal position of H_β line center. If the peaks of the periodic structure observed are assumed to be the above–mentioned satellites then at $N/p \sim 1.45 \cdot 10^{20}$ m^{-3}·Pa^{-1} ($p = 324$ Pa, $N = 4.7 \cdot 10^{22}$ m^{-3}, $T = 300$ K) the spectral distance between the peaks is about 0.035 Å and the corresponding field strength $E_0 = 840$ V/cm ($E_{0\mathrm{eff}} = E_0/\sqrt{2} = 600$ V/cm). From these calculations it follows that $n_e \sim 2.3 \cdot 10^{11}$ cm^{-3} what is of the same order of magnitude as the experimental value. Thus we can conclude that the Langmuir oscillations are responsible for appearance of the periodic structure in the H_β line profile rather than the Stark effect. Of course, we can alternatively assume that some periodic process is initiated in the electric discharge in which the atomic hydrogen plays a catalytic role in direct and reverse reactions.[16]

CONCLUSIONS

In conclusion we can state that even the simplest spectroscopy of electric discharge in humid air is much more laborious than spectroscopy of homogeneous gases. Most suitable for spectroscopic studies of the discharge are emission lines of hydrogen of Balmer series. However, selection of a particular line of the series is critical with respect to the measurement goal. Strong distortions of the H_β line profile due to the action of intraplasma microfields can cause large measurement errors and, finally, mislead in understanding the physicochemical processes in the discharge. When determining temperature of neutral particles using a spectral line profile one should subtract the instrumental function of the Fabry and Perot etalon from the measured profile.

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