NONEQUILIBRIUM OF THE DENSE ELECTRIC ARC PLASMA CASED BY RADIATION TRANSFER

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The results of the tomographic spectroscopy study of the free burning electric arc plasma between evaporating copper electrodes are presented briefly. The role of resonance radiation in departure of the dense plasma from the state of local thermodynamic equilibrium is evaluated. The transfer of radiation in plasma is taken into consideration unlike well-known Griem criterion. The results of numerical modeling demonstrate the effects of non-equilibrium between the ground, metastable and resonant levels.

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INTRODUCTION

The using of electric arc plasma equipment allows to rich the extreme temperatures in any technologies. That is why this equipment is widely applied in metallurgy, welding and deposition of structural and functional coatings. Nowadays it finds new area of application in waste processing and converting of carbon containing raw materials into alternative gaseous fuels [1]. Individual direction, based on the using of quasi equilibrium electric arc plasma, is separated nowadays in the modern plasma chemistry [2]. The using of nonequilibrium effects will allow to optimize the operation of plasma equipment or to decrease the energy cost of charge particles production in plasma technologies. Either way, the account of violation of local thermodynamic equilibrium (LTE) in electric arc plasma resulting from the transfer of radiation is necessary for the adequate modelling of these plasma properties.

The revealing and justification of deviation from LTE in atmospheric electric arc plasma in connection with the transfer of radiation, which will be discussed in the present work, was quite complicated and has long history. As early as in the 80-s one of the authors with his co-worker in Kyiv University, taking advantage of the fact that the plasma arc in a copper vapour is a convenient object for the quantitative spectroscopy, have found the following. If in the electric arc, freely burning in the atmosphere between copper electrodes, carefully measure the electron density and temperature of particles, then the test for compliance atmospheric pressure according to Dalton's law in the standard assumption of equilibrium plasma gives the result of higher than expected at times. At the same time we have shown, that there has been a significant increase of population of copper atom metastable levels, corresponding to the lower level one of the resonance spectral lines at the periphery of the arc and in the near area outside of her channel [3]. It may be explained as the deviation from LTE due to selective absorption of the resonance radiation emitted from high-temperature near axial zone at the arc channel periphery, where the temperature is relatively small. The result is a partial LTE (PLTE), characterized by the overpopulation of the resonance level of the copper atom [4].

The similar plasma object – wall-stabilised arc between vaporized electrodes was studied by two groups of French researchers slightly earlier [6, 7]. They were also observed outwardly similar effect of increasing the content of metal vapour on the periphery of the arc. But they explained its nature by separation of the diffusion component of plasma forming mixture in the process of diffusion, well known as demixing [8]. It can significantly influence on the composition of plasma, increasing the concentration of the elements in some cases by a factor three. We were checking the role of demixing later by direct numerical modelling of the diffusion processes concerning our experiments. This simulation have shown negligible role of this effect [9]. Thus we can't consider demixing as essential factor in electric arc copper-air plasma.

1. EXPERIMENT

The arc was ignited between the end surfaces of the non-cooled copper electrodes in air, each having a diameter of 6 mm. Interelectrode distance l_{ak} could be varied between 2 and 8 mm and discharge current I from 3,5 to 100 A. The electrodes were placed in a vertical position. A pulsing mode was used to avoid the metal droplets appearing: the single current pulse up to 100 A was put on the "duty" weak-current discharge. The pulse interval ranged up to 30 ms. The quasi-steady mode was investigated.

In view of absence of the arc stabilizing wall, it could chaotically move on the end-electrode surfaces. Therefore the fast recording of the arc space distribution parameters during single current impulse is necessary. The initial experimental data acquisition was accomplished by the tomographic spectrometer based on the astigmatic light-high monochromator, Fabry-Perot interferometer (FPI) and image sensor. This spectrometer provided practically simultaneous recording of spectral line shapes in various space elements of plasma as well as space distribution of the spectral line emission and absorption [5]. The example of registered with this devise pattern is presented in Fig. 1,a.

Naturally, the FPI could be excluded as an optical element; in this case the spectrometer remains a convenient instrument for high-speed measurements of the radial profiles of spectral line radiation (Fig. 1,b). Transformation of observed spectral intensity into radial distribution of the emission of plasma was fulfilled by well-known methods of Abel inversion. As the result a space distribution of plasma particle species may be obtained.

The spectral diagnostic of plasma follows the next methods [3]:

-relative intensity of spectral lines CuI (in *nm*) 521.8 / 510.5, 465.1 / 510.5;

-absolute intensity of spectral line 465.1;

-Stark width of lines CuI 515.3 and 510.5;

-absorption in the centre of line 510.5 nm.

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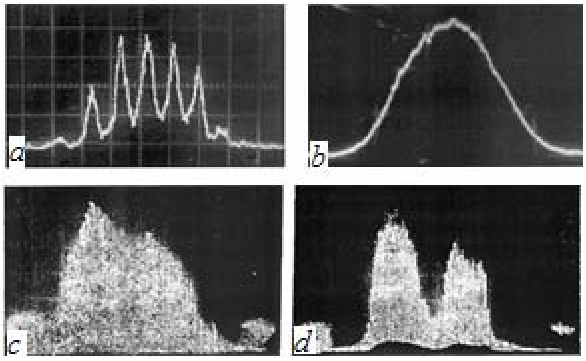

Fig. 1. The examples of signals recorded by tomographic spectrometer in the regime of emissive spectroscopy (a, b) with FPI (a) and without it (b) and in the regime of laser absorption spectroscopy (c, d). In the last case the radial distribution of intensity in incident laser beam (c) and transmitted one through the region of electric arc (d) are presented. The visible diameter of arc corresponds to lower part of dip at oscillogram (d)

The direct experimental observations of the near channel region of free-burning electric arc between melting electrodes were made by the method of laser absorbing spectroscopy [3]. The arc was lighted by wide parallel beam of radiation from cooper laser with wave length 510.5 nm. It spectral luminance was higher than the radiation of spectral line of the electric arc. This radiation corresponds to electron transition in energy structure of cooper atom from resonance state E_u=3.82 eV (upper) into metastable one E_l=1.39 eV (lower). Arc's «shadow» in parallel laser beam was registered by tomographic spectrometer during a short time, until the arc remained practically immovable (Fig. 1, c-d).

It should be emphasized that the effects observed in this study could go undetected with conventional spectrometer. That is why the state of the art in plasma spectroscopy involves application of tomographic spectrometry.

2. EXPERIMENTAL RESULTS

The example of radial distribution of measured temperature *T(r)* and electron density $N_e(r)$ as the calculated in LTE-assumption copper contents x_{Cu} in the average cross section is shown In Fig. 2,a. *T(r)* was obtained from the ratio of local emission coefficients of spectral lines CuI 510.5 and 521.8 nm. $N_e(r)$was determined by two temperature-independent methods based on the measurements of spectral line CuI 515.3 nm widths Δλ and absolute intensity of the line CuI 465.1 nm. These data allow calculating the radial profiles of plasma composition.

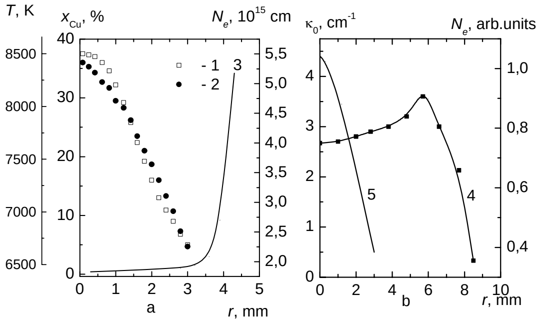

Fig. 2. Radial distributions of temperature T (1), electron density N_e (2) and copper vapour content x_{Cu} (3) (a), coefficient of absorption in the centre of spectral line 510.5 nm (4) and relative density N_e (5) (b) in electric arc of I = 30 A and interelectrode gap l_{ak} = 8 mm

As may be seen the calculated in such manner $x_{Cu}(r)$ reveal the abnormal increasing of the metal vapor contents at the arc periphery. This non-physically high content is observed only at the discharge periphery in plasma of the arc mode of a current 30 A and a gap *lak* = 8 mm. The copper content is already more than 5 % on an axis in a case of electrode gap l_{ak} = 2 mm and the same current. Though, the metal impurity contents in plasma of a wall-stabilized arc in copper vapor did not exceed 1 % even in the vicinity of the melting electrode [6]. The reason of these discrepancies may be deviation from LTE in plasma in specified areas.

This conclusion follows qualitatively from the Fig. 2,b, obtained with account of data in Fig. 1, d. Here experimentally obtained radial distributions of absorption coefficient $\kappa_0(r)$ in the centre of spectral line 510.5 nm and relative electron density are shown. The last one corresponds with the data of Fig. 2,a (curve 2). It should be emphasized that the distributions $N_e(r)$ is incompatible in LTE-assumption, to be adheres to Boltsmannian, with the profile $\kappa_0(r)$ presented in Fig. 2,b (curve 4). Really, the profile $\kappa_0(r)$ of the law-lying metastable state *E* = 1.39 eV corresponds closely with radial distribution of copper atom density $N_{Cu}(r)$ as well as with copper contents profile $x_{Cu}(r)$.

This effect may be refereed to the influence of self-absorption of cooper resonance radiation during its propagation transverse to electric arc channel. The periphery volume of plasma may be identified as non-equilibrium. Really, the radiation from the hot arc core is able to overpopulate the resonance level of Cu atom at the arc periphery, where temperature is relatively small.

The sharp non-uniform zones are observed in the vicinity of electrodes. That is why the similar effect of deviation from LTE takes place here too. Plasma may be in PLTE even in arc axis due to the influence of near-electrode zones in short electric arc, where $l_{ак} \leq d$ (d – diameter of the arc channel). Thus, one can speak about short and long free-burning arcs in respect with its equilibrium due to radiation transfer [10].

This non-LTE has a qualitatively another character comparing with the widely known non-equilibrium in plasma of low current discharges, where the radiation leaves free volume of plasma and as a result the resonance state of plasma's atoms is found to be under-populated.

The concerned here non-equilibrium may takes a place, when on the free path of resonance photons in plasma $<l>$ the considerable drop of kinetic temperatures of plasma's particles takes a place. However, it is very rough estimation. The decision of this problem is fulfilled strictly in a variant of LTE criterion determining by taking into account a role of radiation transfer in plasma and their escape from the arc in our previous paper [11]. This variant simplifies a solution of problem, as it allows restrict consideration of the state of plasma with LTE assumption.

3. DEVIATION FROM LTE CASED BY RADIATION TRANSFER

Resonance spectral transition is determining factor to plasma be in LTE [12]. This leads to the spread of so-called two-level model of atom with two energy levels - the basic *1* and excited *2*. The balance of the population of the excited level in this model in the stationary case can be represented in the form

$$n_1\omega_{12} = n_2\omega_{21} + n_2 A_{21}^{*},$$

where A_{21} – probability of spontaneous radiating transition 2 → 1.

The basic Biberman-Holstein equation for the kinetics of resonant level population in a stationary plasma with radiative transfer [12] is

$$n_2(r)(A_{21}+\omega_{21}) - \int_V n_2(r')A_{21}K(|r-r'|)dr' - n_1(r)\omega_{12} = 0$$

Here the integral term takes into account the radiative transfer energy. The kernel $K(|r-r'|)$ is the probability that photon emitted from the arbitrary point *r'*, is absorbed in the volume of coordinate *r*:

$$K(\rho) = (4\pi\rho^2)^{-1}\int \varepsilon_\nu k_\nu \exp(-k_\nu \rho)d\nu \,, \rho \equiv |r-r'|, (1)$$

where ε_ν is normalized per unit distribution of the frequencies of photons, emitted from upper level of spectral transition, k_ν – spectral absorption coefficient. The calculations took into account the next broadening mechanisms of spectral lines: natural, due to collisions of atoms, Doppler and Stark effects. The list of the copper atom spectral lines emitted from the resonant levels of E_u = 3,79 and 3,82 eV is presented in the table. The role of the effects of radiation transfer is studied just in relation to these lines. Some of their have ground (non-exited) level of the spectral transition, another one – metastable levels of E_l = 1,39 and 1,64 eV. The table also presents the statistical weight *g* of the levels (indices *u* and *l* denote the upper and lower levels of the transition, respectively), the oscillator strength *f* (which are proportional to the probabilities of transition), as well as the parameters $\Delta\lambda_s^*$ of the Stark broadening et electron density N_e = 10^{17} cm^{-3}. For more detailed consider of spectral intensities problem, see our recent paper [11].

Resonance spectral lines of copper atom and their spectroscopy parameters

Line, nm	E_u, eV	g_u	E_u, eV	g_l	$\Delta\lambda_s^*$, nm	f
324,7	3,82	4	0	2		0,430
510,5	3,82	4	1,39	6	0,021	0,0051
570,0	3,82	4	1,64	4	0,026	0,0011
327,3	3,79	2	0	2		0,220
578,2	3,79	2	1,64	4	0,027	0,0042

* at N_e = 10^{17} cm^{-3}

In the final version the kernel (1) includes integration to take into account the self-absorption along each beam, where the exponent contains planimetric integral along the line connecting the points with coordinates *r* and *r*′:
:

$$K(r',r) = \frac{1}{4\pi}\int_0^\infty \iiint_V \frac{k_\nu(r')\varepsilon_\nu(r')}{|r-r'|^2} \times$$

$$\times \exp\left[-\int_r^{r'} k_\nu(r'')dl\right] dV d\nu \cdot \qquad (2)$$

The original system of equations for three-level model of the atom in the quasistatic approximation with the account of the splitting of resonant and metastable levels has the following form consistently for the resonance – the upper and the lower – and for the metastable (in the same order) levels [13]:

$$-n_r^u\left(\omega_{rg}^u + \omega_{rm}^{ul} + \omega_{rm}^{uu}\right) + n_g\omega_{gr}^u + n_m^l\omega_{mr}^{lu} + n_m^u\omega_{mr}^{uu} +$$

$$+ R_{rg}^u + R_{rm}^{ul} + R_{rm}^{uu} = 0 \,, \qquad (3)$$

$$-n_r^l\left(\omega_{rg}^l + \omega_{rm}^{lu} + \omega_{rm}^{ll}\right) + n_g\omega_{gr}^l + n_m^u\omega_{mr}^{ul} + n_m^l\omega_{mr}^{ll} +$$

$$+ R_{rg}^l + R_{rm}^{lu} = 0 \,. \qquad (4)$$

Here introduced separate designations of terms connected with the radiation. It has, for example, such a view for spectral line emitted from the upper of the resonance level on the ground one:

$$R_{rg}^u = A_{rg}^u(n_r^u - I_{rg}^u)\,, \qquad (5)$$

where I_{rg}^u is the integral term:

$$I_{rg}^u = \int_V n_r^u(r')K_{rg}^u(r,r')dr' \cdot \qquad (6)$$

In these equations subscripts *g, m, r* correspond to the ground, metastable and resonant levels, and the top *u, l* - upper and lower sublevels for metastable and resonant levels. There is taken into account also in this equation, that in accordance with the principle of detailed equilibrium the rate of transitions within the equilibrium between the resonance and metastable sublevels are mutually compensating [12, 13]:

$$n_u^0 \omega_{ul} = n_l^0 \omega_{lu} \,. \qquad (7)$$

Here the upper index (0) corresponds to the state of equilibrium.

For the accounting of active energy exchange between the sublevels they are combined between themselves; and such level are attributed to the following statistical weight and the average energy of [12]:

$$g = \Sigma g_j \,, \ E = \Sigma g_j E_j / \Sigma g_j \,. \qquad (8)$$

In this setting, the end result reflects the combined effect of the transfer of all of the resonance spectral lines. It should, however, be borne in mind that this combination and, respectively, averaging only applies to collision processes. Emission of lines, as well as their transfer, is considered individually for the corresponding pairs of energy levels; here simplification is associated with the only value of the population of the upper radiating layer n_r under the integral I in each of the integral terms R in equations (3), (4).

By entering the population of combined levels n_r and n_m, and the frequency of collision processes of excitation and deactivation of these states, we obtain a system of equations for approximate describing the kinetics of the processes among all groups of levels:

$$-n_r\left(\omega_{rg} + \omega_{rm}\right) + n_g\omega_{gr} + n_m\omega_{mr} + \frac{g_r^u}{g_r}\left(R_{rg}^u + R_{rm}^{ul} + R_{rm}^{uu}\right) + \frac{g_r^l}{g_r}\left(R_{rg}^l + R_{rm}^{lu}\right) = 0 \,, \qquad (9)$$

$$n_r\omega_{rm} - n_m\left(\omega_{mr} + \omega_{mg}\right) + n_g\omega_{gm} - \frac{g_m^u}{g_m}\left(R_{rm}^{uu} + R_{rm}^{lu}\right) - \frac{g_m^l}{g_m} R_{rm}^{ul} = 0 \,. \qquad (10)$$

Here is taken into account that the radiative processes do not refer to the totality of the combined levels, but only to the part of them. This is evidenced by the relationship of the statistical weights of individual sublevels g_r^u and g_r^l to the statistical weight of the combined level $g_r = g_r^u + g_r^l$ on the example of the group of resonance levels in equation (9).

The system of equations (9), (10) is added by the simplified Dalton equation, Saha-Boltzmann equation in relation to the population of the resonance level and Elenbaas-Heller equation [11, 13].

The solution of a similar system of equations for the formulation of criterion version of problem is presented in [11]. The main difficulty is the calculation of the integral terms (2). For the determining of their numerical values was carried out the transition to a local spherical coordinate system associated with the point of observations r. The system is solved by the Newton method. The integral part is founded by the method of successive approximations, where in the integrand applied the radial profiles of the sought functions obtained in the previous step. The results of numerical solution relating to wall-stabilized arc in copper vapour in the atmosphere of nitrogen of the radius r_w = 3 mm and current of I = 30 A are presented in Fig. 3.

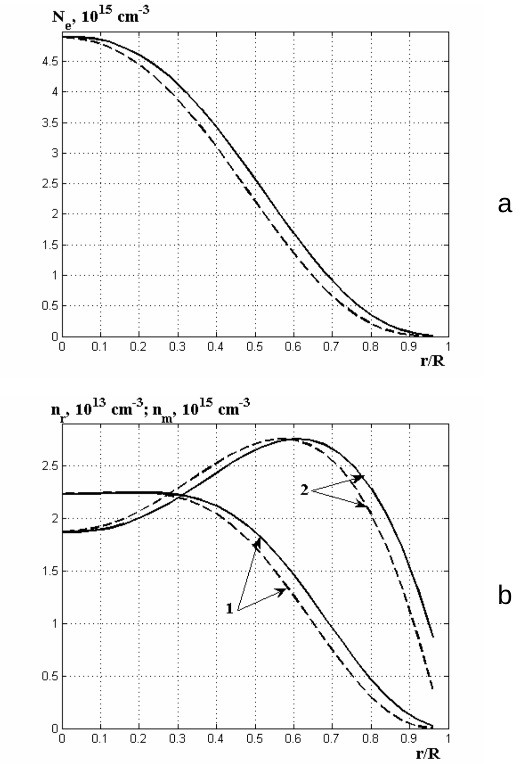

Fig. 3. Radial distribution of electron density (a), populations of resonance (1) and metastable (2) levels of copper atom (b) in electric arc (non-LTE values are a continuous curve, LTE values – dotted lines); copper contents x_{Cu} = 1%; current – 30 A

CONCLUSIONS

The effect of non-equilibrium plasma (as well as deviations from LTE) due to radiation transfer actually exists, at least in the electric arc, burning in metal vapors.

The mathematical apparatus and algorithm for calculation of such non-LTE plasma are proposed.

REFERENCES

1. O.V. Chernets, V.M. Korzhyk, G.S. Marynsky, S.V. Petrov, V.A. Zhovtyansky. Electric arc steam plasma conversion of medicine waste and carbon containing materials // *Proc. XVII GD (7th – 12th Sept. 2008, Cardiff, Wale)/* Ed. J.E.Jones, Cardiff University, 2008, p. 465 – 468.
2. D.I. Slovetsky. Plasma chemical processes in the oil chemistry (Review)// *Oil Chemistr.* 2006, v. 46, p. 323 – 332 (in Russian).
3. I.L. Babich, A.N. Veklich, V.A. Zhovtyansky. Investigation of the role of self-absorption of radiation in freely burning arcs in copper vapors by laser diagnostics // *J. Appl. Spectroscopy.* 1989, v. 51, p. 1028 – 1031.
4. I.L. Babich, A.N. Veklich, V.A. Golovkina, V.A. Zhovtyansky. Non-equilibrium state of plasma of the electric arc in a copper vapour due to the transfer of

the resonance radiation // *Zhurn. Prikl. Spectr.* 1992, v. 56, p. 323 – 326 (in Russian).

5. V.A. Zhovtyansky. High-speed tomographic spectrometry of a plasma // *Jour. of Engineering Physics and Thermophysics* (translated from Russian). 1992, v. 62, №. 5, p. 545-550.
6. A.M. Rahal, B. Rahhaoui, S. Vacquie. Copper vapour diffusion in a nitrogen arc chamber // *J. Phys. D: Appl. Phys.* 1984, v. 17, p. 1807 – 1822.
7. H. Ouajji, B. Cheminat, P. Andanson. Composition and conductivity of a copper-air plasma // *J. Phys. D: Appl. Phys.* 1986, v. 19, p. 1903 – 1916.
8. A.B. Murphy. Diffusion in equilibrium mixtures of ionized gases // *Phys. Rev. E.* 1993, v. 48, p. 3594 – 3603.
9. V.A. Zhovtyansky, A.B. Murphy, V.M. Patriyuk, Yu.I. Lelyuh. The diffusion processes and the role of demixing in arcs with copper electrodes // *Proc. XVII GD (7th – 12th Sept. 2008, Cardiff, Wales)*/ Ed. J.E.Jones, Cardiff University, 2008, p. 569 – 572.
10. V.A. Zhovtyansky. The interrelation between the departure from LTE and the space modes of electric arc plasma and diagnostic problems // *Proc. XXIII ICPIG (Toulouse, France. July 17-22, 1997)*/ University Paul Sabatier of Toulouse, 1997, v. 2, p. 152 – 153.
11. V.A. Zhovtyansky, Yu.I. Lelyukh, Ya.V. Tkachenko. Effect of radiation transfer on a deviation of dense electric-arc plasma from the equilibrium state: criterion approach // *Ukr. J. Phys.* 2012, v. 57, p. 311 – 321.
12. L.M. Biberman, V.S. Vorob'yov, I.T. Yakubov. *The kinetic of non-equilibrium low temperature plasma.*, Moscow: «Nauka»,. 1982, 375 p.(in Russian).
13. V.A. Zhovtyansky, Yu. I Lelyukh and Ya.V. Tkachenko. Nonequilibrium of the dense nonuniform plasma due to radiation transfer / Invited lecture // *XIX Int. Conf. on Gas Discharges and their Applications (2nd – 7th September 2012, Beijing, China). Proceedings* / Ed. Z.C Guan. – Beijing: Tsinghua University, 2012, p. 40 – 47.

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НЕРАВНОВЕСНОСТЬ ПЛОТНОЙ НЕОДНОРОДНОЙ ПЛАЗМЫ ВСЛЕДСТВИЕ ПЕРЕНОСА ИЗЛУЧЕНИЯ

В.А. Жовтянский, Ю.И. Лелюх, Я.В. Ткаченко

Кратко изложены результаты томографической спектроскопии плазмы свободно горящих электрических дуг между медными испаряющимися электродами. Оценивается роль резонансного излучения в отклонении от состояния локального термического равновесия плотной электродуговой плазмы. В отличие от хорошо известного критерия Грима принимается в расчет перенос излучения в плазме. Результаты численного моделирования показывают наличие эффектов неравновесности между основным, метастабильным и резонансным уровнями.

НЕРІВНОВАЖНІСТЬ ЩІЛЬНОЇ НЕОДНОРІДНОЇ ПЛАЗМИ ВНАСЛІДОК ПЕРЕНЕСЕННЯ ВИПРОМІНЮВАННЯ

В.А. Жовтянський, Ю.І. Лелюх, Я.В. Ткаченко

Коротко викладено результати томографічної спектроскопії плазми вільно горілих електричних дуг між мідними електродами, що випаровуються Оцінюється роль резонансного випромінювання у відхиленні від стану локальної термічної рівноваги щільної електродугової плазми. На відміну від добре відомого критерію Гріма ураховується перенесення випромінювання в плазмі. Результати чисельного моделювання показують наявність ефектів нерівноважності між основним, метастабільним і резонансним рівнями.