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Solar radiation spectrum and biospheric evolution^(*)

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Summary. — It has been known since long ago that the solar radiation is not only the sole source of energy for the Earth but also an important factor governing the evolution of life on the Earth due to changes both in the incoming energy and its spectral composition. The latter fact has determined a wide application in medical practice of phototherapy and laser means of treatment. Problems of phototherapy and laser means of treatment are numerous and diverse. We will only discuss specific problems connected with the recent investigations of the effect of the fine structure of the solar radiation spectrum on the biospheric evolution. This new problem is specific in that it illustrates a critical importance of interdisciplinary studies in the interests of medicine, biology, environmental sciences, and astrophysics.

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1. – Solar radiation spectrum and Fraunhofer lines

Passing through the atmosphere, the radiant solar energy suffers complicated transformations. On its way from the external atmospheric boundary to the Earth's surface the radiant energy is absorbed and scattered, with solar radiation attenuation in the atmosphere being selective, that is, depending on wavelength. Changes in the spectral composition of the passing solar radiation are determined by the following three factors:

- 1) molecular (Rayleigh) scattering;
- 2) aerosol scattering and absorption on large particles (dust, water droplets, etc.);
- 3) absorption by water vapor, carbon dioxide, ozone and other optically active trace gases.

In the UV spectral region, ozone is crucially important for changes in the solar radiation spectrum.

(*) The authors of this paper have agreed to not receive the proofs for correction.

Results of theoretical and observational studies of changes in the solar radiation spectrum near the Earth's surface have been widely discussed in the literature. New important results of studies of the fine structure of the solar radiation spectrum with the use of DOAS methods (Differential Optical Absorption Spectrometry) have been obtained by Sierk *et al.* [1]. Below will be discussed only special features of the solar spectrum connected with the presence of Fraunhofer lines.

In astronomy, studies of Fraunhofer lines have been in focus for a long time, since from the data on these lines a lot of information about the Sun has been obtained. Observations of Fraunhofer lines have shown, for instance, which chemical elements are present on the Sun, and enabled one to assess the physical conditions in the atmosphere of the Sun (temperature, pressure, magnetic field, etc.).

Fraunhofer lines' intensity depends on a relative amount of atoms of the respective element, with six metals (Na, Me, Si, K, Ca, and Fe) constituting 95% of the mass of the solar atmosphere, and magnesium and iron are its dominating components. The chemical composition of the solar and terrestrial atmospheres is known to be somewhat similar. However, an exception is hydrogen which is more abundant on the Sun than on the Earth.

It should be noted that solar radiance within Fraunhofer lines can substantially change in the lower atmosphere. Grainger and Ring [2] were the first to pay attention to this phenomenon. They observed the $H(3968\text{\AA})$ line in the spectrum of light reflected by the Moon to discover possible luminescent radiation.

Noxon and Goody [3] confirmed the results obtained by Grainger and Ring and showed that in the scattered skylight there is a non-polarized component with an intensity constituting about 1–3% of total scattered light intensity, and the spectrum of this component does not contain Fraunhofer lines. Noxon and Goody [3] believe that the most probable cause of the non-polarized component is "incoherent scattering" as a result of aerosol fluorescence. Investigating the line of iron ($\lambda \sim 4300\text{\AA}$), they found out that an additional brightness in the daytime is not constant. At noon, it constitutes $\sim 3\%$ of the sky brightness outside Fraunhofer line, and in the afternoon, two hours before sunset, the relative intensity at this wavelength reaches only 1%. This testifies the fact that additional brightness depends on the atmospheric mass and, hence, one may suppose that the brightness of an additional component forms in the atmosphere itself, in its rather low layers. Noxon and Goody [3] made an attempt to locate this phenomenon. With this aim in view, they compared the results of surface and aircraft observations at the height 13 km. Measurements were made for the line $K(\lambda \sim 3934\text{\AA})$ in skylight and sunlight. It was found out that an additional component can completely form within the layer of the order of several km thick above the Earth's surface.

Thus investigations accomplished by Noxon and Goody [3] suggested the conclusion that the magnitude of an additional brightness in the visible averages 2% of the sky brightness, that is, approximately $1.5 \cdot 10^3 \text{ erg/cm}^2$.

Also, it should be emphasized that a decrease of Fraunhofer lines' depth due to their additional illumination changes strongly depending on wavelength. In the long-wave UV ($\lambda \sim 3986\text{\AA}$), this effect can reach 25% [3], while in the dark blue ($\lambda \sim 4383\text{\AA}$) and yellow ($\lambda \sim 5890\text{\AA}$) spectral regions it constitutes only 1–3%. This effect depends much on cloud conditions. Under conditions of overcast cloudiness and in case of K line it constitutes about 17% and for H line 15%, that is it remains substantial.

The work by Lukshin *et al.* [4] has been also dedicated to a study of Fraunhofer lines' transformation in the spectrum of direct solar radiation. The authors believe that there is an additional atmospheric radiation propagating in the direction of solar rays, and

as a result, Fraunhofer lines get smoothed (lines 3933 and 3968Å as well as a totality of lines near 4305Å were studied). It was found out that the depth of lines (H , K) in direct solar radiation is time-variable, whereas the depth of Fraunhofer lines near 4305Å remains practically the same.

Without dwelling upon the cause of this phenomenon, Lukshin *et al.* [4] believe that smoothing of Fraunhofer lines is due to the atmospheric self-emission. The fact should be noted that Fraunhofer lines get transformed, and this directly concerns the biological processes taking place in the organisms of plants and animals.

If Fraunhofer lines are observed in the spectrum of not direct but scattered radiation, they turn out to be less deep, which has been first discovered from observations of the sky brightness in H -line Call ($\lambda = 396.8$ nm) and has been defined as “the Ring Effect” (RE). It was also found out that the degree of linear polarization in the intervals of strong Fraunhofer lines is lower compared to the surrounding continuum. Various explanations have been suggested with respect to the nature of RE as connected, in particular, with the effect of aerosol fluorescence, airglow, and reflection of light by the surface.

It has been reliably established, however, that the main cause of ER is the rotational Raman scattering (RRS) by molecules residing in the atmosphere [2]. RRS is a non-elastic process, the wavelength of scattered light shifts with respect to the direct solar radiation. With the process of non-elastic scattering taken into account, the RE can be explained by the fact that in the spectral intervals containing Fraunhofer lines the radiation flux whose wavelength shifts from the region of continuum into the interval of the line exceeds substantially the scale of transformation in the opposite direction. Therefore Fraunhofer lines in the scattered light turn out to be “filled in”. An analysis of observational data has justified such an interpretation.

Since the information about the RE intensity and variability is of interest, in particular, for the solution of numerous problems of the remote sounding of the atmosphere, including the retrieval of the content of trace gases in the atmosphere, Stam *et al.* [2] have undertaken an analysis of the observed spectra of the cloudless sky polarization in the zenith. An examination of the spectra in the wavelength interval 350–400 nm revealed the presence of the fine structure coinciding with Fraunhofer lines in the direct solar radiation spectrum (RE). The observational data indicate that the fine-structure intensity depends not only on the solar zenith angle but also on atmospheric conditions, especially on the content of aerosol in the atmosphere. With the use of an algorithm of the theory of radiation transfer considering RRS (with an approximation of primary and secondary scattering) in the presence of atmospheric aerosol it is quite possible to adequately simulate the fine structure observed in the spectra of skylight polarization and its angular dependence.

2. – Spectral composition of solar radiation and biospheric evolution

All physical, chemical and biological processes taking place on the Earth’s surface, in the atmosphere and water basins are known to be governed by solar radiation. The light reaching the Earth is characterized by intensity (quantity) and spectral composition (quality) [5-16]. Since from the very beginning of its existence the Earth has been under the influence of direct solar radiation, irradiance and spectral composition of solar radiation determined the composition of organic substances formed under the influence of solar radiation —the main source of energy for the synthesis of biochemically important compounds in the pre-biological period.

In the period of the pre-biological-chemical evolution resulting in the beginnings of life

on Earth, during first 1-2 billion years of the Earth's existence, when there was little free oxygen in the planetary atmosphere and, hence, the formation of a powerful ozone screen protecting the Earth's surface from UV radiation on wavelengths shorter than 300 nm was impossible, this spectral region of solar radiation provided energy for synthesis of various biochemically important compounds. The elementary substances residing in the atmosphere, hydrosphere, and lithosphere as well as in the near space (H_2O , N_2 , CO , CO_2 , CH_2O_2 , HCN , etc.) formed the basis for the formation of various biochemically important compounds — amino acids, bases of nucleic acids, etc., later on being the basis for biopolymers. The absorption spectra of aromatic amino acids and bases of nucleic acids cover the wavelength interval 260–280 nm, which corresponds to a “depression” in the solar spectrum. Further formation of the Earth's ozone screen promoted the formation and protection from photo-destruction of compound polymers of amino acids (proteins) and polymers of the bases of nucleic acids (nucleic acids) absorbing radiation in the interval 260–280 nm. In this connection, there is no doubt that the problem of the ozone screen depletion has important ecological aspects to be investigated at the biochemical level.

Below is given an analysis of the importance of participation of metals in the biochemical processes of the origin and evolution of life and of the role of Fraunhofer lines of the Sun in these processes.

Such metals as Mg, Fe, and Ca are known to be major metals ensuring practically all most important metabolic processes in living organisms. At present, an enormous value of basic metals (Fe, Zn, Mg, Ca, Mo, etc.) for the living systems' functioning has been widely recognized, and in this connection, a new field of science — inorganic biochemistry — is rapidly developing. The importance of trace metals becomes especially evident, if we take into account that several hundred ferments (more than one third of all ferments known) are metal-enzymes, and their functioning is impossible without participation of metals. Apparently, the metals not only stabilize the structure and create an active conformation of the ferment but also directly participate in the processes of catalysis. So, metals with variable valency such as Fe, Cu participate in the catalytic act (in reduction-oxidation processes) indirectly, and metals such as Zn and Mg function as Lewis oxygen in enzymatic reactions of hydrolysis, synthesis, etc.

Apparently, in the period of pre-biological evolution resulting in life on the Earth, ions of metals had served as catalysts which then functioned in combination with organic substances giving proto-ferments whose further evolution led to an appearance of metal-ferments. According to Egami *et al.* (see [13], those metals which dominated in sea waters were included in metal complexes evolving then to metal-enzymes. Apparently, also important is a consideration of the effect of special features of the solar radiation spectrum and especially Fraunhofer lines, on the processes of inclusion of metals into proto-ferments and other metal-organic biological complexes.

Consider now some features of the photosynthesis evolution. It is known that first plants originated in water. As a result of photosynthesis of these plants, the spectral composition of the incoming radiation was gradually changing due to solar radiation absorption by atmospheric oxygen and its derivatives: ozone, carbon dioxide, nitrogen oxide, and others. When the amount of ozone grew so that it formed a shell around the Earth, this created conditions for plants' growing on land. In this connection, however, a problem appeared to protect the plants from excess intensity of sunlight received by the plants. Already K. A. Timiriazev had pointed out that the photosynthesis intensity was not proportional to that of sunlight.

The light saturation level of photosynthesis for most of the plants is within (100–300)·

10^3 erg/cm² s. Further increase of light intensity reduces the rate of photosynthesis. It was shown [17] that under conditions of excessively high illumination when the light intensity exceeds $(300-400) \cdot 10^3$ erg/cm²s, the processes of pigments' biosynthesis, inhibition of photosynthetic reactions as well as growing processes are drastically violated, which reduces the total plant productivity. At the same time, the intensity of sunlight reaching the Earth's surface can exceed this limit several times, especially on cloud-free days. Therefore, the plants had to develop some protecting mechanism against destructive changes in the excessive solar radiation intensity. This mechanism has been developed in the process of evolution.

Note that the photosensibilizing systems of plants include two major groups of pigments: tetra-pyrrols (chlorophylls, cytochromes, phycobilines) and pigments of isoprenoid nature combined into the group of carotenoids. The structural base of all tetra-pyrrol compounds is porphyrin.

The solar spectrum has two abrupt and deepest minima in the wavelength intervals 390–400 nm and 430–440 nm. A maximum of the porphyrin absorption band coincides with the first of the indicated minima. This strong-absorption band corresponds to a pure electron transition and is present in all tetra-pyrrol macro-cycles.

The second deep minimum in the solar spectrum corresponds to a maximum of the basic absorption band of carotenoids constituting the second group of plants' pigments. An artificial synthesis of isoprene testifies to a possibility of abiogenous synthesis of the main carotenoid precursors in conditions of the initial Earth. Therefore, precursors of all pigments of plants could have formed in the abiogenous way in the course of chemical evolution, and their photochemical properties could have been pre-determined by special features of the solar spectrum.

A question arises: why did the main absorption bands of all pigments' precursors turn out to be bound with two abrupt and deepest minima in the visible region of the solar spectrum? One of the possible answers to this question may be the following: the molecules whose spectral absorption maxima are in the interval of an abrupt variation in the incoming solar radiation intensity, can (due to either weak conformational changes or local environment) change (within several nm) the location of its maximum absorption—shift it towards either increase or decrease of light intensity in a given solar spectral region. A realization of this possibility might be a step towards regulating the intensity of the process of light absorption. The presence of two close conformational conditions of the same molecule sharply differing in the probability of the light absorption, could stimulate a specialization of photoactive molecules, their transformation into precursors of future light-collecting complexes and centres of transformation, processing of the light energy into chemical one.

Proceeding from chemical to biochemical evolution, one can also observe the coincidence between spectral maxima of absorption of the completely formed pigments with the deepest minima in the solar spectrum. The older are the organisms with the pigment, the wider and deeper is a minimum in the solar spectrum which corresponds to a maximum of absorption.

Major maxima of absorption for bacteriochlorophyll-a correspond to deeper depressions in the solar spectrum (365–375, 390–400, 760–765) compared to absorption maxima for chlorophyll-a (410, 430, 660 nm). This can be explained by two circumstances:

- 1) Photosynthesis of bacteria with only one photo-system is accomplished without separation of oxygen and is the most primitive process. This suggests a supposition that photosynthetic pigments of bacteria had appeared at earlier stages of evolution compared with chlorophyll-a. It can be assumed that in the process of evolution,

bacteriochlorophyll-a had formed independently, beginning from synthesis of uroporphyrinogen. Also, it should be noted that a coincidence of the red absorption maximum for chlorophyll-a with the atmospheric oxygen absorption band (760 nm) can favor the hypothesis of an abio-genous origin of oxygen on the Earth.

2) For bacteria, one molecule of bacteriochlorophyll-a in the reactionary centre falls on 20 to 100 molecules of bacteriochlorophyll-b constituting the light-collecting system. For higher plants this quantity varies between 200 and 400. On this basis, one can state that the level of specialization of pigments of the photosynthetic apparatus for bacteria is much lower than for higher plants. The way of adaptation to the level of solar radiation intensity for bacteria is more primitive than for higher plants: bacteria mostly use the mechanisms for adjusting the absorption bands of their pigments to solar spectrum minima, and their antenna systems are far from being perfect. The basic pigment of higher plants (chlorophyll-a) is less oriented towards minima in the solar spectrum: higher plants are characterized by larger light-collecting complexes which include, apart from chlorophyll-a, a highly specialized pigment: chlorophyll-b.

3. – Stability of biomolecules' geometry and Fraunhofer lines of the Sun

As has been mentioned already, the solar atmosphere contains many metals, with two of them (Mg and Fe) constituting about 50% of the solar atmosphere mass. Besides, it is important that only Mg and Fe determine strong Fraunhofer lines in the biologically important spectral region.

On the other hand, results of studies in the field of inorganic biochemistry indicate that major metal-containing molecules performing the most important functions in catalytic reactions, are metal-ferments containing Mg and Fe in the active centre: chlorophylls, cytochromes, ferredoxins, haemoglobin, myoglobine, and others. The nature of metals inclusion into the most important biologic molecules is not clear. At least, their existence on the Earth does not play a decisive role.

Thus molecules residing the solar photosphere and determining the formation of strong Fraunhofer lines, are also present on the Earth as parts of living organisms. To prove that this coincidence is not occasional and that it is Mg and Fe that should be present in the most important biological molecules, it is necessary to remind of the role of these metals in the biological molecules. For instance, magnesium plays a unique role in the molecule of chlorophyll and its protein complexes in case of the transformation of light energy into chemical potential of the plant cell. All chlorophylls participating in photosynthesis are coordinating compounds of magnesium. The coordinating role of magnesium in the chlorophyll molecule cannot be played by any other metal contained in chlorophyll.

One of the important functions of magnesium is to ensure the work of molecular electric pumps (proton ATPase (Na^+ - K^+)-ATPase). Due to ferments' functioning, on the surface of membranes of vegetative and animal cells the electric potential difference is maintained of the order of 600–100 mV needed to transport substances through the cell's wall. During the functioning of ferments, magnesium penetrates the active centre of the ferment ensuring its necessary conformational condition when bounding and releasing ions of hydrogen, sodium, and potassium.

Magnesium plays a unique role in fermentative reactions connected with the functioning of the genetic apparatus: Mg-activated ferments guarantee a transcription, translation, and replication of the genetic code. Of great importance is the stabilizing role of magnesium in maintaining the geometry of the DNA dual spiral, tertiary structure of t-RNA. In these examples, in many cases, metal as a component of the active centre of

the ferment is in a strained state, when the electron state of the metal strongly affects the conformational properties of protein and, hence, its catalytic activity.

It is known that the basic factor of the formation of the chlorophyll absorption spectrum is its tetra-pyrrol structure. An inclusion of magnesium into the tetra-pyrrol system substantially changes the spectral properties of the whole molecule of chlorophyll. At the same time, the chlorophyll molecule becomes more symmetric, the electron density becomes the same for all nuclei and the four pyrrol nuclei become equivalent. Besides, the atom of magnesium determines the capability of the chlorophyll molecule to form associates due to additional coordinative bonds.

Light absorption in the lines of magnesium is negligibly small in energy compared with absorption determined by the porphyrin ring, since magnesium lines are very narrow (2–3Å). However, despite a small energy contribution to net radiation absorption by the chlorophyll molecule, magnesium-determined absorption plays an important coordinative role in the topology of the chlorophyll-protein complex. Therefore, for instance, an artificial illumination of the chlorophyll molecule in the lines of magnesium may be important as a factor breaking the coordinative chlorophyll-protein bonds leading to macro-changes in the course of the whole photosynthetic process.

Due to the presence in a chlorophyll molecule of four atoms of nitrogen, the carbonyl and carboxyl groups containing oxygen (CO, COOH) can form the coordinative bonds at the expense of undivided electrons. Therefore an illumination in magnesium lines is efficient from the viewpoint of the influence on undivided electrons of magnesium which form the coordinative bonds (magnesium gives a part of electrons to the common "P" cloud of porphyrin).

Like an atom of magnesium, an atom of iron owns coordinative properties. As a result of specific construction of ligands of the active centre directly bound with the atoms of iron, low excitations can lead to substantial shifts of ligands, which in its turn can lead to marked changes even in the parts of protein molecules which are far from an atom of metal and active centre. It can be exemplified by a well-studied molecule of hemoglobin in which an interaction of the iron atom with ligands in the fifth and sixth coordinative positions plays a decisive role in determination of the catalytic activity of the ferment when binding oxygen.

Recent numerous studies in the field of quantum biochemistry and molecular biology testify to a unique role of metals, especially magnesium and iron, in the functioning of biological objects. So, for instance, iron and magnesium are part of most important biological ferments (metal-containing proteins) as a constituent of the catalytically active centre of the ferment. Among such ferments are, first of all, the oldest iron-containing proteins — cytochromes, forming the basis of respiratory systems for all living objects; magnesium-containing chlorophyll-protein complexes of green plants; iron-containing proteins of hemoglobin; magnesium activated ferments; sodium-potassium ATPase and proton ATPase maintaining an electric potential on the surfaces of all living cells, which provides the ATPase synthesis and an active transport of substances through the walls of a cell, and many others.

A characteristic feature of the functioning of the metal-containing ferments mentioned is a necessity to maintain a strongly defined geometry of the active centre of the ferment at the moment of its functioning and spatial orientation of the substratum molecule with respect to the active centre. These requirements, most important for biochemical reactions, are met by the electron structure of the atom of metal as part of the active centre and bound with the atoms of the centre by its electron orbits. A change in the radii of the electron orbits of the metal due to light-forcing of its electron levels can change

both the geometry of the ferment's active center and geometry of the whole molecule, which strongly affects the ferment's catalytic activity and negatively tells upon the course of biochemical reaction.

In this sense, metal is a stabilizer of certain conformations of protein molecules needed to provide the catalytic activity of ferments. Besides, an atom of metal can affect a molecule of substratum changing its electron structure so that it more easily reacts with ferment or it may play the role of a bridge connecting the ferment and the substratum when they form an intermediate compound, and stabilizes the conformation of this intermediate compound [2].

Thus the maintenance of the electron structure of an atom of the metal of active centre in a quiet state is the most important requirement for the normal course of biochemical reactions with the participation of metal-containing proteins. This requirement can be met by including into the active centers of ferments, through natural selection, of the metals whose absorption lines are not sun-irradiated (within Fraunhofer lines), that is, metals in the solar photosphere.

Another possible way to reduce the probability of light-exciting the atom of metal is its screening with an electron cloud of adjacent atoms. It can be exemplified by the porphyrin ring with an atom of magnesium in the center (the base of the chlorophyll molecule). Here a maximum of one of the absorption bands of the electron cloud of generalized electrons of the porphyrin ring exactly coincides with the strongest (in the visible) electron transition of magnesium atom in the interval 517–518 nm. The need to ensure a strict geometric stability of the structure of molecule —ferment— is one of the causes of coincidence between the composition of basic metals as part of both the most important ferments of the cells of living organisms and the photosphere of the Sun, which is due to the presence (in the latter case) of Fraunhofer lines.

On the whole, metals as part of the most important biologic molecules play a very important role in a number of processes: formation of the spatial structure of many proteins which are the most important ferments in reactions of nucleic acids formation through their binding and twisting into one macromolecule forming a tertiary structure; binding nucleic acids with proteins; stabilization of the t-RNA tertiary structure; formation of light-absorbing pigment-protein complexes of plants and organization of the spatial structure of many other sub-molecular complexes (ribosomes, molecular pumps of membrane, etc.). Quite probable is the bond between chlorophyll and protein in the pigment-protein complex via magnesium atom. The magnesium atom plays in this complex the same role of stabilizer of the molecular structure (topology) like the atom of iron in iron-containing ferments, which indicates a common topological principle of the spatial structure organization for most of the ferments: metal + protein. In this respect, the chlorophyll-protein complex with the atom of magnesium is a valid system [2].

Entering the porphyrin ring, which in its turn is a part of protein, a metal gets surrounded with protein ligands (atoms of the porphyrin ring and atoms in the fifth and sixth coordinative bond). The complex containing metal-porphyrin and adjacent atoms of aminoacid residia of protein is characterized by energy levels (which are partially levels of metal), partially almost pure levels of metals with weak additions of the levels of ligands, and the remaining part represents the combined levels of ligand ($\pi \rightarrow \pi^*$), metal \rightarrow ligand, ligand \rightarrow metal.

In metal-porphyrins, the main contribution to the light absorption energy is made by the levels ligand \rightarrow ligand ($\pi \rightarrow \pi^*$), whereas the levels ligand \rightarrow metal are insignificant. In the net spectra of metal-ferments of the pigment-protein complexes there are pure metal lines. However, the intensity of transitions connected with them is weak. Therefore

from the energy point of view, the absorption due to metal lines (contribution to the absorption by the whole complex molecule) is not that significant and, hence, the role of metal in the energy of light absorption by the metal-containing complex organic molecule is not very significant.

As has been mentioned, metals play a very important role in the structure of the molecule acting as a stabilizer of geometry (topology of a molecule) of the element as well as a coordinator in the course of catalytic reactions with the participation of metal-ferments. To perform these functions, it is necessary to keep the metal electron shell stable, since its weak disturbances amplify and are transmitted to remote parts of biomolecule, which leads to undesirable macroscopic consequences connected with the conformational changes of the active centres of ferments and the molecule on the whole [11].

It should be noted that only for Mg and Fe was it reliably established that it is they that perform important biological functions in the porphyrin complexes, whereas the role in photosynthesis of Cu contained in the porphyrin complexes has been poorly studied. Cu-uroporphyrin determines the colour of the feathers of some birds and does not perform any important biological functions. An attempt to determine the role of Zn-porphyrins *in vivo* was not a success either.

Thus the conclusion can be drawn that the stable electron structure of metals contained in the active centres of ferments is the most important condition for the normal functioning of metal-ferments closely connected with the conformational states. The stability of the electron structure of metals is achieved by two ways:

- 1) including into ferments of the metals that constitute the atmosphere of the Sun (however, the solar spectrum lacks the absorption lines of these metals);
- 2) screening the metals with the porphyrin ring (with its π -electrons). Thus the metal strengthens the ferment's topology without its participation in the radiation absorption by pigment molecules.

From this point of view, one can also explain the fact that the mechanism for the evolutionary stability of the tertiary structure of protein molecules containing Fe and Mg is based on the absence of radiation at the wavelengths of Fe and Mg Fraunhofer lines in the solar spectrum.

4. – Dependence of some biological processes on the metal electron shell photoexcitation

As has been mentioned, for the atom of metal to perform the most important functions in the course of biochemical reactions, it is necessary to protect its electron shell from the solar radiative forcing. Bearing in mind a great value of Fraunhofer lines as spectral reference points in the mechanisms of adjustment and functioning of the pigment systems, it can be supposed that artificial photoexcitation of the metal atom's electron shell can substantially affect the basic metal-containing molecules which perform the most important functions in the course of catalytic reactions. In this connection it is important to understand what happens with the disappearance (or partial disappearance) of Fraunhofer lines. Such a situation can really happen due to emissions produced by anthropogenic admixtures in the atmosphere which lead to blocking Fraunhofer lines [3].

Following these assumptions, a number of laboratory experiments have been conducted with the use of the most important metal-ferments. This made it possible to prove the biological value of Fraunhofer lines and to analyze the role of their emissions dueto anthropogenic admixtures in the atmosphere.

Irradiation of etiolated plants in the intervals of Fraunhofer lines and the transformation of pigments [18].

The existence of the evolutionary adaptation of green plants to the solar spectrum does not raise doubts. Already K. A. Timiriazev in his outstanding studies had proved the capability of green chlorophyll to absorb solar radiation in red and dark blue spectral regions.

Later on, attention was focused on studies of the biological role of various solar spectral regions. The evolutionary approach to the solution of this problem has been mainly confined to the analysis of the importance of the UV spectral region, since in this region the atmospheric absorptance plays a significant role [19]. Most interesting are studies of the regulating role of radiation which affects the phytochrome.

The recently established coincidence of spectral maxima of absorption for basic pigments of plants with characteristic minima of solar spectrum (Fraunhofer lines) deserves attention. Based on this fact, there is a possibility to assume a universal functional significance of Fraunhofer lines, which can play the role of spectral reference points in the functioning mechanisms of the pigment systems responsible for various processes related to plants' growth and directly or indirectly depend on light (photosynthesis, photoperiodicity, photoregulation).

Accepting this hypothesis has led to the discovery of a new phenomenon consisting in the biological effect of the strong variability of solar spectral irradiance within intervals of corresponding Fraunhofer lines. Firstly, a study has been undertaken of the mechanism of protochlorophyll reproduction with resulting chlorophyll formation in case of irradiation of etiolated germs by solar and additional light within the iron Fraunhofer lines. As known, in the course of biospheric evolution, the process of chlorophyll biosynthesis developed (and is developing now) in the direction of increasing its energetic efficiency. Gradually, the mechanism of this evolution has adapted itself to the use of available light energy. It is this evolution that determines the possibility of further chlorophyll phytolization and the structural reorganizations of the photosynthetic apparatus which is responsible for its functional activity.

As far back as 1962, Sud'ina and Lozovaya [14] developed a combined method of the chromatographic and spectral analysis to determine the light-dependent transformation of green precursors of chlorophyll. In its time, this method made it possible to exactly establish the sequence of reactions of reduction and phytolization in the process of chlorophyll biosynthesis in the course of evolution of photosensibilization. It is based on the chromatographic division (depending on hydrophoby) of the pigments pairs protochlorophyllid-chlorophyllid, protochlorophyll-chlorophyll, as well as on the consideration of the spectral difference between the pairs protochlorophyllid-protochlorophyll, chlorophyllid-chlorophyll depending of the degree of reconstruction of the fourth pyrrol ring.

In this context, an attempt has been undertaken to experimentally discover the dependence of the protochlorophyll reproduction reaction on additional solar irradiation at certain Fraunhofer lines. An additional irradiation was carried out on Fraunhofer lines of iron in the interval 340–480 nm. The total intensity of the additional irradiation within Fraunhofer lines at the moment of illumination did not exceed 1% of the integral solar irradiance.

The experiment has shown that the solar irradiation of etiolated wheat germs during 10–30 minutes leads to a total transformation of protochlorophyllid (precursor of chlorophyll) into chlorophyllid. Therefore in this case the fluorescence spectra revealed only a

maximum of chlorophyllid. An additional irradiation within the Fraunhofer lines of iron did not lead to marked changes in the phytol-free precursors of chlorophyll immediately after irradiation, which indicates the complete transformation of protochlorophyllid into chlorophyllid independent of the irradiation conditions under study.

It has been also established [14] that a long irradiation of the etiolated germs leads to the transformation of protochlorophyllid into chlorophyllid only under conditions of repeated darkening. With this fact taken into account, the ratio was determined between the chlorophyll precursors in the repeatedly darkened etiolated germs one day after their irradiation with sunlight during 10 and 30 minutes for control purposes and in the respective versions with an additional irradiation within the Fraunhofer lines of iron.

It turned out that the germs irradiated with only sunlight differed from the samples with a 10-minute irradiation by the relationship between maxima of fluorescence of protochlorophyllid and chlorophyllid due to accelerated reaction of reproduction, that is, a 10-minute preliminary irradiation and 24-hour darkness led to a larger content of protochlorophyllid compared to chlorophyllid, whereas with a 30-minute irradiation their ratio was equal to unity.

In the versions with an additional sunlight irradiation within Fraunhofer lines (in combination with solar radiation) the 24-hour aftereffect has made it possible to detect a considerable inhibition (in both cases of 10 and 30 minutes of preliminary irradiation) and accumulation of chlorophyll precursors. This can indicate an effect of additional irradiation within Fraunhofer lines on reactions of chlorophyll biosynthesis in the darkness, which precede the formation of protochlorophyllid. However, this does not exclude a possibility of rapid reactions of further transformation of protochlorophyllid.

Special attention should be paid to a decrease of chlorophyll as a consequence of sunlight irradiation within Fraunhofer lines. A 30-minute illumination leads to a much weaker formation of chlorophyll (only traces have been observed) compared to a 10-minute illumination. This can reflect either a retarded response of protochlorophyllid or an accelerated chlorophyll phytolization with the formation of chlorophyll.

Also, it should be noted that with irradiation of etiolated germs in darkness only within Fraunhofer lines (the time of irradiation is 10 or 30 minutes with their subsequent diurnal stay in darkness), the same effect as with only sunlight irradiation has been obtained: protochlorophyllid completely transformed into chlorophyllid.

Thus the results of the experiments suggest the conclusion that an additional irradiation of etiolated germs of wheat and rye within the Fraunhofer lines of iron during their illumination with sunlight seriously hampers the biosynthesis of basic pigments, whereas an irradiation of the germs in darkness only within Fraunhofer lines does not lead to principal differences compared to the germs irradiated only by sunlight. These results confirm the hypothesis of a specific (not energy dependent) mechanism of the light effect within intervals of Fraunhofer lines. The mechanism of biosynthesis is based on the principle of breaking the balance of the spectral composition of the physiologically active light simultaneously within several Fraunhofer lines.

Photoexcitation of the magnesium atom's electron shell and the functioning of (Na⁺-K⁺) [20].

It has been theoretically proven that the rigid electron structure of metals contained in the most important biomolecules is due to the existence of Fraunhofer lines in the solar spectrum. To confirm this conclusion, an experiment has been carried out to determine dependences of some fermentative reactions in a living cell on photoexcitation of the

magnesium atom's electron shell.

As is known, an inclusion of magnesium into biological molecules is necessary for a number of the most important fermentative reactions taking place in a living cell. The condition of the electron shell of Mg atom determines necessary conformational changes in the molecule of ferment and substratum in the course of fermentation reactions. Therefore the absence in the solar spectrum of radiation within the lines of Mg is of a great biological importance [16]. One of the important functions of Mg is to provide the functioning of the molecular electric pumps (proton ATPase, $(\text{Na}^+ - \text{K}^+) - \text{ATPase}$). Due to the functioning of these ferments, the electric potential difference of the order of 60–100 mV is maintained at the surface of membranes of plant and animal cells, needed for the transport of substances through the wall of a cell. During the ferments' functioning, Mg-ion enters the ferment's active centre providing the needed conformational conditions of the ferment when binding and releasing ions H^+ , Na^+ , and K^+ .

Proceeding from the earlier studies [21, 18], it can be supposed that photoexcitation of the Mg atom's electron shell can strongly affect the functioning of $(\text{Na}^+ - \text{K}^+) \text{ATPase}$.

To confirm this supposition, a special experiment has been undertaken. In laboratory conditions, a fermentative reaction was modeled with the participation of Mg atoms through splitting-off of inorganic phosphate from ATPase by Mg-dependent adenosine triphosphate (Mg-ATPase).

A sample was illuminated with the Mg d.c. arc. Between the arc and the sample colour filters ЖС-17 and СЗС-7 were placed (ensuring an isolation of three basic lines of magnesium — 516.7, 517.2, and 518.2 nm) and a collecting lens.

For the reaction to take place, the microsome fractions of the cattle brain were used. The sample was obtained by differential centrifugation and was a suspension of microsomes in 0.625 M sucrose. Apart from the ferment sample, the reaction medium contained: $\text{Na}_2 \text{ATPase}$ 2 mM, MgCl_2 2 mM HCl ($\text{pH} \sim 7.2$) 60 mM. Protein (1 mg) was introduced into the sample 1 ml in volume. The reaction going on during 1.5 minute at 25°C was stopped by adding a 5% trichloroacetic acid (TCA). The ferment's activity was determined from the amount of inorganic phosphate split-off from ATPase due to ferment. Inorganic phosphate was determined by the Fiske-Subbarow method. Three versions of the experiments were carried out.

1) The ferment sample (0.2 ml) containing 1 mg of protein was irradiated within the three lines indicated above during 90 s. Upon irradiation, the sample was immediately added to the reaction medium. The reaction lasted 90 s, then it was stopped with TCA.

2) The mixture of ferment (1 mg of protein) with 2 mM MgCl_2 was irradiated with the subsequent reaction as in item 1.

3) The mixture was irradiated containing the reaction media with protein, and then the reaction was stopped with TCA immediately after irradiation.

In all experiments there were control samples kept under the same conditions as the test samples but not irradiated and samples in which the substratum reaction medium without ferment was irradiated. The latter control was made to exclude a possibility of spontaneous splitting of inorganic phosphate from the Mg-ATPase complex under the influence of the magnesium electric arc irradiation.

The results of the experiments are as follows. In the first series, with irradiation of an isolated ferment medication, the ATPase activity did not change, but in the second series, with irradiation of the ferment sample with an addition of 2 mM MgCl_2 the activity of the Mg-ATPase ferment increased by 25–30%. And, finally, in the third series of experiments, with irradiation of the vat with the ferment sample and complete mixture of the reaction medium, the Mg-ATPase activity increased by a factor of 1.5.

Thus the Mg-ATPase activity changes with irradiation of samples within Mg lines only in the presence of Mg^{++} ions in the irradiated sample. This indicates the functional biological value of Fraunhofer lines (516.7, 517.2, 518.2) of the solar spectrum for Mg. An irradiation within these lines (in our case with the magnesium arc) can strongly affect the fermentative reaction in which Mg^{++} ions are a constituent of the ferment-substratum complex.

Therefore the absence in the solar spectrum of radiation corresponding to Mg absorption lines stabilizes the regime of reactions with the participation of Mg-ATPase and makes these reactions independent of light.

Similar experiment was undertaken by Dreval and Girnyk [22]. The effect was studied of photoexcitation of the electron shells of Ca and Mg atoms on the ATPase activity. It was shown that Mg-ATPase and Ca-ATPase demonstrated a selective sensitivity in photoexcitation of Ca and Mg shells. With irradiation of the reaction mixture within Mg (518 nm) lines, the Mg-ATPase activity increased by a factor of 1.8 and practically did not change with irradiation on Ca line, whereas on the wavelength 445.5 nm the Ca-ATPase activity increased by a factor of 1.9.

Dreval and Girnyk [22] noted also that a change in the structure of the ferment active centre can affect either the stage of formation of the ferment-substratum complex or the stage of disintegration of this complex.

These changes have been estimated by evaluating the Michaelis constant (K_m) and maximum rate of reaction (V_{max}). It was found out that with irradiation of Mg-ATPase within Mg wavelength the Michaelis constant K_{ATP_h} increases by a factor of 1.7 and V_{ATP_h} increased by a factor of 1.4. Based on these data, Dreval and Girnyk [22] drew the conclusion that with irradiated Mg-ATPase a decrease takes place of affinity of the complex Mg-ATPase to the ferment active centre and an increase of the velocity constant of the ferment-substratum complex disintegration with the formation of reaction products.

Since the Ca-ATPase of plasmatic membranes accomplishes an active transport of calcium due to the energy of ATPase hydrolysis, the kinetic parameters for the Mg-ATPase (K_{ATP_h} , V_{ATP_h}) complex and for Ca (K_{Ca} , V_{Ca}) were determined both in the control sample and irradiating the incubating medium within Ca wavelength. It was shown that as a result of Ca-ATPase irradiation the value of K_{ATP_h} increased by a factor of 1.3 and that of V_{ATP_h} by a factor of 2.1.

Thus the results obtained by Dreval and Girnyk [22] confirmed our hypothesis that an increase of the ATPase activity of the investigated ferments is connected with the initial photoexcitation of the electron shells of Mg and Ca atoms.

It has to be pointed out that the character of fermentative reactions in which the Mg atom directly participates can be only affected by irradiation within the respective Mg absorption line. Irradiation at a wavelength even slightly differing from the Mg absorption line, does not affect the reaction at all. To confirm this conclusion, these reactions were repeated but irradiating with the laser of the wavelength 514.5 nm. This irradiation did not produce even a small effect on the course of the fermentative reaction.

The results obtained show that an inclusion of Mg, Fe, and Ca into the most important biological molecules is a unique property of biomolecules acquired in the process of evolution in order to adapt the optical characteristics of biomolecules to characteristic minima of solar radiation spectrum (Fraunhofer lines) to stabilize the functionally important chemical bonds determining the conformation as a function of photoexcitation due to sunlight.

5. – The impact of the solar radiation spectral composition on biological processes

The functional value of the solar Fraunhofer lines for biological objects has been demonstrated above. It was shown the basic metal-containing molecules performing the most important functions in catalytic reactions are metal-ferments containing in their active centres the metals which exist in the photosphere of the Sun and form powerful Fraunhofer lines in the biologically important spectral region. Such metals are magnesium and iron. Entering the active center of the molecule, the atom of metal determines its conformation and controls the molecule's geometry. Therefore the problem of protection of the metal atom's electron shell from external forcings is an important aspect of the evolutionary biochemistry.

Absorption bands in the solar spectrum exist due to the terrestrial atmosphere and are called telluric. In the UV, the solar spectrum sharply breaks and practically the rays with wavelengths shorter than 290 nm do not reach the Earth. Ozone with Hartley, Huggens and Chappui absorption bands is responsible for the solar radiation absorption in the UV. Molecular oxygen has absorption bands at wavelengths 759, 687, and 628 nm. In the IR, there are numerous absorption bands of water vapour [23].

As for the absorption bands of some biomolecules, one can see that they exactly coincide with the absorption bands of atmospheric gases. For example, a maximum of absorption for the DNA molecule coincides with the ozone absorption band, that is, this molecule never "sees" the Sun. On this basis one can draw the conclusion about the functional value of this spectral feature of the Sun and DNA for life on the Earth protected with the ozone screen from the destructive mutagen effect of the UV [19]. A feature has been observed consisting in location of the long-wave maximum of absorption spectrum for chlorophyll-b between two deep minima of the solar spectrum (970–1150 nm) due to solar energy absorption by water vapour.

The fact that the spectral composition of light exhibits a complicated and diverse effect on various biological processes is not new. At present there are many publications dedicated to this problem. There is no doubt that the spectral composition of light plays a significant role in the development and growth of plants. Usually, this role is explained by relationships between red, dark blue, and far red light, that is, this is a question of energy.

However, as our studies have shown, not only energy plays an important role in the most complicated biological processes. The absorption of solar radiation in the intervals of Fraunhofer lines is negligibly small compared to absorption determined by the porphyrin ring, since magnesium lines are very narrow (2–3Å). In spite of this, an irradiation of the chlorophyll molecule within magnesium lines can be important as a factor of breaking the coordinative chlorophyll-protein bonds. And this, in its turn, leads to breaking the whole photosynthesis process.

At present there are many studies dedicated to the effect of dark blue light on the growth, development and metabolism of numerous compounds. It has been shown, for instance, that small doses (of the order of mW/cm²) of solar radiation between 350 and 500 nm can substantially affect the growth and development both of hetero- and phototrophic organisms. Despite an extensive experimental material indicating an amazing similarity of the effects of the electromagnetic radiation in the UV and dark blue spectral regions on various physiological processes, a detailed mechanism of the effect of dark blue light as well as initial photoreceptors have not been identified so far. The results of preliminary theoretical and experimental studies on the basis of analysis of the fine structure

of the solar spectrum and comparison of its characteristic minima with spectral maxima of a number of most important biological compounds (pigments, electron carriers, co-factors) enable one, in our opinion, to consider anew the problem of photo-regulation in biology and make some suggestions connected with the evolution of photo-dependent systems (see [13]).

The main idea of the new approach consists in the fact that the correspondence of major spectral maxima of absorption for some biomolecules in basic functional conditions (oxidized or reduced) at main stages of the cell energy metabolism to characteristic minima of the solar spectrum is not occasional. Oxidation or reduction of respective molecules leads to natural shifts of their spectral maxima of absorption with respect to the minima in the solar spectrum. Thus the functioning molecules can catch different amounts of the solar radiation photons. Flavins and some components of the electron transport terminal chain, cytochrome in particular, are most typical compounds with the characteristics mentioned above.

In the case of flavins, the ratio of probabilities of absorption of photons corresponding to the basic and oxidized states of flavins can change by a factor of > 2.5 due to a sudden change in the spectrum of solar radiation near 400 nm.

The main maximum of absorption due to the reduced form of cytochrome corresponds to the second in value minimum in the dark blue region of the solar spectrum (430 nm), and the difference of irradiance available for absorption by the reduced or oxidized form of this pigment constitutes several tenths of mW/cm^2 due to the presence of a minimum in the solar spectrum in the interval 430–432 nm. Even such small differences in energy absorbed in the dark blue spectral region can be physiologically important [13].

Thus the molecules whose major spectral absorption maxima are in the region of rapid change of the sunlight irradiance (in the region of Fraunhofer lines) can regulate the probability of their photoexcitation by shifting their absorption maxima into the regions of a rapid change of solar irradiance. The availability of the suggested hypothetical mechanism for photo regulation can be exemplified by proteins located in the knot chains of the energy metabolism. In this case one molecule rigidly bound with the regulation process can serve as a photoregulator.

Basic structural components of the iron-containing proteins are: iron ion included into the porphyrin ring and a protein globule surrounding iron-porphyrin. Due to electron d-orbitals of the iron atom, one of the main interactions of iron-porphyrin with molecule's protein is accomplished (coordination with axial ligands). The iron ion itself is in a state, when weak disturbances of its electron orbitals can lead to conformational reorganizations of the whole protein part of the molecule [16]. The π -electrons of the porphyrin ring can play here the role of light-collectors (antennas) and transmit the excitation energy to the electrons of the d-orbitals of the ions of iron acting as a sensor which transmits the disturbance to the protein part of the molecule and starts the mechanism of photo-regulation. The conformational protein changes can affect the membrane which it is set into, and substantially increase microscopic effects [24]. The flavin-protein complex where flavin acts as an antenna may be another possible version of photo-regulation. In order to test this hypothesis, special experiments with mitochondrions have been undertaken, in the course of which individual elements of the electron-transport chain (ETC) inclusive of flavins and iron-proteins were photoactivated.

The experiments were carried out on mitochondrions from white underbred mice selected by the usual method of differential centrifugation. The succinate-dehydrogenated activity (SDHA) of mitochondrions was determined from varying decrease of optical density of 2,6-dichlorophenolindophenol being reduced with oxidation of succinate by

mitochondrions. Measurements were made in a thermostatically controlled cell at 30°C with an introduction into the system of an additional acceptor of phenosinmetasulphate electrons.

The cytochrome-C-oxidase activity of mitochondrions was determined from measurements of the formation of blue and neo-phenol from dimethyl-paraphenylendiamine and α -naphtho in the presence of the reduced cytochrome C, and the content of protein was determined by the Lowry method.

The activity of mitochondrions was determined under usual daylight conditions and with an additional irradiation with monochromatic light (406, 420, 426, 430, 445, 446 nm). Apart from the halogen lamp, whose light was filtered out through narrow-band interference filters, a d.c. electric arc between iron electrodes was used as an irradiation source. The spectrum of the arc included a number of frequencies corresponding to absorption bands for iron-porphyrins located in the reaction centres of electron carriers in the electron transport chain of mitochondrions.

As a result of experiments, the effect of dark blue light on SDHA of mitochondrions has been studied. Instead of the earlier discovered broad maximum in the dark blue spectral region (400–480 nm), two narrower bands with maxima at 430 and 465 nm were discovered. The presence of a minimum near 445 nm can be explained by blocking the terminal electron carriers of cytochrome-C-oxidase. The short-wave maximum (430 nm) is due to, first of all, cytochrome absorption and a possible contribution of cytochrome C and C₁. The long-wave maximum (465 nm) is determined by an excitation of flavin of the prosthetic group of succinate-dehydrogenase.

The arc irradiation resulted in more than a twofold increase of SDHA of mitochondrions.

The results of experiments with the aim to investigate the cytochrome-C-oxidase activity (COA) of mitochondrions have shown that, practically, it is not affected by the monochromatic light in the dark blue spectral region whereas the arc light caused a 20–30% increase of COA. This indicates a possible simultaneous arc-activation of several ETC components, which is of principal importance for COA increase. The arc ensures an irradiation simultaneously at several frequencies in the dark blue interval, which strongly distinguishes it from the monochromatic source.

Thus a possibility has been demonstrated of activation with dark blue light of individual ETC components, and on this basis a hypothesis has been suggested on photoregulation with due consideration of specific features of the fine structure of sunlight and optical properties of the most important ETC components, located at focal points of the cell energy exchange. It should be noted that the flavin-containing ferments accomplish a “rough” photo-regulation, and cytochrome-b — a finer regulation in correspondence with specific features of solar spectral irradiance.

It has to be pointed out in conclusion that the photoregulation mechanism described could form at early stages of the pre-biological evolution. For instance, the basic maximum of absorption of the precursor of the whole class of porphyrin pigments coincides with the most abrupt change in the spectrum of solar irradiance (396 nm).

According to Krasnovsky [25], a transition to photosynthesis could have been accomplished through photochemical activation of molecules similar to present co-ferments. Hemoproteids could be the initial photosensitizers whose chemical evolution led to the origin of porphyrin-dependent photosynthesis.

Thus both an analysis of available publications and our studies suggest the conclusion that the fine structure of the solar radiation spectral composition significantly and specifically affects various biological processes (photosynthesis, photo-regulation, etc.).

Studies carried out by Nikolsky *et al.* [26] are worthy of special attention. They put forward a hypothesis of the bioprotective role of water vapour clusters formed during solar flares.

6. – Conclusion

1) A decrease of Fraunhofer lines' depth because of their additional irradiation due to atmospheric emissions impacts biological processes taking place in plant and animal organisms.

2) The solar spectrum is characterized by two abrupt and deepest minima in the intervals 390–400 nm and 430–440 nm. The first minimum coincides with the absorption band of porphyrin, the second minimum with that of carotinoids.

3) The molecules whose spectral maxima of absorption are in the interval of a sudden change of the incoming solar irradiance, are capable (either due to weak conformational changes or due to local environment) of re-locating (within several nm) their absorption maximum, shifting it towards light intensity decrease or increase in a given spectral interval. A realization of this possibility could be a first step towards regulating the light absorption intensity.

4) An artificial irradiation of the chlorophyll molecule on magnesium lines can be very important as a factor of breaking the chlorophyll-protein coordinating bonds, leading to macrochanges in the course of the whole photosynthesis process.

5) Maintenance of the “quiet” state of the electron structure of a metal atom in the active centre is the most important requirement for the normal process of biochemical reactions taking place with the participation of metal-containing proteins. This requirement can be met by inclusion (through natural selection) into active centres of ferments of the metals whose absorption lines are free of solar irradiation (*i.e.* coincide with Fraunhofer lines).

6) An inclusion of magnesium, iron and calcium into most important biological molecules is a unique property of biomolecules acquired in the process of evolution to adapt the optical characteristics of biomolecules to characteristic minima of solar radiation (Fraunhofer lines) in order to stabilize the functionally valuable chemical bonds which determine the conformation depending on the sunlight photoexcitation.

7) An artificial irradiation of the metal atom's electron shell can strongly affect the basic metal-containing molecules performing major functions in the course of catalytic reactions. This situation can happen since the anthropogenic admixtures emitted to the terrestrial atmosphere shine (luminesce), “jamming” the Fraunhofer lines.

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