ION-PHOTON SPECTROMETRY STUDY OF THE ORGANIC DYE–LIPID SYSTEM

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The spectral composition, quantum yield, and spatial distribution of excited particles emitted from the surface of the organic dye-lipid system bombarded with argon ions have been studied. The presence of lipids in a target was found to change the number of excited particles emitted from the surface in comparison with the case of pure dye. On the basis of the data obtained, a mechanism of influence of lipids on the excited particle yield has been proposed.

1. Introduction

Last decades, the significant progress has been observed in researches of processes that occur when medium-energy ions interact with a solid surface [1]. An important place among them is occupied by the studies of the ion-photon emission (IPE) phenomenon which consists in knocking the excited particles out from the surface which afterwards emit photons. This is related to the fact that only such researches allow one to obtain simultaneously the information concerning the nature of particles that escape from the surface and their kinetic energy. It is also possible to determine a character of the distribution of particles over their excited states. In this case, the more complex a target to be studied, the larger the number of different processes that give rise to the formation of excited particles.

In recent years, biosensors – devices on the basis of bimolecular structures for the analysis and processing of information – have been widely used. Biosensors are analytical devices which use biological materials to "recognize" certain molecules. Biosensors include lipids, proteins, and indicator dyes which are active identification elements or compose their basis [2]. Various methods of analysis are used to determine the processes, where the biosensor elements are engaged [3]. The ion-photon spectrometry (IPS) is one of the promising research methods which is based on the IPE phenomenon.

In this work, we report the results of our studies of main IPE parameters (the spectral composition, the quantum yield, and the spatial distribution of radiation from excited particles that escape from the surface). The researches aimed at elucidating the processes, in which the excited particles are formed under the ionic bombardment of organic systems. This work is a continuation of work [4].

2. Experimental Technique

When studying the complex organic systems with the use of ion beams, it is very important to consider the chemical environment of molecules in a target [1]. Therefore, the method used for the preparation of targets of organic systems, which are to be investigated, should be taken into account. In this work, we used targets of two types prepared from dyes and lipids: 1) a pellet target made up of a powder of the corresponding dye, without any admixtures, pressed with the help of a special press mold and 2) saturated alcoholic solutions of dyes, lipids, as well as their mixtures, which were precipitated on the surface of porous graphite and then dried up in vacuum.

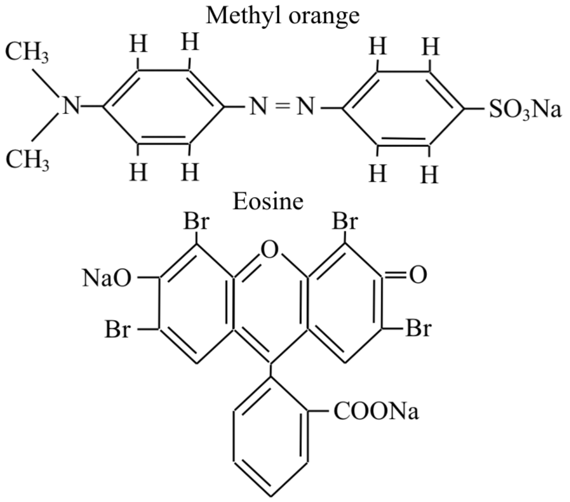

Fig. 1. Structural formulas of dyes

The surface bombardment was carried out using Ar^+ ions with an energy of 20 keV and a current density in the beam of $5 \div 10$ $\mu A/cm^2$. The target was arranged in such a manner that the total radiation emitted by both the target surface and the glowing halo over it was registered. The radiation emission spectra in the wavelength interval of 250–800 nm were registered with the help of a photo-electric registration system which operated in the photon-counting mode.

Dyes, the composition of which includes atoms of alkaline metals, were chosen as targets. These were methyl orange (MO) with the Na atom, and eosine (EO) with either the Na or the K atom. Our choice was based on the fact that, according to the structural formulas of those dyes, the atom of alkaline metal joins dye molecules in different ways [5]. In the MO dye, the Na atom joins through the sulfide group SO_3. In the EO dye, Na (or K) atoms join one of the carbon atoms through the oxygen one and the other carbon atom through the COO group (Fig. 1). Lipids are known [6] to be compounds of biological origin which can be dissolved in nonpolar solvents, but are insoluble in water; these are fats, fat-soluble vitamins, steroids, and so forth. In this work, we studied cholesterol (Cho), cortisone (Cor), and progesterone (Pro) which are classed to steroids. A typical feature of steroids is that they have an identical carbohydrate frame. Steroids are designated using the numeration of carbon atoms in a definite order [7]. Then, the hydroxyl group OH joins the carbon atom at position 3 in the case of Cho and at position 17 in the case of Cor. In the Pro case, the OH group is absent (Fig. 2).

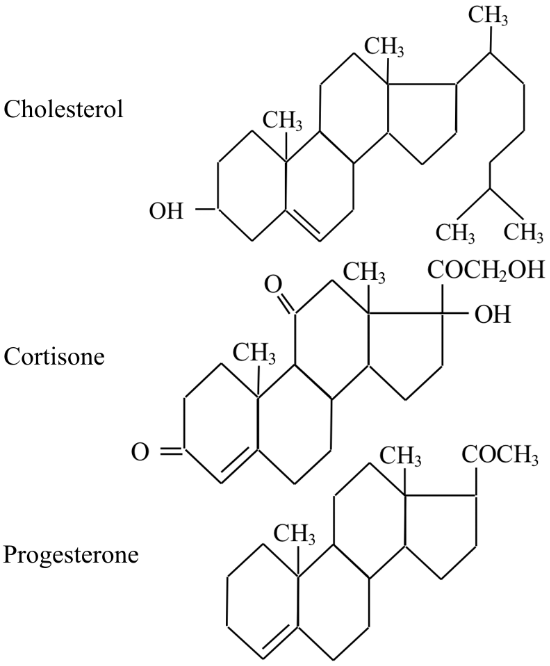

Fig. 2. Structural formulas of lipids

3. Experimental Results

3.1. Spectral composition and quantum yield of radiation emission

The results of our researches testify that, for all types of dye targets, the radiation emission by CH atomic group (λ 431.2 nm, the Q-edge of $^2\Delta \rightarrow {}^2\Pi$ transition; and λ 387 nm, the R-edge of $^2\Sigma \rightarrow {}^2\Pi$ transition) and excited hydrogen atoms (emission at $\lambda\lambda$ 410.1 nm (line H_δ), 434.0 nm (line H_γ), 486.1 nm (line H_β), and 656.2 nm (line H_α) of the Balmer series). A number of lines of the Na I and K I spectra emitted by excited sodium and potassium atoms, respectively, which are included into the composition of corresponding dyes were also observed. The most intensive among them are the Na I ($\lambda\lambda$ 588.9, 589.6 nm) and K I ($\lambda\lambda$ 766.4, 769.8 nm) resonance doublets.

For the basic spectral emissions, we determined the quantum yield of radiation, γ_λ, i.e. the number of emitted photons per one incident ion (see Table) [8]. The numbers in parentheses mean the relative values of γ_λ with respect to the quantum yield of the CH atomic group. The table demonstrates that the resonance doublets $\lambda\lambda$ 588.9, 589.6 nm of the Na I spectrum and $\lambda\lambda$ 766.4, 769.8 nm of the K I spectrum are the most sensitive to the target type. The largest γ_λ-values for them were observed, when the pellet targets were bombarded.

Quantum yield of radiation for basic spectral lines

Target	γ_λ $\times 10^6$, photon/ion				
	CH, 431.2 nm	H$_\alpha$, 656.2 nm	H$_\beta$, 486.1 nm	Na I, 588.9 nm	K I, 766.4 nm
MO, pellet	5.5 (1)	33 (6)	3.3 (0.6)	1150 (210)	–
MO, alcoholic solution	1.7 (1)	15 (8.9)	0.7 (0.4)	500 (294)	–
MO + Cho, alcoholic solution	3.3 (1)	22 (6.8)	1.5 (0.45)	1.8 (0.5)	–
MO + Cor, alcoholic solution	7.8 (1)	62 (7.9)	3.0 (0.4)	770 (99)	–
MO + Pro, alcoholic solution	8.4 (1)	68 (8.1)	3 (0.4)	210 (25)	–
EO, pellet	4.4 (1)	22 (4.9)	1.6 (0.4)	1020 (233)	890 (202)
EO, alcoholic solution	3.3 (1)	15 (4.6)	1.2 (0.4)	650 (196)	690 (209)
EO + Cho, alcoholic solution	3.3 (1)	16.5 (5.0)	1.5 (0.45)	47 (14.2)	47 (14.2)
EO + Cor, alcoholic solution	5.5 (1)	28 (5.1)	1.7 (0.3)	1150 (209)	800 (145)
EO + Pro, alcoholic solution	5.3 (1)	39 (7.4)	2.2 (0.4)	650 (130)	520 (98)
Cho, alcoholic solution	1.7 (1)	8.9 (5.2)	0.5 (0.3)	–	–
Cor, alcoholic solution	2.7 (1)	15 (5.5)	0.9 (0.3)	–	–
Pro, alcoholic solution	3.3 (1)	28 (8.5)	1.6 (0.5)	–	–

For the precipitations of saturated alcoholic solutions of the dyes under consideration, the γ_λ-values decrease, which may probably be associated with the solubility degree of each dye in ethyl alcohol.

The most interesting are data describing the influence of lipids on the yield of excited particles. For the resonance doublets of Na and K atoms, a substantial reduction of γ_λ–different for different dyes–is observed for the dye–Cho system, in comparison with the precipitation of the alcoholic solution of pure dye. For the dye–Cor mixture, the γ_λ-values increase, and, in the case of dye–Pro mixture, some reduction of γ_λ-values with respect to the precipitate of the alcoholic solution of pure dye is observed. A confrontation of γ_λ-values for characteristic emission spectral lines for excited hydrogen atoms (H$_\alpha$, H$_\beta$) and a CH atomic group shows that, although their relative quantum yields are almost identical, some differences in the absolute values are observed. As was in the case of alkaline metal atoms, a change from the pellet target to the alcohol solution precipitate results in a reduction of γ_λ-values for all emissions. The presence of lipids in Cho, Cor, and Pro targets–in that order–brings about an insignificant increase of γ_λ-values.

3.2. The number of knocked-out excited particles

We used the data obtained for γ_λ to determine the number of knocked-out excited particles of different types (CH, H, Na, K). According to the results of work [9], the number of particles excited to the i-th level, N_i, is connected with γ_{ik} by the relation

$$N_i = \frac{\gamma_{ik}}{A_{ik}\tau_i}, \tag{1}$$

where $i{\rightarrow}k$ is a transition which is responsible for the radiation emission of the line λ, A_{ik} is the transition probability, and τ_i is the lifetime of the i-th level. This relation allows the obtained γ_λ-values to be used for the determination of the number of particles excited to the i-th level. For the lines in Na I and K I spectra, the dominant contribution to radiation is given by resonance doublets, i.e. $N_{(\mathrm{Na}^*)} = \sum \gamma_{\lambda_{R\mathrm{Na}}}$ and $N_{(\mathrm{K}^*)} = \sum \gamma_{\lambda_{R\mathrm{K}}}$, because $\tau_i = \frac{1}{A_{ik}}$ for them.

In the case of hydrogen, we observed transitions 3→2(H$_\alpha$); 4→2(H$_\beta$), and 5→2(H$_\gamma$), where 2, 3, 4, and 5 are principal quantum numbers. To evaluate the occupation number for the lowest excited level of a hydrogen atom, $2p^2P^0$ – the $2 \rightarrow 1$ transition from it is responsible for the radiation of the line L_α in the ultra-violet spectral range, which was not observed experimentally – we plotted the dependences $\ln \gamma_\lambda = f(n)$. For $n = 3$, 4, and 5, the $f(n)$-plot is a straight line, which can be used to evaluate, by the extrapolation method, the γ_λ-value for $n = 2$. Then, in accordance with formula (1), we calculated the values of N_2, N_3, N_4, and N_5. Their sum gives almost the total number of excited hydrogen atoms.

For a CH radical, we observed the band with a wide Q-edge with violet shadowing and the R-branch with a widely branched structure. In this work, we determined the γ_λ-value in the Q-edge maximum, γ_{λ_m}. The spectral analysis demonstrated that γ_{λ_m} amounts to one tenth of the quantity $\sum \gamma_\lambda$ for the whole band, so that $N_{\mathrm{CH}} = 10\gamma_{\lambda_m}$.

Excited Na and K atoms were found to compose the majority of particles knocked out from the pure-dye targets. Their number was a few units of 10^{-2} at/ion, depending on the dye and target types. For the dye-

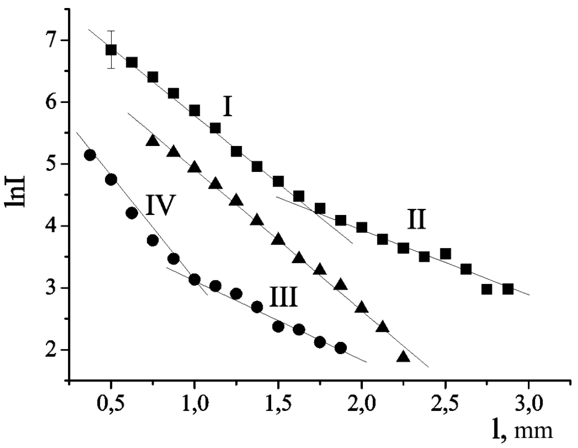

Fig. 3. Dependences of the intensity of the Na atom resonance doublet on the distance to the target surface for various targets: an EO pellet target (■), the precipitate of an EO alcoholic solution (▲), and the precipitate of an alcoholic solution of the EO+cholesterol mixture (●)

cholesterol mixture, the number of excited Na and K atoms decreased by two orders of magnitude in comparison with the corresponding alcoholic solution of pure dye. For the dye mixtures with Cor and Pro, no substantial change in the number of knocked-out excited atoms with respect to the precipitate of an alcoholic solution of pure dye was observed. The number of knocked-out H atoms fell within the interval $10^{-3} \div 10^{-5}$ at/ion and substantially depended on the target type. The number of knocked-out CH atomic group was a few units of 10^{-5} molecules/ion for all target types.

3.3. Spatial distribution of radiation

To evaluate the kinetic energy of knocked-out excited particles, we used a method that is based on the measurement of the spatial extension of a glowing halo. The spectral line intensity was determined by the formula

$$I = A_{ik} N_i h\nu_{ik}, \tag{2}$$

where ν_{ik} is the frequency of radiation emitted at the $i \rightarrow k$ transition, and h is Planck's constant. At distances larger than 10 Å, the excited particles can be considered free; therefore, a variation of the occupation number of the upper excited state during the time t can be described by the law of spontaneous radiation emission only [6],

$$N_i = N_{0i} \exp(-t/\tau_i), \tag{3}$$

where N_{0i} is the occupation number of the level concerned at $t = 0$. Substituting this formula into expression (2) and bearing in mind that $t = l/v$, we obtain the following dependence of the radiation intensity on l:

$$I(l) \approx \exp\left(-\frac{l}{v_\perp^*}\right). \tag{4}$$

Here, $v_\perp^*$ is the normal component of the effective velocity of a group of particles that flow away; and l is the distance from the target surface. If excited particles belong to the same velocity group, the dependence $\ln I(l)$ is linear. So that, knowing τ_i and the slope of this dependence, one can determine $v_\perp^*$ and the energy of particles E_k flying away from the surface of the solid. Not every time can the dependence $\ln I(l)$ be approximated by a straight line. There are cases where the excited particles belong to several groups with different velocities. Since different groups of particles located at different distances from the target surface give different contributions to the halo radiation, the plot of the dependence $\ln I(l)$ will have a number of linear sections with transition regions between them. The tangents of the slope angles of those sections can be used to determine $v_\perp^*$ and E_k for every group.

In the experiment, we determined the dependence of the number of excited particles N_i giving the contribution to the analyzed line on the distance from the target surface l. According to formula (2), the number of particles excited to the i-th level is proportional to the intensity I_{ik} of the line concerned. This fact allowed us to derive the dependence $I_{ik} = f(l)$ and make estimation of the velocity of excited particles flying away from the surface.

The analysis of the spatial distribution of radiation emission by excited Na atoms showed that, when studying the pellet targets of MO and EO dyes, the radiation was observed that was emitted by knocked-out excited Na atoms belonging to two velocity groups (squares in Fig. 3): the first group with a kinetic energy of 60–150 eV (section I) and the second one with a kinetic energy of 300–900 eV (section II). Na atoms knocked out from the precipitate of an alcoholic solution of pure dye belonged to the same velocity group with $E_k \approx 150$ eV (triangles in Fig. 3). If any dye was mixed with Cho (circles in Fig. 3), there appeared a group of very slow particles with a kinetic energy of 20–40 eV (section IV) in addition to the group of high-energy particles (section III). For the mixtures of dyes with either Cor or Pro, the same spatial distribution was observed as in the case of the precipitate of an alcoholic solution of dye itself. The evaluation of the kinetic energy of knocked-out excited hydrogen atoms and CH atomic group showed that the energy of those particles did not depend on the target type. In particular, hydrogen atoms were knocked out with a kinetic energy of about 20 eV. The kinetic energy of CH atomic group was lower than 1 eV.

The presence of knocked-out particles belonging to various velocity groups testifies to the existence of a number of processes, in which those particles were formed [4]. Low values of kinetic energy (1–50 eV) point to the formation of an excited particle owing to the decay of a complicated complex. High values of kinetic energy are related to the processes, where the atoms of alkaline metals are knocked out, such as the direct knocking out ($E_k \approx 300 \div 900$ eV) and cascade collisions ($E_k \approx 150$ eV). The absence of a group of particles knocked out from the precipitate of the alcoholic solution of pure dye by the direct knocking-out can be associated with a reduction of the corresponding line intensity or with a specific feature of the target itself.

4. Discussion of Results

Generalizing the results obtained, the following hypothesis may be put forward concerning the mechanism of interaction between the dyes and the lipids under consideration.

When the dyes are dissolved in ethyl alcohol, they dissociate into ions, forming the negatively charged frame of a dye and the positively charged ion of a metal [10]. The dissociation degree depends on the properties of both a dye and a solvent – in particular, the dye structural formula. When the dye interacts with the lipid, the metal atom can join the lipid molecule; however, it depends to a great extent on the presence and the position of an OH polar group in the lipid.

In the Cho case where the OH group is located at the third carbon atom, it is most probable that the metal atom is surrounded by Cho molecules, which diminishes the probability of the cascade knocking-out of metal atoms, although a certain number of metal atoms can be knocked out in the course of direct collisions. As a result, the value of γ_λ for the emission of Na and K atoms decreases, as well as the number of knocked-out atoms. The fact of the existence of a group of atoms with a low kinetic energy of 20–40 eV allows an assumption to be made concerning a probable decay of the metal atom–Cho complex hit by an Ar^+ ion. In Cor, the OH group is located at the 16-th carbon atom, which gives rise to considerable variations of γ_λ-values. At the same time, the presence of a very active $\mathrm{COCH_2OH}$ group in Cor can enhance the degree of dye dissociation in the alcoholic solution. As a result, the yield of excited atoms of alkaline metals grows in comparison with the case of dye mixtures with other lipids. The structural formula of Pro does not contain any OH group at all, so that the dye-Pro mixture does not reveal any difference from the case of bombarding the alcoholic solution of pure dye.

5. Conclusions

The method of ion-photon spectrometry is applied to study the spectral composition, quantum yield, and spatial distribution of radiation emitted by excited particles that leave the target surface – in particular, these are organic dyes, the structural formulas of which include atoms of alkaline metals, lipids, and their mixtures – when the target is bombarded with argon ions. It was found that the radiation emission by excited hydrogen atoms (the Balmer series) and the molecular bands inherent to the CH radical were observed for all types of studied targets. Provided that the content of an organic system includes a dye, a series of spectral lines characteristic of alkaline metal atoms (Na I and K I) are observed.

For all kinds of observed emission, the quantum yield of radiation and the numbers of knocked-out excited H atoms, CH atomic group, and atoms of Na and K alkaline metals are determined. The presence of cholesterol in the target was found to substantially reduce the yield of excited Na and K atoms.

The spatial distribution of radiation emitted by excited Na atoms is analyzed. For all targets, the kinetic energy of excited particles that fly away from the surface is determined. Different values of kinetic energy testify to two types of the formation of excited particles: the decay of a complex molecule (slow particles) and a series of cascade collisions or the direct knocking-out by a primary ion (fast particles).

On the basis of the data obtained, a hypothesis concerning the mechanism of interaction between the studied dyes and lipids and the influences of lipids on the yield and the energy of excited particles has been proposed.

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ДОСЛІДЖЕННЯ СИСТЕМИ ОРГАНІЧНИЙ БАРВНИК–ЛІПІД МЕТОДОМ ІОННО-ФОТОННОЇ СПЕКТРОМЕТРІЇ

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Резюме

Проведено дослідження спектрального складу, квантового виходу і просторового розподілу випромінювання збуджених частинок, що покидають поверхню системи органічний барвник–ліпід, під час бомбардування іонами аргону. Встановлено, що наявність у мішені ліпідів змінює кількість збуджених частинок, що покидають поверхню, відносно чистого барвника. На основі отриманих результатів зроблено висновки щодо механізму впливу ліпідів на вихід збуджених частинок.