

FORMATION OF EXCITED PARTICLES UNDER ION BOMBARDMENT OF ORGANIC DYES

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We investigate the basic parameters of ion-photon emission under the bombardment of organic objects with an Ar⁺ ion beam. The spectral composition, quantum yield, and space distribution of radiation of knocked-out excited particles are determined. The obtained results are used to make a conclusion about the mechanism of formation of excited particles.

1. Introduction

Processes accompanying the interaction of medium-energy ions with a solid-body surface have been widely investigated in the recent decades. An important place among them is occupied by researches of the ion-photon emission (IPE) phenomenon consisting in the knocking-out of excited particles with the following radiation of photons. This is due to the fact that only these investigations allow one to simultaneously obtain the information on the nature of knocked-out particles and their kinetic energy, as well as to determine the nature of their state distribution function.

The targets under investigation were presented by one-component compounds (metals and semiconductors), complex compounds (oxides and halides), alloys, and (in the recent years) organic compounds. Moreover, the more complex is the investigated target, the larger number of various processes result in the formation of excited particles knocked out of the surface due to its bombardment by medium-energy ions. In the given work, we present the results of studying the basic IPE parameters (spectral composition, quantum yield, and space distribution of the radiation of excited particles knocked-out of the surface) aimed at clarifying the processes resulting in the formation of excited particles under the ion bombardment of organic dyes.

2. Experimental Technique

The organic targets were bombarded by Ar⁺ ions with an energy of 20 keV and a current density of 10 ÷

20 $\mu\text{A}\cdot\text{cm}^{-2}$. The target was placed in such a way that we could register the total radiation both from the target surface and the above region (aureola). The emission spectra in the wavelength region 250.0 ÷ 800.0 nm were registered with the help of a photoelectric system operating in the pulse-counting mode.

It is known [1] that, in the case of investigations of complex organic systems with the help of ion beams, an important role is played by the chemical surrounding of molecules in a target. Due to this fact, it is necessary to consider the way of preparation of targets of the researched organic systems. We dealt with three kinds of targets: 1) liquid target: glycerol and glycerol solutions of dyes (Eriochrome black – EBk; Rhodamine 6G – Rh6G; Bromthymol blue – BthBl; Bromphenol blue – BphBl; Methylene blue – MthBl) deposited onto a porous graphite surface; 2) pellet target made of a powder of the above-mentioned dyes, as well as Methyl orange – MO and Eosin – EO, with the help of a press mold without any admixtures; 3) saturated water and alcohol solutions of dyes (MO, EBk, and EO) deposited onto a porous graphite surface and dried in vacuum.

3. Investigation of IPE Spectra of Some Organic Objects

3.1. Spectral composition and quantum yield of radiation

The optical radiation spectra of excited particles knocked out of the surface of liquid targets include radiation lines of a hydrogen atom (Balmer series), the band of a CH molecule, and the very weak-intensity resonance line of a Na atom (for MO and EBk). The lines of a hydrogen atom and the band of a CH molecule were also observed in the optical radiation spectra of excited particles knocked out of the surface of solid targets of the second and third kinds. The basic emissions observed in the spectra of all the investigated targets were the lines $\lambda\lambda 486.1$ nm H β , 656.2 nm H α , and the band λ 431.2

Quantum yield of radiation

Emission λ , nm	Interpretation	γ_λ , 10^{-6} photons/ion								
		MO			EBk			EO		
		pellet	alcohol solution	water solution	pellet	alcohol solution	water solution	pellet	alcohol solution	water solution
431.2	Q band head of the transition ${}^2\Delta \rightarrow {}^2\Pi$, CH	5.5 (1)	1.7 (0.3)	1.6 (0.3)	2.6 (1)	4.3 (1.7)	3.1 (1.2)	4.4 (1)	3.3 (0.75)	4.8 (1.1)
486.1	$4d {}^2D \rightarrow 2p {}^2P^0$, H_β	3.3 (1)	0.7 (0.2)	0.9 (0.3)	1.8 (1)	1.6 (0.9)	1.1 (0.6)	1.6 (1)	1.2 (0.75)	1.6 (1)
568.2	$4d {}^2D \rightarrow 3p {}^2P^0$, Na I	13.0	2.6	5.0	19.0	4.4	13.5	13.8	5.8	3.2
568.8		(1)	(0.2)	(0.4)	(1)	(0.2)	(0.7)	(1)	(0.4)	(0.2)
588.9	$3d {}^2P^0 \rightarrow 3s {}^2S$, Na I	1200.0	500.0	1250.0	2190.0	365.0	1140.0	1270.0	650.0	240.0
589.5		(1)	(0.2)	(0.4)	(1)	(0.2)	(0.7)	(1)	(0.4)	(0.2)
656.2	$3d {}^2D \rightarrow 2p {}^2P^0$, H_α	53.1 (1)	15.1 (0.3)	12.0 (0.2)	15.4 (1)	22.5 (1.5)	17.8 (1.2)	21.7 (1)	15.3 (0.7)	21.7 (1)
766.4	$4p {}^2P^{0,3/2} \rightarrow 4s {}^2S_{1/2}$, K I	–	–	–	–	–	–	890.0 (1)	690.0 (0.8)	190.0 (0.2)
769.8	$4p {}^2P^{0,1/2} \rightarrow 4s {}^2S_{1/2}$, K I	–	–	–	–	–	–	590.0 (1)	290.0 (0.5)	110.0 (0.2)

nm (Q band head of the ${}^2\Delta \rightarrow {}^2\Pi$ transition) of a CH molecule. In addition, we registered a series of emissions of Na and K atoms (according to their presence in the structural formula of a dye). For the MO dye, we observed a series of band heads (372.4, 377.4, 382.6, 367.9, and 395.4 nm) of a Na_2 molecule. In addition, a wide molecular band with a large number of indistinct band heads was observed for these two types of solid targets, which was probably caused by the radiation of a polyatomic molecule of the undetermined nature.

The quantum yield of radiation γ_λ (the number of photons with a certain wavelength corresponding to one incident ion) was calculated for all the investigated targets. The comparison of the relative quantum yields of radiation for the basic emissions observed in studies of the radiation of particles knocked out of the liquid and pellet targets (656.2 nm H_α , 486.1 nm H_β , and 431.2 nm CH) has demonstrated that the proportion of the quantum yields for glycerol and glycerol-dye solutions is almost identical and amounts to 43:2.1:1, though the presence of a dye in a solution increases the absolute value of the quantum yield almost by an order of magnitude. In the case of pellet targets, this proportion considerably changes and differs for each dye: MO – 9.5:0.6:1 (5.7), Rh6G – 11.6:0.4:1 (3.6), BthBl – 6.4:0.55:1 (4.5), BphBl – 4.5:0.4:1 (3.4), MthBl – 4.8:0.5:1 (2.4), EBk – 5.9:0.7:1 (2.6), and EO – 5.0:0.4:1 (4.4). The values in the parentheses represent the absolute values of the quantum yield of radiation in the units of 10^{-6} photons/ion. The ra-

diation spectra of particles knocked out of the glycerol solutions of the dyes, whose structural formula includes Na (MO, EBk), practically do not contain any lines of a Na atom. This is most probably due to the fact that a dye in glycerol dissociates into ions (the negative core of a dye and a positive ion of an alkali metal), while the presence of a polar COOH hydroxyl group results in the formation of micelles [2]. Under ion bombardment, the main contribution to the number of the knocked-out particles is made by fragments of a hydroxyl group. For the pellet targets, the quantum yield of radiation of the resonance duplet of the Na I spectrum exceeded that of the basic emissions by three orders of magnitude. As the radiation of Na atoms in the case of glycerol-dye solutions is practically absent, we consider only the results of studies for the solid targets. Table summarizes the absolute values of the quantum yield of radiation of the knocked-out excited particles for the basic emissions and the most intense lines of the Na I and K I spectra for all the solid targets investigated in the work. In the parentheses, we give the relative values of the quantum yields, where γ_λ of a pellet is taken as 1.

One can see that the absolute quantum yields of radiation of alkali metal (AM) particles are considerably higher than those of hydrogen and a CH molecule. Moreover, the maximum quantum yield of radiation (γ_λ of the AM spectral lines) is observed for the pellet targets. As concerns the dried solutions of MO and EBk, γ_λ for the Na I spectral lines is higher in the case of alcohol so-

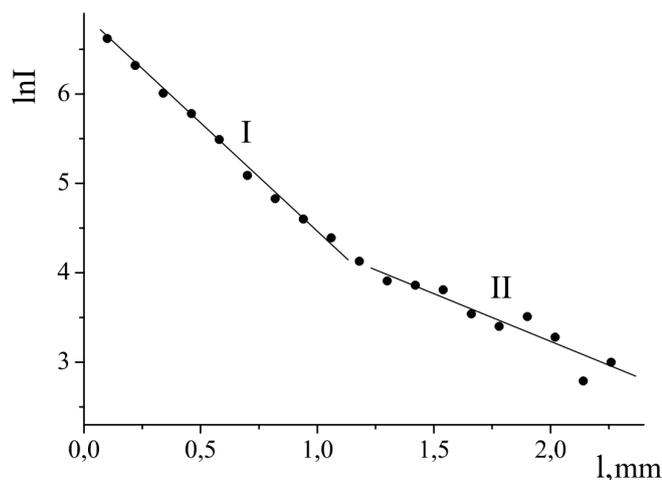


Fig. 1. Space distribution of radiation ($\lambda = 588.9$ nm) of Na atom. Target – EO, pellet; $E_k = 107$ eV (I); $E_k = 944$ eV (II)

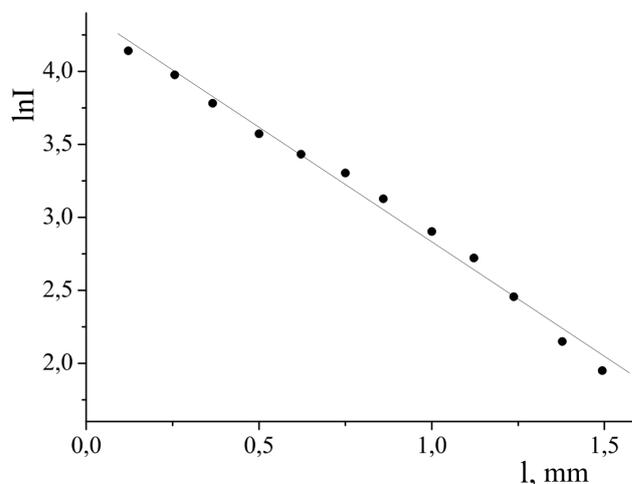


Fig. 2. Space distribution of radiation ($\lambda = 656.2$ nm, H_α) of H atom. Target – MO, pellet; $E_k \sim 14$ eV

lutions as compared with the corresponding water ones. For the EO solutions, one observes the inverse relation between the lines of the Na I and K I spectra. The lines of the basic emission do not obey such a regularity. The obtained results can be explained in the following way. According to [3], the dissolution of dyes results in their dissociation into ions: the negative core of a dye molecule and a positive AM ion. The ionization ability of a solvent is determined by the permittivity that equals 80.4 for water and 27.8 for ethanol [4]. As one can see from Table in the case of the MO and EBk dyes, a larger yield of excited Na atoms is really observed for water solutions. A different proportion for EO is probably caused by the fact that EO poorly dissolves in water. According to [5], MO dissolves well in water and poorly in ethanol, EBk dissolves in ethanol and up to 70% in water, and EO dissolves in ethanol and does not dissolve in water.

3.2. Space distribution of radiation of knocked-out excited particles

The analysis of the data on the space distribution of radiation of the knocked-out particles allows one to estimate their kinetic energy and make a conclusion about the processes resulting in their knocking-out. For the pellet targets of all three dyes, we observed the radiation of Na atoms belonging to two velocity groups with energies of $100 \div 150$ eV and $700 \div 1000$ eV. For sediments of the alcohol- and water-dye solutions, we registered the radiation of only the first group of Na particles for comparatively weak spectra or the radiation of both groups of particles for more intense spectra.

Figure 1 shows the dependence $\ln I = f(l)$, where I is the relative intensity of the investigated line and l is the distance to the target surface. In this dependence, one can mark out two segments (I and II), whose slope gives a possibility to obtain the value of the kinetic energy E_k [7]. Excited Na atoms of group I are formed due to a cascade of collisions in a solid target; excited Na atoms of group II are generated in the course of hard collisions of a primary ion with a knocked-out atom. The value of E_k for the knocked-out hydrogen particles is close to 20 eV (Fig. 2), whereas it is lower than 1 eV for CH molecules. That is, these particles are evidently formed in the course of excitation and the subsequent decay of a complex molecule – dye core.

4. Conclusions

The analysis of the existing literature data and the obtained experimental results allows us to make some conclusions about the processes running under the ion irradiation of organic materials and resulting in the formation of excited particles. As was shown in [1], an important role in investigations of complex organic systems with the help of ion beams is played, first of all, by the chemical surrounding of molecules in a target. Indeed, the results of our researches of the basic IPE parameters of three types of organic-dye targets confirm this statement. In the case of the dissolution of organic dyes in glycerol, the IPE spectra of different dyes are similar to one another. It can be explained by the fact that, under the dissolution of a dye in glycerol, it dissociates into ions that form associative groups with glycerol molecules (micelles) including an active COOH hydroxyl

group. Under the ion irradiation of micelles, one mainly observes the radiation of only fragments of a glycerol molecule, i.e. hydrogen atoms and CH molecules. Solid targets of two kinds (pellets representing a pressed dye or dried sediment of a saturated alcohol- or water-dye solution on the porous-carbon surface) have characteristic IPE spectra. Moreover, the parameters of these spectra are influenced by the nature of both a dye and a solvent. In the case of the dissolution of dyes in water or ethanol, one observes their dissociation into ions: a negative dye core and a positive metal ion. The dissociation degree depends on both properties of a dye (particularly, structural formula and solubility) and a solvent (ionization ability). The analysis of a space distribution of the radiation of excited Na atoms has demonstrated that they can belong to two velocity groups: slow and fast ones with kinetic energies of Na atoms amounting to $100 \div 150$ eV and $700 \div 1000$ eV, respectively. This testifies to the fact that excited Na atoms are formed in two kinds of collisions: the cascade collision of a number of solid-target atoms with a Na atom at the end and the hard collisions of a primary ion with a knocked-out atom. The value of E_k is close to 20 eV for knocked-out hydrogen particles and less than 1 eV for CH ones, i.e. these particles are probably formed under the excitation and the subsequent decay of a complex molecule – organic-dye core.

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УТВОРЕННЯ ЗБУДЖЕНИХ ЧАСТИНОК ПРИ ІОННОМУ БОМБАРДУВАННІ ОРГАНІЧНИХ БАРВНИКІВ

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Резюме

Проведено дослідження головних параметрів іонно-фотонної емісії при бомбардуванні органічних об'єктів пучком іонів Ag^+ . Визначено спектральний склад, квантовий вихід та просторовий розподіл випромінювання вибитих збуджених частинок. На базі одержаних результатів зроблено висновки щодо механізму утворення збуджених частинок.