EFFECTIVENESS OF TWO-STAGE PHOTOIONIZATION OF AROMATIC AND HETEROAROMATIC MOLECULES IN SOLUTIONS UNDER THE ACTION OF UV LASER RADIATION

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When photoexcitation of molecules of organic compounds in solutions is sufficiently intense, there is an effective population of the lower electron states - triplet (2, T₁) or singlet (3, S₁). If the exciting radiation is sufficiently hard, and as a result of the absorption of a second quantum by the electronically excited molecules, there may be a photoionization or some other photoconversions of the excited molecules. The first two-quantum reactions (through the intermediate T₁ level) were observed in the excitation of solid solutions by the radiation of mercury lamps [1, 2]. Subsequently two-quantum photoreactions were observed in liquid solutions in the case of excitation of molecules by pulses of the radiation of solid-state or gaseous nitrogen lasers [3-5].

In this work we determined the effectiveness of the photoionization of certain aromatic and heteroaromatic compounds in polar solvents [ethanol, tetrahydrofuran (THF)] during excitation by pulses of radiation of the third (λ₃ = 353 nm) and fourth (λ₄ = 265 nm) harmonics of a neodymium laser. Part of the investigated compounds are used as active molecules in lasers based on solutions of organic compounds.

Photoionization was studied by measuring the photocurrent I induced by the exiting radiation in the cuvette with the solution. The photocurrent arose as a result of the appearance of solvated electrons and positive ions in the electrode gap, on which the exciting radiation was focused. Electrodes of titanium or platinum were used. The length of the electrodes along the axis of the excitation beam was 3–5 mm; the length of a side turned toward the front face of the cuvette was about 3 mm; width of the electrode gap 3–5 mm. A constant voltage in the range from 200 to 700 V was delivered to the electrodes. The value of the induced photocurrent and its dependence on the time were measured on an oscillograph according to the value of the voltage V = RI, where R is a resistance connected in series with the cell with the electrodes. To obtain the time resolution necessary for the proper recording of the signals, the value of this resistance was varied from 0.1 to 10 kΩ. The lifetime of the current carriers (solvated electrons and positive ions) in the solvents used was usually several or tens of microseconds; therefore, the investigated signals were recorded at a time resolution of the system 0.1–1.0 μsec. The pulse of the photocurrent was recorded on an S-1-17 two-beam oscillograph; the intensity of the exciting light was recorded on the same oscillograph with an FēK-22 SPU photocell. The exciting radiation was focused into the electrode gap by means of a lens with a focal length of ~1 m. The space and time dependence of the photon flux density at the entrance to the cuvette can be approximately described by the formula

\[ f(r, t) = f_0 \exp \left\{ -\left( \frac{r}{a} \right)^2 - \left( \frac{t}{t_0} \right)^2 \right\} \]  

(1)

with parameters a ~ 0.5 mm, t₀ ≈ 15 nsec.

When effects of the space charge are neglected, the value of the current flowing through the resistance R can be expressed as follows:

\[ I(t) = \frac{V_0}{L^2} \sum \mu_i |Q_i| N_i(t), \]  

(2)

where \( V_0 \) is the constant voltage applied to the electrodes; \( L \) is the length of the electrode gap; \( \mu_i \) and \( Q_i \) are the mobility and charge of the \( i \)-th carrier; \( N_i \) is the total number of carriers \( i \) in the electrode gap. As the measure of the intensity of photoionization in the investigated medium, we can take the value of \( y = \frac{IL^2V_0{\mu_i}^2}{a^2} \), which depends only on the number (per unit cross-sectional area of the excited zone) and mobility of the current carriers and pertains to the moment of ending of the excitation pulse. Since the lifetime of the current carriers in the solvents under consideration is much greater than the duration of the excited pulse, the value of \( y \) is determined by the total number of electrons and ions arising during the process of excitation.

Figure 1 presents the dependences of the intensity of photolysis \( y \) on the photon flux density \( f_0 \) of the exciting radiation in a logarithmic scale. The concentration of the solutions of all the investigated compounds was \( 10^{-4} - 10^{-3} \) M and was selected so that the pumping radiation was entirely absorbed along the electrode gap. From Fig. 1 it can be seen that in the region of low excitation densities, these dependences take the form of straight lines with a slope close to two for all the investigated molecules; this means that the photolysis process is of a two-quantum type. Evidently in the region of values of \( f_0 \) where the dependence of the photolysis intensity on the power density of the exciting radiation is linear, the effects of absorption of the exciting radiation by the excited molecules or ions can be neglected, and the experimental results can be analyzed using kinetic equations in a linear approximation. It is also essential that the process of photolysis is recorded at low pumping-power densities (\( \sim 1 \) kW/cm\(^2\)), when all side effects of the powerful photolysis can be neglected. There lies an important advantage of the study of stepwise two-photon processes by the method of photolysis in comparison with methods based on a measurement of the fluorescence intensity and the transmission coefficient of the solutions under conditions of powerful photolysis.

If we assume that photolysis occurs only through an intermediate triplet level, then (in the case of complete absorption of the pumping in the electrode gap), it is easy to find that the number of solvated electrons and positive ions after the end of the excitation pulse is equal to

\[
N_{r1} = a_2 q_2 \eta_T \frac{\pi^2 f_0^2 t_p^2}{4},
\]

where \( a_2 \) is the absorption cross section of a molecule on the triplet level along the pumping wave \( \lambda_p \); \( \eta_T \) is the quantum yield of triplet states; \( q_2 \) is the probability of photolysis of a molecule that has absorbed a second quantum of pumping radiation in the \( T_1 \) state.

If photolysis occurs only through an intermediate excited singlet level \( S_1 \), then the number of electrons and ions is equal to

\[
N_{s1} = a_3 q_3 \frac{f_0}{K_3} \frac{\pi}{4 \sqrt{2}} \frac{\pi^2}{a_2 t_p^2},
\]

where \( a_3 \) is the absorption cross section of the molecule in the state \( S_1 \) at \( \lambda_p \); \( K_3 \) is the total rate of deactivation of the singlet state \( S_1 \); \( q_3 \) is the probability of photolysis of a molecule that has absorbed a second quantum in the \( S_1 \) state.

Evidently, on the strength of the linear approximation of the kinetic equations in the cases \( a_2 q_2 \neq 0 \) and \( a_3 q_3 \neq 0 \), the total number of solvated electrons or positive ions will be the simple sum of (3) and (4).

Substituting the values of (3) and (4) into function (2), we obtain the relationship between the value of the induced photocurrent, the excitation power density, and the parameters \( a_3 q_3 / K_3 \) in the case of photolysis through the \( S_1 \) level or \( a_2 q_2 T \) in the case of photolysis through the \( T_1 \) level. Table 1 presents the values of \( a_3 q_3 T \) and \( a_2 q_2 / K_3 \) calculated by means of formulas (2), (3), and (4) according to the experimental values of \( I \) and \( f_0 \), as well as the values of \( \eta_T K_3 \), known from the literature data. The last two columns give the quantum yields of photolysis of \( q_3 \) and \( q_1 \), on the assumption that there is only channel of photolysis.