Dependence of the Integral Characteristics of Multiquantum Processes on Radiation Intensity

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Submitted May 23, 1971

Zh. Eksp. Teor. Fiz. **61**, 2287–2292 (December, 1972)

The dependence of the integral yield N_k for a k-quantum process occurring in a certain fixed volume on radiation intensity I is analyzed theoretically. It is shown that in the presence of appreciable absorption the dependence $N_k(I)$ may be of the form $N_k \sim I^m$, where $1 \lesssim m(I,z) \lesssim k$. Deviations of the $N_k(I)$ dependence form the $N_k \sim I^k$ law, which is characteristic for the probability of an elementary absorption act, are greater the greater the light beam intensity and the longer the length of the ray path z on the basis of which the integral yield of the multiquantum process is measured.

ARUTYUNYAN, Askar'yan, and Pogosyan[1] analyzed theoretically the multiquantum effect in the focus of a laser beam, and have shown that at large light-flux density the volume of the action expands, owing to the saturation of the absorption, as a result of which an appreciable change takes place in the dependence of the integral yield N_k of the k-quantum process on the radiation intensity I.

It is shown in the present article that noticeable deviations of the $N_k(I)$ dependence from the form $N_k \sim I^k$ which is characteristic of the probability of the elementary absorption act, can also be observed in an unfocused laser beam and in the region far from saturation.

In the medium in which k-quantum absorption takes place, the radiation intensity of a cylindrically-symmetrical light beam parallel to the Z axis decreases like (see, for example, [2,3])

$$I(z,r,t) = \frac{I(0,r,t)}{[1+(k-1)\beta_k I^{k-1}(0,r,t)z]^{1/(k-1)}}, \quad k \geqslant 2, \tag{1}$$

where $\beta_k = \sigma_k n_0 = \text{const}$ is the true coefficient of k-quantum absorption, which is independent of the intensity of the light flux and is equal to the product of the cross section σ_k of k-quantum absorption ($[\sigma_k]$ = (absorbed particle)$^{-1}$photon^{-k+1}cm^{2k}sec^{k-1}) and the concentration of the radiation-absorbing particles n_0, while

$$I(0,r,t) = I_0 f(r)\varphi(t) \tag{2}$$

is the space-time distribution of the radiation intensity on the surface of the medium (z = 0) absorbing the incident radiation. When account is taken of relation (1), which is valid for the case when there is no saturation of the multiquantum absorption, the expression for the experimentally measured integral yield of the k-quantum process

$$N_k = \int\int\int \alpha_k n_0 I^k(z,r,t)\,dt\,dr\,dz \tag{3}$$

takes the form

$$N_k = \alpha_k n_0 \int_t\int_r dt\,dr \int I^k(0,r,t)\,[1+(k-1)\beta_k I^{k-1}(0,r,t)z]^{k/(1-k)}dz, \tag{4}$$

where α_k is the quantum yield of the registered multiquantum process ($[\alpha_k]$ = (number of acts)(absorbed particle)$^{-1}$photon^{-k}cm^{2k}sec^{k-1}, $[N_k]$ = number of acts).[1)]

For the sake of clarity we consider a simple case, when a light pulse has a rectangular shape in time with duration τ_0, and the radial distribution of the intensity is such that f(r) = 1 when $r \le r_0$ and f(r) = 0 when $r > r_0$. We then have for the integral yield of the k-quantum process registered in a length z_0

$$N_k(z_0) = \alpha_k n_0 \tau_0 S I_0^k \cdot \times \int_0^{z_0} \left[1+\frac{\tilde{z}}{z_0}z\right]^{k/(1-k)} dz = \alpha_k n_0 \tau S I_0^k z_0 F\left(\frac{k}{k-1}\,1;2;-\tilde{z}\right) \tag{5}$$

where S is the area of the light beam, $\tilde{z} = (k-1) \times \beta_k z_0 I_0^{k-1}$ is a dimensionless parameter, and $F(\alpha,\beta;\gamma;\tilde{z})$ is the Gauss hypergeometric function. It is known from the asymptotic expressions for the Gauss function[4] that in the region $\tilde{z} \ll 1$, i.e., when

$$z_0 I_0^{k-1} \leqslant [\beta_k(k-1)]^{-1} \text{ or } z_0 \varkappa_k^{(0)} \leqslant 1/(k-1), \tag{6}$$

we have $F \approx 1$, and therefore

$$N_k(z_0) \approx \alpha_k n_0 \tau_0 S z_0 I_0^k \tag{7}$$

(in (6), $\kappa_k^0 = \beta_k I_0^{k-1}$ is the phenomenological coefficient of k-quantum absorption in the region far from saturation and depends on the intensity $[\kappa_k^{(0)}] = \text{cm}^{-1}$).

At $\tilde{z} \approx 1$ and more, the estimates for $N_k(z_0)$ should be carried out in accordance with the formula (see [4])

$$N_k(z_0) = \alpha_k n_0 \tau_0 S I_0^k z_0 \sum_{n=0}^{\infty} (\tilde{z})^n \frac{(-1)^n}{(k-1)^n} \frac{k(2k-1)\ldots(kn-n+1)}{(n+1)!}. \tag{8}$$

In the limit as $z_0 \to \infty$ ($\tilde{z} \to \infty$) we have[4]

$$N_k = \alpha_k n_0 \tau_0 S I_0^k \int_0^{\infty} \left[1+\frac{\tilde{z}}{z_0}z\right]^{k/(1-k)} dz = \frac{\alpha_k}{\beta_k} n_0 \frac{\tau_0 I_0 S}{k-1} B\left(1,\frac{1}{k-1}\right) = \frac{\alpha_k}{\beta_k} n_0 \mathscr{E}, \tag{9}$$

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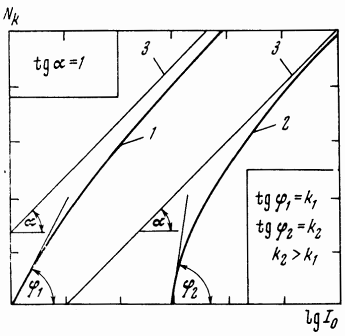
1)In the case of registration of, say, electrons produced in multiquantum ionization, $\alpha_k = \beta_k$. On the other hand, in the case of other multiquantum processes, for example multiquantum fluorescence or multiquantum photochemical reaction, we have $\alpha_k \neq \beta_k$, since β_k characterizes the probability of the primary process of the multiquantum absorption, and α_k represents the probability of the secondary process due to multiquantum absorption.



where B(x, y) are β functions. Thus, the total integral yield of the multiquantum process ($k \geq 2$) for any radiation intensity outside the absorption-saturation region is always proportional to the radiation intensity and is determined in final analysis by the pulse energy $\xi = \tau_0 I_0 S$.

It follows from (5) that, unlike the linear processes, when the expression $N \sim I$ is valid for all fixed values of the layer thickness z_0 in the region far from saturation, the integral yield of the multiquantum processes is a complicated function of the dimensionless parameter $\tilde{z} \sim z_0 I_0^{k-1}$. This occurs because of the nonlinearity of the value of the running absorption dI/dz, which increases with increasing light-flux density, or, which is principally the same, in view of the change of the dependence of the transmission of the layer

$$T(z_0) = I(z_0) / I_0 = [1 + \tilde{z}]^{1/(1-k)}$$

on the intensity of the light flux.[2] The form of the function $N_k(I)$, determined by expression (5) for the case k = const and z_0 = const, is shown in the figure with log N_k and log I_0 as the coordinates (curves 1 and 2 pertain to the cases k_1 and k_2, respectively, with $k_2 > k_1$). The asymptotes 3 are determined in both cases by expression (9). As seen from the figure, in the initial section $N_k \sim I_0^k$, and then with increasing light-flux intensity the $N_k(I_0)$ dependence becomes less steep ($N_k \sim I_0^m$, where $1 \lesssim m(I_0) \lesssim k$) and tends to become linear in the limit regardless of the order of the effect k. This indicates that the $N_k \sim I_0^k$ dependence can be observed only if the condition (6) is satisfied for the quantities z_0 and I_0. Therefore, in work with sufficiently intense light fluxes, it is necessary to organize the experiment in such a way that the measured integral yield of the multiquantum process corresponds to the small dimension of the effective interaction z_0, which, incidentally, decreases very rapidly with increasing intensity of the light flux ($z_0 \sim I_0^{1-k}$).

The values of the parameter $\tilde{z}$ at which a noticeable change takes place in the exponent of the power-law dependence of the integral yield of the multiquantum process can be estimated in accordance with the scheme proposed in [1]. After performing in succession the operations of taking the logarithm and differentiating with respect to I_0 in (8), we obtain, under the condition $\tilde{z} < 1$,

$$\frac{\delta \ln N_k}{\delta \ln I_0} = m \approx k\left[1 - \frac{k}{2(k-1)}\tilde{z}\right],$$

i.e.,

$$\frac{\delta k}{k} \approx -\frac{k}{2(k-1)}\tilde{z} = -\frac{k}{2}[1 - T(z_0)]. \tag{10}$$

It is seen from (10) that noticeable deviations of $N_k(I_0)$ from the form $N_k \sim I_0^k$ (on the order of 10%) can be observed also in the region of values $\tilde{z} < 1$, i.e., in the region where the transmission $T(z_0)$ of the layer differs by several tenths from unity. The quantity $\delta k/k \sim \tilde{z}$ depends little in this case on the order of the effect k, since $1/2 < k/2(k-1) \leq 1$. The condition $\tilde{z} \approx (k-1)/k < 1$, at which the relative change of the exponent in the power-law dependence reaches approximately the value 0.5, can be satisfied completely in that region of light-flux intensities where there is no saturation of the absorption. Indeed, if one works with light beams whose intensity satisfies the condition $I_0 < I^*$, where I^* is the intensity at which the multiquantum-absorption saturation analyzed in [1] comes into play ($I^* \approx 10^{10}$–10^{11} W-cm^{-2}), then, if the conditions

$$z_0 > I_0^{1-k}/k\beta_k, \quad I_0 < I^*,$$

are satisfied, the integral effect of the change of the power-law dependence of the k-quantum process, not connected with the bleaching effect,[2)] is perfectly feasible.

This conclusion confirms fully the critical remarks contained in [1] and concerning the doubt as to the correct interpretation of those experimental data which are reconstructed from the experimentally measured yield of the multiquantum process. By way of illustration of the possible methodological errors that can occur in this manner, let us analyze critically a number of experimental investigations in which the quantitative characteristics of the multiquantum processes (σ_k, α_k) were estimated from the integral yield of the multiquantum process excited by laser emission in a certain volume.

We consider first investigations devoted to the study of multiquantum fluorescence under the influence of laser radiation in condensed media.[3,5-9] The experiment in [3], where nonlinear absorption of picosecond pulses of light in semiconductors was investigated and the possibility of using this phenomenon for the study of the temporal and statistical characteristics of the exciting light pulse was evaluated, was performed quite correctly. Indeed, the integral curve I(z) of the decrease in the brightness of the luminescence track along the laser-beam propagation direction was obtained in this experiment for cases of two- and three-quantum absorption (in ZnS and CdS samples, respectively) by photography of the transmitted light flux from the side of the sample. In both cases, the measured luminescence intensity curve $I(z \pm z_0/2)$, characterizing the light flux of the multiquantum luminescence from a certain layer of matter, located at the point z and having a thickness z_0, did not differ in practice from the true local luminescence brightness curve along the path of the beam. The parameter $\tilde{z} \sim z_0$ for the ZnS samples

2)In other words, the described effect is connected not with saturation of the absorption but with the presence of noticeable absorption in the layer of matter used as a basis for measuring the yield of the process. ($z_0\kappa_k^{(0)} \approx 1$). It is easy to show that allowance for the radial and temporal inhomogeneities of the light beam has qualitatively no effect on the results, since averaging of the intensity over the time of the pulse and over the radius changes only the magnitude of the observed effective quantum yield of the process, and not its functional dependence $N_k(I)$ (see expressions (2)–(4)).

($\beta_2 \approx 2 \times 10^{-3}$ cm/MW) was equal to 4×10^{-2} under the experimental conditions ($I_0 \approx 2$GW/cm^2), since the value of z_0 determined from the geometry of the experiment was of the order of 10^{-2} cm. Accordingly, in the case of CdS samples ($\beta_3 \approx 2 \times 10^{-8}$ cm^3/MW^2), we have $\tilde{z} \approx 10^{-3}$.

Estimates show that measurements of the quantum yield of two-quantum fluorescence in CS_2 ($\beta_2 \approx 10^{-4}$ cm/MW, $I_0 \approx 10$ MW/cm^2, $z_0 = 10$ cm)[5] and ZnS ($I_0 \approx 10$ MW/cm^2, $\beta_2 \approx 2 \times 10^{-3}$ cm/MW, $z_0 \approx 1$ cm)[6] were also correctly performed. The corresponding values of the parameter $\tilde{z}$ in both cases were approximately the same and on the order of 10^{-2}. This has made it possible to estimate correctly the quantitative characteristics of the multiquantum absorption process in accordance with the data of the integral characteristics. At the same time, the estimates of the quantum yield of two-quantum luminescence in CdS samples in [7] were performed insufficiently correctly, since it follows from the experimental conditions that $\tilde{z} \approx 0.15$ ($\beta_2 \approx 2.2 \times 10^{-2}$ cm/MW, $z_0 \approx 0.5$ cm, $I_0 \approx 12$ MW/cm^2). Likewise incorrect are the estimates of the quantum yield of luminescence and of the cross section of two-photon absorption, determined from the integral yield of two-quantum luminescence in [8], where a study was made of the behavior of solutions of a number of organic compounds under the influence of picosecond pulses of a ruby laser. It follows from the experimental conditions ($I_0 \approx (1-3)$ GW/cm^2, $z_0 \approx 10$ cm, $\beta_2 \approx 10^{-3}-10^{-4}$ cm/MW) that $\tilde{z} \approx 0.5-5$, and consequently it is no longer possible to estimate the quantum yield of the luminescence or the two-quantum absorption cross section in accordance with formula (7).[3)] Therefore the recently proposed[9] procedure for measuring the absolute values of the cross sections of multiquantum absorption from data on the integral yield of multiquantum fluorescence is valid only when the condition (6) is satisfied. In turn, the procedure used, for example, in [2, 10, 11], to determine the quantitative characteristics of multiquantum absorption processes from the results of measurement of the light flux passing through a sample is free of the indicated methodological errors, and is therefore preferable when the multiquantum absorption in the sample becomes noticeable ($\tilde{z} \gtrsim 0.1$).

It should be noted in conclusion that the effect described above should always be taken into account in a correct estimate of the quantum yield of multiquantum photochemical reactions occurring in the volume of a substance. For example, the quantum yield of the two-photon reaction of decomposition of silver chloride (AgCl) under the influence of ruby-laser radiation ($\alpha_2 \approx 2.3 \times 10^{-28}$ acts-cm^{-3} sec^{-1} photon^{-1}) was determined correctly in [12], for although the measurements had a bulk character ($z_0 \approx 1$ cm), the value of $\tilde{z}$ did not exceed 10^{-2}. The quantum yields calculated in [13] for two-photon photolysis reactions of solutions of iodoform (CH_3I) in different organic solvents were, to the contrary, determined incorrectly and are noticeably too high, since they were determined with formula (7) on the basis of spectrophotometric measurements of the total number of particles that have absorbed the laser radiation, under the condition $\tilde{z} \gtrsim 1$ ($\beta_2 \approx (0.3-3.0) \times 10^{-2}$ cm/MW, $I_0 \approx 10$ MW/cm^2, $z_0 \approx 10$ cm).

The increase in the two-quantum absorption cross section σ_2 in proportion to the radiation intensity, likewise observed in [13], is the consequence of an incorrect reduction of the experimental data. The point is that σ_2 was determined from data on the integral quantum yield of the photochemical reaction α_2, measured under conditions when $\tilde{z} \gtrsim 1$. It can be shown that in this case the theoretical and experimental values are connected by the relation

$$(\alpha_2)_{\exp} = (\alpha_2)_{\text{theor}}\,(1+\tilde{z}), \tag{11}$$

Since the sum of the series in (8) at $k = 2$ is equal to $(1+\tilde{z})^{-1}$. It follows from (11) that the value $(\alpha_2)_{\exp}$ determined in this manner depends on the radiation intensity ($\tilde{z} \sim I_0$), whereas $(\alpha_2)_{\text{theor}}$ is constant. It is seen from the example presented that for a correct estimate of the quantum yield of multiquantum photochemical reactions from integral measurements of the characteristics of the reaction products, it is necessary either to work with volumes of matter and light-flux densities such as to satisfy the condition (6), or else (if this condition is violated), to reduce the obtained results with relation (8) taken into account.

The author is grateful to L. V. Pilipenko for stimulating critical remarks.

3)The noticeable deviations of $N_k(I_0)$ from a quadratic dependence that were observed in[8] indirectly confirm the existence of the described integral effect wherein the exponent of the power-law $N_k(I)$ dependence decreases.

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Translated by J. G. Adashko
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