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DEFINITION OF PHOTOREACTION QUANTUM YIELD AT TWO-
- QUANTUM EXCITATION OF MOLECULES IN SOLUTION

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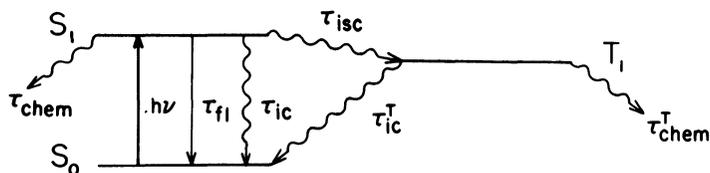
Abstract A new approach to define the photoreaction quantum yield in case of two-quantum excitation of molecules in solution is proposed.

Quantum yield is one of the basic parameters used to describe a photochemical reaction. In accordance with the latest IUPAC recommendations, quantum yield is defined as ratio of the number of molecules which have reacted or formed to the number of photons thereby absorbed [1], that is

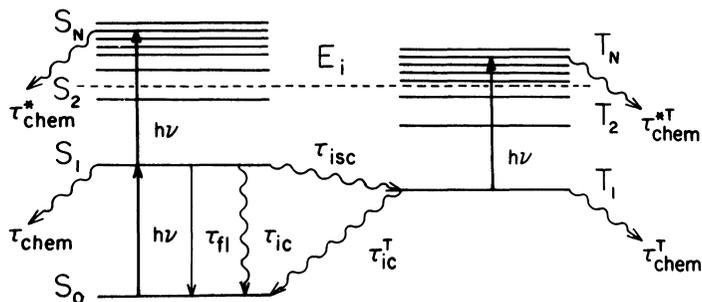
$$\Phi = \frac{\text{the number of molecules which have reacted}}{\text{the number of absorbed photons}} \quad (1)$$

This classical definition of quantum yield was formulated in the pre-laser epoch. It should be noted that it is referred to single-quantum photoreactions resulting from the absorption of one radiation quantum. It is also assumed that all the light quanta are absorbed from the lowest electronic level when organic or biological molecules in solution are excited, the ground singlet S_0 state is this particular level. Photoproducts are formed by single-quantum excitation of one of the low-lying electronic levels, usually the first singlet S_1 level or the first triplet T_1 level (Fig.1a). In other words, the classical definition of quantum yield assumes that the probability of absorption of a second radiation quantum by an excited molecule is negligible. In experi-

ment this situation corresponds to comparatively low-intensity light irradiation (in the case of organic and biological molecules in liquid solutions $I \ll 10^9 \text{ W/m}^2$).



a



b

FIGURE 1. The scheme of electronic state excitation for organic or biological molecules in liquid solution and the ways of excitation energy deactivation in the case of a) single-quantum excitation; b) two-step excitation.

Since in the classical case all the incident quanta are absorbed at a single transition, the number of excited molecules is equal to that of the quanta absorbed. The quantum yield of the single-quantum photoreaction from a singlet level is therefore given by the ratio of the rate constant of the chemical reaction from the given level to the sum of all

the deactivation constants of excitation from the same level, that is:

$$\Phi^s = \frac{1/\tau_{\text{chem}}}{\sum 1/\tau} \quad (2)$$

In the case of the single-quantum reaction from a triplet level the similar expression is valid but considering the probability of triplet level population with one quantum being absorbed at the $S_0 \rightarrow S_1$ transition, that is, with allowance made for the probability of intersystem crossing

$$\Phi^T = \frac{1/\tau_{\text{chem}}^T}{\sum 1/\tau^T} \phi_{\text{isc}} \quad (3)$$

As all the constants from Eqs.(2,3) in the classical case are independent on intensity, the photoreaction quantum yield at low-intensity irradiation does not depend on intensity either (Bunsen-Rosco law).

When transferred to the laser irradiation, as well as at increased lifetime of the excited molecule which is attained under freezing, the probability of absorption of a second quantum by the excited molecule increases drastically. This leads to the realization of two-quantum ("two-step") photoreactions from the highly excited S_N and T_N levels populated at successive absorption of two light quanta through the intermediate S_1 and T_1 levels (Fig. 1b).

It should be noted that for organic and biological molecules in liquid solution the frequency of the $S_0 \rightarrow S_1$ transition lies in the UV spectrum ($E_{S_0 \rightarrow S_1} = 3.5 - 4.5$ eV). Since the ionization threshold of these molecules in liquid phase equals to 5 - 7 eV, the absorption of two quanta corresponds to the excitation above the ionization threshold which leads to the effective realization of chemical reac-

tions from the highly excited S_N and T_N states. It should be marked that since the class of molecules under consideration is characterized by fast vibrational relaxation in the excited electronic S_1 state [2], the excited molecules escape the resonance with the radiation and so in our case the induced emission can be neglected.

At present in scientific literature there is no established definition of quantum yield for the case of two-step photoreaction. The problem we are confronted with is that in two-step photoprocess the incident light quanta are absorbed at both transitions ($S_0 \xrightarrow{h\nu} S_1 \xrightarrow{h\nu} S_N$ or $S_0 \xrightarrow{h\nu} S_1 \xrightarrow{h\nu} T_1 \xrightarrow{h\nu} T_N$), the probability of absorption of a second quantum from the excited S_1 and T_1 levels greatly depending on irradiation intensity. Most of the authors wishing probably to retain the old definition of quantum yield as a quantity independent of intensity believe that two-step photoreaction quantum yield corresponds to the ratio of the number of molecules formed in this reaction to the number of quanta absorbed from an excited intermediate state [3,4,5]. This definition, however, has some essential shortcomings.

First, their aspiration to keep the status of a quantity independent of intensity for two-step photoreaction yield is meaningless because in the case of high-intensity laser irradiation even the quantum yield of single-quantum photoreaction comes to depend on intensity, that is, it decreases with an increase in intensity [6]. This occurs as a result of a considerable depletion of the populations of the intermediate S_1 and T_1 levels due to the transitions to the high-lying electronic S_N and T_N states (Fig.1b). In this case certain members dependent on intensity appear in the denominators of the expressions (2) and (3). As a result, the single-quantum

photoreaction quantum yield drops with increase in intensity.

Another essential shortcoming of the definition for two-step photoreaction quantum yield presented in [3,4,5] is that this quantity cannot be measured in a direct experiment. To find the quantum yield one should predetermine the nature of the intermediate state, to measure its lifetime, the cross-section of absorption from this state, etc. Thus, it is necessary to predetermine all the characteristics of the two-step photoprocess which is not always possible.

The third disadvantage of this definition consists in the fact that it is impossible to compare the quantum yield of the products formed simultaneously by single - and two-quantum channels.

We propose a radically new definition of photoreaction quantum yield free of the shortcomings listed above. The definition given below is a logical generalization of the classical definition of quantum yield for the case of two-quantum photoprocesses. We suggest that quantum yield should be defined as the ratio of the number of molecules reacted to the number of photons absorbed by the system, that is:

$$\Phi = \frac{\text{the number of molecules which have reacted}}{\text{the total number of quanta absorbed}} \quad (4)$$

In this case quantum yield becomes an essentially non-linear quantity because it comes to depend on intensity. Such a definition, however, is more perfect and has, in our opinion, a number of obvious advantages. First, it should be noted that quantum yield, thus defined, is a quantity which can be easily measured in an experiment since it is unnecessary to know "a priori" how the quanta being absorbed

are distributed over separate transitions. Second, such a definition makes it possible to deduce the mechanism of photoproduct formation from the shape of the quantum yield dependence on intensity (Fig. 2) [7]. Third, if there are se-

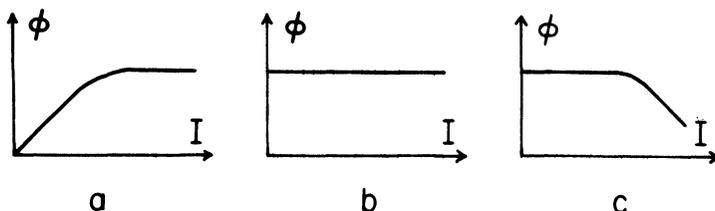


FIGURE 2. The dependence of the photoreaction quantum yield on irradiation intensity in the case of two-step (a), two-photon (b) and single-quantum (c) excitation processes.

veral channels of formation of a single photoproduct, this definition provides an easy differentiation of the contribution of channels with a different number of absorbed quanta.

REFERENCES

1. A.A.Lamola and M.S.Wrighton, *Pure and Appl.Chem.*, 56, 939 (1984).
2. A.Laubereau and W.Kaiser, *Rev.Mod.Phys.*, 50, 607 (1978).
3. U.Lachish, A.Shafferman and G.Stein, *J.Chem.Phys.*, 64, 4205 (1976).
4. Kh.S.Bagdasaryan, Yu.I.Kiryukhin and Z.A.Sinitsina, *Doklady AN SSSR (Moscow)* 243, 385 (1978).
5. D.J.Loungnot and C.R.Goldschmidt, *J.Photochem.* 12, 215 (1980).
6. D.N.Nikogosyan, G.G.Gurzadyan and G.B.Zavilgelsky, *Doklady AN SSSR (Moscow)* 269, 485 (1983).
7. D.N.Nikogosyan and V.S.Letokhov, *Riv.Nuov.Cim.*, 6, serie 3, 1 (1983).