PHOTON EFFICIENCY: RETROSPECTIVE AND PERSPECTIVE

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Concept of the photochemical efficiency was introduced by J. Stark and A. Einstein [1] for the equilibrium case. But it may be developed in Nonliear Optics [2], Relaxed Optics [3] and chemistry [2]. To analyze the efficiency of using absorbed light, we introduced the concept of photon efficiency, which is more general than the Stark-Einstein photochemical efficiency [1– 3].

In general, it makes sense to talk about differential and integral photon efficiency. The differential photon efficiency is introduced at the microlevel for each act of scattering (absorption) of a photon by a medium; integral at the macro level and characterizes macroscopic changes in the properties of the medium or radiated or both radiation and the medium. Appropriate models and theories should be created for each specific case.

According to the level of complexity and scope, photon efficiency can be classified as follows [3]:

1. Radiative photon efficiency.
2. Non-radiative photon efficiency.
3. Mixed photon efficiency.
4. Cascade radiative photon efficiency.
5. Cascade nonradiative photon efficiency.
6. Cascade mixed photon efficiency.

An example of the radiative photon efficiency is the optical pumping of lasers [2, 3], and the nonradiative efficiency is photochemical reactions [2]. The mixed photon efficiency characterizes the optical pumping of a laser with heating of the active medium and autuoscillative chemical reactions of Belousov-Zhabotinskiy type) [3].

Nonlinear optical phenomena are characterized by cascade photon radiative efficiency [3]. Chain chemical reactions [3] and some chains of relaxed-optical processes [3] are represented cascade photon non-radiative efficiency. A number of chains of relaxed-optical processes are characterized by a cascade mixed photon efficiency [3].An example of a mixed optical-electronic system is a photomultiplier tube [3]. It is an electrovacuum device in which the electron flow emitted by a photocathode under the action of optical radiation (photocurrent) is amplified in the multiplier system as a result of secondary electron emission; the current in the anode circuit (collector of secondary electrons) significantly exceeds the initial photocurrent (usually 10^5 times or more). Only first stage of cascade has optical nature.

The integral photon efficiency is connected associated with the direct transformation of the photon flux into photochemical transformations in the irradiated material. It is directly related to differential efficiency. But there is one subtlety in the absorption of radiation by unstable or metastable centers (disordered and amorphous media): the exposure time does not play a big role. At the same time, the radiation saturation mode is of great importance for crystals. For radiative relaxation we have luminescence, generation of laser radiation and various nonlinear optical phenomena; for nonradiative relaxation – relaxed-optical phenomena (phase transformations of the irradiated medium).

Stark-Einstein's law – one quantum of absorbed light causes one elementary chemical reaction [2]. The law allows establishing the relationship between the absorbed energy and the degree of transformation of matter.

It should be noted that in addition to single-photon ionization processes, there can be multiphoton ionization processes and associated dissociation. In this case, the Stark-Einstein law should be corrected.

Now we can formulate the *generalized Stark-Einstein law* [3]: to break (ionize) a certain state, the total energy of a certain number of photons must be greater than or equal to the energy of the excited bond.

The mathematical form of writing for three absorption modes can be represented for the differential photon efficiency δ in the following form [3]:

1) δ <1 for multi photon absorption; (1)
2) δ =1 for one-photon absorption; (2)
3) δ >1 for fractional photon absorption. (3)

Roughly speaking, these three conditions are formalized prsentaion of generalized Stark-Einstein law.

For the estimation the differential photon efficiency of using laser radiation for photochemical irreversible processes for fractional photon absorption we can use next formula for the determination of number of broken chemical bonds per one photon *n* [3]

$$n = 2ln\frac{h\nu}{E_a}, \quad (4)$$

where $h\nu$ – photon energy; E_a – energy of activation (broken) of corresponding bond.

So, for the case of the irradiation *InSb* by Ruby laser pulses (photon energy 1.78 *eV*) we have for the first bond of two-dimensional lattice of *InSb* (E_{1InSb} = 0.18 eV) [3]. These crystals are direct-gap, so the band gap is equal to the energy of the minimum chemical bond [3]. Therefore, n_{InSb} ~ 4.6 bonds/pulse. For case of irradiation *Si* (E_a ~ 1.6 *eV*) by irradiation of eximer laser pulses (photon energy 5 *eV*) we have n_{Si} ~ 2.3 bonds/pulse [3]. These conditions allow increasing the lifetime of excited states and therefore the heating of irradiated matter may be negligible compared to direct photoionization, including phase transformations of the irradiated material.

Formula (3) has large value for the crystals. For the polymers, glasses and amorphous media this condition may be represented as [3, 4]

$$h\nu > E_a. \quad (5).$$

For the determination the differential photochemical efficiency in addition to formulas (4) and (4), the excitation saturation procedure is of great importance.

In other words, for successive *n*-photon absorption for the next absorption event, the medium must be in the excited state that was obtained during previous absorptions.

The integral photochemical (photon) efficiency [3] is connected associated with the direct transformation of the photon flux into photochemical transformations in the irradiated material. It is directly related to differential efficiency. But there is one subtlety in the absorption of radiation by unstable or metastable centers (disordered and amorphous media): the exposure time does not play a big role. At the same time, the radiation saturation mode is of great importance for crystals. For radiative relaxation we have luminescence, generation of laser radiation and various non-linear optical phenomena; for nonradiative relaxation – relaxed-optical phenomena (phase transformations of the irradiated medium). Integral photon efficiency has cascade nature [3].

To increase the photon efficiency, the space-time conditions of irradiation also play an important role. For Nonlinear Optics, they are closely related to coherence and are called phase-matching conditions [2, 3]; for Relaxed Optics, the concept of coherent structures can be used [3].

Main applications of this concept in modern science bare discussed and analyzed in [3, 4].

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