Spectral Dependencies of the Quantum Yield of Photochemical Processes on the Surface of Nano-/Microparticulates of Wide-Band-Gap Metal Oxides. 1. Theoretical Approach

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In this study, we examine theoretically some of the factors that influence the spectral dependencies of the quantum yield, Φ, of photochemical processes on the surface of nano-/microparticulates of wide-band-gap metal-oxide photocatalysts. The approach taken is based on solving the steady-state ($(\mathrm{d}n(t)/\mathrm{d}t) = 0$) continuity equation (eq 7) for a one-dimensional plate with dimensions $x = 0-d$ irradiated on both sides and considering the spatial nonuniformity of photogeneration of charge carriers in the bulk of the solids and their limited probability of diffusion toward the particulate surface. This spatial nonuniformity of charge carrier photogeneration depends on whether the solid photocatalyst is photoexcited in the *intrinsic* or *extrinsic* regions or whether only the surface is photoexcited. Essential conditions required to observe similarities between the spectral dependencies of the quantum yield of surface processes and the absorption spectrum are (i) the relative values of the absorption coefficient α (cm^{-1}) and (ii) the complexity of the absorption spectrum. Spectral selectivity of photocatalysts appears to depend on the different probabilities that electrons and holes reach the photocatalyst surface which are the result of differences in their mobilities and lifetimes (i.e., different diffusion lengths of the carriers).

Introduction

One important characteristic in assessing the efficiency of surface photochemical and photocatalytic processes in heterogeneous (solid/gas, solid/liquid) systems as well as in general photochemistry is the quantum yield (Φ) of reaction, defined as the ratio of the number of molecules taking part in the photoreaction per unit time to the number of absorbed photons per unit of time (eq 1).

$$\Phi(t,C,\rho,h\nu)\ \frac{\dfrac{\mathrm{d}N_{\mathrm{mol}}}{\mathrm{d}t}}{\dfrac{\mathrm{d}N_{h\nu}}{\mathrm{d}t}} \tag{1}$$

where $\mathrm{d}N_{\mathrm{mol}}/\mathrm{d}t$ is the reaction rate (molecules s^{-1}) and $\mathrm{d}N_{h\nu}/\mathrm{d}t$ is the rate of photons absorbed by the system (photons·s^{-1}). In general, the quantum yield is a function of time (t), concentration of reagents (C), light intensity (ρ), and energy of the actinic photons ($h\nu$). The dependence of the quantum yield on time is caused either by decay of the photochemical activity of solids with time in noncatalytic processes, or by a decrease of the concentration of substrates during the photocatalytic reactions. The latter leads to a decrease of the rate of surface photochemical processes. In the majority of studies of surface photochemical processes the dependence of the reaction rate on substrate concentration (pressure in the case of solid/gas systems) can be described by saturation-type kinetics as manifested by the Langmuir−Hinshelwood (LH) approximation[1−6]

$$\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{kKC}{(1 + KC)} \tag{2}$$

where k is an apparent rate constant for the process and K denotes the adsorption coefficient ($k_{\mathrm{ads}}/k_{\mathrm{des}}$) for a process described by the reaction 3

$$\text{gas} + \text{solid} \overset{K}{\rightleftharpoons} \{\text{gas/solid}\} \overset{k}{\rightarrow} \text{intermediates} \ldots \rightarrow \ldots \text{products} \tag{3}$$

Thus, the rate of a photochemical reaction and, therefore, the value of the quantum yield are maximal for $KC \gg 1$ provided all other conditions remain the same. The rate of a surface photochemical process also depends on the intensity of the actinic light. In most studies, these dependencies have been approximated by either linear[7,8] or square-root[7−10] functions. The type of approximation depends on the magnitude of the incident light intensity. In the work of Ollis,[10] carried out at high light intensities, the order of the reaction rate on photon flow, ρ (photons $\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$), was nearly zero because surface intrinsic kinetics were so rapid under the conditions used that the observed reaction rate was limited by the diffusional supply of reactant from the liquid phase. However, diffusional limitation is not the sole factor since dominant recombination decay of surface-active centers also leads to similar kinetic behavior as recently noted for the ZrO_2/O_2 and TiO_2/phenol systems.[11]

To the extent that most photochemical systems are examined at relatively moderate light intensities, the rate of absorption of photons will be proportional to the photon flow (eq 4) (note: henceforth, for convenience we use the terms *light intensity* and

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photon flow interchangeably). Thus,

$$\frac{dN_{h\nu}}{dt} = (\text{const})\rho \tag{4}$$

and any nonlinear dependence of the photochemical reaction rate on light intensity results in the dependence of the quantum yield on light intensity.

Indeed, the dependence of the reaction rate on photon flow can generally be represented by

$$\frac{dC}{dt} = (\text{const})'\rho^m \tag{5}$$

Then according to Eqs 1 and 4, the relationship (Eq 6) given by

$$\Phi = (\text{const})''\rho^{(m-1)} \tag{6}$$

should be observed. Clearly, for $m < 1$ the quantum yield of a surface process decreases as light intensity increases. If the order of the reaction with respect to photon flow, m, is unity, the quantum yield becomes independent of light intensity and yields the maximal value of Φ. Results of recent studies carried out by Emeline and co-workers[11] demonstrate that, in such heterogeneous systems as ZrO_2/O_2 and TiO_2/phenol, the interdependence of the reaction rate on concentration (eq 2) and light intensity (eq 5) may be a common occurrence (see also ref 12) in photoinduced processes taking place in solid/gas and solid/liquid systems, although additional studies are evidently needed to confirm this assertion. In particular, the linear dependence of the reaction rate on light intensity ($m = 1$; eqs 5 and 6) is seen when the dependence of the rate of reaction on concentration is near saturation (when $KC \gg 1$; eq 2); i.e., the reaction order with respect to concentration is 0.

Thus, to characterize the efficiency of solids in surface photochemical reactions necessitates the maximal value of Φ, which is observed at sufficiently high concentration of substrates (i.e., when $KC \gg 1$) and when the reaction order with respect to photon flow, m, equals 1. In general, Φ is time-independent for an ideal photocatalytic process only for small-percent conversion of the reagent substrate. In addition, determination of Φ provides a means to verify the reproducibility of the initial state of the (little understood) surface of the solid.

Quantum yields of photoadsorption of molecules[13−19] and of surface photoreactions[20−23] in several heterogeneous solid/gas and solid/liquid systems have been reported. Typical values for these systems are $\Phi = 0.01-0.1$. Maximal values of quantum yields have been measured for oxygen photoadsorption on ZnO under photoexcitation in the extrinsic absorption band ($\lambda = 445$ nm, ca. 2.8 eV), $\Phi = 0.8$,[13] and for nonsensitized photolysis of surface-adsorbed water on Al_2O_3 at $\lambda < 250$ nm ($\Phi = 0.3$[20]). Note that quantum yields in solid/gas systems may also exceed unity.

Quantum yields of surface photoreactions are, in particular, determined by a whole set of excitation processes and energy (and/or charge) transfer to the surface. One of the more interesting problems regarding quantum yields is the spectral distribution of Φ and its relationship with the absorption spectrum of the system (i.e., the wavelength dependence of Φ). Knowledge of such dependencies is needed to estimate and compare the total efficiencies of photocatalysts.[23] In addition, as with any spectral response of a given system to light action, the quantum yield provides some information concerning the mechanism of photoexcitation of the system (either solids or adsorbed species). The importance of this latter aspect was emphasized long ago in the pioneering studies of Terenin.[24,25]

A few studies[13−15,17−19] have reported the spectral distribution of quantum yields for a variety of surface photoprocesses determined by different actinometric methods to estimate the rate of absorption of photons. Typical distributions of $\Phi(h\nu)$ are the spectral curves with more or less resolved band maxima. In some cases, the spectral dependencies of quantum yields $\Phi(h\nu)$ were arbitrarily indentified[17] as transformed absorption spectra because of their mutual spectral resemblance where the maxima of quantum yields of oxygen photoadsorption on MgO were taken to correspond to the maxima of absorption bands of F-type centers in the absorption spectrum of the adsorber. From studies of the spectral distributions of quantum yields of photoadsorption of different molecules on ZnO, other workers[13,15,18] proposed that some spectral features of the quantum-yield distribution may be connected to the absorption of photochemically inactive light by the system. Thus, features of the spectral distribution of quantum yields of surface photochemical processes and their connection to the absorption spectra of heterogeneous systems remains rather unresolved. Nevertheless, the basic approaches used to establish the factors that determine the values of either the rates or the quantum yields of surface photochemical processes are well-known.

The first approach is based on a consideration of multistep kinetic mechanisms.[2,21,26−32] It considers the importance of such factors as efficiency of charge-carrier generation, their trapping by and their recombination through the solid's defects, and in particular, the chemical stages of surface reactions with the participation of chemical intermediates from which experimental rates of photoprocesses are assessed. This approach was used in several major studies. Concomitantly, the proportionality of the rate of reaction to the rate of carrier photogeneration is typical for all these mechanisms, so that the latter is included in the final expression for the reaction rate and is taken either as constant (e.g., see the work of Turchi and Ollis[26]) or otherwise is represented as $\chi\rho$, where χ is the internal quantum yield of photoeffects intrinsic to the solid and ρ is the incident photon flow.[2,31] In this case, the action spectrum of the photoreaction mirrors the absorption spectrum of a single band of photochemically active light absorption, whereas Φ is independent of the wavelengths of the actinic light.

In the second approach, unlike the first, the spatial separation of carrier photogeneration (in the bulk of solids) and the chemical reaction (at the surface of solids) are taken into consideration. This approach considers carrier photogeneration at some distance x from the surface ($x = 0$ at the surface), their decay through both trapping and recombination, and their diffusion to the surface. All these processes are considered when solving the continuity equation (eq 7) which is described below for a one-dimensional case in which internal and external electrical fields are neglected

$$\frac{\partial n(t,x)}{\partial t} = D\frac{\partial^2 n(x)}{\partial x^2} - \frac{n(x)}{\tau} + G(t,x) \tag{7}$$

where $n(x)$ is the concentration of carriers (either electrons or holes) at a distance x from the surface, D is the diffusion coefficient of the charge carriers and τ is their lifetime, both of which determine their diffusion length L through $L^2 = D\tau$, and $G(t,x)$ is the volume rate of carrier photogeneration in the bulk at the distance x from the surface. Thus, the first term on the right-hand side of eq 7 describes the diffusive migration of carriers in the bulk space from a distance x to the surface, the

second term considers the carrier decay by several pathways as a quasi-first-order decay process, and the third term is the volume rate of carrier photogeneration which typically depends on distance, x, and on time, t.

To our knowledge, this continuity equation (eq 7) was first applied to treat surface photochemical reactions in the electronic theory of photocatalysis[33] using a quasi-steady-state approach for the concentration of carriers ($dn(t,x)/dt = 0$) in a semi-infinite crystal (one-dimensional case) taking into account near-surface internal electrical fields and using standard boundary conditions for the surface-recombination rate, s. Similar approaches have been used by Gerischer and Heller,[34] Albery and Bartlett,[35] and Curran and Lamouche[36] for photocatalytic processes in colloidal sols and in photoelectrochemical cells. The solid was envisaged as consisting of sphere-like particles with radius r to assess the distribution of electrical potentials in the particles.[35] The dependencies of the quantum yield, or of the so-called *collection coefficient*, on particle size and other characteristics of particles have been examined in the work of Curran and Lamouche[36] in which they proposed that the main path of surface carrier decay takes place by electron transfer across the interface rather than by surface recombination. The solution of the non-steady-state eq 7 was also used for solid particles of small radius by Gruzdkov and co-workers[37] to describe the kinetics of luminescence decay of adsorbed molecules.

In all of the above-mentioned studies, the case of uniform carrier generation, $G = \alpha\rho$, which is not a function of x was considered only because of some particular conditions that applied to the problem (for example, small radius of particles, $r \ll \alpha^{-1}$, where α is the absorption coefficient of the solid). This case restricts the general analysis of the spectral distribution of quantum yields of surface photochemical reactions and considers only the particular case of its spectral independence within a single absorption band. Nevertheless, this last approach makes it possible to analyze the spectral distribution of quantum yields of photoprocesses, as done to examine the photoconductivity of solids,[38] the field-assisted photomagnetic effect,[39] or the photolysis of AgBr crystals.[40]

Results and Discussion

The rate of a photochemical reaction of molecules in a gas or liquid phase with a solid surface when that rate does not depend on the concentration of reagent (at sufficiently high concentration, see Introduction) for the simplest reaction or otherwise the first step of a complex process

$$S + e \text{ (or } h) \xrightarrow{k_{tr}} S^- \text{ (or } S^+) \tag{8}$$

is expressed by

$$\frac{dS}{dt} = k_{tr}[S][n_s] \tag{9}$$

where S represents either the adsorbed molecules or the surface defects (i.e., "potential" surface active centers), e and h are the charge carriers (electrons and holes, respectively), S^- and S^+ are either the reaction products or the surface-active centers, k_{tr} is the rate constant of carrier trapping either by surface defects in the case of the Eley−Rideal mechanism or by adsorbed molecules in the case of the Langmuir−Hinshelwood reaction, $[S]$ is the concentration of either the surface defects ("potential" surface active centers) or of the adsorbed molecules, and $[n_s]$ is the surface concentration of carriers of the appropriate sign (electrons or holes). The initial quantum yield at wavelength λ is then given by

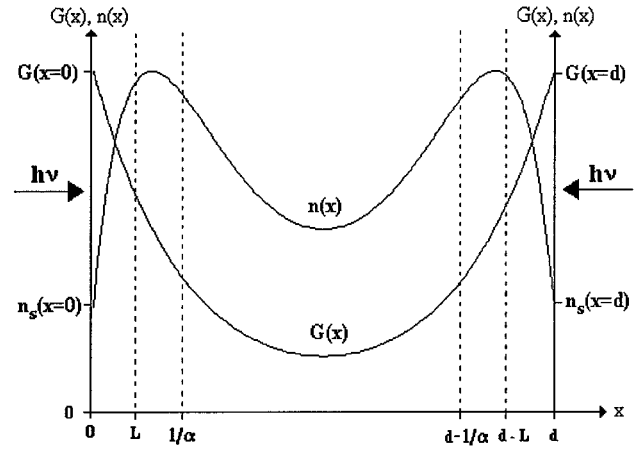

Figure 1. Scheme of an infinite solid plate with thickness d irradiated uniformely from both sides. The curve $G(x)$ describes a nonuniform spatial distribution of carrier photogeneration. The straight vertical lines between the surface and the bulk define a depth equal to the average diffusion length of the carriers L and average length $1/\alpha$ of light penetration into the bulk. The carriers generated within the diffusion length can reach the plate surfaces by diffusion migration. Those generated in the remaining part of the lattice bulk cannot take part in surface chemical processes. The curve $n(x)$ represents the spatial distribution of the concentration of free-charge carriers.

$$\Phi = \frac{k_{tr}[S_o][n_{so}]}{A\rho} \tag{10}$$

where the subscript "o" defines the initial quasi-steady-state concentrations of carriers and their corresponding traps, ρ is the photon flow, and A is the absorbance of the system at a given wavelength λ, e.g., the dimensionless coefficient representing the fraction of photons absorbed by the solid.

In the present study we consider the process of a photochemical reaction on the surface of an infinite plate of a solid with uniformly irradiated surfaces (both sides of plate; see Figure 1). This model simplifies the system to a one-dimensional case to facilitate the interpretation of the results obtained, by using the final expressions for single crystals (semi-infinite crystals) assuming the thickness of the crystal $d \rightarrow \infty$, and to analyze the dependence of the quantum yield on the thickness d of the crystal plate. At a given initial concentration of "potential" surface-active centers or of adsorbed molecules, Φ is determined by the initial quasi-steady-state surface concentration of the corresponding charge carriers, which generally varies with the spectral-dependent absorption coefficient, α, of the adsorber. The spectral dependence of the surface concentration of charge carriers $[n_s(\alpha)]$ can be found by solving the continuity equation (eq 7).

1. Case of Light Absorption in the Bulk of the Crystal. We first consider that light absorption by the bulk of the solid follows the Lambert−Beer law and leads to bulk generation of photocarriers and their subsequent diffusion toward the surface (see Figure 1). In this case, the absorbance in eq 10 is defined as

$$A = 2[1 - e^{-\alpha d}] \tag{11}$$

where the number 2 is introduced to indicate that the plate absorbs light at both extremes. The solution to the continuity eq 7 for the quasi-steady-state approach at given boundary

conditions yields the spatial distribution of the carrier density *n(x)* and the surface concentration of charge carriers at $x = 0$ and at $x = d$. The function of the photogeneration of carriers in the bulk in eq 7 for the infinite-crystal plate then becomes

$$G(x) = \chi\alpha\rho[e^{-\alpha x} + e^{-\alpha(d-x)}] \tag{12}$$

where χ is the quantum yield of internal photoeffects or, otherwise, the probability of formation of free carriers after absorption of a single photon. In a given case, the boundary conditions can be written as

$$D\frac{\partial n}{\partial x} = sn \qquad \text{for } x = 0 \tag{13}$$

$$D\frac{\partial n}{\partial x} = -sn \qquad \text{for } x = d \tag{14}$$

where s is the rate of surface recombination of the carriers (note that carriers decay on the surface).[41]

The continuity equation 7, with the function of carrier photogeneration, eq 12, denotes a nonuniform second-order differential equation with constant coefficients. Taking into consideration the boundary conditions, eqs 13 and 14, one obtains the expression for the surface concentration of charge carriers, namely

$$n_s = \frac{2(1 - e^{-\alpha d})\chi\rho\alpha L^2}{D\left(\tanh\left(\frac{d}{2L}\right) + \xi\right)(1 - \alpha^2 L^2)}\left[\tanh\left(\frac{d}{2L}\right)\coth\left(\frac{\alpha d}{2}\right) - \alpha L\right] \tag{15}$$

where $L = (D\,\tau)^{1/2}$ is the diffusion length of the carriers and $\xi = s\,L/D$ can be considered as a ratio of the surface recombination and bulk recombination rates. Substituting eqs 11 and 15 into eq 10 yields

$$\Phi = \frac{k_{tr}S_o\chi\alpha L^2}{D\left(\tanh\left(\frac{d}{2L}\right) + \xi\right)(1 - \alpha^2 L^2)}\left[\tanh\left(\frac{d}{2L}\right)\coth\left(\frac{\alpha d}{2}\right) - \alpha L\right] \tag{16}$$

Note that a general solution of eq 7 for *n(x)* can also be obtained. As an example, we present graphically (see Figure 1) the possible profile of *n(x)* at a given rate of surface recombination, $0 < s < \infty$, corresponding to the carrier-generation function, *G(x)*, depicted in the same plot. Clearly, the curve for *n(x)* is different from the *G(x)* plot owing to diffusion of carriers and their decay at the surface.

Equation 16 suggests that the quantum yield of a surface photoreaction on a given photocatalyst depends on the ratio $d/2L$, which in the one-dimensional model is proportional to the ratio between the total volume of the bulk crystal ($V_{crys} \propto d$) and the volume of the bulk space near the surface ($V_{dif} \propto 2L$) from which the photogenerated carriers can reach the surface through diffusion. The greater this ratio is, the smaller the fraction of carriers photogenerated in the bulk crystal that can diffuse to the surface and the higher the fraction of the absorbed light that is photochemically inactive. As a result, the quantum yield decreases as the ratio $d/2L$ increases. In other words, on one hand, the smaller the thickness of the crystal plate is (i.e., the smaller the size of the crystalline solid particles), the smaller the ratio $d/2L$ will be and the higher the quantum yield for a given type of photocatalyst.[42] On the other hand, the greater the mobility of carriers is, and as a result, the longer their diffusion length L, the greater the quantum yield Φ for a given crystal size d and absorption coefficient α.

The quantum yield also depends on the ratio of the surface recombination rate to the bulk recombination rate, $\xi = sL/D$, which determines the direction of the diffusion flow of photocarriers: either toward the surface or toward the bulk. Note that the surface recombination rate indirectly corresponds to the surface potential that determines the magnitude of band bending in the space charge layer.[43,44] Clearly according to eq 16, the quantum yield also depends on the rate constant of the surface process, k_{tr}, and on the initial concentration of the reagent substrate, S_o. Note that the conditions assumed in this model result in the independence of the quantum yield relative to the intensity of the actinic light, which corresponds to the maximal quantum yield of the surface photochemical process for a given system (see Introduction).

Assuming generation of thermalized charge carriers at moderate light intensities, the rate of surface recombination, s, and the carrier lifetime, τ, may be considered constant. Then L and ξ are also constant, and the spectral dependence of the quantum yield is determined by the spectral variation of the absorption coefficient $\alpha(h\nu)$ or, to be precise, by the co-relationship αL. The physical sense of this relation corresponds to the number of photons absorbed in the space near the surface with a depth similar to the diffusion length L. Hence, absorption of photons leads to the appearance of photocarriers which can reach the surface and take part in the surface photochemical process. The greater the value of αL (i.e., the greater the absorption coefficient α at a given diffusion length L) the closer is the spatial distribution of carrier photogeneration to the surface and the greater is the number of photocarriers that can participate in surface processes. The co-relationship αd determines the spatial nonuniformity of the density of carrier photogeneration in the bulk of the crystal and also sets the value of the quantum yield.

Note that the quantum yield $\Phi \rightarrow 0$ under two otherwise distinct conditions: (i) the recombination of carriers in the bulk is fast because either the lifetime of the carriers in the bulk $\tau \rightarrow 0$ and their diffusion length $L \rightarrow 0$ or (ii) the total consumption of surface photocarriers taking part in the chemical reaction is much smaller than that for all other possible decay pathways of surface carriers in surface recombination processes, so that $s \gg k_{tr}S_o$ for reasonable values of the other parameters in eq 16. However, when bulk recombination of carriers is negligible, i.e., $\tau \rightarrow \infty$ and so $L \rightarrow \infty$, and if the chemical process is the only path for the decay of surface carriers (i.e., $s = k_{tr}S_o$), then the quantum yield approaches its maximal value limited only by the quantum yield of internal photoeffects (i.e., $\Phi = \chi$).

Some particular cases of the spectral dependence of the quantum yields under different types of photoexcitation of the photocatalyst are considered below. Assuming that all the parameters (excluding α) in eq 16 are constants, we may then consider excitation of a solid in a single absorption band.

(1a) Case Where $d \rightarrow \infty$. This case corresponds to a photochemical process on the surface of large (semi-infinite) single crystals. Assuming $\alpha d \rightarrow \infty$ and $d/2L \rightarrow \infty$ in eq 15 one obtains

$$\Phi = k_{tr}S_o\left[\frac{\chi\alpha L}{1 + \alpha L}\right]\left[\frac{L}{D(1 + \xi)}\right] \tag{17}$$

or

$$\Phi = (\text{const})\left[\frac{\chi\alpha L}{1 + \alpha L}\right] \tag{18}$$

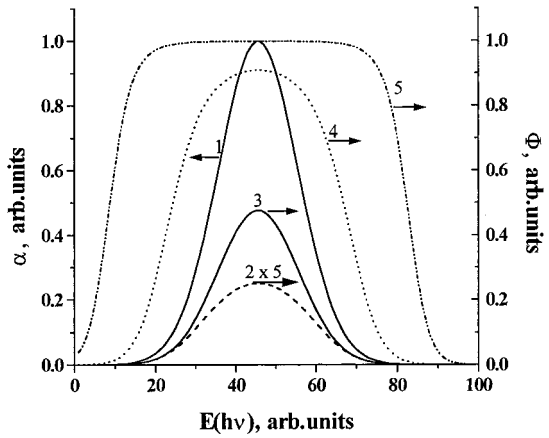

Figure 2. Spectral dependencies of the quantum yield within a single absorption band (curve 1) for different maximal values of the co-relationship αL: (curve 2), $\alpha L = 0.1$; (curve 3), $\alpha L = 1$; (curve 4), $\alpha L = 10$; (curve 5), $\alpha L = 1000$.

Thus, within a single absorption band and for $\chi =$ const, the shape of the spectral dependence of the quantum yields is determined by the value of αL. In the case of strong photon absorption, when $\alpha L \gg 1$, the quantum yield is spectral independent (i.e.,$\Phi(h\nu) \rightarrow$ const) since this condition signifies that photocarrier generation occurs in the space near the surface at a depth smaller than the diffusion length, thereby providing a high probability that carriers reach the surface and take part in surface photochemical reactions. For $\alpha L \ll 1$, the quantum yield distribution, $\Phi = \alpha L$ (const), closely follows the absorption spectrum. Obviously, for small values of αL a significant fraction of the photocarriers is generated far from the surface and cannot reach the surface; consequently, their decay occurs by a recombination process in the bulk of the lattice. With increasing αL, a greater number of carriers are generated within the diffusion length from the surface and so there is an increase in the quantum yield with an increase of the absorption coefficient α. The evolution of the spectral dependence of the quantum yield with increasing $\alpha L = 0.1$ to $\alpha L = 1000$ for a model Gaussian shaped single-absorption band in accordance with eq 17 is presented in Figure 2.

Equations 17 and 18 can also be used to clarify the spectral dependence of quantum yields of photochemical processes taking place on the surface of single semiconductor crystals, e.g., preadsorbed molecules photodesorbing from the surface of semiconductors (e.g., see the studies of Young et al.[45] and Lu and co-workers[46]) on reaction with the holes as the photocarriers and assuming the pathway described by reaction 19 for the photodesorption of oxygen[46]

$$O_2^{\bullet -}{}_{ads} + h \rightarrow O_{2(g)}\uparrow \tag{19}$$

Note that the spectral dependence of the quantum yield, as might be given by eqs 17 and 18, was also considered in order to interpret the experimental results of studies of the photolysis of single crystals of AgBr.[40]

(1b) Case Where $\alpha \rightarrow \infty$. The condition $\alpha d \rightarrow \infty$ (see above) may also be satisfied for an infinite crystal plate in the case of strong light absorption, as may occur in the spectral region of *intrinsic* absorption[47] of the solid. In this case, the quantum yield is expressed by

$$\Phi = k_{tr} S_o \left[\frac{\chi \alpha L}{1 + \alpha L}\right]\left[\frac{L}{D\left(\tanh\left(\frac{d}{2L}\right) + \xi\right)}\right] \tag{20}$$

or more simply as

$$\Phi = (\text{const})\left[\frac{\chi \alpha L}{1 + \alpha L}\right] \tag{21}$$

Thus, the shape of the spectral dependence of the quantum yield is similar to the case of a semi-infinite crystal considered earlier (eqs 17 and 18) and is determined by the value of αL. Equation 20 can be reduced to eq 17 assuming that $d \rightarrow \infty$ or that $2L \ll d$ so that $\tanh(d/2L) \rightarrow 1$. Condition $2L \ll d$ for $\alpha \rightarrow \infty$ signifies, in practice, that the plate can be considered as a single crystal since processes on each of the crystal surfaces are isolated from one another.

In the case of very strong light absorption, for $\alpha L \gg 1$ (at all wavelengths), eq 20 reduces to

$$\Phi = \frac{k_{tr} S_o \chi L}{D\left(\tanh\left(\frac{d}{2L}\right) + \xi\right)} \tag{22}$$

that is, $\Phi \neq f(\alpha)$, which means that the quantum yield is spectrally independent of light excitation within a single absorption band, provided that photogeneration of carriers occurs mostly on the surface (this corresponds closely to the case of surface light absorption considered below).

(1c) Case Where $\alpha \rightarrow 0$. This case corresponds to weak light absorption by the crystal when $\alpha L \rightarrow 0$ and $\alpha d \rightarrow 0$ in eq 15. In practice, this represents a case of *extrinsic* light absorption by the solid, for which the quantum yield is given by

$$\Phi = \frac{2 k_{tr} S_o \chi L^2}{Dd}\left[\frac{\tanh\left(\frac{d}{2L}\right)}{\tanh\left(\frac{d}{2L}\right) + \xi}\right] \tag{23}$$

that is,

$$\Phi \neq f(\alpha) \tag{24}$$

At moderate light intensities when the photocatalyst is excited within a single absorption band and for $\chi =$ (const), the quantum yield, Φ, is a spectrally independent, constant value. This case corresponds to the spatially uniform photogeneration of carriers in the bulk of the solid crystal. Thus, the fraction of carriers able to reach the surface is given by the ratio $2L/d$. Consequently, in multistep mechanisms, the stages that implicate photoexcitation of the solid which, in turn leads to surface photochemical reactions, such as those reported in earlier studies,[26−32,48] must also be applied to the region near the surface space, i.e., within the diffusion length L of those carriers that can participate in surface reactions. Note that the independence of the quantum yield, Φ, on the absorption coefficient, α, (see eqs 23 and 24) also infers its independence on the concentration of light absorption centers N, since $\alpha = \sigma N$, where σ is the cross section of light absorption by the absorption centers. Causes for relaxing this independence were observed by Emeline and co-workers[32] in the heterogeneous system Sc_2O_3/H_2, in which Φ of oxidation of H_2 was dependent on α. Note that the condition $\alpha d \rightarrow 0$ is also valid for the case of strong *intrinsic* light absorption in a very thin crystal plate, i.e., for $d \rightarrow 0$. In this case, the spatially uniform generation of carriers is achieved because of the small size of the crystals.

2. Surface Light Absorption. Light absorption by *intrinsic* and/or *extrinsic* surface states of the solids may lead to photogeneration of charge carriers directly on the surface. The continuity equation under steady-state conditions applied to the

carrier concentration is then given by

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau} = 0 \tag{25}$$

with the boundary conditions

$$D\frac{\partial n}{\partial x} = sn + G_s \qquad \text{for } x = 0 \tag{26}$$

$$D\frac{\partial n}{\partial x} = -sn + G_s \qquad \text{for } x = d \tag{27}$$

where

$$G_s = \chi\kappa\rho(2 - \kappa) \tag{28}$$

is a function of the surface photogeneration of carriers, κ is the *dimensionless* coefficient of surface light absorption defined as the fraction of incident light absorbed by the surface states. In such a case, the surface concentration of photocarriers is expressed as

$$n_s = \kappa\rho(2 - \kappa)\frac{\kappa L}{D\left(\tanh\left(\frac{d}{2L}\right) + \xi\right)} \tag{29}$$

Taking the absorbance $A = \kappa(2 - \kappa)$ and making the substitution of eq 29 into eq 10, we obtain for the quantum yield of reaction for the case of surface light absorption the expression

$$\Phi = k_{tr}S_o\frac{\chi L}{D\left(\tanh\left(\frac{d}{2L}\right) + \xi\right)} \tag{30}$$

We conclude from eq 30 that photoexcitation in the spectral region within a single absorption band (χ = const) and for moderate light intensities (ξ = const), the quantum yield is spectrally independent since the rate of carrier photogeneration on the surface is proportional to the rate of absorption of photons. In general, the value of the quantum yield Φ is less than χ because photocarriers are consumed not only by the chemical reaction(s) but also by other processes of carrier surface recombination and by diffusion to and decay in the bulk. The efficiency of these processes is determined by ξ and $d/2L$ (the physical sense of these parameters has been defined above). Note that the expression for the quantum yield in the case of surface light absorption is identical to that in the case of very strong absorption by the lattice bulk, provided that $\alpha L \gg 1$ (see eq 22).

3. Multiband Absorption Spectrum. All the cases considered above have dealt with the spectral dependencies of the quantum yield within a single absorption band for the photoexcitation of the catalyst. In practice, however, the actual absorption spectrum of the photocatalyst is the result of several overlapping absorption bands of different origins (*intrinsic* bulk and surface absorption, absorption of different types of defects, and free-charge-carrier absorption, among others). As a result, the spectral dependence of the quantum yield of a surface photochemical reaction is a composite of the superposition of different types of photoexcitation of the solid. Hence, the total rate for the simplest photochemical reaction (reaction 8) is the sum of the rates of elementary processes considering the

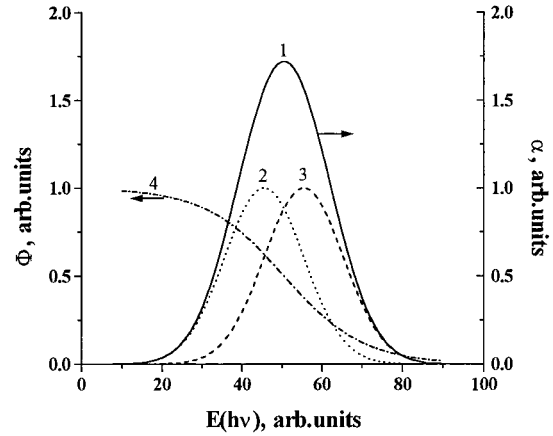

Figure 3. Spectral dependence of the quantum yield (curve 4) within the absorption spectrum (curve 1) formed by the overlap of two single-absorption bands: (curve 2), band corresponding to the photochemically active light absorption; (curve 3), band corresponding to the photochemically inactive light absorption.

photoexcitation in each single absorption band separately; thus,

$$\frac{dS}{dt} = R = \sum_i R_i = \rho\sum_i A_i\Phi_i \tag{31}$$

assuming from eq 10 that

$$R_i = A_i\rho\,\Phi_i \tag{32}$$

where R_i is the rate of the elementary reaction under excitation in the *ith* single absorption band, A_i is the absorbance in the *ith* single absorption band, and Φ_i is the corresponding quantum yield of the reaction. Taking the total number of absorbed photons per unit time to be given by $A\rho = \rho\sum_i A_i$ (where A is the total absorbance at a given wavelength) we obtain from eq 10 that the total quantum yield is

$$\Phi = \frac{R}{A\rho} = \frac{\sum_i A_i\Phi_i}{\sum_i A_i} \tag{33}$$

where Φ_i can be estimated from eqs 16−18, 20, 21, 23, 24, and 30, taking α as the absorption coefficient resulting from all the different types of light absorption.

In general, excitation in each of the single absorption bands differs from others by the values of the quantum yield of internal photoeffects χ, the corresponding lifetime τ, and the diffusion coefficient D of the carriers (and hence by the diffusion length L) depending on the type of delocalized excitation (electrons, holes, or excitons), its energy (hot or thermalized carriers) and type of excitation (direct or indirect electronic transitions), the rate of surface recombination, s, and the rate constant k_{tr} of carrier trapping either by adsorbed molecules or by the "potential" surface-active centers (surface defects). All these parameters must be considered in the interpretation of the spectral dependence of the quantum yield of surface photochemical processes when using eq 33.

As an example of this interpretation of the spectral dependence of the quantum yield (eq 33), we consider the hypothetical absorption spectrum (curve 1) illustrated in Figure 3. The absorption spectrum is the result of the overlap of two single Gaussian-shaped bands of equal amplitudes and half-widths. One of these is a photochemically active absorption band (χ = 1; curve 2) while the other is a photochemically inactive one (χ = 0; curve 3). The case of weak light absorption ($\alpha d \ll 1$) is illustrated in Figure 3. In this case, the quantum yield $\Phi(h\nu)$

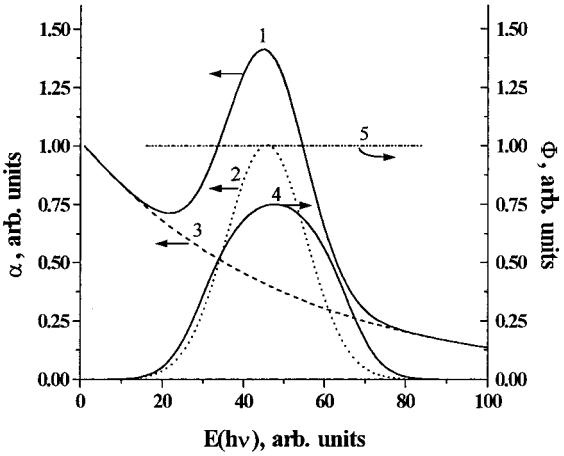

Figure 4. Spectral dependence of the quantum yield (curve 4) when the absorption spectrum (curve 1) is formed by the overlap of a single absorption band of photochemically active light (curve 2) and a photochemically inactive background absorption (curve 3). Curve 5 represents the spectral dependence of the quantum yield, provided, only, that the photochemically active light absorption (curve 2) takes place in a given spectral region.

remains constant within the spectral region of the single active absorption band and within the inactive band $\{\Phi(h\nu) = 0\}$. However, for multiband absorption (i.e., for their sum, curve 1), $\Phi(h\nu)$ consists of two spectral regions in which the quantum yield is practically constant (at least initially; see Figure 3) and, subsequently, a "transition" region is evident where $\Phi(h\nu)$ changes with photon energy. Note that other types of overlap of active and inactive absorption bands result in multiband light absorption that can yield different types of spectral dependencies of the quantum yield.

Figure 4 shows another typical situation. Here the absorption spectrum (curve 1) is formed by the overlap of a photochemically active single Gaussian-like absorption band (herein considered as absorption by the surface states, curve 2) and of a photochemically inactive and exponentially decaying background absorption (considered herein as absorption by the crystal bulk, curve 3). According to eq 30, the quantum yield is constant (curve 5) within the single band of light absorption by the surface states, provided that this type of light absorption only occurs in a given spectral region. However, if we take into account the total light absorption (curve 1) resulting from the overlap of the active band (curve 2) and the inactive background absorption (curve 3) and further assume that the quantum yield Φ_i for the photochemically inactive light absorption is 0 (because $\chi = 0$), then from eq 33 the shape of the spectral dependence of the quantum yield (curve 4) will be rather similar to the absorption band of the active light absorption. Thus, in the general case, an active absorption-bandlike peak in the $\Phi(h\nu)$ dependence appears because of the inactive absorption background. Obviously, the shift of its maximum with respect to the maximum of the active absorption band is more significant the more abruptly the background absorption changes with wavelength. Zero shift would be observed at constant background absorption. On the other hand, the greater the inactive light absorption is the smaller the quantum yield is, and the greater the resemblance of the shape of the $\Phi(h\nu)$ peak will be to the shape of the single absorption band provided that χ is constant. The latter should be kept in mind when one observes the correspondence between $\Phi(h\nu)$ and $\alpha(h\nu)$. For example, the model presented can explain the similarity between $\Phi(h\nu)$ and $\alpha(h\nu)$ for the photoadsorption of simple molecules on the surface of MgO within the spectral region of the absorption bands of F-type centers.[17] Note that in practice the systematic experimental error involved in measuring the sample absorbance (in particular, by the method of diffuse reflectance spectroscopy[17]) can play the role of apparent inactive absorption background (that is, false absorption with $\chi = 0$). This model can be also used to interpret the spectral dependence of the quantum yield of photostimulated adsorption of oxygen on the system CaO/CO by excitation of the surface carbonate groups.[14]

Note that secondary chemical steps following reaction 8 can also affect the spectral dependence of the quantum yield.

4. Spectral Selectivity of Photocatalysts. Solving the continuity equation (eq 7) offers an opportunity to both predict and explain the spectral selectivity(ies) of photocatalysts. We consider two possible reactions a molecule M may undergo with electrons and holes

$$M + e_s \rightarrow M^- \tag{34a}$$

$$M + h_s \rightarrow M^+ \tag{34b}$$

followed by secondary reactions which lead to formation of different intermediates and products. The rates of the corresponding primary steps (34a, 34b) can then be presented as

$$\frac{d[M^-]}{dt} = k'[M][e_s] \tag{35a}$$

$$\frac{d[M^+]}{dt} = k''[M][h_s] \tag{35b}$$

and thus their ratio is given by

$$\frac{\dfrac{d[M^-]}{dt}}{\dfrac{d[M^+]}{dt}} = (\text{const})\frac{[e_s]}{[h_s]} \tag{36}$$

which depends on the ratio of the surface concentration of electrons to that of holes. These concentrations can be found using the solution to the continuity equation (eq 7) with the corresponding, appropriate boundary conditions. As disclosed above, the surface concentrations of carriers depend on the value of the absorption coefficient α, and thus, the ratio of the surface concentration of electrons to that of holes in eq 36 will be spectrally dependent. Consequently, the direction of the overall surface photoreaction of molecules M with surface carriers toward either the formation of radical anions, M^-, or radical cations, M^+ , depends on the wavelength of the actinic light.

In the simplest case, a semi-infinite crystal, the spectral dependence of the surface concentration of the corresponding charge carriers (electrons or holes) presented by eq 15 can be rewritten as

$$n_s = \frac{\alpha L}{(\alpha L + 1)}[F(s,D,\rho)] \tag{37}$$

where $[F(s,D,\rho)]$ represents a term that is a function of s, D, and photon flow, ρ.

In general, the diffusion length, L, is different for electrons and holes because of their different mobilities. The ratio between the surface concentration of electrons and that of holes ($[e_s]/[h_s]$) can be described by

$$\frac{[e_s]}{[h_s]} = (\text{const})\frac{\alpha L_e + \beta}{\alpha L_e + 1} \tag{38}$$

where $\beta = L_e/L_h$ is the ratio between the diffusion length of electrons and that of holes, respectively. This implies that the ratio $[e_s]/[h_s]$ depends on the absorption coefficient α, and the shape of the spectral dependencies is determined by the value of β. The ratio $[e_s]/[h_s]$ decreases for $\beta > 1$ (i.e., for $L_e > L_h$) and increases for $\beta < 1$ (i.e., for $L_e < L_h$) with increasing absorption coefficient, α. Thus, in the simplified example illustrated by reactions 34, the direction of the overall reaction with increasing absorption coefficient, α, would be turned toward the production of the radical anions M^- if the diffusion length of electrons is less than the diffusion length of the holes (i.e., $L_e < L_h$, and $\beta < 1$). The overall reaction would favor the formation of radical cations M^+ for the case where $L_e > L_h$, and $\beta > 1$. Note that the spectral changes in the ratio between the surface concentration of carriers could affect the secondary chemical steps through different interactions between the carriers and the reaction intermediates, thereby leading to a more complex spectral selectivity of the photocatalysts.

Obviously, the strongest alteration of the ratio $[e_s]/[h_s]$ occurs at the edge of the *intrinsic* absorption band where the absorption coefficient, α, changes by a few orders of magnitude, which, in turn, may alter the overall reaction pathway. Indeed, such an experimental alteration of the reaction pathway has been observed by Kuzmin and co-workers[49] for the photostimulated reaction of methane on TiO_2 particulates under photoexcitation near the fundamental absorption edge of the photocatalyst. These workers detected more complex hydrocarbons as the major reaction products for TiO_2 photoexcitation near the band edge of the fundamental absorption for $\alpha \approx 10^2$ cm^{-1}, whereas oxidation products were observed mainly for excitation in the fundamental absorption band where $\alpha \approx 10^4$ cm^{-1}. In addition, complex hydrocarbons were also the major products when TiO_2 was subjected to X-ray radiation absorption that paralleled exciting of TiO_2 in the fundamental absorption edge of 3.2 eV (i.e., 385 nm).

It must be emphasized that variations in the concentration of electrons and that of holes on the photocatalyst surface with changes in the spectral region of photoexcitation of the solid are not the sole reason for the spectral selectivity of a photocatalyst. For example, the different selectivities observed in the photooxidation of H_2 on KBr were attributed to different oxygen species formed on the surface by preadsorbed oxygen upon photoexcitation of KBr.[50] This difference in selectivity was closely connected to the different mechanisms of photoexcitation of the solid in different spectral regions that generate either excitons or electrons which ultimately lead to formation of chemically different species of the preadsorbed oxygen.

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(41) An astute reviewer queried as to when carrier diffusion might dominate the surface flux relative to carrier mobility (μ) which is driven by band bending. In the present article we have taken $D(\mathrm{d}n/\mathrm{d}x) \gg n\,\mu\,E$, where E is the electric field strength, and all other considerations depend on the particular conditions for the given system. The depth of the band bending is determined by the screening efficiency of the surface charge by the bulk mobile and immobile carriers. In semiconductors, free carriers play a major role in this screening, whereas charge defects play this role in insulators. Consequently, in semiconductors the width of the band bending

is smaller than in insulators. Considering that the size of crystals in powdered or colloidal photocatalysts is around $10^{-6}-10^{-4}$ cm (i.e., 10−1000 nm) the band bending can be neglected in most cases, especially for insulators. In the general case, one would need to consider both diffusion and drift of carriers, which would add a term to the continuity equation (eq 7) to describe the motion of carriers caused by the near-surface electric field. This renders a solution to eq 7 to be a more complex problem, something we are presently working on. In the present instance, initial conditions were established which correspond to the case when the near-surface electric field is negligible (see text).

(42) It should be emphasized that eq 16 affords an analysis of both (i) the spectral dependence of the quantum yield of reaction, Φ, on the surface of the photocatalyst specimen of a given size d when the absorption coefficient α changes with the wavelength of the incident light, and separately (ii) the dependence of Φ on $d/2L$ when Φ increases with decreasing $d/2L$ for a given value of the absorption coefficient α. When the size of the photocatalyst specimen is in the quantum-size regime, that is, as d gets very small to nanometer dimensions, Φ should decrease as $d/2L$ decreases. However, in the quantum-size regime, the absorption coefficient α at a given wavelength also changes: it decreases near the absorption threshold, whereas at shorter wavelengths the changes may be different owing to variations in the probabilities of electronic transitions between the valence and conduction bands. This infers that, in general, even the shape of the absorption spectrum may be different in this regime. Hence, changes in the absorption spectrum (α(d)) caused by the quantum-size effect also need to be considered in the estimation of changes in the quantum yield of reaction, Φ. In the present case, the focus is on an analysis of the spectral dependence of Φ for a given specimen for a constant value of $d/2L$ (see item (i) above).

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(47) Absorption of light by a solid is said to be *intrinsic* when light absorption leads to electronic transitions between states of the regular lattice (bulk and surface), hence to transitions between the valence and conduction bands to generate delocalized excitons and/or free electrons and holes. Absorption is said to be *extrinsic* when light is absorbed by lattice defects, impurities, and irregularities among others. It is worth noting that some confusion may arise with respect to light absorption by surface states, regardless of whether they are regular or irregular. In some cases light absorption by surface states is said to be *extrinsic* because the surface is always a defect relative to the bulk of the lattice. In the case treated herein, we refer to light absorption by the regular surface as *intrinsic surface absorption* and light absorption by surface defects as *extrinsic surface absorption.*

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