Zeitschrift für Physikalische Chemie, **214**, 2, S. 149 – 167 (2000)

Quantitative Determination of Photokinetic Parameters for Reversible Photoisomerizations in Light Scattering Adsorbent-Adsorbates

By R. Gade and Th. Porada

Institut für Phys. Chemie, Universität Jena, Steiger 3, D-07743 Jena, Germany

(Accepted February 22, 1999)

Photoisomerization / Light Scattering / Absorption Coefficients / Quantum Yields / Azobenzene

Based on an approximate solution of the differential equations describing the rate of a reversible photoisomerization and the attenuation of the actinic light in a powdered adsorbent-adsorbate a method is presented permitting us to predict the irradiation time dependence of the sample reflectance and to determine both the quantum yields of the partial reactions and the absorption coefficients of the reactant and the product from the reflectance-time-curves measured at two different wavelengths. The present method, thus, is an improved version of the peviously reported procedure [1] which enables the quantum yield of a simple photoreaction to be calculated from the initial slope of the $R(t)$-curve. To test the method proposed here it has been used for calculating the photokinetic parameters of azobenzene adsorbed on disperse silica.

1. Introduction

Based on the recent progress in the photocatalytic purification of waste waters [2, 3] and in the photoelectrochemical conversion of solar energy [3, 4] the photochemistry of molecules adsorbed on heterogeneous systems has received increasing attention during the last few years [5, 6].

However, the spectroscopic investigations of heterogeneous systems are much more complicated than those of homogeneous ones. This is firstly due to the circumstance that the light propagation in heterogeneous systems is strongly influenced by scattering effects. Since, in addition, the adsorbed molecules are relatively fixed within the light scattering medium the attenuation of the actinic light owing to absorption and scattering gives rise to the formation of concentration gradients varying with time. In contrast to stirred solutions, hence, the concentrations of all species involved in the photoreaction depend on both the irradiation time and the penetration depth of the light so that the rate equations in general become nonlinear, partial differential equations. On these conditions the common way to determine the desired kinetic parameters, e.g. quantum yields or rate constants then consists in fitting a numerical solution of these differential equations to available spectroscopic data. Using this method Oelkrug and coworkers [7] determined the isomerization quantum yields of various organic compounds adsorbed on alumina. With this procedure being rather complicated Simmons and coworkers [8, 9] presented several models which enable the quantum yields of some solid state reactions in powders to be directly calculated from diffuse reflectance data. All of these models, however, are founded on drastic and inconsistent assumptions so that they can only be employed in a limited degree. That is why we have recently proposed another method [1] which in contrast to Simmons' approach strictly uses the Kubelka-Munk theory without any additional presumptions to describe the light propagation in the scattering medium. Based on the power series expansions of both the concentrations and the intensities of the light-fluxes we succeeded in relating the quantum yield of the photoreaction to the slope of the measured reflectance-time curve. Hence, the afore-mentioned procedure may be regarded as a generalization of the "*initial-slope method*" [10] developed for stirred solutions to the case of light scattering materials.

Employing our method to the photobleaching of an azo-dye adsorbed on nanodisperse titania [11] we could quantitatively determine the quantum yield of this TiO_2-catalysed photodegradation from diffuse reflectance data. It must be noted, however, that the knowledge of the absorption coefficient of the photoproduct either at the irradiation wavelength λ_i or at some detection wavelength λ_d is a prerequisite for applying this method. If, in general, the absorption coefficient of the product is unknown at any wavelength and should be determined together with the quantum yields the procedure outlined above will fail. On the other hand, a generally applicable method for determining both the quantum yields and the absorption coefficients of the photoproducts did also not exist for stirred solutions. Since in this case the relation between the absorbance $A_{\lambda_i}(t, \lambda_d)$ of the irradiated solution and the kinetic parameters desired was much simpler than in the case of light scattering adsorbent-adsorbates we dealt with this problem first and developed a procedure [12] which combines the method of Fischer [13] with techniques for calculating the absorbance $A_{\lambda_i}(\infty, \lambda_d)$ in the photostationary state, particularly with the "method of transformed time" [14]. The needed absorbance values $A_{\lambda_i}(\infty, \lambda_d)$ are then determined from a least-squares fit of the irradiation-time function [15]

$$A_{\lambda_i}(t,\lambda_d) = A_{\lambda_i}(\infty,\lambda_d) - (A_{\lambda_i}(\infty,\lambda_d) - A_{\lambda_i}(0,\lambda_d))\, e^{-p_{\lambda_i} I_{\lambda_i} \Theta(t)} \tag{1}$$

to the points $\{\Theta(t_n), A_{\lambda_i}(t_n,\lambda_d)$ of the experimental absorbance-time curve where

$$\Theta(t) = \int_0^t dt' \, \frac{1-10^{-A_{\lambda_i}(t',\lambda_i)}}{A_{\lambda_i}(t',\lambda_i)} \tag{2}$$

denotes the so-called "*transformed time*" [14] which may easily be calculated from measured reaction spectra of the illuminated solution.

So as to be able to analyse photoreactions in light scattering systems in a similar way as those in stirred solutions we searched for an approximate solution of the differential equations describing the reaction rate and the attenuation of the actinic light. Based on the approximation found an analytic expression for the time-dependence of the diffuse reflectance $R_{\lambda_i}(t,\lambda_d)$ could be derived whose form is analogous with Eq. (1). Accordingly, in the present case the extent of conversion $\beta_{\lambda i}(\infty)$ in the photostationary equilibrium can be obtained from a least-squares fit of the points $\{t_n, R_{\lambda_i}(t_n,\lambda_d);\ n = 0, \ldots N\}$ to this analytic expression. Once the quantity $\beta_{\lambda i}(\infty)$ is determined the quantum yields and the absorption coefficient of the photoproduct are easy to calculate by means of the method developed below.

2. Theory

2.1 Rate equations for photoisomerizations in powdered adsorbent-adsorbates

As it is illustrated in Fig. 1 the surface ($z = 0$) of a powdered adsorbent-adsorbate sample is homogeneously illuminated with monochromatic light having the wavelength λ_i and the irradiance $I_0(\lambda_i)$. Due to the irradiation with light a reversible photoisomerization

$$\mathrm{A} \overset{h\nu}{\rightleftharpoons} \mathrm{B}$$

is supposed to be induced in the disperse adsorbent-adsorbate. According to a preceding paper [1] the rate equations of this photoreaction can be written as

$$\frac{\partial c_{A\lambda_i}}{\partial t} = (-\,\Phi_B^A \varepsilon_A(\lambda_i) c_{A\lambda_i}(z,t) + \Phi_A^B \varepsilon_B(\lambda_i) c_{B\lambda_i}(z,t))\, \delta[I_{+\lambda_i} + I_{-\lambda_i}] \tag{3}$$

$$\frac{\partial c_{B\lambda_i}}{\partial t} = -\,\frac{\partial c_{A\lambda_i}}{\partial t} \tag{4}$$

where $\varepsilon_A(\lambda_i)$ and $\varepsilon_B(\lambda_i)$ designate the molar absorption coefficients of the species A and B, respectively, at the wavelength λ_i. Furthermore, Φ_B^A denotes the partial quantum yield for the production of B when A is excited

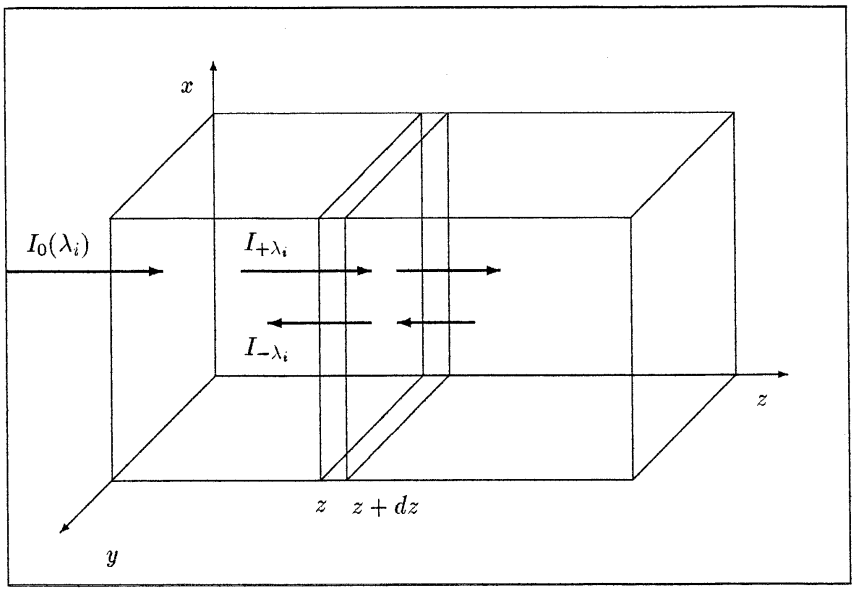

Fig. 1. Illustration of the light fluxes penetrating the volume element dV inside a light scattering sample.

and Φ_A^B the corresponding one for the reverse case. In the case considered here the concentrations $c_{A\lambda_i}(z,t)$ and $c_{B\lambda_i}(z,t)$ of the species A and B, respectively, depend not only on the exposure time t but also on the irradiation wavelength λ_i and the penetration depth z. The irradiances $I_{+\lambda_i}$ and $I_{-\lambda_i}$ of the penetrating (+) and backscattered (−) irradiation light fluxes obey the Kubelka-Munk equations

$$\frac{\partial I_{+\lambda_i}}{\partial z} = -\,(K+S)\,I_{+\lambda_i}(z,t) + S\,I_{-\lambda_i}(z,t) \tag{5}$$

$$\frac{\partial I_{-\lambda_i}}{\partial z} = -\,S\,I_{+\lambda_i}(z,t) + (K+S)\,I_{-\lambda_i}(z,t) \tag{6}$$

where K and S designate the absorption and the scattering coefficient, respectively, of the powdered adsorbent-adsorbate. The absorption coefficient K is assumed to be composed additively of contributions of the particulate substrate and the adsorbed species A and B, viz:

$$K = K_S + K_A + K_B \tag{7}$$

where K_A and K_B in each case are proportional to the absorption coefficient of the corresponding species and its concentration, i.e.

$$K_A(z,t,\lambda_i) = \delta\varepsilon_A(\lambda_i)\, c_{A\lambda_i}(z,t) \tag{8}$$

$$K_B(z,t,\lambda_i) = \delta\varepsilon_B(\lambda_i)\, c_{B\lambda_i}(z,t) \tag{9}$$

The proportionality factor δ can easily be determined by taking into account that Eqs. (7)−(9) hold for any irradiation time t, especially also for $t = 0$ where

$$c_{B\lambda_i}(z,0) = 0 \tag{10}$$

and hence

$$K(z,0,\lambda_i) = K_S(\lambda_i) + \delta\varepsilon_A(\lambda_i)\, c_0\,. \tag{11}$$

Due to the spatial constancy of K at $t = 0$ the Kubelka-Munk relationship

$$F(R_0) = \frac{(1 - R_0)^2}{2\,R_0} = \frac{K(t = 0)}{S} \tag{12}$$

may be applied, finally yielding

$$\delta = \frac{S[F(R_0(\lambda_i)) - F(R_S(\lambda_i))]}{c_0\varepsilon_A(\lambda_i)}\,. \tag{13}$$

Here, $R_0(\lambda_i)$ denotes the diffuse reflectance of the unirradiated sample while $R_S(\lambda_i)$ designates that of the pure adsorbent and both are taken at the wavelength λ_i. Because of Eq. (4) the concentrations of A and B satisfy the local balance equation

$$c_{A\lambda_i}(z,t) + c_{B\lambda_i}(z,t) = c_0 \tag{14}$$

allowing one concentration to be eliminated in Eqs. (3) and (4) so that the remaining rate equation can be rewritten in terms of the *extent of conversion*

$$\beta_{\lambda_i}(z,t) = \frac{c_{B\lambda_i}(z,t)}{c_0} \tag{15}$$

which leads to

$$\frac{\partial\beta_{\lambda_i}(z,t)}{\partial t} = (m_{\lambda_i} - p_{\lambda_i}\,\beta_{\lambda_i})\,\delta[I_{+\lambda_i} + I_{-\lambda_i}] \tag{16}$$

where c_0 is the total concentration of the adsorbate and the quantities m_{λ_i} and p_{λ_i} are given by

$$m_{\lambda_i} = \Phi_B^A\,\varepsilon_A(\lambda_i) \tag{17}$$

$$p_{\lambda_i} = \Phi_B^A\,\varepsilon_A(\lambda_i) + \Phi_A^B\,\varepsilon_B(\lambda_i)\,. \tag{18}$$

Since because of Eq. (10) the extent of conversion $\beta_{\lambda_i}(z,t)$ obeys the initial condition

$$(\beta_{\lambda_i}(z,t))_{t=0} = 0 \tag{19}$$

and its time derivation has a positive value at this time the function $\beta_{\lambda_i}(z,t)$ increases with increasing t while $(\partial\beta_{\lambda_i}/\partial t)$ decreases. Hence, in the photostationary equilibrium, i.e. as $t \to \infty$ the time derivative of $\beta_{\lambda_i}(z,t)$ vanishes

$$0 = \left(\frac{\partial \beta_{\lambda_i}(z,t)}{\partial t}\right)_{t\to\infty} = (m_{\lambda_i} - p_{\lambda_i}\,\beta_{\lambda_i}(\infty))\,\delta[I_{+\lambda_i} + I_{-\lambda_i}] \tag{20}$$

and for arbitrary values of z the function $\beta_{\lambda_i}(z,t)$ tends to the limit

$$\beta_{\lambda_i}(\infty) = \frac{m_{\lambda_i}}{p_{\lambda_i}}\,. \tag{21}$$

Eq. (16) manifests that the time derivative of β_{λ_i} depends on the irradiances $I_{+\lambda_i}$ and $I_{-\lambda_i}$ obeying the Kubelka-Munk Eqs. (5) and (6). On the other hand, according to Eqs. (7)−(9) the absorption coefficient K of the powdered medium is a linear function of β_{λ_i}. For this reason the rate Eq. (16) and the Kubelka-Munk Eqs. (5) and (6) are coupled to each other so that the kinetic description of a photoisomerization in a powdered absorbent-adsorbate requires solving the following set of differential equations

$$\frac{\partial \beta_{\lambda_i}}{\partial t} = p_{\lambda_i}[\beta_{\lambda_i}(\infty) - \beta_{\lambda_i}]\,\delta[I_{+\lambda_i} + I_{-\lambda_i}] \tag{22}$$

$$\frac{\partial I_{+\lambda_i}}{\partial z} = -\,[b_1(\lambda_i) + b_2(\lambda_i)\,\beta_{\lambda_i}]\,I_{+\lambda_i} + S\,I_{-\lambda_i} \tag{23}$$

$$\frac{\partial I_{-\lambda_i}}{\partial z} = -\,S\,I_{+\lambda_i} + [b_1(\lambda_i) + b_2(\lambda_i)\,\beta_{\lambda_i}]\,I_{-\lambda_i} \tag{24}$$

where for the sake of clearness the following abbreviations have been used

$$b_1(\lambda_i) = S + K_S + \delta c_0\,\varepsilon_A(\lambda_i) \tag{25}$$

$$b_2(\lambda_i) = \delta c_0(\varepsilon_B(\lambda_i) - \varepsilon_A(\lambda_i))\,. \tag{26}$$

In order that well-determined and unique solutions β_{λ_i}, $I_{+\lambda_i}$, and $I_{-\lambda_i}$ are obtained, of course, the boundary-value problem of Eqs. (22)−(24) needs to be solved, i.e. in addition to the differential Eqs. (22)−(24) these functions are required to satisfy the boundary conditions

$$(\beta_{\lambda_i})_{t=0} = 0 \tag{27}$$

$$(I_{+\lambda_i})_{z=0} = I_{0\,\lambda_i} \tag{28}$$

$$(I_{-\lambda_i})_{z\to\infty} = 0 \tag{29}$$

the physical content of which can easily be understood. With the right-hand sides of Eqs. (22)−(24) obviously exhibiting product termes of the functions to be calculated these equations must be classified as a set of nonlinear partial differential equations. That is why standard methods developed for solving linear differential equations fail in this case so that any analytical solution cannot be obtained in general.

2.2 Approximate solution of the differential equations

So as to obtain at least an approximate solution of Eqs. (22)−(24) being suitable for determining the quantum yields Φ_B^A and Φ_A^B and the absorption coefficient $\varepsilon_B(\lambda_i)$ the differential equations will be transformed into a set of equivalent integral equations which may subsequently be solved by the *method of successive approximation*.

For this purpose the variables in Eq. (22) are separated and both sides of the resulting equation are integrated from 0 to t_n with respect to time which gives

$$-\ln\left(\frac{\beta_{\lambda_i}(\infty)-\beta_{\lambda_i}(z,t_n)}{\beta_{\lambda_i}(\infty)-\beta_{\lambda_i}(z,0)}\right)=\int_0^{t_n} dt\, p_{\lambda_i}\,\delta[I_{+\lambda_i}(z,t)+I_{-\lambda_i}(z,t)]$$

Solving this equation for β_{λ_i} and using Eq. (19) finally leads to

$$\beta_{\lambda_i}(z,\mathrm{t}_n)=\beta_{\lambda_i}(\infty)\left\{1-e^{-p_{\lambda_i}\delta\int_0^{t_n} dt(I_{+\lambda_i}+I_{-\lambda_i})}\right\} \tag{30}$$

On the other hand the integration of the differential equations (23), (24) yields the integral equations

$$\begin{aligned} I_{+\lambda_i}(z,t) &= I_{0\lambda_i}+S\int_0^z dz' I_{-\lambda_i}(z',t) \\ &\quad -\int_0^z dz'[b_1(\lambda_i)+b_2(\lambda_i)\,\beta_{\lambda_i}(z',t)]\,I_{+\lambda_i}(z',z) \end{aligned} \tag{31}$$

and

$$\begin{aligned} I_{-\lambda_i}(z,t) &= I_{0\lambda_i}\,R_{\lambda_i}(t,\lambda_i)-S\int_0^z dz' I_{+\lambda_i}(z',t) \\ &\quad +\int_0^z dz'[b_1(\lambda_i)+b_2(\lambda_i)\,\beta_{\lambda_i}(z',t)]\,I_{-\lambda_i}(z',z) \end{aligned} \tag{32}$$

describing the propagation of the penetrating and the backscattered irradiation light within the powdered sample the optical properties of which have been altered by the photoreaction. As the alterations caused by the light-induced transformation in the irradiated sample vary with the irradiation wavelength λ_i both the extent of conversion and the light intensities depend not only on z and t but also on λ_i. The last-mentioned dependence on λ_i which results from the spectral behaviour of the absorption coefficient is expressed by an index λ_i at the corresponding observables throughout this paper.

Moreover it is noted that the unknown reflectance value $R_{\lambda_i}(t,\lambda_i)$ of the infinitely thick irradiated sample which appears on the right-hand side of Eq. (32) will only be determined by the boundary condition (29). So as to spectroscopicly detect the photoinduced concentration changes within the irradiated adsorbent-adsorbate the powdered sample is to be analysed by means of monochromatic light of appropriate wavelength. This is usually done with a common spectrophotometer equipped with a diffuse reflectance accessory. In this case the irradiance $I_{0\lambda_d}$ of the analysing light is choosen so low that in this way the sample reflectance

$$R_{\lambda_i}(t,\lambda_d) = \frac{I_{-\lambda_i}(0,t,\lambda_d)}{I_{+\lambda_i}(0,t,\lambda_d)} \tag{33}$$

may be measured at the observation wavelength λ_d but no photoinduced transformation of the sample will be caused.

Naturally, the intensities $I_{+\lambda_i}(z,t,\lambda_d)$ and $I_{-\lambda_i}(z,t,\lambda_d)$ of the penetrating and the backscattered analysing light respectively also satisfy Kubelka-Munk equations of the form (23, 24) but in contrast to the latter the coefficients b_1 and b_2 now have to be taken at the observation wavelength λ_d.

So as to get the approximate solution desired of the integral Eqs. (30)−(32) we have to proceed as follows. As the starting point of the iteration procedure the state of the unirradiated sample is choosen where the extent of conversion is given by

$$\beta^{(0)}_{\lambda_i}(z,t) = 0\ . \tag{34}$$

Inserting this approximation in the Kubelka-Munk Eqs. (23) and (24) specified for the analysing light and taking into account the boundary conditions (28, 29) we obtain the following expressions for the forward and backward directed fluxes of the analysing light

$$I^{(0)}_{+\lambda_i}(z,0,\lambda_d) = I_{0\lambda_d}\, e^{-z\kappa(\lambda_d)} \tag{35}$$

$$I^{(0)}_{-\lambda_i}(z,0,\lambda_d) = I_{0\lambda_d}\, R_0(\lambda_d)\, e^{-z\kappa(\lambda_d)} \tag{36}$$

i.e. the Kubelka-Munk solutions for an homogeneous semiinfinite medium. Here $R_0(\lambda_d)$ is the diffuse reflectance of the unirradiated sample at the detection wavelength λ_d whereas

$$\kappa(\lambda_d) = \sqrt{K_0(\lambda_d)(K_0(\lambda_d) + 2\,S)} \tag{37}$$

denotes the attenuation coefficient and

$$K_0(\lambda_d) = K_S + \delta c_0 \varepsilon_A(\lambda_d) = b_1(\lambda_d) - S \tag{38}$$

the absorption coefficient of the unirradiated powder material at this wavelength. On the other hand, according to the Kubelka-Munk relationship

$$\frac{K_0(\lambda_d)}{S} = F(R_0(\lambda_d)) = \frac{[1 - R_0(\lambda_d)]^2}{2R_0(\lambda_d)} \tag{39}$$

the absorption coefficient $K_0(\lambda_d)$ may be expressed by the reflectance value $R_0(\lambda_d)$ and the scattering coefficient S of the pure adsorbent so that we finally have

$$\kappa(\lambda_d) = \frac{S[1 - R_0^2(\lambda_d)]}{2\,R_0(\lambda_d)}\,. \tag{40}$$

In an analogous way, i.e. by inserting Eq. (34) into the Kubelka-Munk Eqs. (23) and (24) we get the zero-order approximation for the intensities of the scattered irradiation light fluxes

$$I^{(0)}_{+\lambda_i}(z,0,\lambda_i) = I_{0\,\lambda_i}\,e^{-z\kappa(\lambda_i)} \tag{41}$$

$$I^{(0)}_{-\lambda_i}(z,0,\lambda_i) = I_{0\,\lambda_i}\,R_0(\lambda_i)e^{-z\kappa(\lambda_i)} \tag{42}$$

where $R_0(\lambda_i)$ is the diffuse reflectance of the unirradiated sample at the irradiation wavelength λ_i and the attenuation coefficient $\kappa(\lambda_i)$ at this wavelength is given by

$$\kappa(\lambda_i) = \sqrt{K_0(\lambda_i)(K_0(\lambda_i) + 2\,S)} = \frac{S[1 - R_0^2(\lambda_i)]}{2\,R_0(\lambda_i)}\,. \tag{43}$$

Substituting for the intensity profiles from Eqs. (41) and (42) into Eq. (30) within the next iteration cycle we find the following expression for the first-order approximation of β_{λ_i}

$$\beta^{(1)}_{\lambda_i}(z,t) = \beta_{\lambda_i}(\infty)\,\{1 - e^{-tu_{\lambda_i}\exp(-z\kappa(\lambda_i))}\} \tag{44}$$

where the abbreviation

$$u_{\lambda_i} = p_{\lambda_i}\,\delta I_{0\,\lambda_i}[1 + R_0(\lambda_i)] \tag{45}$$

has been used. So as to calculate the first-order approximations of the irradiances of the scattered analysing light then the zero-order approximations (35, 36) of these intensity profiles as well as the first-order approximation (44) of the extent of conversion are to be inserted in the right-hand sides of the integral Eqs. (31) and (32) where the coefficients b_1 and b_2, of course, must be taken at the detection wavelength λ_d. Thus we get

$$\begin{aligned}\frac{I^{(1)}_{+\lambda_i}(z,t,\lambda_d)}{I_{0\lambda d}} &= 1 + (SR_0(\lambda_d) - b_1(\lambda_d))\int_0^z dz'\,e^{-z'\kappa(\lambda_d)} \\ &\quad - b_2(\lambda_d)\beta_{\lambda_i}(\infty)\int_0^z dz' e^{-z'\kappa(\lambda_d)}\,[1 - e^{-tu_{\lambda_i}\exp(-z'\kappa(\lambda_i))}]\end{aligned} \tag{46}$$

and

$$\begin{aligned}\frac{I^{(1)}_{\lambda_i}(z,t,\lambda_d)}{I_{0\,\lambda_d}} &= R_{\lambda_i}(t,\lambda_d) + (b_1(\lambda_d)R_0(\lambda_d) - S)\int_0^z dz' e^{-z'\kappa(\lambda_d)} \\ &\quad + b_2(\lambda_d)R_0(\lambda_d)\beta_{\lambda_i}(\infty)\int_0^z dz' e^{-z'\kappa(\lambda_d)}\,[1 - e^{-tu_{\lambda_i}\exp(-z'\kappa(\lambda_i))}]\end{aligned} \tag{47}$$

In the same way also the first-order approximations for the intensity profiles $I^{(1)}_{+\lambda_i}(z,t,\lambda_i)$ and $I^{(1)}_{-\lambda_i}(z,t,\lambda_i)$ of the irradiation light may be calculated which enable the second-order approximation of the extent of conversion to be subsequently obtained from Eq. (30). The hitherto unknown reflectance value $R_{\lambda_i}(t, \lambda_d)$ in Eq. (47) can be determined if the limiting approach $z \longrightarrow \infty$ is applied to this equation and the boundary condition (29)

$$\lim_{z \to \infty} I_{-\lambda_i}(z, t, \lambda_d) = 0$$

is taken into account. At the end of this iteration cycle, thus, the time-dependence of the diffuse reflectance $R_{\lambda_i}(t, \lambda_d)$ can be expressed as

$$R_{\lambda_i}(t, \lambda_d) = Q_{1\lambda_i}(\lambda_d) - Q_{2\lambda_i}(\lambda_d) P(v, u_{\lambda_i}, t) \tag{48}$$

where the function $P(v, u_{\lambda_i}, t)$ has the integral representation

$$P(v, u_{\lambda_i}, t) = \kappa(\lambda_i) \int\limits_0^\infty dz' e^{-\kappa(\lambda_d) z'} \, e^{-t u_{\lambda_i} \exp(-\kappa(\lambda_i) z')} = \int\limits_0^1 dw \, w^{v-1} e^{-t u_{\lambda_i} w} \tag{49}$$

v denotes the ratio

$$v = \frac{\kappa(\lambda_d)}{\kappa(\lambda_i)}$$

and the parameters $Q_{1\lambda_i}$ and $Q_{2\lambda_i}$ are given by

$$Q_{1\lambda_i}(\lambda_d) = \frac{S - R_0(\lambda_d)[b_1(\lambda_d) + b_2(\lambda_d)\beta_{\lambda_i}(\infty)]}{\kappa(\lambda_d)} \tag{50}$$

$$Q_{2\lambda_i}(\lambda_d) = -\frac{R_0(\lambda_d) b_2(\lambda_d) \beta_{\lambda_i}(\infty)}{\kappa(\lambda_i)} . \tag{51}$$

The illustrative meaning of the parameters $Q_{1\lambda_i}$ and $Q_{2\lambda_i}$ becomes clear if we let t approach 0 and ∞, respectively, in Eq. (48). Because of

$$\lim_{t \to \infty} P(v, u_{\lambda_i}, t) = 0$$

we get in the former case

$$Q_{1\lambda_i}(\lambda_d) = R_{\lambda_i}(\infty, \lambda_d) \tag{52}$$

whereas taking into consideration that

$$\lim_{t \to 0} P(v, u_{\lambda_i}, t) = \frac{1}{v}$$

in the latter the relationship

$$Q_{2\lambda_i}(\lambda_d) = v[R_{\lambda_i}(\infty, \lambda_d) - R_{\lambda_i}(0, \lambda_d)] \tag{53}$$

follows.

Hence, formula (48) discussed above has a similar form as Eq. (1) describing the irradiation-time dependence of the absorbance of a stirred solution in which a reversible photoisomerization proceeds.

2.3 Determining quantum yields and absorption coefficients of the products from reflectance-time curves

According to a proposal previously made by Fischer [13] the quantum yields of a reversible photoisomerization in a stirred solution as well as the absorption coefficients of the photoproduct can be calculated if the sample absorbances in two different photostationary states are known. Unfortunately, the photostationary states of many photoisomerizations, however, cannot be attained because of the occurrence of side reactions. In such a case we can gain the spectroscopic data needed for a kinetic analysis by illuminating the powdered absorbent-adsorbate successively with light of two different wavelengths $\lambda_i = \lambda_1, \lambda_2$ and measuring in each case a set of diffuse reflectance spectra $R_{\lambda_i}(t_n, \lambda)$ of the irradiated powder sample for a sequence of increasing exposure times t_n ($n = 1, \ldots, N$). From each of the two series of spectra assigned to different irradiation wavelengths $\lambda_i = \lambda_1, \lambda_2$ afterwards two reflectance-time curves $R_{\lambda_i}(t_n, \lambda_d)$ were extracted at the detection wavelengths $\lambda_d = \lambda_1$, λ_2 so that altogether four such curves are available. A least-squares fit of the points $\{t_n, R_{\lambda i}(t_n, \lambda_d)\}$ of these experimental reflectance-time curves to the analytical expression (48) describing the irradiation-time dependence of the diffuse reflectance then enables the unknown parameters $Q_{1\lambda_i}(\lambda_d)$, $Q_{2\lambda_i}(\lambda_d)$ and u_{λ_i} of this expression to be determined. Taking into account the definition (51) of the parameter $Q_{2\lambda_i}$ and, in addition, Eq. (21) for the parameters $\beta_{\lambda_i}(\infty)$ appearing there we are able to establish the following six equations

$$\frac{Q_{2\lambda_1}(\lambda_1)\kappa(\lambda_1)}{R_0(\lambda_1)\delta c_0} = [\varepsilon_A(\lambda_1) - \varepsilon_B(\lambda_1)]\beta_{\lambda_1}(\infty) \tag{54}$$

$$\frac{Q_{2\lambda_2}(\lambda_2)\kappa(\lambda_2)}{R_0(\lambda_2)\delta c_0} = [\varepsilon_A(\lambda_2) - \varepsilon_B(\lambda_2)]\beta_{\lambda_2}(\infty) \tag{55}$$

$$\frac{Q_{2\lambda_1}(\lambda_2)\kappa(\lambda_1)}{R_0(\lambda_2)\delta c_0} = [\varepsilon_A(\lambda_2) - \varepsilon_B(\lambda_2)]\beta_{\lambda_1}(\infty) \tag{56}$$

$$\frac{Q_{2\lambda_2}(\lambda_1)\kappa(\lambda_2)}{R_0(\lambda_1)\delta c_0} = [\varepsilon_A(\lambda_1) - \varepsilon_B(\lambda_1)]\beta_{\lambda_2}(\infty) \tag{57}$$

$$\beta_{\lambda_1}(\infty) = \left[1 + \frac{\varepsilon_B(\lambda_1)}{\varepsilon_A(\lambda_1)}\left(\frac{\Phi_A^B}{\Phi_B^A}\right)\right]^{-1} \tag{58}$$

$$\beta_{\lambda_2}(\infty) = \left[1 + \frac{\varepsilon_B(\lambda_2)}{\varepsilon_A(\lambda_2)}\left(\frac{\Phi_A^B}{\Phi_B^A}\right)\right]^{-1} \tag{59}$$

obviously not being linearly independent. Dividing Eq. (54) by Eq. (57), Eq. (56) by Eq. (55), and adding the resulting equations we arrive at

$$\left(\frac{Q_{2\lambda_1}(\lambda_1)}{Q_{2\lambda_2}(\lambda_1)} + \frac{Q_{2\lambda_1}(\lambda_2)}{Q_{2\lambda_2}(\lambda_2)}\right)\frac{\kappa(\lambda_1)}{\kappa(\lambda_2)} = 2\,\frac{\beta_{\lambda_1}(\infty)}{\beta_{\lambda_2}(\infty)}\,.$$

Thus, by combining the last equation with Eqs. (54), (55), (58), (59) we may extract the following five linearly independent equations

$$a_{\lambda_1}(\lambda_1) = [\varepsilon_A(\lambda_1) - \varepsilon_B(\lambda_1)]\beta_{\lambda_1}(\infty) \tag{60}$$

$$a_{\lambda_2}(\lambda_2) = [\varepsilon_A(\lambda_2) - \varepsilon_B(\lambda_2)]\beta_{\lambda_2}(\infty) \tag{61}$$

$$1 = \left[1 + \frac{\varepsilon_B(\lambda_1)}{\varepsilon_A(\lambda_1)}\,\varphi\right]\beta_{\lambda_1}(\infty) \tag{62}$$

$$1 = \left[1 + \frac{\varepsilon_B(\lambda_2)}{\varepsilon_A(\lambda_2)}\,\varphi\right]\beta_{\lambda_2}(\infty) \tag{63}$$

$$\beta_{\lambda_1}(\infty) = r\beta_{\lambda_2}(\infty) \tag{64}$$

where for the sake of clearness the abbreviations

$$a_{\lambda_1}(\lambda_1) = \frac{Q_{2\lambda_1}(\lambda_1)\kappa(\lambda_1)}{R_0(\lambda_1)\delta c_0} \tag{65}$$

$$a_{\lambda_1}(\lambda_1) = \frac{Q_{2\lambda_2}(\lambda_2)\kappa(\lambda_2)}{R_0(\lambda_2)\delta c_0} \tag{66}$$

$$r = \frac{1}{2}\left(\frac{Q_{2\lambda_1}(\lambda_1)}{Q_{2\lambda_2}(\lambda_1)} + \frac{Q_{2\lambda_1}(\lambda_2)}{Q_{2\lambda_2}(\lambda_2)}\right)\frac{\kappa(\lambda_1)}{\kappa(\lambda_2)} \tag{67}$$

$$\varphi = (\Phi_A^B/\Phi_B^A) \tag{68}$$

have been introduced. Solving the nonlinear, algebraic Eqs. (60)−(64) for the unknown variables $\varepsilon_B(\lambda_1)$, $\varepsilon_B(\lambda_2)$, $\beta_{\lambda_1}(\infty)$, $\beta_{\lambda_2}(\infty)$, and φ by means of a substitution method finally yields

$$\varphi = \frac{(r - \ 1)\varepsilon_A(\lambda_1)\varepsilon_A(\lambda_2)}{a_{\lambda_1}(\lambda_1)\varepsilon_A(\lambda_2) - r a_{\lambda_2}(\lambda_2)\varepsilon_A(\lambda_1)} \tag{69}$$

$$\beta_{\lambda_2}(\infty) = \frac{a_{\lambda_1}(\lambda_1)\varepsilon_A(\lambda_2) - a_{\lambda_2}(\lambda_2)\varepsilon_A(\lambda_1)}{\varepsilon_A(\lambda_2)(a_{\lambda_1}(\lambda_1) - \varepsilon_A(\lambda_1)) - r\varepsilon_A(\lambda_1)(a_{\lambda_2}(\lambda_2) - \varepsilon_A(\lambda_2))} \tag{70}$$

$$\beta_{\lambda_1}(\infty) = r\beta_{\lambda_2}(\infty) \tag{71}$$

$$\varepsilon_B(\lambda_1) = \varepsilon_A(\lambda_1) - \frac{a_{\lambda_1}(\lambda_1)}{\beta_{\lambda_1}(\infty)} \tag{72}$$

$$\varepsilon_B(\lambda_2) = \varepsilon_A(\lambda_2) - \frac{a_{\lambda_2}(\lambda_2)}{\beta_{\lambda_2}(\infty)}\,. \tag{73}$$

Here the absorption coefficients $\varepsilon_A(\lambda)$ ($\lambda = \lambda_1, \lambda_2$) of the reactant are directly calculated from the reflectance spectrum $R_0(\lambda)$ of the unirradiated adsorbent-adsorbate sample by using a previously reported statistical model of coated particles [16]. Provided that the absorption coefficients $\varepsilon_B(\lambda_1)$ and $\varepsilon_B(\lambda_2)$ of the photoproduct have already been obtained from Eqs. (72), (73) a favourable way to determine the quantum yields consists in using the quantity

$$p_{\lambda_i} = \varepsilon_A(\lambda_i)\Phi_B^A + \varepsilon_B(\lambda_i)\Phi_A^B = \Phi_B^A[\varepsilon_A(\lambda_i) + \varepsilon_B(\lambda_i)\varphi] \tag{74}$$

which may be calculated according to Eq. (45) from the parameter u_{λ_i} of the experimental reflectance-time curves. Taking into account Eq. (68) and the right-hand side of Eq. (74) we find for the quantum yields the relationships

$$\Phi_B^A = \frac{p_{\lambda_i}}{\varepsilon_A(\lambda_i) + \varepsilon_B(\lambda_i)\varphi} \tag{75}$$

$$\Phi_A^B = \varphi\Phi_B^A \tag{76}$$

where the ratio $\varphi = \Phi_A^B/\Phi_B^A$ is assumed to be already known from Eq. (69).

3. Experimental details

To test the method developed above we have used it to determine the quantum yields of the photoinduced *cis-trans*-isomerization of azobenzene adsorbed on disperse silica gel as well as the absorption coefficients of the photoproduct *cis*-azobenzene. Here, azobenzene has been choosen as an appropriate adsorbate because its photoisomerization can be sufficiently well observed in the adsorbed state too and, on the other hand, no fluorescence could be measured "brightening'' the powdered sample and, hence, enhancing the diffuse reflectance.

The adsorbate azobenzene was obtained from Merck (Darmstadt) and used without further purification. To prepare the adsorbent-adsorbate samples needed the azobenzene was dissolved in n-hexane (Merck, UVSOL grade) and adsorbed on the disperse silica (Merck, particle size 15−20 μm) from this solution. For this purpose, hexanic solutions of azobenzene with different concentrations were mixed with 4.8 g of the adsorbent and the resulting suspensions have been stirred for 2 hours. After the adsorption equilibrium had been established the solution was sucked from the suspension and the powder was dried at 40 °C.

The diffuse reflectance measurements were performed by means of a SPECORD M40 UV/VIS-spectrophotometer (Carl Zeiss Jena) equipped with a (45°/0°) diffuse reflectance accessory using a pressed powder sample of pure MgO (Merck) as reference.

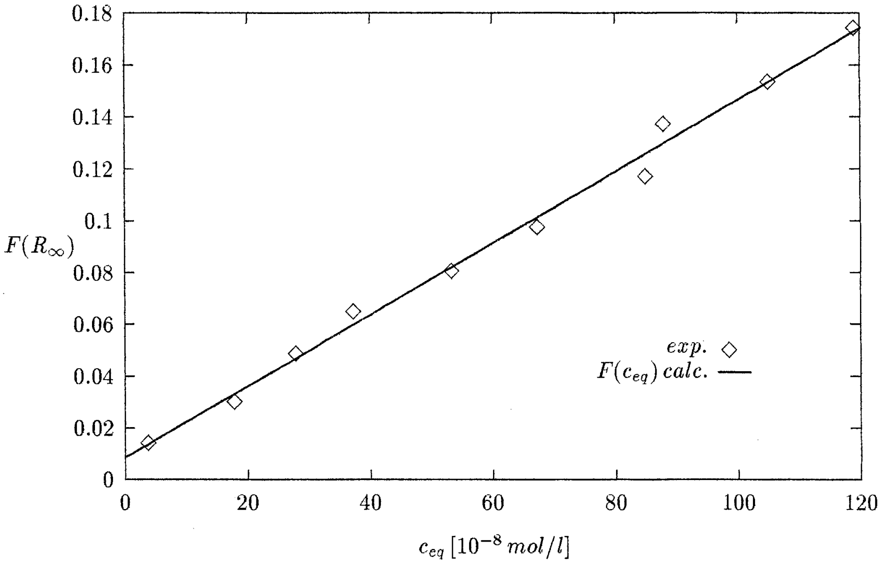

Fig. 2. Adsorption isotherm of *trans*-azobenzene adsorbed on silica gel from n-hexane.

To study the photoisomerization of the adsorbed azobenzene the powder samples were monochromaticly illuminated with a home-made photochemical irradiator consisting of a mercury lamp HBO200, a heat protection accessory and a interference filter for selecting the monochromatic light of the corresponding wavelength. The light intensities required for the calculation of the quantum yields were determined by using both a calibrated pyroelectric detector RS5900 (Polytec) and a chemical actinometer.

4. Results and discussion

A prerequisite for the application of the statistical model [16] used in sect. 2.3 to determine the absorption coefficients of the adsorbed azobenzene is the existence of a monomolecular layer of the adsorbate on the surface of the adsorbent particles. That is why we have first measured the adsorption isotherm shown in Fig. 2 to elucidate the way in which the azobenzene is adsorbed on the disperse silica gel. Since all our adsorbent-adsorbate samples prepared as described in sect. 3 are within the linear range of the adsorption isotherm the adsorbent particles are assumed to be coated with a submonomolecular azobenzene layer so that the afore-mentioned prerequisite for using the statistical model [16] is fulfilled.

After that the powdered adsorbent-adsorbate samples were step by step irradiated with monochromatic light of the wavelengths λ_1 = 297 nm and

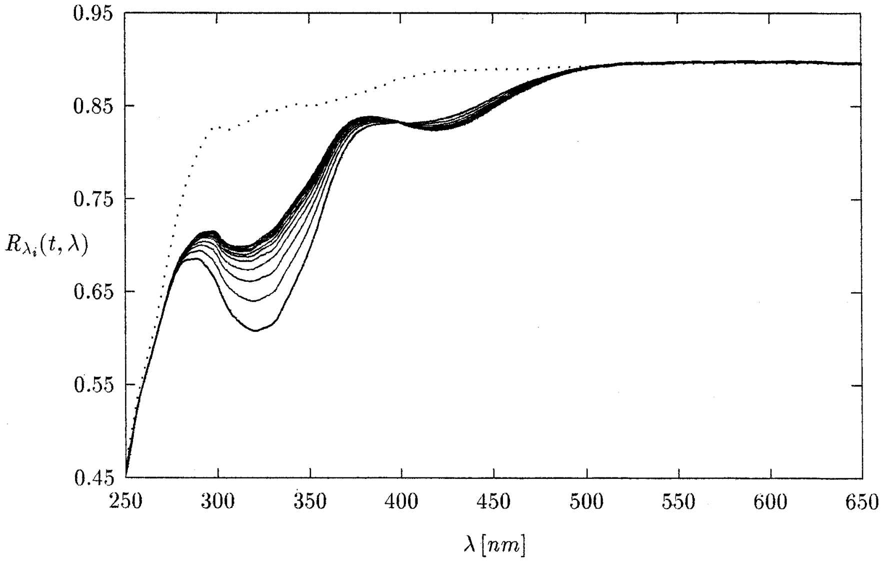

Fig. 3. Diffuse reflectance spectra of an adsorbent-adsorbate sample irradiated with light of $\lambda_i = 297$ nm wavelength (dotted line: spectrum of the pure silica gel; $\Delta t = 20$ s).

$\lambda_2 = 313$ nm respectively and N diffuse reflectance spectra were measured of each of the irradiated samples characterizing its state after each irradiation step t_n; $n = 1,\dots,N$. In Fig. 3 and Fig. 4 two such sets of spectra are illustrated referring to the samples with the highest adsorbate molality.

Finally, two $R_{\lambda_i}(t,\lambda_d)$-curves were extracted at the detection wavelengths $\lambda_d = \lambda_1, \lambda_2$ from both these series of spectra assigned to the irradiation wavelengths $\lambda_i = \lambda_1, \lambda_2$ so that a total of four such reflection-time curves are obtained which are shown in Fig. 5. Using these data and the procedure described in sect. 2.3 we could then calculate the quantum yields and absorption coefficients which are summarized in Table 1.

From Table 1 it can be seen that the absorption coefficients of the adsorbed azobenzene isomers calculated at the wavelengths $\lambda_1 = 297$ nm and $\lambda_2 = 313$ nm hardly differ from those ones measured in solution. In contrast to this the photoisomerization quantum yields calculated in the adsorbed state differ remarkably from those ones determined in n-hexane as it is shown in Table 2.

Studying the photoisomerization of aromatic azocompounds adsorbed on silica Kerzhner and coworkers [17] arrived at similar results. They found that in the adsorbed state both the reaction rate of the *trans*-*cis*-photoisomerization and the extent of conversion in the photostationary equilibrium are considerably higher than in a nonpolar solvent like pentane. Since in contrast to pentane the surface of the silica gel particles represents a strongly

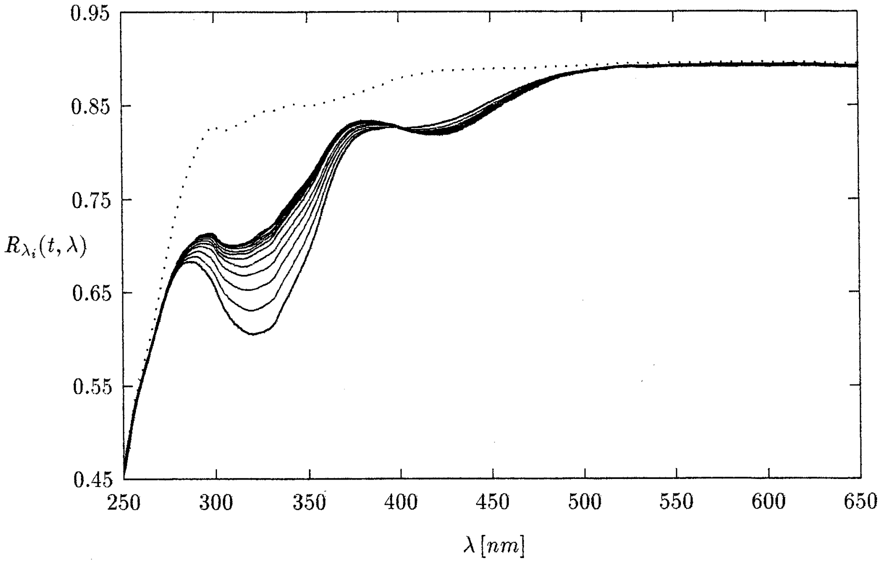

Fig. 4. Diffuse reflectance spectra of an adsorbent-adsorbate sample irradiated with light of $\lambda_i = 313$ nm wavelength (dotted line: spectrum of the pure silica gel; $\Delta t = 5$ s).

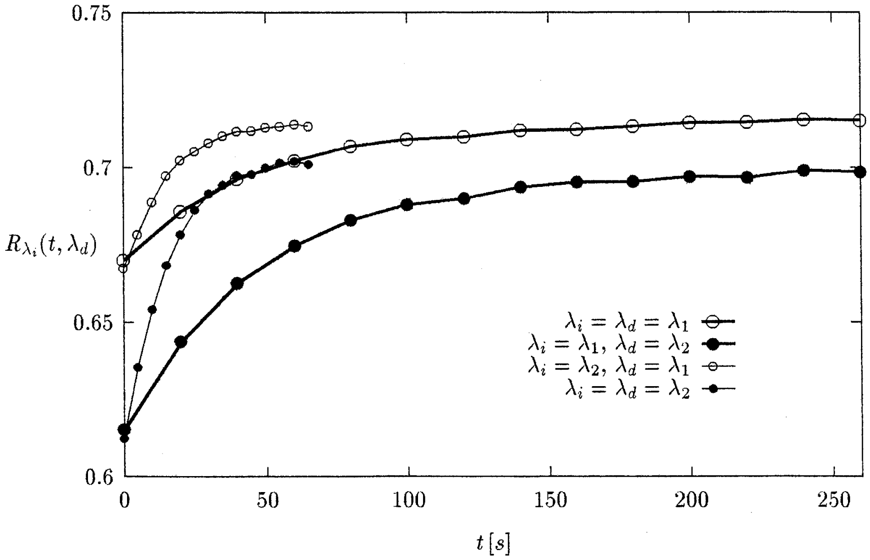

Fig. 5. Reflectance-time-curves of the adsorbent-adsorbate samples irradiated with light of different wavelengths λ_i (azobenzene molality $= 1.12 \cdot 10^{-7}$ mol/g).

Table 1. The calculated quantum yields of the partial reactions and the absorption coefficients of the reactant and the product respectively at the wavelengths $\lambda_1 = 297$ nm and $\lambda_2 = 313$ nm ($I_{0\,\lambda_1} = 4.4 \cdot 10^{-10}$ Einst cm^{-2} s^{-1}, $I_{0\,\lambda_2} = 1.15 \cdot 10^{-9}$ Einst cm^{-2} s^{-1}).

Molality [10^{-7} mol/g]	Φ_B^A	Φ_B^A	$\varepsilon_B(\lambda_1)$ $\left[\frac{\text{cm}^2}{\text{mmol}}\right]$	$\varepsilon_B(\lambda_2)$ $\left[\frac{\text{cm}^2}{\text{mmol}}\right]$	$\varepsilon_A(\lambda_1)$ $\left[\frac{\text{cm}^2}{\text{mmol}}\right]$	$\varepsilon_A(\lambda_2)$ $\left[\frac{\text{cm}^2}{\text{mmol}}\right]$
0.9354	0.20	0.17	6100	1500	18900	31000
1.1243	0.20	0.13	7900	3300	20000	32800
1.3054	0.20	0.15	7300	2600	19400	31700
1.6725	0.21	0.10	7800	3000	20000	33000
1.8694	0.19	0.15	7200	1900	19200	31600

Table 2. Comparison of the photoisomerization quantum yields of azobenzene solved in n-hexane with those of azobenzene adsorbed on silica gel.

Azobenzene adsorbed on silica gel[a]		Azobenzene solved in n-hexane[b]	
$\Phi_{t\rightarrow c} = \Phi_B^A$	$\Phi_{c\rightarrow t} = \Phi_A^B$	$\Phi_{t\rightarrow c} = \Phi_B^A$	$\Phi_{c\rightarrow t} = \Phi_A^B$
0.2	0.14	0.1	0.4

[a] see Table 1.
[b] see Ref. [12].

polar milieu it seems to be reasonable to explain the observed differences of the quantum yields by polarity effects. Usually the polarity of solvents may be characterized not only by the dielectric constant but also by a number of other parameters among them e.g. by the Kossower number Z [18]. Based on UV-spectroscopic investigations of various solvatochromic compounds adsorbed on silica gel Nicholls and Leermakers [19] determined a Kossower number $Z = 88$ for weakly hydrated silica gel. This Z-value is higher than that of methanol ($Z = 83.6$) and lower than that of water ($Z = 96.4$). On the other hand studying the solvent effects on the photoisomerization of azobenzene Bortolus and Monti [20] determined the following values of the photoisomerization quantum yields $\Phi_{t\rightarrow c}$ and $\Phi_{c\rightarrow t}$ which are compiled in Table 3.

This table clearly points out that with increasing polarity of the solvent the *trans-cis*-photoisomerization quantum yield $\Phi_{t\rightarrow c}$ increases whereas the *cis-trans*-photoisomerization quantum yield $\Phi_{c\rightarrow t}$ decreases. Since according to the above considerations the silica gel is expected to have a similar polarity as the ethanol-water mixture does the photoisomerization quantum yields $\Phi_{t\rightarrow c}$ and $\Phi_{c\rightarrow t}$ calculated by means of our method (cf. Table 1) fit in with the polarity dependence of Table 3.

Table 3. Dependence of the photoisomerization quantum yields of azobenzene on the solvent polarity according to Bortolus and Monti [20].

Solvent	Dielectric constant	$\Phi_{t \to c} = \Phi_B^A$	$\Phi_{c \to t} = \Phi_A^B$
Ethylbromide	9.2	0.115	0.255
Ethanol	24.3	0.150	0.240
Acetonitrile	37.5	0.158	0.210
H_2O/Ethanol	74	0.210	0.150

The dependence of the quantum yields $\Phi_{t \to c}$ and $\Phi_{c \to t}$ on the polarity of solvents found by Bortolus and Monti [20] can be explained by the fact that *cis*-azobenzene has a nonzero electric dipole moment whereas that of *trans*-azobenzene vanishes by reason of symmetry. In a nonpolar solvent the ground state of the *cis*-isomer is known to be above that of the trans-isomer because of steric reasons. With increasing polarity of the solvent, however, the ground state of the *cis*-isomer will be more and more stabilized relative to that of the *trans*-isomer due to the polarization effect of the molecular dipole. Hence, in polar solvents the rate of the *trans*-*cis*-photoisomerization becomes greater and the rate of the reverse process becomes smaller so that the quantum yields of the photoisomerizations $\Phi_{t \to c}$ and $\Phi_{c \to t}$ will alter in the way exhibited in Table 3.

On the other hand, according to Kerzhner *et al.* [17] the different adsorptive interactions between the azobenzene isomers and the adsorbent account for the observed difference in the quantum yields shown in Table 2. Apparently, in solution of nonpolar solvents both the isomers interact only weakly with the solvent molecules so that the relative positions of their energy levels will hardly be altered and particularly the *trans*-isomer remains the more stabilized one. In the adsorbed state, however, the *cis*- and the *trans*-isomer show a quite different behaviour. While the adsorption of the planar-shaped *trans*-isomer is realized by the weak interaction of the π-electrons of the azobenzene with the electron acceptor centers of the silica gel surface the adsorption of the nonplanar *cis*-isomer is due to the formation of strong hydrogen bonds between the n-orbitals of the nitrogen atoms and the proton-donor centers of the adsorbent. These hydrogen bonds can also be considered as an acid-base interaction between the azo-group of the adsorbate having a rather high basicity in this case and the Broensted acid centers on the surface of the silica gel.

Since the adsorptive interaction of the *cis*-isomer is much stronger than that of the *trans*-isomer the molecular state of the former will be lowered with respect to the latter. Consequently, the quantum yield of the *trans*-*cis*-photoisomerization will be greater and that of the *cis*-*trans*-photoisomerization will be smaller than the corresponding quantum yields measured in solution of nonpolar solvents. This prediction is in good agreement with the quantum yields collected in Table 2.

Acknowledgement

The research work described herein was supported by a grant of the Deutsche Forschungsgemeinschaft which is gratefully acknowledged.

References

1. R. Gade, Z. Phys. Chem. **189** (1995) 99.
2. M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, Chem. Rev. **95** (1995) 69.
3. A. Mills and S. LeHunte, H. Photochem. Photobiol. A: Chem. **108** (1997) 1.
4. A. Hagfeldt and M. Grätzel, Chem. Rev. **95** (1995) 49.
5. M. Anpo and T. Matsuura (Eds.), *Photochem. on Solid Surfaces*, Elsevier 1989.
6. P. V. Kamat, Chem. Rev. **93** (1993) 267.
7. D. Oelkrug, W. Flemming, R. Füllemann, R. Günther, W. Honnen, G. Krahbichler, M. Schäfer and S. Uhl, Pure Appl. Chem. **58** (1986) 1207.
8. E. L. Simmons, J. Phys. Chem. **75** (1971) 588.
9. E. L. Simmons, J. Chem. Phys. **66** (1977) 1413.
10. H. Mauser, *Formale Kinetik*, Bertelsmann Universitätsverlag, Düsseldorf 1974.
11. Th. Porada and R. Gade, Z. Phys. Chem. **210** (1999) 113.
12. R. Gade and Th. Porada, J. Photochem. Photobiol. **A 107** (1997) 27.
13. E. Fischer, J. Phys. Chem. **71** (1967) 3704.
14. H. Mauser and J. Polster, Z. Phys. Chem. **268** (1987) 481.
15. P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, New York 1969.
16. R. Gade, U. Kaden and D. Fassler, J. Chem. Soc., Faraday Trans. 2, **83** (1987) 2201.
17. B. K. Kerzhner, V. I. Kofanov and T. L. Vrubel, Zh. obshch. khim. **53** (1982) 2303.
18. E. M. Kossower, J. Am. Chem. Soc. **80** (1958) 3259.
19. C. H. Nicholls and P. A. Leermakers, Adv. Photochem. **8** (1971) 315.
20. P. Bortolus and S. Monti, J. Phys. Chem. **83** (1979) 648.