

Kinetics of Triplet Sublevel Selective Photochemical Reactions in the Solid State

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A detailed description of the overall kinetics of photochemical reactions has to deal with photo-physical activation and de-activation rates as well as with true photochemical rates. Based on the hypothesis that for photoreactions involving the lowest excited triplet state the chemical reaction rates of the individual triplet zero-field levels have different values, a method is presented for the evaluation of these rates from bulk measurements under steady state illumination conditions. The complications arising from the detection of solid state reactions are discussed, and a simple solution is given, illustrated by a numerical example.

1. Introduction

Photochemistry in the solid state has gained increasing interest recently [1]. This includes possible technological applications (e.g. storage of data [2, 3]) as well as the field of topochemistry [4]. Investigations of solid state photochemical reactions so far mainly dealt with the evaluation of quantum yields [5–7] and the dynamical differences between one and two photon processes [8].

In this contribution, we concentrate on the detailed kinetics of photochemical reactions. Especially we are interested in the relations between the rates for chemical de-activation of excited states and the physical relaxation processes. Quantum theory of chemical reactivity [9] already has given hamiltonians and matrix elements [10] governing photochemical reaction rates. These matrix elements are very similar to the ones controlling photo-physical de-activation processes [11, 12].

As a first step we investigated [13] reactions involving the lowest excited triplet state T_1 in order to test the hypothesis [14] that the by now well known T_1 -sublevel-selectivity of physical relaxation processes [11, 12] carries over to the chemical de-activation processes.

The experiments had to be undertaken in solid state at very low temperature ($T < 5$ K) in order to avoid thermal equilibrium of the T_1 -zero-field levels [15].

Here we present considerations on how to evaluate detailed chemical de-activation rates from

measurements of the overall reaction rates of a solid state photochemical reaction. Despite of difficulties connected with the correct initial condition for the appropriate differential equations, which has not been discussed before, we show that, after all, a simple approximation can be obtained, and comment on its limitations by giving a numerical example. Although not necessarily restricted to this case, our considerations deal with the photoisomerization reaction $A \xrightarrow{h\nu} B$ with thermal backreaction $B \xrightarrow{kT} A$.

2. Microscopic Reaction Kinetics

2.1. The Model Used

Normally, photochemistry is discussed in terms of the Three State Concept [16] which claims that only three electronic states of an organic molecule undergoing a photochemical reaction have to be considered. These are the ground state S_0 and the lowest excited singlet and triplet states, S_1 and T_1 , respectively. Here, we extend this concept by taking into account the zero-field splitting (ZFS) of T_1 [17, 18]. Although the ZFS (~ 0.1 cm $^{-1}$) seems to be negligible as compared to the energy separation (~ 20.000 cm $^{-1}$) of the electronic states involved, it is well established experimentally and theoretically that the three triplet sublevels have considerably different photophysical population and depopulation rates. By hypothesis, we assume this sublevel selectivity to be also true for the photochemical reaction rates. This can be justified by a comparison of the quantum mechanical matrix elements governing photophysical relaxation pro-

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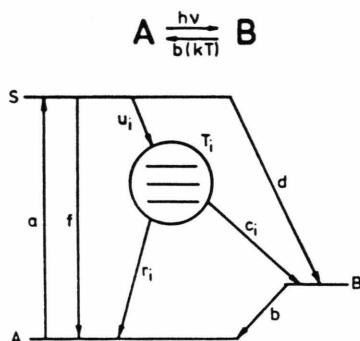


Fig. 1. Jablonski Type Diagram for a Photoisomerization Reaction. The physical de-activation rates f and r comprise radiative and radiationless relaxation of the lowest excited singlet and triplet states, S and T_i , respectively; a is the excitation rate and the u_i 's describe the intersystem crossing processes populating the triplet sublevels T_i . The chemical de-activation of S and the T_i 's is governed by d and the c_i 's, respectively. The rate of (thermal) backreaction is b .

cesses on the one hand [11, 12] and photochemical reactions on the other hand [10]. Such a treatment has to be restricted to diabatic reactions, i.e. to reactions where the actual chemical step is taking place between an excited state of the reactant and the ground state of the product [19]. Our model outlined so far is summarized in a Jablonski type diagram (Fig. 1) where we used a somewhat unconventional notation in order to avoid confusing multiple subscripts.

The kinetic equations governing the dynamics within this scheme now simply read:

$$\dot{A} = -aA + fS + \sum r_i T_i + bB, \quad (1)$$

$$\dot{S} = -fS + aA - \sum u_i S - dS, \quad (2)$$

$$\dot{T}_i = -(r_i + c_i) T_i + u_i S, \quad (3)$$

$$\dot{B} = dS + \sum c_i T_i - bB, \quad (4)$$

and the relation connecting the initial condition with stoichiometric requirements is:

$$A_0 = A + S + \sum T_i + B. \quad (5)$$

Here and in the following, $i = x, y, z$ designate the triplet sublevels.

In order to decouple this set of equations one first has to assume that the chemical rates d and c_i are smaller than the rates for the competing physical de-activation respectively, by several orders of magnitude. This assumption seems to be justified by preliminary experiments. Under steady state illumination conditions therefore, and monitored

on the (slow) photochemical time scale, the photophysical cycle is stationary. Consequently, the populations of the ground and excited states of the reactant are proportional:

$$S = sA \quad \text{with } s = a/(f + \sum u_i), \quad (6)$$

$$T_i = t_i A \quad \text{with } t_i = s(u_i/r_i) = t_i^0, \quad (7)$$

and hence, using (5):

$$B = A_0 - (1 + s + \sum t_i) A. \quad (8)$$

2.2. Local Reaction Progress

Within the framework of our model, the increase in the population of the product ground state B, as governed by (4), is connected with the decrease in the population of the reactant ground state A via (8). The rate equation therefore reads:

$$\dot{A} = - \left(\frac{sd + \sum t_i c_i}{1 + s + \sum t_i} + b \right) A + \frac{b}{1 + s + \sum t_i} A_0, \quad (9)$$

which describes an exponential approach to the photochemical stationary state:

$$A = \tilde{A} = \frac{b/k}{1 + s + \sum t_i} A_0 \quad (10)$$

with the rate constant:

$$k = \frac{sd + \sum t_i c_i}{1 + s + \sum t_i} + b. \quad (11)$$

Obviously, one cannot obtain the chemical rates d and c_i from a single measurement of k , even if the photophysical quantities s and t_i are known. One has to make use of the possibility to alter, in a well defined manner, the relative population numbers of the triplet sublevels. This can be achieved with the help of an ODMR-spectrometer [20] which is also used to determine the selective photophysical quantities.

2.3. Coupling of Triplet Sublevels

In general, the triplet zero-field levels T_i are populated (u_i) and depopulated (r_i) within the photophysical cycle selectively [11, 12, 14, 20] (cf. Figure 1). At very low temperatures ($T < 5$ K), spin lattice relaxation (SLR) as a coupling mechanism between the sublevels can be neglected [21], and the relative population numbers are $t_i = t_i^0$, given

by the intrinsic molecular parameters (cf. (7)). The t_i 's can be manipulated in two ways:

First, one can simply raise the temperature until SLR begins to equilibrate the populations according to the Boltzmann distribution. Using typical orders of magnitude of the zero-field splittings in organic molecules, for $T > 10$ K the result can be approximated quite accurately to yield:

$$t_i = \sum t_i^0/3 \text{ for all three sublevels.} \quad (12)$$

Note that this can lead to a sharp temperature effect on k in the range $2 \text{ K} < T < 15 \text{ K}$, even for a pure photoreaction without any activation energy barrier involved. If the back reaction rate, however, is dependent on temperature in the given range, this method is not applicable, as will become apparent in the following subsection.

Secondly, under still very low temperature conditions, one can equalize the populations of two (or three) of the sublevels by coupling them with resonant microwave radiation, e.g.:

$$t_x = t_y = (t_x^0 + t_y^0)/2, \quad t_z = t_z^0. \quad (13)$$

Including the case of isolated triplet sublevels, one can therefore obtain five values for the rate constant k . The redundancy of one should be useful in actual measurements and calculations (*vide infra*) for discussing error margins.

2.4. Evaluation of Chemical Rates

Clearly, from a knowledge of the photophysical quantities and the above-mentioned five k 's one could calculate the absolute values of d and the c_i 's. This will not be discussed here. If, as was the case in our ODMR-experiments [17], s is not accessible and only relative triplet sublevel populations $t_i^0/\sum t_i^0$ can be obtained, the following procedure yields relative chemical rates $c_i/\sum c_i$: The influence of the reaction from the singlet state and of the back reaction is eliminated by subtracting one of the k 's, e.g. the one measured with isolated sublevels, $k^{(0)}$, from the other four (note that the denominator N in the expression for k does not change when the various coupling cases (j) are employed):

$$\Delta^{(j)} = k^{(j)} - k^{(0)}. \quad (14)$$

Dividing this by the appropriate quantity for all sublevels T_x, T_y, T_z being coupled and taking into

account (12):

$$\begin{aligned} \Delta^{(xyz)} &= k^{(xyz)} - k^{(0)} \\ &= \left(\sum \left(\frac{\sum t_i^0}{3} \right) c_i - \sum t_i^0 c_i \right) / N \\ &= (\frac{1}{3} \sum t_i^0 \sum c_i - \sum t_i^0 c_i) / N \end{aligned} \quad (15)$$

and rearranging, one obtains:

$$Q^{(j)} = \frac{\Delta^{(j)}}{\Delta^{(xyz)}} = \frac{\sum (n_i x_i) - \sum (n_i^0 x_i)}{\frac{1}{3} \sum n_i^0 x_i}. \quad (16)$$

where $n_i^0 = t_i^0/\sum t_i^0$, $n_i = t_i/\sum t_i^0$ and $x_i = c_i/\sum c_i$. Inserting the experimental quantities $Q^{(j)}$, n_i^0 and n_i , after some simple algebra one can solve for the relative chemical rates x_i .

2.5. Numerical Considerations

Before we turn our attention to the question of how to measure k we briefly discuss some estimates on the order of magnitude of the effects to be expected. These are most significant, clearly, if reactions originating from the singlet state can be excluded:

$$s d \ll \sum t_i c_i \quad (17)$$

and if the back reaction is substantially slower than the triplet forward reaction. Under these circumstances one further can dispense with the subtraction in (14) which can result in large error margins. The requirement that the reaction from the triplet state by far predominates, therefore, should be carefully considered when choosing the molecular system to be investigated.

The relative changes of k upon altering the triplet sublevel populations are then governed by the right hand side of inequality (17). They were estimated to lie in the range of $\pm 10\%$ to $\pm 30\%$ and to reach $\pm 50\%$ in exceptional cases only. Here we used typical data for the zero-field level populations of organic molecules [18] as well as the assumption that the triplet sublevel chemical rates c_i differ by factors of 1 to 100 which is the same order of magnitude as for the physical radiationless de-activation [17, 20].

3. Bulk Reaction Kinetics

The problem can now be stated as following: In order to measure the effect of microwave irradiation on chemical reactivity and to extract values of

triplet sublevel chemical de-activation rates to an accuracy of about 10%, one has to bring down the error margin of k — or some related quantity — to a few percent, preferably 1%.

As can be seen from subsection 2.3 the experiments have to be done at very low temperature and therefore inevitably in the solid state. Now some severe complications arise, some of which have been discussed already by several workers in the field [5–8]. In the following we present additional aspects, before we offer our approximate solution and comment on it giving a numerical example.

3.1. The Model Used

First of all — and most important — it has to be ascertained whether chemistry is actually rate determining. Alternative possibilities which have to be examined are e.g.: Is energy transfer to X-traps or structural defects of the solid the slowest step; or do the mechanical properties of the reactant crystal determine the growth rate of macroscopic product clusters (cf. the concept of homogeneous vs. heterogeneous reaction [22])?

In order to substantially facilitate the further discussion here and also the evaluation of experimental data one should take care of two more requirements: i) There should be no overlap of reactant and product absorption bands at the excitation wavelength; ii) The intensity of the exciting light should not vary markedly over the cross section used for driving the photoreaction so that a one-dimensional treatment (e.g. along the z -axis) is feasible.

Under these conditions the bulk reaction kinetic is governed first by the differential Lambert-Beer-law:

$$\frac{\partial}{\partial z} I(z, t) = -\varepsilon I(z, t) A(z, t), \quad (18)$$

where ε is the extinction coefficient of the reactant which has the local concentration $A(z, t)$, and $I(z, t)$ is the local intensity of the exciting light relative to its value at the front of the sample.

Secondly, the rate equation (9) is now modified by taking into account that the relative population numbers s and t_i are proportional to the intensity via the excitation rate a (cf. Eqs. (6) and (7)):

$$\frac{\partial}{\partial t} A(z, t) = -\left(\frac{I(s\bar{d} + \sum t_i c_i)}{1 + I(s + \sum t_i)} + b \right) A(z, t) + \frac{b}{1 + I(s + \sum t_i)} A_0, \quad (19)$$

where $I = I(z, t)$ again is the relative local intensity.

Whereas the boundary condition for $z = 0$ can be evaluated very simply by inserting $I = 1$ into (19), the initial condition has to be discussed more carefully. Clearly, before the exciting light has been turned on ($t = 0$), the reactant concentration $A(z, 0)$ is constant and equals A_0 . But immediately after the onset of the illumination and after the stationarity of the photophysical cycle is established ($t = 0^+$), (8) is valid with $B = 0$:

$$A(z, 0^+) = \frac{A_0}{1 + I(s + \sum t_i)}. \quad (20)$$

Together with (18) this leads to an equation implicitly determining $I(z, 0^+)$:

$$\ln I(z, 0^+) + (s + \sum t_i)(I(z, 0^+) - 1) + \varepsilon A_0 z = 0 \quad (21)$$

which cannot be solved analytically.

This difficulty has not been considered before. Exact solutions to (18) and (19) which have been given previously [23, 24], rest on the assumption that initially the concentration distribution is homogeneous and equals A_0 . Equations (20) and (21) show this not to be true in general; for an example cf. subsection 3.3. and Figs. 2, 3 and 4.

The non-uniform intensity and concentration profiles evolving from (19) through (21) are never measured directly. When using e.g. an optical method for monitoring the reaction progress, the detector inevitably samples radiation from a range $z_1 \leq z \leq z_1 + \delta z$, corresponding to the solid angle spanned by the imaging system. In any case, an additional integration

$$Y(t) = \int_{z_1}^{z_1 + \delta z} A(z, t) dz \quad (22)$$

has to be taken into account, the range of which often has to be extended over the whole sample thickness $0 \leq z \leq z_{\max}$.

3.2. An Approximate Solution

As was discussed in connection with (21) an exact and analytical solution of the problem posed by Eqs. (18) through (22) cannot be obtained.

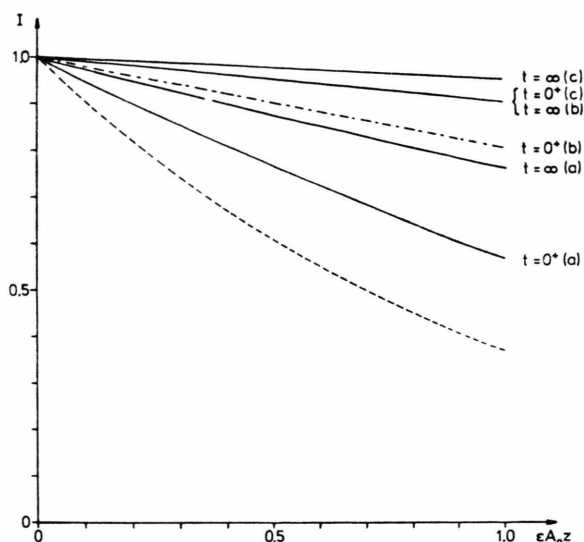


Fig. 2. Variation of relative intensity I across the sample, calculated with the data sets quoted on the right of the pertinent curves (—), as compared to $\exp(-\epsilon A_0 z)$ (---).

A substantial simplification is feasible if — as is not unusual for organic molecules — the populations of the excited states (esp. T_i) by far exceed the

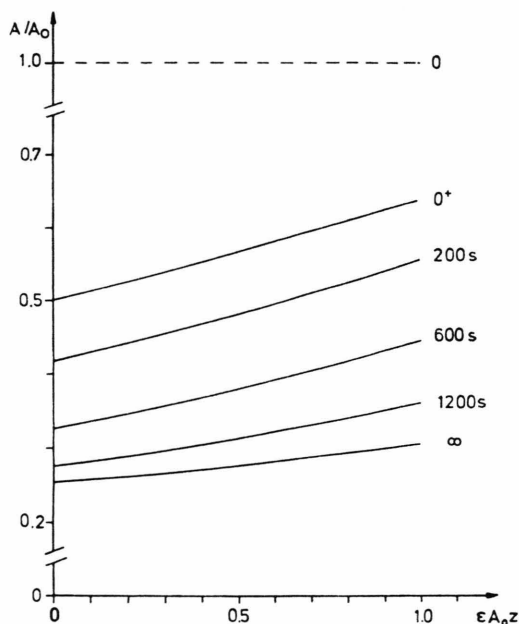


Fig. 3. Variation of relative reactant ground state concentration A/A_0 across the sample approaching its steady state, for times quoted on the right of the pertinent curves, calculated with data set (a).

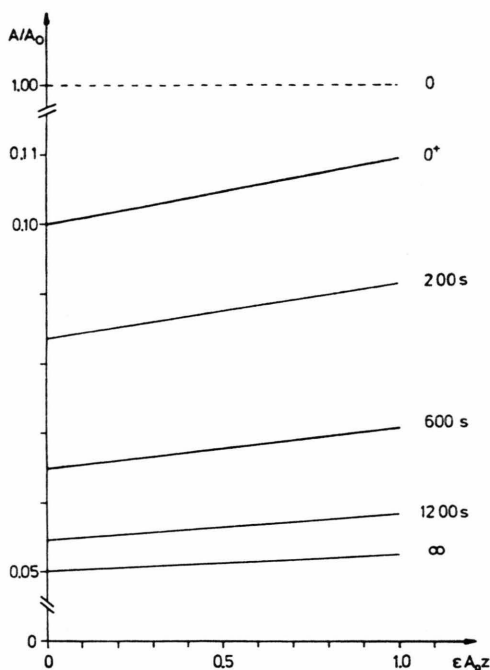


Fig. 4. Variation of relative reactant ground state concentration A/A_0 across the sample approaching its steady state, for times quoted on the right of the pertinent curves, calculated with data set (c).

population of the ground state:

$$1 \ll s + \sum t_i \quad (23)$$

which (for samples with not too high an optical density) renders the rate constant in (19) independent of z and t :

$$K = \frac{s d + \sum t_i c_i}{s + \sum t_i} + b. \quad (24)$$

As will not be discussed here in detail, the time behaviour of the quantity of experimental interest $Y(t)$, then simply reflects the microscopic kinetics described in connection with (9). The consequences of spatial variations enter as unessential constants only. In general however, inequality (23) is not valid to sufficient accuracy and a "trivial" approximation has to be applied. Therein one dispenses with taking into account any spatial or time variations of the relative intensity, by setting $I \equiv 1$. Obviously then, the bulk reaction kinetic equals the simple microscopic reaction kinetic, and the integration in (22) consists merely of multiplying by δz .

The basic assumption $I \equiv 1$ is not as unfounded as it may seem: Consider the diminished reactant concentration at time $t = 0^+$ which in turn leads to an intensity distribution (cf. Eqs. (20) and (21)) substantially less damped in space than it would be for the original concentration A_0 . Moreover, as the reaction proceeds, the sample becomes more and more transparent ($I \rightarrow 1$). These features will be illustrated in the following subsection.

The proposition $I \equiv 1$ does not prohibit the detection of the chemical reaction progress, because it can be followed by monitoring the absorption of the product or the luminescence of the excited states S and T_i of the reactant as well. The latter method clearly also yields the correct rate k due to the proportionality between the ground and excited state populations (cf. Equations (6), (7)).

3.3. A Numerical Example

In order to test for the reliability of the "trivial" approximation, a model calculation was undertaken. As will become apparent, the crucial parameter is

$$p = s + \sum t_i. \quad (25)$$

We therefore used three sets of data (a, b and c) for our calculations, consistent with preliminary experimental results, with three different values for p (cf. Table 1).

With these data, first, (21) and the corresponding one for the photochemical stationary state $t = \infty$ were solved by iteration (cf. Figure 2). Note that the basis of our approximation, $I \equiv 1$, is valid to an accuracy of, say, 5% within a range of z strongly dependent on p .

Next, (18) and (19) were solved by numerical integration, with the initial condition as expressed in (20). The results shown in Figs. 3 and 4 illustrate the approach of the concentration distribution to its photochemical stationary state for data set (a) and (c), respectively. The "trivial" approximation

	a	b	c
$s + \sum t_i$	1	4	9
d	0	0	0
$\sum c_i t_i / 10^{-3} \text{ s}^{-1}$	2	5	10
$b / 10^{-3} \text{ s}^{-1}$	1	1	1
$k = 2 \cdot 10^{-3} \text{ s}^{-1}$			

Table 1. Data sets a, b, and c, used for the calculations in subsection 3.3.

is represented by the points $A(0, t)$, i.e. by the points on the ordinate. Note that for each data set chosen:

$$A(0, \infty)/A(0, 0^+) = 0.5. \quad (26)$$

This ratio could be obtained from our experiments and was used, in turn, to select the data in Table 1. It should not be confused with \bar{A}/A_0 given by (10), which is different for the three data sets. Note that these two ratios are connected, within the limits of our approximation, simply by a factor of $1 + p$ (cf. Eqs. (10) and (25)), and that therefore an estimation of p should be possible, in principle. Without going into experimental details we only remark that it depends on the detection method used which of the ratios is actually measured. Clearly, as the reader may readily verify, there exist other possibilities to estimate p ; we propose to use the above-mentioned one, because it takes advantage of the nearly homogeneous concentration distribution in the photochemical stationary state (cf. Figs. 3 and 4).

The quantity of experimental interest, $Y(t)$, was obtained by numerical integration of (22) over $0 \leq z \leq z_{\max}$. From this, $L(t)$ was calculated:

$$L(t) = -\ln \left(\frac{Y(t) - Y(\infty)}{Y(0) - Y(\infty)} \right) \quad (27)$$

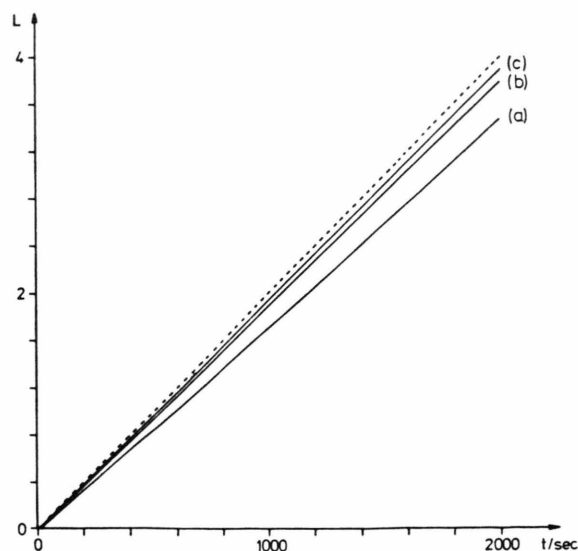


Fig. 5. $L(t)$ (cf. Eq. (27)) calculated for an optical density of 1.0 and with data sets quoted on the right of the pertinent curves (—), as compared to the "trivial" approximation (---).

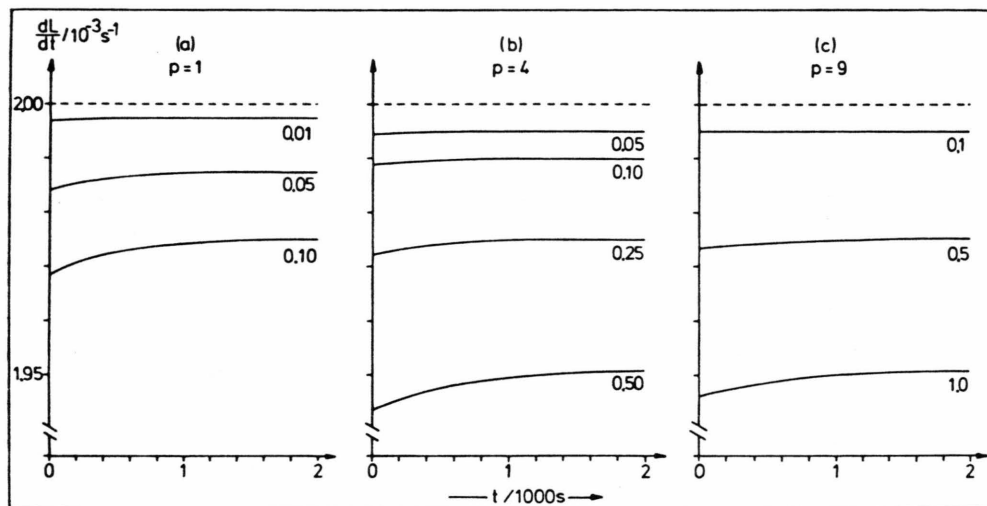


Fig. 6. Time derivatives of $L(t)$ for several values of the optical densities, quoted on the right of the pertinent curves (—), calculated for all three data sets, as compared to the “trivial” approximation (---).

which should be exactly linear for the trivial approximation being valid strictly (Figure 5).

In order to get more thorough evidence for the limits of validity of the approximation, $dL/dt(t)$ was evaluated numerically from $L(t)$ -curves calculated for several z_{\max} (cf. Figure 6). Two aspects are important: i) The mean deviation from the value obtained for the “trivial” approximation being valid exactly (numerical error), which should not exceed 1% (vide supra); and ii) the deviation from constancy which can be viewed as a measure of the functional error. Our results comprised in Fig. 6 show that both errors can be suppressed to any reasonable value (e.g. given by the limitations of the apparatus) by simply using a sample with the appropriate optical density. Furthermore — and this is most important — they show how the appropriate optical density can be estimated even from an only approximate knowledge of p (note that the essential difference between the data sets used is the value of p ; cf. Table 1).

Coming back now to the problem posed at the beginning of this section, we conclude that the approximation used describes the kinetics of a solid state photochemical reaction with an accuracy which, after some relatively simple adjustment, is sufficient to measure even the small microwave effects on the overall reaction rate (cf. Section 2.5.).

4. Conclusion

A method is described for the evaluation of excited state chemical de-activation rates, especially for the triplet zero-field levels, under steady state illumination conditions. It is based on the possibility to alter, in a well defined manner, the sublevel populations by applying resonant microwave irradiation. In a favorable case (the requirements of which have been discussed) the overall reaction rate will be changed by about 20% when two of the triplet sublevels are coupled.

The measurements have to be done in the solid state at very low temperature in order to avoid thermal equilibration of the sublevel populations. The differential equations governing the bulk reaction kinetics are given. The most important feature therein is that the reaction rate is not simply proportional to the local intensity of the light driving the photoreaction. This complication can be circumvented for a special case only, the requirement of which has been considered.

For the general case, a “trivial” approximation is proposed which consists merely of neglecting any spatial or time variations of the intensity as the reaction proceeds. Its applicability is based on the diminished reactant ground state population under the steady illumination. A numerical example,

calculated with three typical sets of data, shows that this approximation can be used to any desirable accuracy if the measurements are done on samples with an appropriate value of the optical density, and gives a method to estimate this value.

It is therefore possible to measure the expected changes of the overall reaction rate even with the

“trivial” approximation needed to treat the complications of solid state photochemistry.

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