[4] *A. G. Andersen & G. Berkelhammer*, J. Amer. chem. Soc. *80*, 992 (1958); *K. Wallenfels et al.*, Liebigs Ann. Chem. *621*, 106, 137, 178, 198 (1959).

[5] *P. Karrer & O. Warburg*, Biochem. Z. *285*, 297 (1936).

[6] *W. Traber & P. Karrer*, Helv. *41*, 2066 (1958); *G. W. Rafter & S. P. Colowick*, J. biol. Chemistry *209*, 773 (1954); *R. F. Hutton & F. H. Westheimer*, Tetrahedron *3*, 73 (1958); *H. E. Dubb, M. Saunders & J. H. Wang*, J. Amer. chem. Soc. *80*, 1767 (1958); *G. Cilento, E. de Carvalho Filho & A. C. Giora Albanese. ibid. 80*, 4472 (1958); *W. L. Meyer, H. R. Mahler & R. H. Baker*, Biochem. biophys. Acta *64*, 353 (1962).

[7] *K. Schenker & J. Druey*, Helv. *42*, 1960 (1959).

[8] *K. Schenker & J. Druey*, Helv. *42*, 2511 (1959).

[9] *R. A. Sulzbach & Abul F. M. Iqbal*, Angew. Chem. *83*, 758 (1971).

[10] *R. M. Acheson & N. D. Wright*, Chem. Commun. *1971*, 1421.

[11] *H. Gilman & S. M. Spatz*, J. org. Chemistry *16*, 1485 (1951).

[12] *H. Meyer & H. Tropsch*, Mh. Chem. *35*, 210 (1914).

[13] *M. Marti, M. Viscontini & P. Karrer*, Helv. *39*, 1451 (1956); *C. A. Grob & F. Ostermeyer*, Helv. *45*, 1119 (1962).

[14] a) *E. Wenkert, K. G. Dave, F. Haglid, R. G. Lewis, Takoshi Oishi, R. V. Stevens & M. Terashima*, J. org. Chemistry *33*, 747 (1968); b) vgl. a. *M. Freifelder, ibid. 29*, 2895 (1964).

[15] *M. Marti, M. Viscontini & P. Karrer*, Helv. *39*, 1451 (1956); *Hoffmann-La Roche*, Schweiz. Pat. 345005 (*P. Karrer*).

[16] *L. D. Quin & D. O. Pinion*, J. org. Chemistry *35*, 3130 (1970); *N. J. Leonard & A. S. Hay*, J. Amer. chem. Soc. *78*, 1984 (1956).

[17] *E. Wenkert*, Accounts chem. Research *1*, 78 (1968); s.a. *M. E. Kuehne*, Synthesis *2*, 510 (1970) (pp. 522 ff.).

[18] *G. Stork, A. Bizzolara, H. Landesman, J. Szumuszkovicz & R. Terrell*, J. Amer. chem. Soc. *85*, 207 (1963); s.a. *G. H. Alt* in: *A. G. Cook*, «Enamines; Synthesis, Structure und Reactions», (S. 115, M. Dekker, New York und London, 1969).

[19] *G. Opitz*, Liebigs Ann. Chem. *650*, 122 (1961).

[20] *M. Perelman & St. Miszak*, J. Amer. chem. Soc. *84*, 4988 (1962); *G. Opitz & J. Koch*, Angew. Chem. *75*, 167 (1963).

[21] *A. K. Bose & G. Mina*, J. org. Chemistry *30*, 812 (1965).

[22] US Pat. 2977360; *M. L. Weiner*, J. org. Chemistry *26*, 951 (1961).

[23] *P. Karrer & F. Blumer*, Helv. *30*, 1157 (1947).

[24] *P. Karrer & F. J. Stare*, Helv. *20*, 418 (1937).

[25] *F. Troxler, F. Seemann & A. Hofmann*, Helv. *42*, 2073 (1959), Tabelle 1.

[26] *E. Wenkert & B. Wickberg*, J. Amer. chem. Soc. *87*, 1580 (1965).

30. Kinetics of Photochemical Systems with Modulated Optical Excitation

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Summary. The kinetic equations of a photochemical system are discussed in which the transitions from the ground to the first excited state are produced by a sinusoidally modulated photon source. The system includes irreversible reactions starting from the first excited singlet state S_1 and the first triplet state T_1 (*cf.* Fig. 1). Explicit solutions are given for a linear approximation of the equations of motion for the parametrically modulated system. The solutions apply only when there is weak optical pumping, low quantum yields of the photochemical end-products and for

certain conditions of the modulation frequency. The concentrations of all particles occurring are shown to consist of modulated and unmodulated components where the amplitudes of the modulated components are slowly decaying exponentials. The phases of the modulated components are shown to be non-decreasing along a sequence of irreversible steps. Formulae are given which permit determination of the photochemical system rate constants and location of a particle in a sequence of irreversible reactions.

1. Introduction. – In recent years modulation methods have become an important tool for the improvement of sensitivity and resolution in many fields of physical chemistry. Modulation excitation spectroscopy was proposed first by *Hexter* [1] for the measurement of life times of excited electronic states and has actually been used similarly by *Labhart* [2] and others. *Birks et al.* [3] have discussed extensively phase fluorimetry methods. Modulated excitation has also been applied very efficiently to the study of triplet life times, including energy transfer by excited metal atoms [4]. *Johnston et al.* [5] have reported the development of a modulated excitation infrared (MEIR.) gas spectrometer, and *Fringeli et al.* [6] have very recently described an MEIR. spectrometer including its sensitivity. An application of this spectrometer to the study of a photochemically induced sequence of irreversible reactions has been reported by *Fringeli* [7].

During this work, it became obvious that the same principle may be applied to a variety of spectroscopic techniques, which allow the modulation of the concentration of transient particles, *e.g.* ESR. and microwave spectroscopy. In many cases the molecular systems, investigated by modulated excitation, behave approximately according to Fig. 1, with the additional specification that the exciting light source produces only small populations of the excited singlet S_1 as compared to that of the ground state singlet S_0. According to the kinetic scheme Fig. 1, irreversible reactions either from the S_1 or T_1 state are included and are assumed to form chains of irreversible first order steps. Owing to the irreversible sequences, continuous pumping in the cycle $S_0 \rightleftarrows S_1 \rightarrow T_1$ leads to irreversible changes of the populations of these states, superimposed on the modulation. From a general point of view the exciting light source acts as a parametric modulator.

In this paper we give a complete approximate solution of the kinetic equations of this system for the case of a weak pump modulated sinusoidally. The solution is based on a treatment usually applied in the theory of quantum mechanical perturbation. It includes both the aperiodic (exponential) and periodic components (amplitudes and phases) of the populations, but is restricted to the fundamental of the modulation frequency and to times comparable with or greater than the modulation period. It will be shown that the exponential behaviour for 'large' times is dominated by the smallest eigenvalue of the constant part of the kinetic matrix, *i.e.* by the pump coefficient. The phase shifts of the periodic components of the populations in the side chains increase monotonically along the chain, but also depend on the phases of the populations in the cycle $S_0 \rightleftarrows S_1 \rightarrow T_1$. The formulae may be extended to include first harmonic modulation components, which, however, may be shown to be negligible for classical light sources. The solution presented in this paper is considered to be applicable to a wide variety of photochemical systems. In a forth-

coming paper it will be used in the kinetic analysis of MEIR. spectra of photo-generated radicals of polyhydroxy-benzenes [8].

2. Definition of the kinetic system and equations of motion. – The kinetic equations discussed in this paper are based on the kinetic diagram shown in Fig. 1, where S_0, S_1 and T_1 denote the ground state, the first excited singlet and the first triplet state, respectively. B_1, B_2, ... B_m denote particles forming a sequence of irreversible reactions starting from the excited singlet S_1, and C_1, C_2, ... C_n form a similar irreversible first order sequence starting from the first triplet T_1.
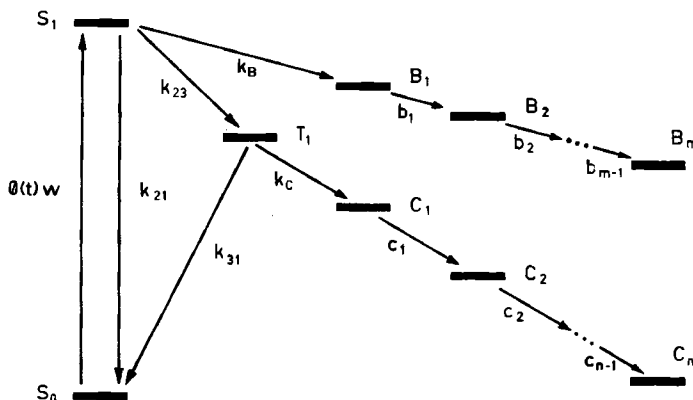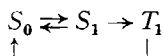

Fig. 1. *First order kinetics of a photochemical system with modulated excitation $\Phi(t) = \frac{1}{2} \Phi_0 w (1 + \cos \omega t)$ and sequences of irreversible reactions (B and C). The constants k_{21} and k_{31} contain radiative and nonradiative contributions. The cycle $S_0 \rightleftarrows S_1 \rightarrow T_1$ represents the A cycle (see section 2).*

For the cycle

$$S_0 \rightleftarrows S_1 \rightarrow T_1$$

the important assumption will be made that only the transition $S_0 \rightarrow S_1$ will be excited, with transition rate $\Phi(t)w$, by the photon-flux $\Phi(t)$.

The spontaneous transition probability k_{21}, from S_1 to S_0, may contain thermal (non radiative) and optical (radiative) contributions. Similarly, the spontaneous transition probability k_{31}, from T_1 to S_0, may consist of radiative and non radiative contributions. Finally the photon-flux is assumed to be modulated harmonically, *viz.*

$$\Phi(t) = \frac{1}{2} \Phi_0 (1 + \cos \omega t) \tag{2-1}$$

For the mathematical treatment we shall now denote the cycle $S_0 \rightleftarrows S_1 \rightarrow T_1$ as the cycle A with the notation $A_1 = S_0$, $A_2 = S_1$, $A_3 = T_1$ (see Fig. 1). With this notation the equations of motion of the system for $t \geqslant 0$ are obtained from Fig. 1 directly in matrix form

$$\frac{d}{dt} \begin{pmatrix} A(t) \\ B(t) \\ C(t) \end{pmatrix} = \left(K + \frac{1}{2} \Phi_0 (1 + \cos \omega t) w \, W \right) \begin{pmatrix} A(t) \\ B(t) \\ C(t) \end{pmatrix} \qquad (2\text{-}2')$$

where $A(t)$, $B(t)$ and $C(t)$ represent the column vectors of the instantaneous particle concentrations ($\tilde{A}(t) = A(t)$ transposed, etc.), *i.e.*

$$(\tilde{A}(t)) = ([A_1](t),\ [A_2](t),\ [A_3](t))$$

$$(\tilde{B}(t)) = ([B_1](t),\ [B_2](t),\ \ldots\ [B_m](t)) \qquad (2\text{-}2'')$$

$$(\tilde{C}(t)) = ([C_1](t),\ [C_2](t),\ \ldots\ [C_n](t))$$

K is the kinetic matrix of the whole system and may be divided into submatrices according to the subdivision of the concentration vector $(\tilde{A}(t),\ \tilde{B}(t),\ \tilde{C}(t))$, *i.e.*

$$K = \begin{pmatrix} K^{AA} & K^{BA} & K^{CA} \\ K^{AB} & K^{BB} & K^{CB} \\ K^{AC} & K^{BC} & K^{CC} \end{pmatrix} \qquad (2\text{-}3')$$

where according to Fig. 1

$$K^{BA} = K^{CA} = K^{BC} = K^{CB} = 0 \qquad (2\text{-}3'')$$

$$K^{AA} = \begin{pmatrix} 0 & k_{21} & k_{31} \\ 0 & -k_2 & 0 \\ 0 & k_{23} & -k_3 \end{pmatrix} \qquad (2\text{-}4')$$

where

$$k_2 = k_{21} + k_{23} + k_B \qquad k_3 = k_{31} + k_C \qquad (2\text{-}4'')$$

$$K^{AB} = \begin{pmatrix} 0 & k_B & 0 \\ 0 & 0 & 0 \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ 0 & 0 & 0 \end{pmatrix} \qquad K^{AC} = \begin{pmatrix} 0 & 0 & k_C \\ 0 & 0 & 0 \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ 0 & 0 & 0 \end{pmatrix} \qquad (2\text{-}5)$$

K^{BB} and K^{CC} are lower triangular singular matrices of the form (*cf.* Fig. 1)

$$
K^{BB} = \begin{pmatrix}
-b_1 & 0 & 0 & . & . & . & 0 \\
+b_1 & -b_2 & 0 & & & & . \\
0 & +b_2 & & & & & . \\
0 & & & & & & \\
. & & & & & & . \\
. & & & & & & . \\
0 & . & . & . & +b_{m-1} & 0
\end{pmatrix}
$$

$$
K^{CC} = \begin{pmatrix}
-c_1 & 0 & 0 & . & . & . & . & 0 \\
+c_1 & -c_2 & 0 & & & & & . \\
0 & +c_2 & & & & & & . \\
. & & & & & & & . \\
. & & & & & & & . \\
. & & & & & & & . \\
0 & . & . & . & . & 0 & +c_{n-1} & 0
\end{pmatrix}
$$

$(2\text{-}6)$

The matrix $\frac{1}{2}\,\Phi_0\,(1 + \cos\omega t)\,wW$ is time-dependent for a modulated system. W may be subdivided into submatrices similarly to (2-3')

$$
W = \begin{pmatrix}
W^{AA} & W^{BA} & W^{CA} \\
W^{AB} & W^{BB} & W^{CB} \\
W^{AC} & W^{BC} & W^{CC}
\end{pmatrix}
\tag{2-7}
$$

where all submatrices except W^{AA} are zero and

$$
W^{AA} = \begin{pmatrix}
-1 & 1 & 0 \\
1 & -1 & 0 \\
0 & 0 & 0
\end{pmatrix}
\tag{2-8}
$$

if induced emission is included.

It is evident from Eqs. (2-2) to (2-8) that the equations of motion may be decomposed into three subsystems:

$$
\frac{d}{dt}\,(A(t)) = (K^{AA} + \frac{1}{2}\,\Phi_0\,wW^{AA} + \frac{1}{2}\,\Phi_0\,wW^{AA}\cos\omega t)\,(A(t))
\tag{2-9'}
$$

$$
(\tilde{A}(0)) = ([A_1](0), 0, 0))
$$

$$
\frac{d}{dt}\,(B(t)) = K^{AB}(A(t)) + K^{BB}(B(t))
\tag{2-9''}
$$

$$
(\tilde{B}(0)) = (0, 0, \ldots 0)
$$

$$\frac{d}{dt}\,(C(t)) = K^{AC}(A(t)) + K^{CC}(C(t))$$

$$(\tilde{C}(0)) = (0, 0, \ldots 0) \tag{2-9'''}$$

The solutions of the non-homogeneous Eqs. (2-9″) and (2-9‴) may be obtained from the general equations:

$$(B(t)) = \int_0^t e^{K^{BB}\,(t-t')}\,K^{AB}(A(t'))\,dt' \qquad (C(t)) = \int_0^t e^{K^{CC}\,(t-t')}\,K^{AC}(A(t'))\,dt' \tag{2-10}$$

if the solution $(A(t))$ of Eq. (2-9′), i.e. of the cycle A of the kinetic graph, is known. Therefore, we must first give an appropriate solution for the time behaviour of the concentrations of the cycle A.

3. Solution of the kinetic equation of the cycle A. – Eq. (2-2′) represents a linear system with periodic coefficients. Since these coefficients are continuous for $t > 0$, a unique solution exists, which may be written in the form

$$(A(t)) = \overline{X}(t)\,(A(0)) \tag{3-1}$$

where $\overline{X}(t)$ is the unique matrix satisfying the matrix differential equation [9]

$$\frac{d\overline{X}}{dt} = \left(K^{AA} + \frac{1}{2}\,\Phi_0\,(1 + \cos \omega t)\,wW^{AA}\right)\overline{X}(t) \qquad \text{with} \qquad \overline{X}(0) = I \tag{3-2}$$

Though the theory of systems of this type has been treated intensively, solutions in closed form are difficult to obtain [10].

For the case of a weak pump, an approximate solution, adapted to the situation prevailing usually in modulated excitation spectroscopy (MES) [5] [6], may be obtained as follows. At present, for this technique, the following relations hold

$$k_2 \approx 10^8\,\text{s}^{-1}, \quad k_3 = 10^0 \cdots 10^6\,\text{s}^{-1}, \quad \Phi_0 w \approx 1\,\text{s}^{-1}, \quad k_2 \gg \omega, \quad \Phi_0 w < k_3 \ll k_2. \tag{3-3}$$

Under these conditions for $t \gg T = 2\,\pi/\omega$ the concentrations of the particles, averaged over a modulation period, may be shown to be slowly varying functions of time. An approximate solution of the equations of motion may then be found by the *ansatz*

$$\overline{X}(t) = e^{\overline{K}t}\,X(t) \tag{3-4}$$

where

$$e^{\overline{K}t} = e^{(K^{AA} + \frac{1}{2}\,\Phi_0 wW^{AA})t}$$

is the solution of the equation

$$\frac{d}{dt}\,U(t) = \overline{K}U(t), \quad U(0) = I \tag{3-5}$$

and $X(t)$ is a new, as yet unknown, matrix. The *ansatz* (3-4) means that the solution matrix $\overline{X}(t)$ is a product of a matrix $e^{\overline{K}t}$ containing only unmodulated terms and a matrix $X(t)$, which describes the effects of the parametric modulation of the system in addition to unmodulated components of the concentrations.

By combining Eq. (3-2) with (3-4) we obtain

$$\frac{d}{dt} X(t) = \frac{1}{2} \Phi_0 w \cos \omega t \, e^{-\overline{K}t} \, W^{AA} \, e^{\overline{K}t} \, X(t) \tag{3-6}$$

A solution of Eq. (3-6) may be obtained either by the use of the *Baker-Haussdorff* formula [11], or by the *matrizant* method [12].

The former apparently does not yield formulae easily applicable to actual experiments, and so a solution based on the *matrizant* in the pump factor $^1/_2 \Phi_0 w$ will be given.

Considering for the moment only the first iteration term of the *matrizant* solution of Eq. (3-6) one obtains:

$$X(t) = I + \frac{1}{2} \Phi_0 w \int_0^t \cos \omega \, t' e^{-\overline{K}t'} \, W^{AA} e^{\overline{K}t'} \, dt' + 0 \left(\left(\frac{1}{2} \Phi_0 w \right)^2 \right) \tag{3-7}$$

As will be discussed later, numerically calculated solutions up to second order proved this approximation to be justified for conditions of MES. using classical light sources. For high energy pulsed laser sources extension to higher approximations may be required. It should be pointed out that the matrix $e^{(K^{AA} + \frac{1}{2} \Phi_0 w W^{AA})t}$ itself contains terms of the order $(^1/_2 \Phi_0 w)^2$ and higher, and therefore the integral term in Eq. (3-7) also contains $0((^1/_2 \Phi_0 w)^2)$ terms. In order to obtain a solution useful practically, it proved important to retain terms at least up to $(^1/_2 \Phi_0 w)$ in the matrix exponential $e^{(K^{AA} + \frac{1}{2} \Phi_0 w W^{AA})t}$.

This requirement on the other hand allows the calculation of the eigenvalues and eigenvectors of $\overline{K}$ by perturbation technique.

Assuming that the matrix $\overline{K}$ may be diagonalized by similarity transformation [13][1]), *i.e.*

$$\overline{T}^{-1} \overline{K} \, \overline{T} = \overline{\Lambda}, \quad e^{\overline{K}t} = \overline{T} \, e^{\overline{\Lambda}t} \, \overline{T}^{-1} \tag{3-8}$$

one obtains from Eq. (3-7)

$$X(t) = I + \frac{1}{2} \Phi_0 w \, \overline{T} \int_0^t \cos \omega \, t' \, e^{-\overline{\Lambda}t'} \, \overline{T}^{-1} \, W^{AA} \overline{T} \, e^{\overline{\Lambda}t'} \, dt \, \overline{T}^{-1} \tag{3-7'}$$

Expanding both $\overline{T}$ and $\overline{\Lambda}$

$$\overline{T} = \sum_{k=0}^{\infty} \left(\frac{1}{2} \Phi_0 w \right)^k T^{(k)} \qquad \overline{\Lambda} = \sum_{k=0}^{\infty} \left(\frac{1}{2} \Phi_0 w \right)^k \Lambda^{(k)} \tag{3-9}$$

and using for the inverse $\overline{T}^{-1}$ the expansion

$$\overline{T}^{-1} = T^{(0)-1} - \frac{1}{2} \Phi_0 w \, T^{(0)-1} \, T^{(1)} \, T^{(0)-1} + 0 \left(\left(\frac{1}{2} \Phi_0 w \right)^2 \right) \tag{3-10}$$

---

[1])   It should be pointed out that the matrix $\overline{K}$ is not normal, nevertheless its eigenvalues are, in general, all distinct and therefore $\overline{K}$ can be diagonalized by similarity.

where $0((^1/_2\,\Phi_0 w)^2)$ contains all terms of the order $(^1/_2\,\Phi_0 w)^2$, one obtains with the approximations

$$\overline{T} \simeq T^{(0)} + \frac{1}{2}\,\Phi_0 w\,T^{(1)}$$

$$\overline{T}^{-1} \simeq T^{(0)-1} - \frac{1}{2}\,\Phi_0 w\,T^{(0)-1}\,T^{(1)}\,T^{(0)-1} \qquad (3\text{-}11)$$

$$\overline{\Lambda} \simeq \Lambda^{(0)} + \frac{1}{2}\,\Phi_0 w\,\Lambda^{(1)}$$

by insertion into Eq. (3-8) the commutator equation

$$[\Lambda^{(0)}, Z] = \Lambda^{(1)} - Y \qquad (3\text{-}12)$$

where

$$Z = T^{(0)-1}\,T^{(1)} \qquad Y = T^{(0)-1}\,W^{AA}\,T^{(0)} \qquad (3\text{-}12')$$

Eq. (3-12) may be solved for Z by a technique usually applied in the *Rayleigh-Schrödinger* perturbation theory of quantum mechanical systems [14], giving

$$Z_{mm} = 0 \qquad (3\text{-}13')$$

$$Z_{mm} = (T^{(0)-1}\,T^{(1)})_{mn} = -\frac{Y_{mn}}{\lambda^{(0)}{}_m - \lambda^{(0)}{}_n} \qquad (m \neq n) \qquad (3\text{-}13'')$$

$$\Lambda^{(1)}{}_{mm} = Y_{mm} \qquad (3\text{-}13''')$$

Explicitely, using the coefficients of $\overline{K}$ and W^{AA} given in Eqs. (2-4') and (2-8), Eqs. (3-9) to (3-13''') give

$$T^{(0)} = \begin{pmatrix} 1 & (k_{21}\,k_2 - k_{21}\,k_3 - k_{31}\,k_{23})/k_2 & -k_{31} \\ 0 & (k_3 - k_2) & 0 \\ 0 & k_{23} & k_3 \end{pmatrix} \qquad (3\text{-}14')$$

$$T^{(0)-1} = \begin{pmatrix} 1 & (k_{23}\,k_{31} + k_{21}\,k_3)\,(k_2 k_3)^{-1} & k_{31}/k_3 \\ 0 & (k_3 - k_2)^{-1} & 0 \\ 0 & -k_{23}\,(k_3\,(k_3 - k_2))^{-1} & 1/k_3 \end{pmatrix} \qquad (3\text{-}14'')$$

$$\Lambda^{(0)} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & -k_2 & 0 \\ 0 & 0 & -k_3 \end{pmatrix} \qquad (3\text{-}14''')$$

Introducing the abbreviations

$$\alpha = (- k_2 k_3 + k_{23} k_{31} + k_{21} k_3) (k_2 k_3)^{-1}$$
$$\beta = - ((k_{21} + k_2) (k_3 - k_2) + k_{31} k_{23})/k_2 \qquad (3\text{-}15')$$
$$\gamma = (k_3 - k_2)^{-1}$$

gives for Y and Z respectively

$$
\mathrm{Y} = \begin{pmatrix} \alpha & \alpha\beta & -k_{31}\alpha \\ \gamma & \beta\gamma & -k_{31}\gamma \\ -k_{23}\gamma/k_3 & -k_{23}\beta\gamma/k_3 & k_{31}\,k_{23}\gamma/k_3 \end{pmatrix} \qquad (3\text{-}15'')
$$

$$
\mathrm{Z} = \begin{pmatrix} 0 & -\alpha\beta/k_2 & k_{31}\alpha/k_3 \\ \gamma/k_2 & 0 & -k_{31}\gamma^2 \\ -k_{23}\gamma/k_3{}^2 & -k_{23}\beta\gamma^2/k_3 & 0 \end{pmatrix} \qquad (3\text{-}15''')
$$

The eigenvalues, up to first order, are

$$\bar{\lambda}_1 = -\frac{1}{2}\,\Phi_0 \mathrm{w}\,(k_{23}\,k_\mathrm{C} + k_{31}\,k_\mathrm{B} + k_\mathrm{B}\,k_\mathrm{C})\,(k_2\,k_3)^{-1}$$

$$\bar{\lambda}_2 = -k_2 - \frac{1}{2}\,\Phi_0 \mathrm{w}\,(1 + k_{21}/k_2 + k_{31}\,k_{23}\,(k_2\,(k_3 - k_2))^{-1}) \qquad (3\text{-}16)$$

$$\bar{\lambda}_3 = -k_3 + \frac{1}{2}\,\Phi_0 \mathrm{w}\,k_{31}\,k_{23}\,(k_3\,(k_3 - k_2))^{-1}$$

Eq. (3-16) shows that $\bar{\lambda}_1$ is proportional to the pump coefficient $\frac{1}{2}\,\Phi_0 \mathrm{w}$ and in most practical applications the following relationship of order of magnitude is fulfilled:

$$|\bar{\lambda}_2| \geqslant |\bar{\lambda}_3| \gg |\bar{\lambda}_1| \qquad (3\text{-}16')$$

The behaviour over a long period $(t \gg T = 2\pi/\omega)$ will therefore be dominated by $\bar{\lambda}_1$. Since $\lambda_1{}^{(0)} = 0$, the reason for the inclusion in Eq. (3-7′) of terms up to first order in $\bar{\Lambda}$ now becomes apparent. Omission of the first order terms would have given an unacceptable approximation of the slowly varying components of the populations within both the cycle A of the kinetic graph and the side chains B and C.

By inserting the approximation (3-11) in Eq. (3-7′) and ordering the terms in powers of the pumping factor $\frac{1}{2}\,\Phi_0 \mathrm{w}$, the solution of the kinetic equation (2-9′) of the cycle A becomes, after some lengthy manipulation,

$$(\mathrm{A}(t)) = T^{(0)} \left(e^{\bar{\Lambda}t} + \frac{1}{2}\,\Phi_0 \mathrm{w}\,[Z, e^{\bar{\Lambda}t}] + \right.$$

$$\left. + \frac{1}{2}\,\Phi_0 \mathrm{w}\,e^{\bar{\Lambda}t} \int_0^t \cos\omega t'\,e^{-\bar{\Lambda}t'}\,\mathrm{Y}\,e^{\bar{\Lambda}t'}\,\mathrm{d}t' \right) T^{(0)-1}\,(\mathrm{A}(0)) \qquad (3\text{-}17)$$

The solution $\mathrm{A}(t)$ now becomes separated into unmodulated and modulated terms with frequency ω:

$$[A_1](t) = [A_1](0) \left\{ e^{\bar{\lambda}_1 t} \left\{ 1 - \frac{1}{2} \, \Phi_0 w \, (k_{31} k_{23} \, (k_3^2 - k_2^2) + k_{21} k_3^2 \, (k_3 - k_2)) \, (k_2^2 k_3^2 \, (k_3 - k_2))^{-1} \right\} \right.$$

$$+ \, e^{\bar{\lambda}_2 t} \frac{1}{2} \, \Phi_0 w \, (k_{21} \, (k_3 - k_2) + k_{23} k_{31}) \, (k_2 \, (k_3 - k_2))^{-1} \{ a_2^2 \, (\bar{\lambda}_1 - \bar{\lambda}_2) + k_2^{-1} \}$$

$$\left. - \, e^{\bar{\lambda}_3 t} \frac{1}{2} \, \Phi_0 w \, k_{23} k_{31} \, (k_3 \, (k_3 - k_2))^{-1} \{ a_3^2 \, (\bar{\lambda}_1 - \bar{\lambda}_3) + k_3^{-1} \} \right\}$$

$$+ \, [A_1](0) \, \frac{1}{2} \, \Phi_0 w \, e^{\bar{\lambda}_1 t} \left\{ a_1 \, (k_3 \, (k_{21} - k_2) + k_{23} k_{31}) \, (k_2 k_3)^{-1} \sin \omega t \right.$$

$$- \, a_2 \, (k_{21} \, (k_3 - k_2) + k_{23} k_{31}) \, (k_2 \, (k_3 - k_2))^{-1} \, \cdot$$

$$\cdot \cos (\omega t + \mathrm{arc\,tg} \, (- \omega / (\bar{\lambda}_1 - \bar{\lambda}_2)))$$

$$\left. + \, a_3 \, k_{23} k_{31} \, (k_3 \, (k_3 - k_2))^{-1} \cdot \cos (\omega t + \mathrm{arc\,tg} \, (- \omega / (\bar{\lambda}_1 - \bar{\lambda}_3))) \right\}$$

$$[A_2](t) = [A_1](0) \, \frac{1}{2} \, \Phi_0 w \, \left\{ e^{\bar{\lambda}_1 t} k_2^{-1} - e^{\bar{\lambda}_2 t} \{ a_2^2 \, (\bar{\lambda}_1 - \bar{\lambda}_2) + k_2^{-1} \} \right\}$$

$$+ \, [A_1](0) \, \frac{1}{2} \, \Phi_0 w \, e^{\bar{\lambda}_1 t} \, a_2 \cos (\omega t + \mathrm{arc\,tg} \, (- \omega / (\bar{\lambda}_1 - \bar{\lambda}_2)))$$

$$[A_3](t) = [A_1](0) \, \frac{1}{2} \, \Phi_0 w \, \left\{ e^{\bar{\lambda}_1 t} k_{23} \, (k_2 k_3)^{-1} \right.$$

$$- \, e^{\bar{\lambda}_2 t} k_{23} \, (k_3 - k_2)^{-1} \{ a_2^2 \, (\bar{\lambda}_1 - \bar{\lambda}_2) + k_2^{-1} \}$$

$$\left. + \, e^{\bar{\lambda}_3 t} k_{23} \, (k_3 - k_2)^{-1} \{ a_3^2 \, (\bar{\lambda}_1 - \bar{\lambda}_3) + k_3^{-1} \} \right\}$$

$$+ \, [A_1](0) \, \frac{1}{2} \, \Phi_0 w \, e^{\bar{\lambda}_1 t} k_{23} \, (k_3 - k_2)^{-1} \left\{ a_2 \cos (\omega t + \mathrm{arc\,tg} \, (- \omega / (\bar{\lambda}_1 - \bar{\lambda}_2))) \right.$$

$$\left. - \, a_3 \cos (\omega t + \mathrm{arc\,tg} \, (- \omega / (\bar{\lambda}_1 - \bar{\lambda}_3))) \right\}$$

$$a_1 = \omega^{-1} \qquad a_2 = ((\bar{\lambda}_1 - \bar{\lambda}_2)^2 + \omega^2)^{-1/2} \qquad a_3 = ((\bar{\lambda}_1 - \bar{\lambda}_3)^2 + \omega^2)^{-1/2}$$

(3-1

Eq. (3-18) may be written more generally for $t \gg \max \, (|\bar{\lambda}_2|^{-1}, |\bar{\lambda}_3|^{-1})$

$$[A_i](t) \approx e^{\bar{\lambda}_i t} \, (A_{i0} + A_{i1} \cos (\omega t + \varphi_i)), \, i = 1, 2, 3 \qquad (3\text{-}19)$$

where A_{i0} and A_{i1} denote the amplitudes of the unmodulated and modulated parts, respectively, of the concentration $[A_i](t)$. φ_i is the phase shift of the modulated part relative to the exciting light function $^1/_2 \, \Phi_0 w \, (1 + \cos \omega t)$. By reason of causality the phaseshifts φ_i must be $< 0°$ in every case.

4. Explicit asymptotic solution for chains B and C. – Insertion of the solution (3-19) for the cycle A in equation (2-10) for the chains B and C yields two completely analogous solutions for the instantaneous concentrations of these chains.

Calculation may be either by matrix calculus, according to Eq. (2-10), or by direct substitution in Eqs. (2-9″) and (2-9‴), respectively. Both methods are straightforward, though rather lengthy, and yield solutions in two different forms, shown to be identical by rather tedious rearrangement of terms and application of trigonometric formulae. It should be remembered that all solutions given below are valid only for $t \gg T = 2\pi/\omega$, i.e. for the asymptotic behaviour of the modulated system.

4.1. *Solution by direct substitution.* For the explicit solutions of a chain C with 3 steps, see appendix A.

From these solutions, a simple general expression may be found for the modulated part of the concentration $[C_j](t)$ of the particle C_j in a chain of arbitrary length n $(n > j)$

$$[C_j](t)_{\text{mod.}} = \frac{A_{31}e^{\bar{\lambda}_1 t}\, k_C \prod\limits_{i=1}^{j-1} c_i}{\prod\limits_{i=1}^{j}\sqrt{(\bar{\lambda}_1 + c_i)^2 + \omega^2}} \cos\left(\omega t + \varphi_3 + \sum_{i=1}^{j}\text{arctg}\left(-\frac{\omega}{\bar{\lambda}_1 + c_i}\right)\right)^{2)} \quad (4\text{-}1')$$

and the endpoint of chain C is given by:

$$[C_n](t)_{\text{mod.}} = \frac{A_{31}e^{\bar{\lambda}_1 t}\, k_C \prod\limits_{i=1}^{n-1} c_i}{\sqrt{\bar{\lambda}_1^2 + \omega^2}\ \prod\limits_{i=1}^{n-1}\sqrt{(\bar{\lambda}_1 + c_i)^2 + \omega^2}}$$

$$\times \cos\left(\omega t + \varphi_3 + \sum_{i=1}^{n-1}\text{arctg}\left(-\frac{\omega}{\bar{\lambda}_1 + c_i}\right) + \text{arctg}\left(-\frac{\omega}{\bar{\lambda}_1}\right)\right)^{2)} \qquad \left.\vphantom{\begin{array}{c}a\\a\\a\\a\\a\\a\end{array}}\right\} \quad (4\text{-}1'')$$

Since in general $|\omega/\bar{\lambda}_1| \gg 1$, the modulated part of the concentration of particle C_n has a phase shift differing by $\sim -90°$ from its precursor C_{n-1}.

4.2. *Solution by matrix method.* Eqs. (2-6) show that the kinetic matrices of both the B and C sequence are lower triangular matrices. The kinetic eigenvalues are given directly by the diagonal elements. Furthermore, K^{BB} and K^{CC} may be analytically diagonalized and therefore the exponentials $\exp(K^{BB}t)$, $\exp(K^{CC}t)$ may be expressed in closed form according to Eq. (3-8).

For instance the exponential matrix $\exp(K^{CC}(t - t'))$ in Eq. (2-10) reads, for a chain with three steps

$$e^{K^{CC}(t-t')} = \begin{pmatrix} e^{-c_1(t-t')} & 0 & 0 \\[2mm] \dfrac{c_1}{-c_1 + c_2}\left(e^{-c_1(t-t')} - e^{-c_2(t-t')}\right) & e^{-c_2(t-t')} & 0 \\[3mm] \dfrac{-c_2 e^{-c_1(t-t')} + c_1 e^{-c_2(t-t')}}{-c_1 + c_2} + 1 & -e^{-c_2(t-t')} + 1 & 1 \end{pmatrix} \quad (4\text{-}2)$$

---

2)   The arctg function in these expressions has to be taken as follows in the neighbourhood of the point infinity:

$$\text{arctg}\,(\pm\infty) = -\frac{\pi}{2}$$

Hence, Eq. (2-10) may be exploited directly. For the explicit solutions of chain C with 3 steps, see appendix A.

5. Discussion. – The asymptotic solution of the kinetic equations will be discussed mainly from two points of view:

  i. accuracy of the asymptotic solutions

  ii. information obtainable from modulation spectroscopy experiments.

5.1. Accuracy of the solution. – *5.1.1. Limitations.* The use of the *matrizant* solution for the asymptotic behaviour may seem objectionable since it is usually only appropriate for short time behaviour. However, by the *ansatz* (3-4) the behaviour over a period is taken into account before the iteration step. We therefore consider its use as an asymptotic solution to be justified in essentially the same way as is usual in quantum mechanical treatments of time dependent perturbations of first order radiation processes [15].

Another important fact related to the eigenvalues of $\overline{K}$ should be mentioned. In the discussion it has been assumed so far that Eq. (3-16') holds. Although the second inequality therein will be fulfilled for experiments with classical light sources, an accidental degeneracy could occur, *viz.*

$$\lambda_2^0 = \lambda_3^0 \quad \text{or} \quad \overline{\lambda}_2 = \overline{\lambda}_3 \tag{5-1}$$

In this case the solution changes into a form with terms $t \cdot \exp(\overline{\lambda}_2 t)$ etc. [16]. Though such degeneracies might not appear frequently, they should be kept in mind.

The most important simplification is the neglect of higher iteration steps, *e.g.* terms with $(^1/_2 \, \Phi_0 w)^2$, $(^1/_2 \, c_0 w)^3$ ... which contain frequencies 0, ω, 2ω .... To investigate the convergence of the approximate solution of cycle A, terms with 0ω (with order 0 and 1st order in $^1/_2 \, \Phi_0 w$), 1ω (1st and 2nd order in $^1/_2 \, \Phi_0 w$) and 2ω (2nd order in $^1/_2 \, \Phi_0 w$) have been calculated numerically and compared with each other (see appendix B).

From these calculations one could derive some conditions which have all to be fulfilled if the asymptotic solution is to be correct to within a few percent:

$$t \gg \max \left(|\overline{\lambda}_2|^{-1}, \quad |\overline{\lambda}_3|^{-1}, \quad 2\pi\omega^{-1} \right) \tag{5-2}$$

$$0 \leqslant |\overline{\lambda}_1| \ll \min \left(|\overline{\lambda}_2|, \quad |\overline{\lambda}_3| \right) \tag{5-3}$$

$$\omega \gg |\overline{\lambda}_1| \tag{5-4}$$

and for practical applications

$$\Phi_0 w \leqslant 10 \text{ s}^{-1} \tag{5-5}$$

$$t \geqslant \max \left(10 \, |\overline{\lambda}_2|^{-1}, \quad 10 \, |\overline{\lambda}_3|^{-1}, \quad 20 \, \pi\omega^{-1} \right) \tag{5-6}$$

$$\omega \geqslant 20 \, \pi \, |\overline{\lambda}_1| \tag{5-7}$$

From Eq. (3-16) it is obvious that for $k_B = k_C = 0$, $\overline{\lambda}_1 = 0$. Furthermore, in this case $\lambda_1^{(i)} = 0$, $i = 1 \ldots \infty$ for all orders of approximation. Thereby Eqs. (5-4) and (5-7) become meaningless. It should be pointed out that Eq. (3-18) still holds for the

case where no irreversible photochemistry takes place, which can be shown by inserting $k_B = k_C = 0$ in Eqs. (2-4) and recalculating as in sect. 3. Furthermore, in this case it can be shown that by decreasing ω to zero, Eq. (3-18) is converted to the solution of the unmodulated system

$$\frac{d}{dt}(A(t)) = (K^{AA} + \Phi_0 w W^{AA})(A(t)) \tag{5-8}$$

(cf. Eq. (2-9')), that is, for $k_B = k_C = 0$, no lower limit exists for ω.

Provided all the inequalities (5-2) to (5-7) are valid, the solution (3-18) may now be simplified

$$
\begin{aligned}
[A_1](t) &\simeq [A_1](0)\, e^{\bar{\lambda}_1 t}\left\{1 + \frac{1}{2}\Phi_0 w\{a_1\,(k_3\,(k_{21} - k_2) + k_{23}k_{31})\,(k_2 k_3)^{-1}\sin\omega t\right.\\
&\quad - a_2(k_{21}(k_3 - k_2) + k_{23}k_{31})(k_2(k_3 - k_2))^{-1}\cdot\cos(\omega t + \text{arctg}(-\omega/(\bar{\lambda}_1 - \bar{\lambda}_2)))\\
&\quad \left. + a_3\,k_{23}k_{31}\,(k_3\,(k_3 - k_2))^{-1}\cos(\omega t + \text{arctg}(-\omega/(\bar{\lambda}_1 - \bar{\lambda}_3)))\}\right\}\\[2mm]
[A_2](t) &\simeq [A_1](0)\,\frac{1}{2}\Phi_0 w\, e^{\bar{\lambda}_1 t}\left\{k_2^{-1} + a_2\cos(\omega t + \text{arctg}(-\omega/(\bar{\lambda}_1 - \bar{\lambda}_2)))\right\}\\[2mm]
[A_3](t) &\simeq [A_1](0)\,\frac{1}{2}\Phi_0 w\, e^{\bar{\lambda}_1 t} k_{23}\left\{(k_2 k_3)^{-1} + (k_3 - k_2)^{-1}\right.\\
&\quad \left.\times\{a_2\cos(\omega t + \text{arctg}(-\omega/(\bar{\lambda}_1 - \bar{\lambda}_2))) - a_3\cos(\omega t + \text{arctg}(-\omega/(\bar{\lambda}_1 - \bar{\lambda}_3)))\}\right\}
\end{aligned}
\tag{5-9}
$$

with abbreviations a_1, a_2, a_3 the same as in Eq. (3-18). The three expressions for $[A_1](t)$, $[A_2](t)$ and $[A_3](t)$ in Eq. (5-9) contain those parts of the solution (3-18) which may now be observed experimentally by use of the modulation systems at present available.

5.1.2. Conservation of particle number. If in Fig. 1 $k_B = k_C = 0$ the particle number is conserved within cycle A, then according to Eq. (3-4) $\overline{K}$ becomes singular, hence $\bar{\lambda}_1 = 0$ (cf. Eq. (3-16)). Thus for $t \gg T = 2\pi/\omega$ all components of the populations A_1, A_2, A_3 (modulated and unmodulated) are constant in time.

The eigenvalue 0 of the matrices K^{BB} and K^{CC} expresses the fact that for $t \to \infty$ the total particle number $A_1(0)$ must be either in the state B_m or C_n. This may be verified for chains B and C with three steps from Eq. (A-3) (see appendix) which yields:

$$[B_3](\infty) = k_3\,k_B[A_1](0)\,(k_{23}\,k_C + k_3\,k_B)^{-1} + 0(\bar{\lambda}_2^{-1})$$

$$[C_3](\infty) = k_{23}\,k_C[A_1](0)\,(k_{23}\,k_C + k_3\,k_B)^{-1} + 0(\bar{\lambda}_2^{-1}) \tag{5-10}$$

As to be expected, the populations of the endpoints of the chains B and C for $t \to \infty$ depend on the kinetic constants of only the A cycle.

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5.2. Experimental information derivable from the asymptotic solutions. – 5.2.1. Relation to MES.-Experiments. The use of the solutions (3-18), (5-9), (4-1′) and (4-1″) may be classified according to two typical systems (Fig. 2) [6]

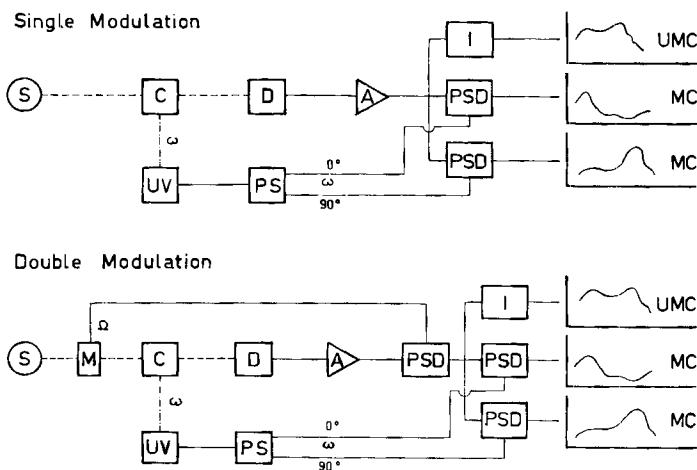 i. single modulation experiments

  ii. double modulation experiments.

Fig. 2. *Schemes for Modulation Spectroscopy*

S: source for analysing radiation, M: modulator with frequency Ω for the analysing radiation, UV.: UV.-light modulated with frequency ω, C: cell with reaction under examination, D: Detector, A: Amplifier, dc- or ac-coupled, PS: phase splitter, PSD: phase sensitive detector with reference frequency ω or Ω, I: Integrator, MC: signal originating from the modulated components of particle concentrations, UMC: signal excluding modulated components of particle concentrations.

In these types, the signal $S(t, \nu)$ observed is either proportional to the modulated concentrations, *i.e.*

$$S(t, \nu) \; \propto \; \sum_m \varepsilon_m(\nu) \; c_m(t) = \tilde{\varepsilon}(\nu) \; c(t)\,^3) \tag{5-11}$$

or is proportional to the exponential of the concentrations (modulated and unmodulated)

$$S(t, \nu) \; \propto \; \exp\{- L\sum_m \varepsilon_m(\nu) \; c_m(t)\} = \exp\{- L\, \tilde{\varepsilon}(\nu) \; c(t)\}\,^3) \tag{5-12}$$

where

$\varepsilon_m(\nu)$ = molar extinction coefficient of particle m at spectrometer setting ν
$c_m(t)$ = instantaneous particle concentration of particle m
L = thickness of absorption cell

Eq. (5-11) relates to situations often encountered in ESR., NMR. and MW. spectroscopy (weak absorption), whereas the second case (5-12) is realised in the *Lambert-Beer* type, *e.g.* optical experiments such as MEUV.- and MEIR.-spectroscopy. For the latter type the expression (5-12) may be simplified, by taking into account the fact that the modulated components of the instantaneous concentrations

---

[3]   For the sake of simplicity we denote the vector $(\tilde{A}(t), \tilde{B}(t), \tilde{C}(t))$ by $\tilde{c}(t)$, *cf.* Eq. (2-2″).

of all reacting particles fulfil the inequality

$$L \,\tilde{\varepsilon}(\nu) \; c''(t) < 0.2 \tag{5-13}$$

Hence, in this case

$$S(t, \nu) \;\propto\; \exp\{-L \,\tilde{\varepsilon}(\nu) \; c'(t)\} \, (1 - L \,\tilde{\varepsilon}(\nu) \; c''(t)) + 0 \, ((L \,\tilde{\varepsilon}(\nu) \; c''(t))^2) \tag{5-14}$$

where $L \,\tilde{\varepsilon}(\nu) \; c''(t)$ contains all the modulated and $L \,\tilde{\varepsilon}(\nu) \; c'(t)$ all the unmodulated components of the particle concentrations.

Information about the modulated and unmodulated components of particle concentrations may be obtained directly by using appropriate phase-sensitive detector systems, *e.g.* single and double modulation for (5-11) and double modulation for (5-12).

5.2.2. Information derivable from amplitude and phase measurements. We restrict ourselves to weak pump experiments and situations where all the inequalities (5-2) to (5-7) hold.

i) *Smallest eigenvalue* $\bar{\lambda}_1$. Since the vector of the modulated concentrations is proportional to $\exp(\bar{\lambda}_1 t)$, the eigenvalue $\bar{\lambda}_1$ may be obtained directly from the modulated signal component at any fixed spectrometer-setting ν, where at least one occurring particle absorbs.

ii) *Reaction rate constants of the kinetic system.*

a) Spectra of occurring particles are non-overlapping:

If at distinct spectrometer settings ν_1, ν_2, ... only distinct particles contribute to the modulated signal component and the latter is measured as a function of the modulation frequency ω at these settings ν_1, ν_2, ..., then sufficient data is obtained for calculation of the reaction rate constants. This is achieved using the explicit solutions (5-9), (4-1') and (4-1'') and performing a nonlinear regression. Considering
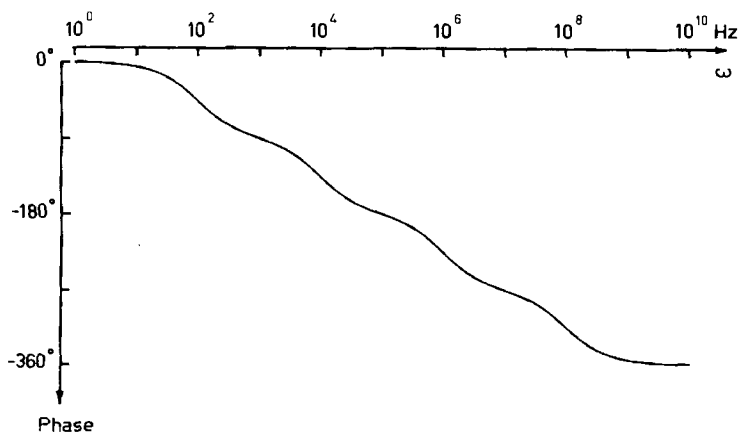

Fig. 3. *Phase of the modulated component of the particle concentration* $[B_3](t)$ *as a function of the modulation frequency* ω *(chain B with arbitrary length)*.

Calculated (according to Eq. (4-1')) for a system with the parameters:

$\varphi_3 = \mathrm{arctg}\,(-\omega/(-\bar{\lambda}_2 + \bar{\lambda}_1))$

$\bar{\lambda}_1 = -10^{-3}\ \mathrm{s}^{-1},\ b_1 = 10^2\ \mathrm{s}^{-1},\ b_3 = 10^6\ \mathrm{s}^{-1}$

$\bar{\lambda}_2 = -10^8\ \mathrm{s}^{-1},\ b_2 = 10^4\ \mathrm{s}^{-1}$

only the chains B and C, the monotonic increase in phase (along the chain) of the modulated component of particle concentrations gives information about the structure of the kinetic graph. If the phase of the modulated component of the particle concentration $[B_j](t)$ (according to Eq. 4-1') is plotted against ω, the number of vertical inflexion points directly yields information about the rate constants and the position of the particle B_j in the sequence (see Fig. 3).

b) Spectra of occurring particles are overlapping: In this case the analysis of the modulated signal component as a function of the excitation frequency ω is more complicated. Here again nonlinear regression is needed using Eqs. (5-9), (4-1') and (4-1''), but many more spectrometer settings ν_1, ν_2, ... and a detailed line shape analysis of the overlapping spectra are required. Derivation of kinetic data in this case requires extended numerical analysis by specific computer programmes and these are being developed in our laboratory.

c) By variation of the photon flux Φ_0, additional information about the kinetic behaviour of each species may be derived. This follows from the fact that $\bar{\lambda}_1$ is proportional to Φ_0 for low values of Φ_0.

Appendix

A. Solution of the kinetic equations of the reaction sequences B and C. The solutions of Eqs. (2-9'') and (2-9''') may be obtained either from a step by step integration (direct substitution) or by a matrix technique (cf. sect. 4). The solutions for chain B or C are completely analogous.

1. Direct substitution. Inserting the cycle A solution in the abbreviated form (3-19) of either (3-18) or (5-9) in (2-9''') one obtains by straightforward algebraic manipulation the solution given below for a chain C with three steps.

$$
\begin{aligned}
[C_1](t) =\ & k_C\, A_{30}\, (e^{\bar{\lambda}_1 t} - e^{-c_1 t})\, (\bar{\lambda}_1 + c_1)^{-1} \\
& + k_C\, A_{31}\, A(c_1)\, \left\{ e^{\bar{\lambda}_1 t} \cos(\omega t + \varphi_3 + \chi_1) - e^{-c_1 t} \cos(\varphi_3 + \chi_1) \right\} \\[4pt]
[C_2](t) =\ & c_1\, k_C\, A_{30}\, \left\{ e^{\bar{\lambda}_1 t}\,((\bar{\lambda}_1 + c_1)\,(\bar{\lambda}_1 + c_2))^{-1} - e^{-c_1 t}\,((\bar{\lambda}_1 + c_1)\,(-c_1 + c_2))^{-1} \right. \\
& \left. + e^{-c_2 t}\,((\bar{\lambda}_1 + c_2)\,(-c_1 + c_2))^{-1} \right\} \\
& + c_1\, k_C\, A_{31}\, A(c_1)\, \left\{ e^{\bar{\lambda}_1 t}\, A(c_2)\, \cos(\omega t + \varphi_3 + \chi_1 + \chi_2) - e^{c_1 t}\,(-c_1 + c_2)^{-1} \cos(\varphi_3 + \chi_1) \right. \\
& \left. + e^{-c_2 t}\{ -A(c_2)\cos(\varphi_3 + \chi_1 + \chi_2) + (-c_1 + c_2)^{-1}\cos(\varphi_3 + \chi_1) \} \right\} \\[4pt]
[C_3](t) =\ & c_1\, c_2\, k_C\, A_{30}\, \left\{ (e^{\bar{\lambda}_1 t} - 1)\,(\bar{\lambda}_1\,(\bar{\lambda}_1 + c_1)\,(\bar{\lambda}_1 + c_2))^{-1} \right. \\
& + (e^{-c_1 t} - 1)\,(c_1\,(\bar{\lambda}_1 + c_1)\,(-c_1 + c_2))^{-1} \\
& \left. - (e^{-c_2 t} - 1)\,(c_2\,(\bar{\lambda}_1 + c_2)\,(-c_1 + c_2))^{-1} \right\} \\
& + c_1\, c_2\, k_C\, A_{31}\, A(c_1)\, \left\{ A(c_2)\, A(c_3)\, \{ e^{\bar{\lambda}_1 t} \cos(\omega t + \varphi_3 + \chi_1 + \chi_2 + \chi_3) \right. \\
& - \cos(\varphi_3 + \chi_1 + \chi_2 + \chi_3) \} \\
& + (e^{-c_1 t} - 1)\,(c_1\,(-c_1 + c_2))^{-1}\cos(\varphi_3 + \chi_1) \\
& + (e^{-c_2 t} - 1)\,\{ A(c_2)\, c^{-1}\cos(\varphi_3 + \chi_1 + \chi_2) \\
& \left. - (c_2\,(-c_1 + c_2))^{-1}\cos(\varphi_3 + \chi_1) \} \right\}
\end{aligned}
\qquad\text{(A-1)}
$$

where

$$A(c_i) = ((\bar{\lambda}_1 + c_i)^2 + \omega^2)^{-1/2}, \quad \chi_i = \text{arctg}\,(-\omega/(\bar{\lambda}_1 + c_i))^2) \tag{A-2}$$

$$i = 1, 2, 3, \quad c_3 = 0$$

2. Matrix method. By using standard matrix algebra technique for functions of triangular matrices Eq. (4-2) is obtained. If combined with the cycle A solution (3-19) Eq. (2-9''') may be solved in a straightforward manner, yielding the following expression (notation as in Eqs. A-2).

$$
\begin{aligned}
[C_1](t) &= k_C\, A_{30}\, (e^{\bar{\lambda}_1 t} - e^{-c_1 t})\,(\bar{\lambda}_1 + c_1)^{-1} \\
&\quad + k_C\, A_{31}\, A(c_1)\,\{e^{\bar{\lambda}_1 t}\cos(\omega t + \varphi_3 + \chi_1) - e^{-c_1 t}\cos(\varphi_3 + \chi_1)\} \\[4pt]
[C_2](t) &= c_1\, k_C\, A_{30}\,\{e^{\bar{\lambda}_1 t}\,((\bar{\lambda}_1 + c_1)\,(\bar{\lambda}_1 + c_2))^{-1} - e^{-c_1 t}\,((\bar{\lambda}_1 + c_1)\,(-c_1 + c_2))^{-1} \\
&\qquad\qquad + e^{-c_2 t}\,((\bar{\lambda}_1 + c_2)\,(-c_1 + c_2))^{-1}\} \\
&\quad + c_1\, k_C\, A_{31}\,(-c_1 + c_2)^{-1}\{e^{\bar{\lambda}_1 t}\{A(c_1)\cos(\omega t + \varphi_3 + \chi_1) - A(c_2)\cos(\omega t + \varphi_3 + \chi_2)\} \\
&\qquad\qquad - e^{-c_1 t}\, A(c_1)\cos(\varphi_3 + \chi_1) + e^{-c_2 t} A(c_2)\cos(\varphi_3 + \chi_2)\} \\[4pt]
[C_3](t) &= c_1\, c_2\, k_C\, A_{30}\,\{e^{\lambda_1 t}\,(\bar{\lambda}_1\,(\bar{\lambda}_1 + c_1)\,(\bar{\lambda}_1 + c_2))^{-1} + e^{-c_1 t}\,(c_1\,(\bar{\lambda}_1 + c_1)\,(-c_1 + c_2))^{-1} \\
&\qquad\qquad - e^{-c_2 t}\,(c_2\,(\bar{\lambda}_1 + c_2)\,(-c_1 + c_2))^{-1} - (\lambda_1\, c_1\, c_2)^{-1}\} \\
&\quad + c_1\, c_2\, k_C\, A_{31}\,\{e^{\bar{\lambda}_1 t}\{-A(c_1)\,(c_1\,(-c_1 + c_2))^{-1}\cos(\omega t + \varphi_3 + \chi_1) \\
&\qquad\qquad + A(c_2)\,(c_2\,(-c_1 + c_2))^{-1}\cos(\omega t + \varphi_3 + \chi_2) \\
&\qquad\qquad + A(c_3)\,(c_1\, c_2)^{-1}\cos(\omega t + \varphi_3 + \chi_3)\} \\
&\qquad + e^{-c_1 t}\, A(c_1)\,(c_1\,(-c_1 + c_2))^{-1}\cos(\varphi_3 + \chi_1) \\
&\qquad - e^{-c_2 t}\, A(c_2)\,(c_2\,(-c_1 + c_2))^{-1}\cos(\varphi_3 + \chi_2) \\
&\qquad - A(c_3)\,(c_1\, c_2)^{-1}\cos(\varphi_3 + \chi_3)\}\}^2)
\end{aligned}
\tag{A-3}
$$

3. Interrelation of the two forms of integrals in the sequences B and C. Comparison of the two sets of equations (A-2) and (A-3) reveals that the solutions of the kinetic equations of the sequences B and C appear in quite a different form, though they must represent identical functions.

The form obtained by direct substitution, (A-2), has the definite advantage that the modulated component of each particle concentration in the sequence is expressed as a product of an amplitude and a phase function (see Eq. 4-1). Thereby it is directly related to the signals observed by phase sensitive detection.

In solution (A-3), the modulated component is divided into a set of harmonic oscillations with different amplitude and phase functions, thereby showing the origin of the contributions to the modulated component.

Thus each of the two forms of solution has its merits. They may be transformed into each other by continuous application of elementary trigonometric relations of the type

$$a\cos(\omega t) + b\sin(\omega t) = \sqrt{a^2 + b^2}\,\cos(\omega t + \varphi) \tag{A-4}$$

However the transformation is quite laborious and so will not be reproduced here.

B. Numerical Calculation of Higher Iteration Terms of Eq. (3-17). For the calculation of terms of first order in $1/_2\, \Phi_0 w$ only the transformation matrices $T^{(0)}$ and $T^{(0)-1}$ have been used (Eq. (3-17)). Since T and T^{-1} are given by Eqs. (3-11) to (3-13''') up to first order in $1/_2\, \Phi_0 w$, the calculation of the modulated terms up to 2nd order containing the matrices Y and Z is straightforward, though rather tedious. Further contributions to the modulated 2nd order term result from the second iterated integral in the *matrizant* solution (Eq. 3-7). The integrals which contribute to the modulated components of 2nd order in $1/_2\, \Phi_0 w$ become

$$+ \left(\frac{1}{2}\Phi_0 w\right)^2 T^{(0)} \left\{ e^{\bar{A}t} \int_0^t \cos\omega t'\, e^{-\bar{A}t'}\, Y[Z, e^{\bar{A}t'}]\, dt' \right.$$

$$+ e^{\bar{A}t} \int_0^t \cos\omega t'\, [Z, e^{-\bar{A}t'}]\, Y e^{\bar{A}t'}\, dt'$$

$$+ [Z, e^{\bar{A}t}] \int_0^t \cos\omega t'\, e^{-\bar{A}t'}\, Y e^{\bar{A}t'}\, dt'$$

$$\left. + e^{\bar{A}t} \int_0^t \cos\omega t'\, e^{-\bar{A}t'}\, Y e^{\bar{A}t'} \int_0^{t'} \cos\omega t''\, e^{-\bar{A}t''}\, Y e^{\bar{A}t''} dt''\, dt' \right\} T^{(0)-1} \cdot (A(0)) \qquad \text{(B-1)}$$

Table. *Numerical values of the iterative solution Eq. (3-18) and its higher order terms* [a])

$\omega = 6.283 \times 10^1$ Hz	Amplitudes and phases of components with frequency [b])			
Particle	0ω (zero + 1st)	1ω (1st)	1ω (2nd)	2ω (2nd)
A_1	7.786×10^{-1}	1.637×10^{-3} -212.7	4.018×10^{-6} -34.6	1.268×10^{-6} -84.3
A_2	1.951×10^{-9}	1.951×10^{-9} -1.8×10^{-5}	8.519×10^{-12} -195.1	2.047×10^{-12} -212.7
A_3	1.932×10^{-3}	1.637×10^{-3} -31.8	4.014×10^{-6} -212.7	1.268×10^{-6} -263.9
$\omega = 6.283 \times 10^3$ Hz				
A_1	7.786×10^{-1}	3.105×10^{-5} -269.1	7.610×10^{-8} -89.1	3.088×10^{-10} -178.6
A_2	1.951×10^{-9}	1.951×10^{-9} -1.8×10^{-3}	4.784×10^{-12} -180.9	3.881×10^{-14} -269.1
A_3	1.932×10^{-3}	3.105×10^{-5} -89.1	7.610×10^{-8} -269.1	3.088×10^{-10} $+13.7$
$\omega = 6.283 \times 10^5$ Hz				
A_1	7.786×10^{-1}	3.105×10^{-7} -269.8	7.611×10^{-10} -89.8	3.089×10^{-14} -179.4
A_2	1.951×10^{-9}	1.951×10^{-9} -1.8×10^{-1}	4.782×10^{-12} -180.2	3.882×10^{-16} $+89.8$
A_3	1.932×10^{-3}	3.105×10^{-7} -90.2	7.611×10^{-10} $+89.8$	3.089×10^{-14} -1.7×10^{-1}

[a]) Calculated for a system with the parameters
$w\Phi_0 = 1$ s^{-1}, $k_{21} = k_{23} = 10^8$ s^{-1}, $k_{31} = 10^2$ s^{-1}, $k_B = 10^3$ s^{-1}, $k_C = 1$ s^{-1}, $t = 100$ s, $A_1(0) = 1$ Mol/l
resulting eigenvalues:
$\bar{\lambda}_1 = -2.478 \times 10^{-3}$ s^{-1}, $\bar{\lambda}_2 = -2.000 \times 10^8$ s^{-1}, $\bar{\lambda}_3 = -1.012 \times 10^2$ s^{-1}

[b]) 1ω (1st) means: component with frequency ω and first order in $1/2\,\Phi_0 w$ etc. The amplitude and phase pairs read:
$1.637 \times 10^{-3}/-212.7 \triangleq 1.637 \times 10^{-3} \cos(\omega t - 212.7°)$ Mol/l

In the table, three typical numerical examples are given for the sake of comparison. The data clearly show that the terms of 2nd order in $^1/_2\,\varPhi_0\mathrm{w}$ with frequency ω and 2ω are several orders of magnitude below the fundamental components (1st order in $^1/_2\,\varPhi_0\mathrm{w}$ with frequency ω).

REFERENCES

[1] *R. M. Hexter*, J. opt. Soc. *53*, 703 (1962).

[2] *H. Labhart*, Helv. *47*, 2279 (1964).

[3] *J. B. Birks* & *I. H. Munro*, Progress in Reaction Kinetics, Vol. 4, ed. *G. Porter* (Pergamon Press, Oxford, 1967), p. 239.

[4] *H. E. Hunziker*, Chem. Phys. Letters *3*, 504 (1969); *C. S. Burton* & *H. E. Hunziker*, J. Chem. Physics *52*, 3320 (1970); *idem*, Chem. Phys. Letters *6*, 352 (1970); *H. E. Hunziker*, IBM J. of Res. and Develop. *15*, 1 (1971).

[5] *H. S. Johnston, G. E. McGraw, T. T. Pankert, L. W. Richards* & *J. van den Bogaerde*, Proc. Nat. Acad. Sci. U.S. *57*, 1146 (1967).

[6] *U. P. Fringeli* & *Hs. H. Günthard*, Appl. Optics *10*, 819 (1971).

[7] *U. P. Fringeli*, Thesis Nr. 4366, ETH Zürich (1969).

[8] *U. P. Fringeli, M. Forster* & *Hs. H. Günthard*, to be published.

[9] *R. Bellmann*, Introduction to Matrix Analysis (Mc Graw Hill, New York, 1960), p. 163.

[10] *R. Bellmann, loc. cit.* p. 202; *E. L. Ince*, Ordinary Differential Equations (Dover Publications, New York, 1956), pp. 175, 381; *W. I. Smirnow*, Lehrgang der Höheren Mathematik (VEB. Deutscher Verlag der Wissenschaften, Berlin, 1963), Vol. 3, *2*, p. 369.

[11] *W. Magnus*, Commun. on Pure and Appl. Mathematics 7, 649 (1954); *G. H. Weiss* & *A. A. Marudin*, J. Math. Phys. *3*, 771 (1962).

[12] *E. L. Ince, loc. cit.*, p. 408; *R. A. Frazer, W. J. Duncan* & *A. R. Collar*, Elementary Matrices (Cambridge, The University Press, 1952), p. 217, 327.

[13] *R. Bellmann, loc. cit.*, p. 187.

[14] *K. Kumar*, Perturbation Theory (North Holland Publishing Co., Amsterdam, 1962), p. 12.

[15] *W. Heitler*, The Quantum Theory of Radiation (Oxford University Press, 2nd Edition, 1944).

[16] *R. Bellmann, loc. cit.*, p. 192.

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31. Methode zur Konstitutionsaufklärung von Celluloseforꞥalen von niedrigem Substitutionsgrad

29. Mitteilung über textilchemische Untersuchungen[1])

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Summary. A method is described which allows the determination of the hydroxyl group(s) in glucose units of cellulose which react with formaldehyde at low degrees of substitution (0.2 to 1.5% CH_2O on cellulose). It consists of permethylation of the cellulose by a sequence of two methylations with dimethylsulfate and NaOH (without solvent) followed by 2 exchange methylations with methyl iodide and sodium *n*-butoxide and further steps described earlier [2]. The results demonstrate that the use of the new permethylation method leads to a loss of material of less than 5%.

1. Einleitung. – Die Umsetzung von Cellulose mit Formaldehyd unter Bildung von Celluloseformalen hat für die Entwicklung pflegeleichter Baumwolltextilien eine grosse technische Bedeutung [3].

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[1])   28. Mitteilung vgl. *A. Mohn, H. K. Rouette* & *H. Zollinger* [1].