Analysis of Spin Polarisation Transients in Periodically Photo-excited Triplet States

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The behaviour of spin sublevel populations with time following periodic photo-excitation is examined. The treatment is limited to conditions of magnetic field strength and temperature for which the spin lattice relaxation rates dominate the individual spin sublevel decay rates.

The response of the system to three modes of excitation is considered: (i) continuous excitation using a time-independent intensity (ii) periodic rectangular pulse excitation and (iii) periodic waveform excitation.

A convenient correspondence between the various forms of solutions is pointed out. The requirements of an experiment to determine spin-lattice relaxation rates in organic triplets at 77 K are discussed.

1. Introduction

In recent years several groups have studied photo-excited triplet states at low temperatures ($\leqq 4.2$ K) by high field [1] and zero field [2,3] magnetic resonance techniques, in order to determine the individual sublevel photo-kinetics. These methods take advantage of the fact that at low temperatures spin-lattice relaxation ceases to dominate the control of population differences.

In 1971 Levanon and Weissman [4] reported the study of transient ESR in high field at ca. 77 K following pulsed and modulated photo-excitation. This and subsequent studies [5,6] demonstrated that the pulse timing or modulation frequency of the excitation source could be chosen such that a transient departure from Boltzmann equilibrium in the triplet sublevels was observed. Potentially, all the photo-kinetic and spin-lattice information is contained in the results of such experiments. Clearly, an analysis enabling the relevant kinetic constants to be extracted from the experimental results is much needed. At the time of starting this work such an analysis had not been reported; recently, however, Levanon and Vega [7] have presented one. These workers adopt a simplified model of the spin lattice relaxation (SLR) where the SLR constants between each pair of triplet sublevels are assumed to be equal. The treatment presented in this communication is based on a more flexible assumption and in many respects, as will be discussed more fully in the conclusion, complements that of Levanon and Vega. A subsequent presentation [8] will describe the implementation of this analysis to a series of molecular triplet states; the purpose here is to provide manageable analytical expressions for such experiments.

The following treatment reveals a means of determining SLR constants in triplets at ca. 77 K in high field together with the relative intersystem crossing rates and absolute decay rates of the individual magnetic sublevels. With regard to the latter quantities the method is the high field, high temperature ESR alternative to ODMR [2,3] in zero field.

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2. Preliminary Considerations

Consider the basic photo-kinetic processes in the system represented by Fig. 1, where the photo-excitation is time dependent. This excitation intensity, which might be of wide spectral range, will excite

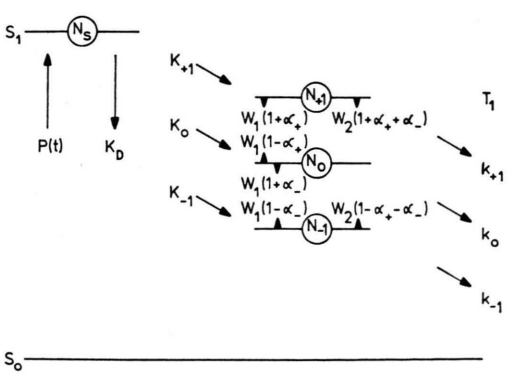

Fig. 1. The kinetic model in high field.

the first and higher excited singlet states in a variety of vibronic levels. The required electronic and vibronic relaxation which occurs before the operative low-lying levels of S_1 (represented by the single level of the diagram) are reached, are assumed to take place in characteristic times ($<10^{-12}$ sec) much shorter than any other represented in the diagram. The rate, $P(t)$, at which photons are absorbed to produce such first excited singlet states will be directly proportional to the time dependent excitation intensity, provided a saturation condition is not reached.

Singlet states thus prepared can then either intersystem cross with rates K_{+1}, K_0, K_{-1} into the respective magnetic sublevels of the first excited triplet state, or can decay directly through radiative and non-radiative processes back to S_0 with a rate K_D.

Within the triplet sublevel manifold spin-lattice relaxation can occur. Between sublevels for which $\Delta m_s = 1$ the rates (W_1) are taken to be equal, but different from that (W_2) between levels for which $\Delta m_s = 2$. In general it has previously been assumed [9] that $W_1 \gg W_2$, although this condition is not rigorously demanded by the following treatment. The characteristic Boltzmann operation of the spin-lattice process, for example between the $|+1\rangle$ and $|0\rangle$ sublevels, is accomodated by representing the up-going rate as $(1-\alpha_+)W_1$ and the down-going rate as $(1+\alpha_+)W_1$. Here:

$$\exp\{-\Delta E(+1,0)/k_B T\} \approx \frac{1-\alpha_+}{1+\alpha_+}$$

i.e. $\alpha_+ \approx \Delta E(+1,0)/(2k_B T)$ when $E \ll k_B T$. Similarly, for the $|0\rangle$, $|-1\rangle$ levels $\alpha_- \approx \Delta E(0,-1)/(2k_B T)$.

The triplet sublevels can decay back to the ground state singlet, S_0, through radiative and non-radiative processes with individual rates k_{+1}, k_0 and k_{-1}. The populations of S_1 and T_1 are denoted by N_s and N_{+1}, N_0 and N_{-1} respectively.

Clearly, in the high field limit, simplification may result [8]. When D, $E \ll g\mu_B H$ then: $K_{+1} \approx K_{-1}$ and $k_{+1} \approx k_{-1}$. To retain the generality of the treatment, the approximations are not adopted at this stage, but are discussed more fully later.

In the following sections use will be made of vector and matrix notation, where

$$\boldsymbol{N} = \begin{pmatrix} N_{+1} \\ N_0 \\ N_{-1} \end{pmatrix} \text{ and } \boldsymbol{K} = \begin{pmatrix} K_{+1} \\ K_0 \\ K_{-1} \end{pmatrix}. \quad (1)$$

The behaviour of the sublevel populations is then conveniently described by the time-differential equation:

$$\dot{\boldsymbol{N}} = -\mathbf{R}\cdot\boldsymbol{N} + N_s\boldsymbol{K} \quad (2)$$

where the matrix

$$\mathbf{R} = \begin{pmatrix} k_{+1} + (1+\alpha_+)W_1 + (1+\alpha_+ + \alpha_-)W_2 & -(1-\alpha_+)W_1 & -(1-\alpha_+ - \alpha_-)W_2 \\ -(1+\alpha_+)W_1 & k_0 + (2-\alpha_+ + \alpha_-)W_1 & -(1-\alpha_-)W_1 \\ -(1+\alpha_+ + \alpha_-)W_1 & -(1+\alpha_+)W_1 & k_{-1} + (1-\alpha_-)W_1 + (1-\alpha_+ - \alpha_-)W_2 \end{pmatrix} \quad (3)$$

The solution of this equation is considered under various excitation possibilities discussed in the following section.

Three further abbreviations are used in the following sections:

$$\begin{aligned} K_s &= K_D + K_{+1} + K_0 + K_{-1} = K_D + 3K_{av}, \\ K_{av} &= \tfrac{1}{3}(K_{+1} + K_0 + K_{-1}) = \tfrac{1}{3}(K_x + K_y + K_z), \\ k_{av} &= \tfrac{1}{3}(k_{+1} + k_0 + k_{-1}) = \tfrac{1}{3}(k_x + k_y + k_z). \end{aligned} \quad (4)$$

3. Method of Approach

The system described in Fig. 1 is examined with a view to obtaining solutions of immediate practical application. The most likely experimental conditions will be either periodic rectangular-pulse excitation of variable duration and separation (laser or flash excitation followed by the ESR detection of the transient spin polarization within one cycle), or modulated excitation by a periodic waveform (mechanically or electro-optically modulated excitation from a continuous source followed by phase sensitive ESR detection of a particular harmonic of the spin polarization). At this level, the approach to cover both these cases is developed in terms of three distinct situations:

1. Continuous time-independent excitation.
2. Periodic rectangular pulse excitation.
3. Periodic waveform excitation.

It is shown how the solutions of all three situations are related and how the ultimate solution resolves to the determination of one transformation. The various situations are considered in order.

3.1. Continuous Time Independent Excitation

The trivial case is that which is time independent. Here $P(t) = P_0$ and the steady state approximation about the S_1 level yields

$$N_s = P_0/K_s . \tag{5}$$

Substitution in Eq. (2) and application of the steady state approximation to the three sublevels gives

$$\mathbf{R}\cdot\mathbf{N} = (P_0/K_s)\cdot\mathbf{K} \tag{6}$$

with the solution:

$$\boldsymbol{N} = (P_0/K_s)\mathbf{S}\cdot\begin{pmatrix} 1/\varrho_1 & & \\ & 1/\varrho_2 & \\ & & 1/\varrho_3 \end{pmatrix}\cdot\mathbf{S}^{-1}\cdot\boldsymbol{K} \tag{7}$$

where

$$\mathbf{S}^{-1}\cdot\mathbf{R}\cdot\mathbf{S} = \begin{pmatrix} \varrho_1 & & \\ & \varrho_2 & \\ & & \varrho_3 \end{pmatrix}. \tag{8}$$

$\mathbf{S}^{-1}$, $\mathbf{S}$ transforms $\mathbf{R}$ to the diagonal form with latent roots ϱ_1, ϱ_2, ϱ_3. This transformation recurs in subsequent sections and it is noted here that $\mathbf{S}^{-1}\cdot\mathbf{S} = \mathbf{S}\cdot\mathbf{S}^{-1} = \mathbf{1}$ but since $\mathbf{R}$ is not symmetric $(\mathbf{S}^{-1})^{\dagger} \neq \mathbf{S}$.

3.2. Pulse Excitation

Here, the behaviour of the populations is examined when a multiple pulse, as shown in Fig. 2, is used to photo-excite. Two regions of time within one complete cycle are defined: region I is of duration T_1 where $t = 0$ is defined by the "on" edge of the pulse, region II is of duration T_2 and $t = 0$ is defined by the "off" edge of the pulse. In both regions N_s is independent of time[16]. It may be readily shown that the solution of Eq. (2) in regions where N_s is constant, but in which the steady state has not necessarily been reached, is:

$$\boldsymbol{N}(t) = \mathbf{S}\cdot\begin{pmatrix} e^{-\varrho_1 t} & & \\ & \ddots & \\ & & \ddots \end{pmatrix}\cdot\mathbf{S}^{-1}\cdot\boldsymbol{N}(0) + N_s\mathbf{S}\begin{pmatrix} \dfrac{1-e^{-\varrho_1 t}}{\varrho_1} & & \\ & \ddots & \\ & & \ddots \end{pmatrix}\cdot\mathbf{S}^{-1}\boldsymbol{K}. \tag{9}$$

Within a continuous sequence of pulses it is required that the starting conditions for each region are:

Region I $(0 \leqq t \leqq T_1)\, \boldsymbol{N}^{\mathrm{I}}(0) = \boldsymbol{N}^{\mathrm{II}}(T_2), N_s = P_0/K_s$,
Region II $(0 \leqq t \leqq T_2)\, \boldsymbol{N}^{\mathrm{II}}(0) = \boldsymbol{N}^{\mathrm{I}}(T_1), N_s = 0$.

Using Eq. (9) to express $\boldsymbol{N}(t)$ at $t = T_1$ in region I and $t = T_2$ in region II two simultaneous equations are obtained from which $\boldsymbol{N}^{\mathrm{I}}(T_1)$, $\boldsymbol{N}^{\mathrm{II}}(T_2)$ are determined. They take the form:

$$\boldsymbol{N}(T) = \frac{P_0}{K_s}\mathbf{S}\begin{pmatrix} h_1 & & \\ & h_2 & \\ & & h_3 \end{pmatrix}\mathbf{S}^{-1}\boldsymbol{K}$$

where for

$$\boldsymbol{N}^{\mathrm{I}}(T_1): \quad h_i = \frac{1}{\varrho_i}\left(\frac{1-\exp\{-\varrho_i T_1\}}{1-\exp\{-\varrho_i(T_1+T_2)\}}\right),$$

and for

$$\boldsymbol{N}^{\mathrm{II}}(T_2): \quad h_i = \frac{\exp\{-\varrho_i T_2\}}{\varrho_i}\left(\frac{1-\exp\{-\varrho_i T_1\}}{1-\exp\{-\varrho_i(T_1+T_2)\}}\right) \tag{10}$$

Substituting back in Eq. (9) for the $\boldsymbol{N}(0)$, N_s appropriate to the region I or II, as required, the time dependent populations take the form

$$\boldsymbol{N}(t) = \frac{P_0}{K_s}\begin{pmatrix} f_1 & & \\ & f_2 & \\ & & f_3 \end{pmatrix}\mathbf{S}^{-1}\boldsymbol{K}$$

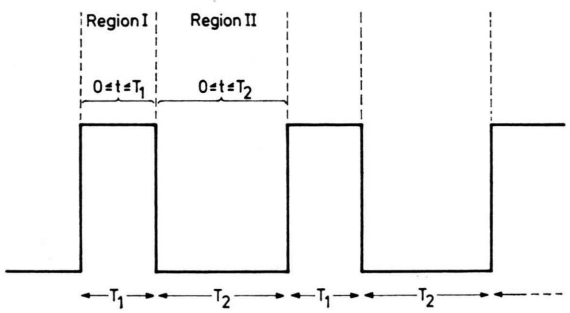

Fig. 2. The time regions in the rectangular pulse experiment.

where for region I

$$(0 \leqq t \leqq T_1)\quad f_i = \frac{1}{\varrho_i}\left\{1-\exp\{-\varrho_i t\}\left(\frac{1-\exp\{-\varrho_i T_1\}}{1-\exp\{-\varrho_i(T_1+T_2)\}}\right)\right\}$$

and for region II

$$(0 \leqq t \leqq T_2)\quad f_i = \frac{1}{\varrho_i}\left\{\exp\{-\varrho_i t\}\left(\frac{1-\exp\{-\varrho_i T_1\}}{1-\exp\{-\varrho_i(T_1+T_2)\}}\right)\right\}. \tag{11}$$

Whilst these equations look rather unwieldy, they are perfectly general for *any* T_1, T_2 [16]. Two useful limiting cases are mentioned at this stage.

(i) Long pulse – long recovery.

$$T_1, T_2 \gg \frac{1}{\varrho_1}, \frac{1}{\varrho_2}, \frac{1}{\varrho_3}$$

Region I $$f_i \approx \frac{1}{\varrho_i}\left(1-\exp\{-\varrho_i t\}\right),$$

Region II $$f_i \approx \frac{1}{\varrho_i}\cdot\exp\{-\varrho_i t\}. \qquad (12)$$

This is the case appropriate to the experiments of Levanon and co-workers [5, 6].

(ii) Short pulse – medium recovery.

$$T_1 \ll T_2 < \frac{1}{\varrho_1}, \frac{1}{\varrho_2}, \frac{1}{\varrho_3}$$

Region I $$f_i \approx \frac{1}{\varrho_i} - \frac{T_1}{1-\exp\{-\varrho_i T_2\}},$$

Region II $$f_i \approx T_1 \cdot \frac{\exp\{-\varrho_i t\}}{1-\exp\{-\varrho_i T_2\}}. \qquad (13)$$

This case describes the δ-pulse limit. T_1 is so short that in region I $\mathbf{N}$ may be considered constant.

3.3. *Periodic Waveform Excitation*

When conditions of the periodic pulse do not apply, that is when the excitation cycle cannot be divided into regions of N_s = constant, a different approach is adopted.

Any physical variable $A(t)$ which is a periodic function of time may be expressed as the real part of a Fourier expansion in the complex exponential form

$$A(t) = \mathrm{Re}\left\{\sum_{n=0}^{\infty} A_n e^{in\omega t}\right\} \qquad (14)$$

where the A_n are complex constants. The excitation may be expressed in this form and time dependent solutions for the various populations of the system having the same form may be sought. It is convenient to consider the problem in the complex domain, extracting the real parts of the solutions as the final step. Furthermore, it is only necessary to consider one general term of each expansion; summations also can be carried out finally as required.

The excitation function is chosen to define the phase origin of the system; in doing so the coefficients for this function are made real. Thus, the response of the system to an excitation of the form

$$P(t) = P_n e^{in\omega t}, \quad 0 \leqq n < \infty \qquad (15)$$

is examined.

The behaviour of the first excited singlet is described by

$$\dot{N}_s = P_n e^{in\omega t} - K_s N_s. \qquad (16)$$

A solution of the form:

$$N_s = S_n e^{in\omega t}, \quad S_n \text{ complex} \qquad (17)$$

is sought. Substitution in Eq. (16) yields

$$S_n = \frac{P_n}{K_s + in\omega}. \qquad (18)$$

For the triplet sublevel populations solutions of a similar form:

$$\mathbf{N} = e^{in\omega t}\cdot\mathcal{N}_n, \quad \mathcal{N}_n \text{ complex} \qquad (19)$$

are sought. Substituting for N_s, $\mathbf{N}$ in Eq. (2) yields, after simplification,

$$\mathcal{N}_n = S_n(\mathbf{R} + in\omega\,\mathbf{1})^{-1}\cdot\mathbf{K}. \qquad (20)$$

It may be easily shown that

$$(\mathbf{R} + in\omega\,\mathbf{1})^{-1} = \mathbf{S}\begin{pmatrix} \frac{1}{\varrho_1 + in\omega} & & \\ & \frac{1}{\varrho_2 + in\omega} & \\ & & \frac{1}{\varrho_3 + in\omega} \end{pmatrix}\mathbf{S}^{-1} \qquad (21)$$

where $\mathbf{S}^{-1}$, $\mathbf{S}$ is the same transformation which diagonalises the rate matrix, $\mathbf{R}$, to give the latent roots ϱ_1, ϱ_2, ϱ_3. The sublevel coefficient may now be determined by substituting S_n [Eq. (18)] and $(\mathbf{R} + in\omega\mathbf{1})^{-1}$ [Eq. (21)] into Equation (20). Remembering that, as solutions for the sublevel populations, only the real part of each harmonic is required, i. e.

$$\mathbf{N}(n\omega, t) = \mathrm{Re}\{e^{in\omega t}\mathcal{N}_n\} \qquad (22)$$

the expression for the n^{th} harmonic component of the sublevel population vector becomes, after some straight forward manipulation,

$$\mathbf{N}(n\omega, t) = \frac{P_n}{K_s}\mathbf{S}\begin{pmatrix} g_1 & & \\ & g_2 & \\ & & g_3 \end{pmatrix}\mathbf{S}^{-1}\cdot\mathbf{K} \qquad (23)$$

where $$g_i(n\omega,t)=\left(\frac{K_s}{K_s^2+n^2\omega^2}\right)\left\{\left(\frac{\varrho_i K_s-n^2\omega^2}{\varrho_i^2+n^2\omega^2}\right)\cos n\omega t+\left(\frac{n\omega(\varrho_i+K_s)}{\varrho_i^2+n^2\omega^2}\right)\sin n\omega t\right\}. \quad (24)$$

The complete expression for the sublevel populations may then be obtained by summing over all such harmonic components:

$$\boldsymbol{N}(t)=\sum_{n=0}^{\infty}\boldsymbol{N}(n\omega,t) \quad (25)$$

although very often all that is required is the behaviour of only one component.

In each of the excitation cases considered in this section, it has been shown that the solutions for the time dependent triplet sublevel populations all take the general form:

$$\boldsymbol{N}=\left(\frac{P_r}{K_s}\right)\mathbf{S}\begin{pmatrix}F_1 & & \\ & F_2 & \\ & & F_3\end{pmatrix}\mathbf{S}^{-1}\cdot\mathbf{K} \quad (26)$$

where $F_i=1/\varrho_i$, $f_i(t)$, $g_i(n\omega,t)$ according to the particular case. It only remains to determine the transformation **S**, expand Eq. (26) and substitute the appropriate F_i.

4. The Transformation and General Form of Solution

As noted previously, the matrix **R** is non-symmetric; this is due to the explicit account of the SLR at a particular temperature. Thus, $\mathbf{S}^{-1}$, **S** do not form a unitary transformation. Moreover, an immediate application of perturbation theory is precluded since the off-diagonal elements of **R** contain terms $\sim W_1$, W_2 which dominate.

The following procedure is adopted. The rate matrix, **R**, may be split into two parts. The first, **A**, contains only the integer parts of terms in W_1. The second, **B**, contains the remainder, i. e.

$$\mathbf{R}=\mathbf{A}+\mathbf{B}$$

where

$$\mathbf{A}=\begin{pmatrix}+W_1 & -W_1 & 0\\ -W_1 & +2W_1 & -W_1\\ 0 & -W_1 & +W_1\end{pmatrix}. \quad (27)$$

The roots and vectors of **A** are easily determined; with

$$\mathbf{U}=\begin{pmatrix}-\frac{1}{\sqrt{6}}+\frac{1}{\sqrt{2}}+\frac{1}{\sqrt{3}}\\ +\frac{2}{\sqrt{6}} \quad 0 \quad +\frac{1}{\sqrt{3}}\\ -\frac{1}{\sqrt{6}}-\frac{1}{\sqrt{2}}+\frac{1}{\sqrt{3}}\end{pmatrix} \quad (28)$$

then

$$\mathbf{U}^{-1}\cdot\mathbf{A}\cdot\mathbf{U}=\begin{pmatrix}3W_1 & & \\ & W_1 & \\ & & 0\end{pmatrix}. \quad (29)$$

Suppose now that

$$\mathbf{S}=\mathbf{U}\cdot\mathbf{X} \quad (30)$$

then

$$\mathbf{S}^{-1}\cdot\mathbf{R}\cdot\mathbf{S}=\mathbf{X}^{-1}\left\{\begin{pmatrix}3W_1 & & \\ & W_1 & \\ & & 0\end{pmatrix}+\mathbf{U}^{-1}\cdot\mathbf{B}\cdot\mathbf{U}\right\}\mathbf{X} \quad (31)$$

$$=\mathbf{X}^{-1}\begin{pmatrix}\left\{\left(3-\frac{\alpha_+-\alpha_-}{2}\right)W_1 & \left\{-\frac{1}{\sqrt{12}}(k_{+1}-k_{-1}) & \left\{\frac{\sqrt{2}}{6}(2k_0-k_{+1}-k_{-1})\right.\\ +\frac{2}{3}k_0+\frac{1}{6}(k_{+1}+k_{-1}).\right\} & -\frac{3}{\sqrt{12}}(\alpha_++\alpha_-)W_1.\right\} & -\sqrt{2}(\alpha_+-\alpha_-)W_1.\right\}\\ \left\{-\frac{1}{\sqrt{12}}(k_{+1}-k_{-1}) & \left\{\left(1+\frac{\alpha_+-\alpha_-}{2}\right)W_1+2W_2 & \left\{\frac{1}{\sqrt{6}}(k_{+1}-k_{-1})+\frac{2}{\sqrt{6}}\right.\\ +\frac{1}{\sqrt{12}}(\alpha_++\alpha_-)(W_1-4W_2)\right\} & +\frac{1}{2}(k_{+1}+k_{-1})\right\} & \cdot(\alpha_++\alpha_-)(W_1+2W_2)\right\}\\ \frac{\sqrt{2}}{6}(2k_0-k_{+1}-k_{-1}) & \frac{1}{\sqrt{6}}(k_{+1}-k_{-1}) & \frac{1}{3}(k_{+1}+k_0+k_{-1})\end{pmatrix}\cdot\mathbf{X}.$$

The new reduced matrix of Eq. (31) is such that all off-diagonal elements are small relative to the differences between the corresponding diagonal elements. A perturbation procedure may now be adopted to determine $\mathbf{X}^{-1}$, **X** and the latent roots $\varrho_1\ldots\varrho_3$.

In general an assymmetric matrix with a pair of small off-diagonal elements may be diagonalized as follows:

$$\begin{pmatrix} 1-\delta_+ & \delta_- & +\frac{1}{2}\delta_-^2 & \dots & +\delta_+ \\ \dots & \dots & \dots & \dots & \dots \\ -\delta_- & \dots & \dots & \dots & 1-\delta_+\delta_-+\frac{1}{2}\delta_+^2 \end{pmatrix} \begin{pmatrix} A & \dots & x_+ \\ \dots & \dots & \dots \\ x_- & \dots & B \end{pmatrix} \begin{pmatrix} 1-\frac{1}{2}\delta_-^2 & \dots & -\delta_+ \\ \dots & \dots & \dots \\ +\delta_- & \dots & 1-\frac{1}{2}\delta_+^2 \end{pmatrix}$$

$$\approx \begin{pmatrix} A+\dfrac{x_+x_-}{A-B} & \dots & 0 \\ \dots & \dots & \dots \\ 0 & \dots & B-\dfrac{x_+x_-}{A-B} \end{pmatrix}, \quad |x_+x_-| \ll (A-B)^2 \qquad (32)$$

where $\delta_\pm = x_\pm/(A-B)$.

The matrix of Eq. (31) has three pairs of such small non-symmetric off-diagonal elements. To a very good approximation diagonalization of this matrix is effected by three such perturbation-type transformations applied consecutively:

$$\mathbf{X} = \mathbf{V}(1,3)\cdot\mathbf{T}(1,2)\cdot\mathbf{Q}(2,3). \qquad (33)$$

where

$$v_+ \approx \frac{\sqrt{2}\,(2k_0-k_{+1}-k_{-1})}{18\,W_1} - \frac{\sqrt{2}}{3}(a_+-a_-),$$

$$v_- \approx \frac{\sqrt{2}\,(2k_0-k_{+1}-k_{-1})}{18\,W_1},$$

$$t_+ \approx \frac{-(k_{+1}-k_{-1})}{4\sqrt{3}\,(W_1-W_2)} - \frac{\sqrt{3}\,(a_++a_-)\,W_1}{4\,(W_1-W_2)},$$

$$t_- \approx \frac{-(k_{+1}-k_{-1})}{4\sqrt{3}\,(W_1-W_2)} - \frac{\sqrt{3}\,(a_++a_-)\,W_1}{4\,(W_1-W_2)} + \frac{(a_++a_-)}{\sqrt{3}},$$

$$q_+ \approx \frac{1}{\sqrt{6}}\frac{k_{+1}-k_{-1}}{W_1+2W_2} + \frac{2}{\sqrt{6}}(a_++a_-),$$

$$q_- \approx \frac{1}{\sqrt{6}}\frac{k_{+1}-k_{-1}}{W_1+2W_2}. \qquad (34)$$

The latent roots of $\mathbf{R}$ become:

$$\varrho_1 = \left(3-\frac{a_+-a_-}{2}\right)W_1 + \frac{1}{2}k_{\mathrm{av}} + \frac{1}{2}k_0 + 3v_+v_-W_1 + 2t_+t_-(W_1-W_2),$$

$$\varrho_2 = \left(1+\frac{a_+-a_-}{2}\right)W_1 + 2W_2 + \frac{3}{2}k_{\mathrm{av}} - \frac{1}{2}k_0 + q_+q_-(W_1+2W_2) - 2t_+t_-(W_1-W_2),$$

$$\varrho_3 = k_{\mathrm{av}} - 3v_+v_-W_1 - q_+q_-(W_1+2W_2). \qquad (35)$$

The elements of $\mathbf{X}^{-1}$, $\mathbf{X}$ become:

$$\mathbf{X} = \begin{pmatrix} 1-\frac{1}{2}v_-^2-\frac{1}{2}t_-^2 & -t_+-v_+q_- & q_+t_+-v_+ \\ +t_- & 1-\frac{1}{2}t_+^2-\frac{1}{2}q_-^2 & -q_+ \\ +v_- & -t_+v_-+q_- & 1-\frac{1}{2}v_+^2-\frac{1}{2}q_+^2 \end{pmatrix},$$

$$\mathbf{X}^{-1} = \begin{pmatrix} 1-t_+t_--v_+v_- & t_+ & v_+ \\ +\frac{1}{2}t_-^2+\frac{1}{2}v_-^2 & & \\ -t_--v_-q_+ & 1-q_+q_-+\frac{1}{2}q_-^2 & -t_-v_++q_+ \\ & -t_+t_-+\frac{1}{2}t_-^2 & \\ +q_-t_--v_- & -q_- & 1-q_+q_--v_+v_- \\ & & +\frac{1}{2}q_+^2+\frac{1}{2}v_+^2 \end{pmatrix}. \qquad (36)$$

In both cases, terms higher than the 2nd power in perturbation coefficients (t_+, q_-, v_+, etc.) have been neglected.

The complete transformation can now be determined in a straightforward fashion. As was pointed out in the previous section, the triplet population vector takes the general form of Equation (26). Whilst it is useful to have expressions for the individual populations, the population differences are of primary interest here and for the sake of

brevity only expressions for the functions

$$\Delta N_+ = N_{+1} - N_0\,, \qquad \Delta N_- = N_0 - N_{-1} \tag{37}$$

are quoted.

$$\begin{aligned}\Delta N_\pm = \frac{P_r}{K_s}\Big\{&\Big[\Big(\mp\frac{1}{\sqrt{2}}v_+ + \frac{1}{\sqrt{6}}v_+ t_-\Big)F_1 + \Big(\mp\frac{1}{\sqrt{2}}t_+ q_- - \frac{1}{\sqrt{6}}v_+ t_- + \frac{1}{\sqrt{6}}q_+\Big)F_2 \\ &+\Big(\pm\frac{1}{\sqrt{2}}v_+ \mp \frac{1}{\sqrt{2}}t_+ q_+ - \frac{1}{\sqrt{6}}q_+\Big)F_3\Big]\cdot 3K_{av} \\ &+\Big[\Big(\mp(1-t_+t_- - v_+v_-) + \frac{2}{\sqrt{12}}t_-\Big)F_1 + \Big(\mp t_+t_- - \frac{2}{\sqrt{12}}t_- - \frac{2}{\sqrt{12}}v_-q_+\Big)F_2 \\ &+\Big(\mp v_+v_- + \frac{2}{\sqrt{12}}v_-q_+\Big)F_3\Big]\Big[K_0 - \frac{1}{2}(K_{+1}+K_{-1})\Big] \\ &+\Big[\Big(\mp\frac{\sqrt{3}}{2}t_+ + \frac{1}{2}t_+t_-\Big)F_1 + \Big(\pm\frac{\sqrt{3}}{2}(t_+ + q_-v_+) + \frac{1}{2}(1-t_+t_- - q_+q_-)\Big) \\ &\cdot F_2 + \Big(\mp\frac{\sqrt{3}}{2}q_-v_+ + q_+q_-\Big)F_3\Big]\cdot(K_{+1}-K_{-1})\Big\}.\end{aligned} \tag{38}$$

5. Particular Forms of Solutions

In general the expression given by Eq. (38) is too unwieldy for normal use. In this section we consider appropriate approximations which render this expression useful with regard to extracting information from experiments.

The discussion of detailed solutions is limited to two examples of the cases generally discussed in the foregoing sections. These are: 1) The "song-pulse long recovery" situation for periodic rectangular pulses and 2) The "first harmonic component" situation for periodic waveform excitation. These are the two situations most commonly used in current ESR experiments [4–7, 10]. The distinction between their respective ΔN-expressions lies in the choice for $F_i(\varrho_i, t)$ in each case.

5.1. General Remarks

Certain remarks regarding the expected range of values for various constants in organic photo-excited triplet systems are pertinent to both the situations to be discussed. Collected together these are:

$$\begin{aligned}&K_s \geqq 10^7\,\mathrm{sec}^{-1}, \quad K_{av} \geqq 10^5\,\mathrm{sec}^{-1}, \quad W_1 \sim 10^5\,\mathrm{sec}^{-1}\ (W_2 \lesssim 0.5\,W_1)\,, \\ &k_B T \geqq 50\,\mathrm{cm}^{-1}, \quad k_{av} \sim 10^0 - 10^3\,\mathrm{sec}^{-1}, \quad |D| + |E| \leqq 0.15\,\mathrm{cm}^{-1}.\end{aligned}$$

Firstly, the consideration of the lifetime of the first excited singlet state for a large number of typical molecules [11] allows the restriction for K_s in nearly all cases. Similar considerations of the quantum yields of intersystem crossing and triplet lifetimes [12] reveal the restriction for K_{av} and range for k_{av} respectively. W_1, W_2 are expected to be in the order of $10^5\,\mathrm{sec}^{-1}$ for organic triplets at 77 K in high field [13, 14]. At this stage experiments at liquid nitrogen temperatures and above are considered so that $k_B T \gtrsim 50\,\mathrm{cm}^{-1}$, where k_B is the Boltzmann constant. Finally, it is noted that for intermediately-sized organic molecules the value of $|D| + |E|$ is not expected to exceed $0.15\,\mathrm{cm}^{-1}$ [12].

When all these conditions are valid it may be shown that the perturbation coefficients: $v_\pm$, $t_\pm$, $q_\pm \ll 1.6\cdot 10^{-2}$ and the latent roots of the rate matrix become $\varrho_1 \approx 3\,W_1$, $\varrho_2 \approx W_1 + 2\,W_2$, $\varrho_3 \approx k_{av}$. In making these approximations terms less than 1% of the total, in each case, have been neglected. Since the principal assumption that the spin lattice rates are much greater than the average triplet depopulation rate is made, then for the two particular examples to be considered in this section the functions F_1, F_2, F_3 adopt the following status at *any time t*

$$F_1(\varrho_1, t) \lesssim F_2(\varrho_2, t) \ll F_3(\varrho_3, t)\,.$$

It is sensible therefore to retain only the zero-order perturbation coefficients of the F_1, F_2 terms and coefficients up to first order for F_3. Noting that $K_0 - 1/2\,K_{+1} - 1/2\,K_{-1} = 3/2\,(K_0 - K_{av})$ and an

analogous expression for the k's, the simplified equation for the population difference becomes

$$\Delta N_{\pm} = \frac{P_r}{K_s}\left\{\left[\pm\frac{1}{\sqrt{2}}v_+ - \frac{1}{\sqrt{6}}q_+\right]3K_{av}F_3 + \frac{1}{2}(K_{+1}-K_{-1})F_2 \mp \frac{3}{2}(K_0-K_{av})F_1\right\}. \quad (39)$$

Substituting for the coefficients and making some rearrangement

$$\Delta N_{\pm} = \left(\frac{P_r}{3W_1}\cdot\frac{K_{av}}{K_s}\right)\left\{\left[\pm\frac{3}{2}\left(\frac{k_0-k_{av}}{k_{av}}\right) - \frac{1}{2}\left(\frac{k_{+1}-k_{-1}}{k_{av}}\right)\cdot\left(\frac{3W_1}{W_1+2W_2}\right) - \frac{6\alpha_{\pm}W_1}{k_{av}}\right]\right.$$
$$\left.\cdot k_{av}F_3 + \frac{1}{2}\left(\frac{K_{+1}-K_{-1}}{K_{av}}\right)3W_1F_2 \mp \frac{3}{2}\left(\frac{K_0-K_{av}}{K_{av}}\right)3W_1F_1\right\}. \quad (40)$$

And for the $\Delta m_s = 2$ transition

$$\Delta N_2 = \Delta N_+ + \Delta N_- = \left(\frac{P_r}{W_1+2W_2}\cdot\frac{K_{av}}{K_s}\right)\left\{\left[-\left(\frac{k_{+1}-k_{-1}}{k_{av}}\right) - \frac{2(\alpha_+ + \alpha_-)(W_1+2W_2)}{k_{av}}\right]k_{av}F_3\right.$$
$$\left. + \left(\frac{K_{+1}-K_{-1}}{K_{av}}\right)(W_1+W_2)F_2\right\}. \quad (41)$$

5.2. *The High-Field Limit*

It is often assumed that at high magnetic field strengths the Zeeman $|\pm 1\rangle$ states are equal mixtures of the zero-field spin function $|\tau_i\rangle$, $|\tau_j\rangle$, where i, j, k are the principal axes of the z.f.s. tensor and the field is directed along the k-axis. This implies that under such conditions $K_{+1} \approx K_{-1}$, etc. and whilst this might be a good approximation at field strengths appropriate to K-band spectroscopy [15], it may not be so in the case of X-band spectroscopy, as has sometimes been supposed [1, 7]. For example, it may be shown:

$$H_0 \parallel x,\ \tfrac{1}{2}(K_{+1}-K_{-1}) \approx \delta/2\,(K_z-K_y) \qquad \delta \approx \frac{D+E}{2g\mu_B H}.$$

At X-band $\delta \ll 0.2$ and when K_z predominates this term becomes significant compared with $\frac{3}{2}(K_x-K_{av})$. At K-band field strengths $\delta \ll 0.05$ for $|D|+|E| \lesssim 0.15\ \mathrm{cm}^{-1}$ and the "high-field" assumption would be a good one for all principal orientations.

The specific examples pertinent to the most commonly used experimental arrangements are now considered in the light of these foregoing remarks.

5.3. *Periodic Rectangular Pulse: "Long-pulse – Long-recovery" Limit*

In this case the behaviour of the populations following the "off"-edge of the pulse (Region II) is considered. Here, the $F_i = e^{-\varrho_i t}/\varrho_i$ and the population differences [Eqs. (40) and (41)] become:

$$\Delta N_{\pm} = \left(\frac{P_0}{3W_1}\cdot\frac{K_{av}}{K_s}\right)\left\{\left[\pm\frac{3}{2}\left(\frac{k_0-k_{av}}{k_{av}}\right) - \frac{1}{2}\left(\frac{k_{+1}-k_{-1}}{k_{av}}\right)\left(\frac{3W_1}{W_1+2W_2}\right) - \frac{6\alpha_{\pm}W_1}{k_{av}}\right]\right.$$
$$\left.\cdot e^{-k_{av}t} + \frac{1}{2}\left(\frac{K_{+1}-K_{-1}}{K_{av}}\right)\left(\frac{3W_1}{W_1+2W_2}\right)e^{-(W_1+2W_2)t} \mp \frac{3}{2}\left(\frac{K_0-K_{av}}{K_{av}}\right)e^{-3W_1t}\right\}, \quad (42)$$

$$\Delta N_2 = \left(\frac{P_0}{W_1+2W_2}\frac{K_{av}}{K_s}\right)\left\{\left[-\left(\frac{k_{+1}-k_{-1}}{k_{av}}\right) - \frac{2(\alpha_+ + \alpha_-)(W_1+2W_2)}{k_{av}}\right]e^{-k_{av}t} + \left(\frac{K_{+1}-K_{-1}}{K_{av}}\right)e^{-(W_1+2W_2)t}\right\} \quad (43)$$

Clearly when t is short with respect to $1/k_{av}$, competition between the fast (e^{-3W_1t}) and slow ($e^{-k_{av}t}$ parts of the decay occurs when $(K_0-K_{av})/K_{av}$ becomes comparable with

$$\pm(k_0-k_{av})/k_{av} - (6\alpha_{\pm}W_1/k_{av}).$$

The result in triplet ESR is the appearance of transient "spikes", sometimes of the opposite sign to the slower part of the decay, as observed by Levanon [5, 6] and Lin [10b].

The same comments hold for the "build up" to the steady state when examining the behaviour following the "on" edge of a long-pulse.

5.4. *The Periodic Waveform: First Harmonic Component*

The periodic waveform solution is less straightforward to handle, but has the advantage of being the most convenient as a basis for experimental design. When $n=0$ or $\omega=0$, the solution, as expected, reduces to that of the steady state i.e. $g_i(0,t)=1/\varrho_i$. Solutions where $n>0$ are more complicated. In the ESR experiment selective examination of the $n=1$ and higher spin polarization harmonics is accomplished by additional phase-sensitive detection. In general, whatever the waveshape, the signal channel is most advantageously arranged to detect the first harmonic[5]. Then, only the $n=1$ term in the complete expansion [Eq. (25)] need be considered and this is done here.

With the provision $\omega^2 \ll k_{av} K_s$, which may be easily met, the g-functions [Eq. (24)] simplify to:

$$g_1 \cong \frac{3W_1}{9W_1^2+\omega^2}\cos\omega t + \frac{\omega}{9W_1^2+\omega^2}\sin\omega t,$$

$$g_2 \cong \frac{(W_1+2W_2)}{(W_1+2W_2)^2+\omega^2}\cos\omega t + \frac{\omega}{(W_1+2W_2)^2+\omega^2}\sin\omega t, \quad (44)$$

$$g_3 \cong \frac{k_{av}}{k_{av}^2+\omega^2}\cos\omega t + \frac{\omega}{k_{av}^2+\omega^2}\sin\omega t.$$

Further simplification arises in the two limits $\omega^2 \gg k_{av}^2$, $\omega^2 \ll W_1^2$ but this may be adopted at a later stage as required.

Equation (40) may then be expressed in the form

$$\Delta N_\pm = A_\pm \cos\omega t + B_\pm \sin\omega t = (A_\pm^2+B_\pm^2)^{1/2}\cos(\omega t+\Phi_\pm) \quad (45)$$

where

$$\tan\Phi_\pm = -B_\pm/A_\pm \quad (46)$$

defines the phase with respect to the excitation waveform and

$$A_\pm \approx \left(\frac{P_1}{3W_1}\frac{K_{av}}{K_s}\right)\left\{\left[\pm\frac{3}{2}\left(\frac{k_0-k_{av}}{k_{av}}\right)-\frac{1}{2}\left(\frac{k_{+1}-k_{-1}}{k_{av}}\right)\left(\frac{3W_1}{W_1+2W_2}\right)-\frac{6\alpha_\pm W_1}{k_{av}}\right]\cdot\frac{k_{av}^2}{k_{av}^2+\omega^2}+\frac{1}{2}\left(\frac{K_{+1}-K_{-1}}{K_{av}}\right)\frac{3W_1(W_1+2W_2)}{(W_1+2W_2)^2+\omega^2}\mp\frac{3}{2}\left(\frac{K_0-K_{av}}{K_{av}}\right)\frac{9W_1^2}{9W_1^2+\omega^2}\right\};$$

$$B_\pm \approx \left(\frac{P_1}{3W_1}\frac{K_{av}}{K_s}\right)\left\{\left[\pm\frac{3}{2}\left(\frac{k_0-k_{av}}{k_{av}}\right)-\frac{1}{2}\left(\frac{k_{+1}-k_{-1}}{k_{av}}\right)\left(\frac{3W_1}{W_1+2W_2}\right)-\frac{6\alpha_\pm W_1}{k_{av}}\right]\cdot\frac{k_{av}\omega}{k_{av}^2+\omega^2}+\frac{1}{2}\left(\frac{K_{+1}-K_{-1}}{K_{av}}\right)\frac{3W_1\omega}{(W_1+2W_2)^2+\omega^2}\mp\frac{3}{2}\left(\frac{K_0-K_{av}}{K_{av}}\right)\frac{3W_1\omega}{9W_1^2+\omega^2}\right\}. \quad (47)$$

Similar expressions may be developed for the $\Delta m_s=2$ population difference, where

$$A_2=A_++A_- \approx \left(\frac{P_1}{(W_1+2W_2)}\frac{K_{av}}{K_s}\right)\left\{\left[-\left(\frac{k_{+1}-k_{-1}}{k_{av}}\right)-\frac{2(\alpha_++\alpha_-)(W_1+2W_2)}{k_{av}}\right]\frac{k_{av}^2}{k_{av}^2+\omega^2}+\left(\frac{K_{+1}-K_{-1}}{K_{av}}\right)\frac{(W_1+2W_2)^2}{(W_1+2W_2)^2+\omega^2}\right\};$$

$$B_2=B_++B_- \approx \left(\frac{P_1}{(W_1+2W_2)}\frac{K_{av}}{K_s}\right)\left\{\left[-\left(\frac{k_{+1}-k_{-1}}{k_{av}}\right)-\frac{2(\alpha_++\alpha_-)(W_1+2W_2)}{k_{av}}\right]\frac{k_{av}\omega}{k_{av}^2+\omega^2}+\left(\frac{K_{+1}-K_{-1}}{K_{av}}\right)\frac{(W_1+2W_2)\omega}{(W_1+2W_2)^2+\omega^2}\right\}. \quad (48)$$

The origin of the interesting frequency dependent phase reversal effects[4-7,10] in $\Delta m_s=1$ ESR experiments now becomes apparent. Consideration of Eqs. (46) and (47) reveals that they arise from the competition of the various terms within $A_\pm$ and $B_\pm$ as ω is increased. For one of the population differences, ΔN_+ or ΔN_-, there exists the possibility for both A and B to change sign with concomitant changes in $\tan\Phi$. Similar consideration of $\tan\Phi$ for ΔN_2 may also be made and Fig. 3 shows the typical phase behaviour of ΔN_+, ΔN_- and ΔN_2 as a function of ω.

The intensity and phase of the first harmonic of the ESR signal may be conveniently measured for each of the two $\Delta m_s=1$ transitions. The intensities, properly considered with respect to linewidth,

transition probability and possible saturation can be taken directly proportional to the population differences, $\Delta N_{\pm}$. Such intensity/phase measurements made for each of the three principal orientations of the magnetic field, and over appropriate ranges of ω, may be analysed using Equations (45) – (47). With careful manipulation, determination of the *relative* populating rates (K_x, K_y, K_z), the *absolute* depopulating rates (k_x, k_y, k_z) and the *absolute* spin lattice rate (W_1) may, in principle, be accomplished. The important point is that the bandwidth of the signal channel prior to the excitation-referenced phase sensitive detector must be wide enough to accomodate a frequency range from which all the necessary information may be obtained. It is also noted that if

$$\frac{1}{2}\left(\frac{K_{+1}-K_{-1}}{K_{\mathrm{av}}}\right)\left(\frac{3W_1}{W_1+2W_2}\right)$$ becomes significant with respect to $$\frac{3}{2}\left(\frac{K_0-K_{\mathrm{av}}}{K_{\mathrm{av}}}\right)$$ for one or more of the orientations, then the absolute rate, W_2, may be additionally estimated.

The procedure used to extract detailed rate information will be described in a following report [8] where it has been applied to a number of photo-excited triplet systems.

6. Conclusion

In this communication the spin population behaviour in the first excited triplet state under conditions of time dependent photo-excitation has been examined. A model involving five levels has been used: the ground state singlet, the first excited singlet and the three magnetic sublevels of the triplet. Between sublevels with $\Delta m_s = 1$ spin lattice relaxation rates are assumed equal, but greater than that between levels with $\Delta m_s = 2$. In most respects this model complements that of Levanon and Vega [7] where all three spin lattice constants are assumed equal. The perturbation treatment required by the $W_1 \neq W_2$ model is valid provided two criteria are met

(i) $$W_1 - W_2 \geqq 5\,k_{\mathrm{av}},$$

(ii) $$\alpha \leqq 10^{-2}.$$

All perturbation coefficients are then less than $5 \cdot 10^{-2}$. The inclusion of the first excited singlet level in the kinetic analysis gives rise to additional characteristics in the "periodic waveform" case when $K_s\,k_{\mathrm{av}} \sim \omega^2$; these have not been discussed in this communication. The essential difference between the $W_1 = W_2$ and $W_1 \neq W_2$ models is that W_2 enters only through small additional terms, e.g. $\frac{1}{2}\frac{(k_{+1}-k_{-1})}{k_{\mathrm{av}}}\frac{3W_1}{W_1+W_2}$, which tend to zero in the high field limit. Otherwise, with due account of the approximations taken, the expressions herein ($W_1 \neq W_2$) may be shown to be the same as those of reference [7] ($W_1 = W_2$).

For $\Delta m_s = 2$ transitions where lower field strengths are required, it might be expected that these W_2 terms become important; thus population difference expressions for the $\Delta m_s = 2$ transition have been developed by retaining terms involving $(K_{+1}-K_{-1})$ and $(k_{+1}-k_{-1})$.

Inspection shows that to effect a complete analysis of the k's, K's and W's in either the "long-pulse" or "periodic waveform" experiments the two constants k_{av}, $3W_1$ must first be determined absolutely, i.e. independent of spectrometer constants. In the "long-pulse" experiment this is done by analysing the decay behaviour for the two dominant exponential decays with constants k_{av}, $3W_1$. In the "periodic waveform" experiment a similar analysis of the phase behaviour is applied; at low frequencies ($\omega \ll 3W_1$) $\tan\Phi$ approximates to a function of (ω/k_{av}) and at high frequencies ($\omega \gg k_{\mathrm{av}}$) to a function of $(\omega/3W_1)$.

The emphasis in this communication has been on the "periodic waveform" experiment and having made the foregoing remarks the criteria necessary for accurate determination of SLR rates may now be discussed.

In the high frequency limit the expression for $\tan\Phi$ takes the very simple form:

$$\tan\Phi_{\pm} = -\omega/3W_1$$
$$\text{provided} \quad (K_{+1}-K_{-1}) \ll (K_0 - K_{\mathrm{av}}). \quad (49)$$

An experiment which absolutely determines W_1 must therefore be capable of measuring the phase of the excitation-coded ESR signal with respect to that of the excitation waveform with sufficient accuracy and at frequencies high enough to compete with $3W_1$. As with any experiment studying the sublevel dynamics which is based on expressions derived in the foregoing sections, low, non-saturating microwave powers must be used.

As seen in Fig. 3, at frequencies high compared with k_{av} the signal to noise ratio is much reduced

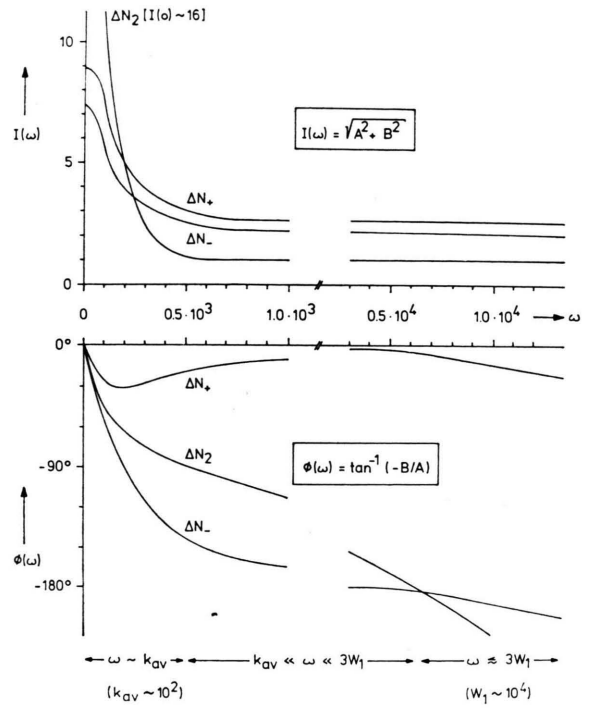

Fig. 3. The behaviour of amplitude and phase of the population differences with frequency.

and this contributes to the overall error in phase determination. Secondly, frequency-independent phase errors originating in the optical system, and frequency-dependent phase errors arising from too narrow a bandwidth in the signal detection channel must be minimised. (It is the restriction of a limited bandwidth at this latter stage which has thus far prevented precise determination of $3W_1$ in the "long-pulse" experiments[7].) A careful prior calibration of these errors is a wise precaution. Finally, consideration of the Bloch equations in the rotating frame reveals additional dependence of the signal phase which will be significant unless $T_1(\sim 1/3\,W_1) \gg T_2$. Fortunately, this condition would generally appear to be met at the temperatures of interest[14].

In emphasizing the possibility of determining W_1, W_2 by means of the ESR experiment it should be noted that the kinetic model adopted in this communication has assumed a constant magnetic field strength. The population difference expressions between any pair of levels involve the same W_1, W_2, α_+, α_-. In the ESR experiment the field is usually varied to observe the different resonance conditions. Whilst this has the advantage that

$$\alpha_+(H_{0\to+1}) = \alpha_-(H_{-1\to0}) = \alpha_+(H_{-1\to+1}) + \alpha_-(H_{-1\to+1}) = h\nu/2\,k_B T\,,$$

the implications may be serious with regard to W_1, W_2. In ordered systems there is evidence[13, 14] that the SLR constants are functions of both the magnitude and direction of the magnetic field. At different resonant fields, or different orientations, different values of the SLR constants may be operating. By using randomly oriented samples the orientational dependence may be relieved. Provided that the resonance fields for the $\Delta m_s = 1$ transitions are not grossly separated, it may also be reasonable to assume that W_1, W_2 remain approximately constant over this region of field strength. However, at the half-field ($\Delta m_s = 2$) resonance appreciably different W_1, W_2 values might be attained. Alternatively, the dependence of W_1 on the orientation and strength of the resonant field may be directly examined, since Eq. (49) is applicable to any $\Delta m_s = 1$ resonance condition. Extraction of the complete kinetic data then becomes more complicated.

Finally, it is emphasized that information in the "periodic waveform" experiment is contained not only in the intensity of the absorption signal but also in its phase with respect to that of the exciting source. In the treatment presented herein it is clear that every transition has a characteristic and distinct phase.

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