Pramāṇa – J. Phys., Vol. 35, No. 1, July 1990, pp. 81–87. © Printed in India.

General transient solutions for the four-coupled Bloch-type equations for a two-level system

J B SHINDE* and S C MEHROTRA

Department of Physics, Marathwada University, Aurangabad 431 004, India
*On deputation from Deogiri College, Aurangabad

MS received 19 December 1988; revised 4 January 1990

Abstract. When the collisional dynamics of two states under consideration for a radiative transition is different, the polarization and population relaxations in gas phase at low pressure are governed by four-, instead of three-, coupled Bloch-type equations. The general transient solutions of these four-coupled equations are solved by using the Laplace transformation technique. It has been found that an additional exponential term appears because of the effect. This is also responsible for the non-exponential character in the decay signal of a transient microwave pulse experiment, besides other factors reported earlier.

Keywords. Microwave Fourier transform spectroscopy; polarization; population relaxation; Laplace transform.

PACS Nos 34·50; 34·10; 33·20

1. Introduction

1.1 *Basic equations*

It has been shown (Liu and Marcus 1975) that for a non-degenerate two-level system, the dynamics of the Feynman–Vernon–Hellworth (FVH) vector, $\mathbf{r}'$, in rotating frame, (Feynman *et al* 1957) is given by

$$\mathrm{d}\mathbf{r}'/\mathrm{d}t = A\mathbf{r}' + B, \tag{1}$$

where

$$\mathbf{r}' = \begin{pmatrix} (\rho'_{ij} + \rho'_{ji}) \\ i(\rho'_{ji} - \rho'_{ij}) \\ (\rho'_{ii} - \rho'_{jj}) \\ (\rho'_{ii} + \rho'_{jj}) \end{pmatrix}, \tag{2}$$

$$A = \begin{pmatrix} -1/T_2 & -\Delta w & 0 & 0 \\ \Delta w & -1/T_2 & -W_1 & 0 \\ 0 & W_1 & -\alpha_1 & -\alpha_2 \\ 0 & 0 & -\gamma_2 & -\gamma_1 \end{pmatrix}. \tag{3}$$

and

$$B=\begin{pmatrix} 0 \\ 0 \\ \alpha_1 r_3'^{(0)}+\alpha_2 r_4'^{(0)} \\ \gamma_1 r_4'^{(0)}+\gamma_2 r_3'^{(0)} \end{pmatrix}. \tag{4}$$

The meaning of the parameters used in (2) to (4) are as follows: ρ'_{ij} are the density matrix elements of a two-level system denoted by i and j with radiative and collisional perturbations. $W_1=\mu_{ab}\varepsilon_0/\hbar$, where μ_{ab}, taken as real, is the dipole matrix element coupling the two levels under consideration, and ε_0 is the amplitude of the microwave field. $\Delta w=w_0-w$ is the difference between the resonant frequency of the system w_0 and the applied frequency w. $1/T_2=\beta,\alpha_1,\alpha_2,\gamma_1$ and γ_2 are relaxation parameters and can be expressed in terms of collisional rates (Liu and Marcus 1975). $r_3'^{(0)}$ and $r_4'^{(0)}$ are the equilibrium values of r'_3 and r'_4 respectively. r'_2 is related to the imaginary part of the polarization and is an observable quantity in a pulse microwave experiment. The different transient microwave experiments will provide different information about the relaxation, depending upon the sensitivity of r'_2 to the relaxation parameters. For example, a $\pi/2$-pulse experiment provides information about $1/T_2$ parameter, while a $\pi-\tau-\pi/2$ experiment about $1/T_1$. There are no such experiments designed yet to determine α_2,γ_1 and γ_2. These relaxation parameters contain useful information regarding collisions of different types, viz,

(i) adiabatic collisions which change only the phase of the colliding molecules,
(ii) collisions which induce transitions between the states under consideration, and
(iii) inelastic collisions other than of type (ii).

If the collisional dynamics of each of the two levels under consideration is the same, the relaxation parameters α_2 and γ_2 will be zero and the fourth equation will be decoupled from the rest of the three equations. The general transient solutions of three coupled Bloch equations are known and applied to different transient experiments (Schmalz and Flygare 1978).

For the inversion lines (Tanaka *et al* 1983), l-doublet transitions and rotational levels with high J quantum numbers, the approximation mentioned above is expected to be good (Mehrotra and Mader 1988), but it is not good enough for the transitions with low rotational quantum number J. For example $J=0\rightarrow 1$ transition of a system, the dynamics of $J=0$ level is different from the dynamics of $J=1$ level. The dynamics of such systems must be described by the four-coupled equations. The objective of the paper is to give the general transient solution of equation (1). The result is applied to two pulse experiments to see the effect of an additional term in the solution.

2. The general transient solution

Equation (1) can be solved by the Laplace transform technique (Schmalz and Flygare 1978). The solution is of the form:

$$r'_i(t)=A_i\exp(-at)+B_i\exp(-bt)\cos(st)+C_i\exp(-bt)\sin(st)/s + D_i+E_i\exp(-ct). \tag{5}$$

The last term $E_i \exp(-ct)$ is an additional term which does not appear in the solution of three-level equation. The following coupled equations have been used to determine the values of a, b, c and s by using an iterative technique.

$$2b + a + c = \alpha_1 + \gamma_1 + 2\beta, \tag{6a}$$

$$b^2 + s^2 + 2b(a + c) + ac = \beta^2 + (\alpha_1\gamma_1 - \alpha_2\gamma_2) + 2\beta(\alpha_1 + \gamma_1) + (\Delta w)^2 + W_1^2, \tag{6b}$$

$$(a + c)(b^2 + s^2) + 2abc = \beta^2(\alpha_1 + \gamma_1) + 2\beta(\alpha_1\gamma_1 - \alpha_2\gamma_2) + (\Delta w)^2(\alpha_1 + \gamma_1) + (\gamma_1 + \beta) W_1^2, \tag{6c}$$

$$ac(b^2 + s^2) = \beta^2(\alpha_1\gamma_1 - \alpha_2\gamma_2) + (\Delta w)^2(\alpha_1\gamma_1 - \alpha_2\gamma_2) + W_1^2\beta\gamma_1. \tag{6d}$$

In the iterative technique the starting values are taken to be the values corresponding to zero microwave power, viz.

$$b = \beta \tag{7a}$$

$$a = -(1/2)\{-(\alpha_1 + \gamma_1) - [(\alpha_1 - \gamma_1)^2 + 4\alpha_2\gamma_2]^{1/2}\}. \tag{7b}$$

$$s = \Delta w, \tag{7c}$$

$$c = -(1/2)\{-(\alpha_1 + \gamma_1) + [(\alpha_1 - \gamma_1)^2 + 4\alpha_2\gamma_2]^{1/2}\}. \tag{7d}$$

The solutions of A_i, B_i, C_i, D_i, E_i can be obtained as

$$A_i = \left(\frac{1}{X}\right)\{a^3[(b - c)^2 + s^2]b_{1i} - a^2[(b^2 + s^2) + c(c - 2b)]b_{2i} - a[c(2b - c) - (b^2 + s^2)]b_{3i} - [(b^2 + s^2) + c(c - 2b)]b_{4i}\},$$

$$B_i = \left(\frac{a - c}{X}\right)\{[(b^2 + s^2)\{(b^2 + s^2) - 2bc - 2ab - ac\} + 4ab^2c]b_{1i} + [(c + a)(b^2 + s^2) - 2abc]b_{2i} + [ac - (b^2 + s^2)]b_{3i} + [2b - (c + a)]b_{4i}\},$$

$$D_1 = \frac{W_1 \Delta w r_3'^{(0)}(\alpha_1\gamma_1 - \alpha_2\gamma_2)}{\beta^2(\alpha_1\gamma_1 - \alpha_2\gamma_2) + (\Delta w)^2(\alpha_1\gamma_1 - \alpha_2\gamma_2) + W_1^2\beta\gamma_1},$$

$$D_2 = \frac{(\alpha_2\gamma_2 - \alpha_1\gamma_1)W_1\beta r_3'^{(0)}}{\beta^2(\alpha_1\gamma_1 - \alpha_2\gamma_2) + (\Delta w)^2(\alpha_1\gamma_1 - \alpha_2\gamma_2) + W_1^2\beta\gamma_1},$$

$$D_3 = \frac{((\Delta w)^2 + \beta^2)(\alpha_1\gamma_1 - \alpha_2\gamma_2)r_3'^{(0)}}{\beta^2(\alpha_1\gamma_1 - \alpha_2\gamma_2) + (\Delta w)^2(\alpha_1\gamma_1 - \alpha_2\gamma_2) + W_1^2\beta\gamma_1},$$

$$D_4 = \frac{r_4'^{(0)}[(\alpha_1\gamma_1 - \alpha_2\gamma_2)(\beta^2 + (\Delta w)^2) + W_1^2\beta\gamma_1 + r_3'^{(0)} W_1^2\beta\gamma_2}{\beta^2(\alpha_1\gamma_1 - \alpha_2\gamma_2) + (\Delta w)^2(\alpha_1\gamma_1 - \alpha_2\gamma_2) + W_1^2\beta\gamma_1}.$$

$$C_i = b_{2i} - A_i(2b + c) - B_i(b + c + a) - (2b + a)(r_i'^{(0)} - D_i - A_i - B_i),$$

$$E_i = r_i'^{(0)} - D_i - A_i - B_i.$$

The values of b_{ij} in the above equations are as follows:

$$b_{11} = r_1'^{(0)} - D_1,$$

$$b_{21} = -D_1(\alpha_1 + \gamma_1 + 2\beta) + r_1'^{(0)}[(\alpha_1 + \gamma_1) + \beta] - \Delta w r_2'^{(0)},$$

$$b_{31} = -D_1\{\beta^2 + (\alpha_1\gamma_1 - \alpha_2\gamma_2) + 2\beta(\alpha_1 + \gamma_1) + (\Delta w)^2 + W_1^2$$
$$+ r_1'^{(0)}[\{\beta(\alpha_1 + \gamma_1) + \alpha_1\gamma_1 - \alpha_2\gamma_2\} + W_1^2] - r_2'\Delta w(\alpha_1 + \gamma_1) + r_3'^{(0)} W_1 \Delta w,$$

$$b_{41} = -D_1\{\beta^2(\alpha_1 + \gamma_1) + 2\beta(\alpha_1\gamma_1 - \alpha_2\gamma_2) + (\Delta w)^2(\alpha_1 + \gamma_1) + (\gamma_1 + \beta)W_1^2\}$$
$$+ r_1'^{(0)}[(\alpha_1\gamma_1 - \alpha_2\gamma_2)\beta + W_1^2\gamma_1] - r_2'^{(0)}\Delta w(\alpha_1\gamma_2 - \alpha_2\gamma_2)$$
$$+ r_3'^{(0)}(\alpha_1 + \gamma_1)\Delta w W_1,$$

$$b_{12} = r_2'^{(0)} - D_2,$$

$$b_{22} = -D_2(\alpha_1 + \gamma_1 + 2\beta) + r_1'^{(0)}\Delta w + r_2'^{(0)}(\beta + \alpha_1 + \gamma_1) - r_3'^{(0)} W_1,$$

$$b_{32} = -D_2\{\beta^2 + (\alpha_1\gamma_1 - \alpha_2\gamma_2) + 2\beta(\alpha_1 + \gamma_1) + (\Delta w)^2 + W_1^2\}$$
$$+ r_1'^{(0)}[(\alpha_1 + \gamma_1)\Delta w] - r_3'^{(0)}(\alpha_1 + \gamma_1 + \beta)W_1$$
$$+ r_2'^{(0)}[\beta(\alpha_1 + \gamma_1) + \alpha_1\gamma_1 - \alpha_2\gamma_2],$$

$$b_{42} = -D_2\{\beta^2(\alpha_1 + \gamma_1) + 2\beta(\alpha_1\gamma_1 - \alpha_2\gamma_2) + (\Delta w)^2(\alpha_1 + \gamma_1) + (\gamma_1 + \beta)W_1^2\}$$
$$+ r_1'^{(0)}(\alpha_1\gamma_1 - \alpha_2\gamma_2)\Delta w + r_2'^{(0)}(\alpha_1\gamma_1 - \alpha_2\gamma_2)\beta$$
$$- r_3'^{(0)}\{\alpha_1(\gamma_1 + \beta) + \beta\gamma_1 - \alpha_2\gamma_2\} W_1,$$

$$b_{13} = r_3'^{(0)} - D_3,$$

$$b_{23} = -D_3(\alpha_1 + \gamma_1 + 2\beta) + r_2'^{(0)} W_1 + (2\beta + \alpha_1 + \gamma_1)r_3',$$

$$b_{33} = -D_3\{\beta^2 + (\alpha_1\gamma_1 - \alpha_2\gamma_2) + 2\beta(\alpha_1 + \gamma_1)(\Delta w)^2 + W_1^2\}$$
$$+ r_1'^{(0)} W_1 \Delta w + r_2'^{(0)} W_1(\beta + \gamma_1)$$
$$+ r_3'^{(0)}[(\Delta w)^2 + \beta^2 + 2\beta(\alpha_1 + \gamma_1) + \alpha_1\gamma_1 - \alpha_2\gamma_2],$$

$$b_{43} = -D_3\{\beta^2(\alpha_1 + \gamma_1) + 2\beta(\alpha_1\gamma_1 - \alpha_2\gamma_2) + (\Delta w)^2(\alpha_1 + \gamma_1) + W_1^2(\gamma_1 + \beta)\}$$
$$+ r_1'^{(0)}\gamma_1 W_1 \Delta w + r_2'^{(0)}\gamma_1 W_1 \beta$$
$$+ r_3'^{(0)}[((\Delta w)^2 + \beta^2)(\alpha_1 + \gamma_1) + 2\beta(\alpha_1\gamma_1 - \alpha_2\gamma_2)],$$

$$b_{14} = r_4'^{(0)} - D_4,$$

$$b_{24} = -D_4(\alpha_1 + \gamma_1 + 2\beta) + r_4'^{(0)}(2\beta + \alpha_1 + \gamma_1),$$

$$b_{34} = -D_4\{\beta^2 + (\alpha_1\gamma_1 - \alpha_2\gamma_2) + 2\beta(\alpha_1 + \gamma_1) + (\Delta w)^2 + W_1^2\}$$
$$- r_2'^{(0)} W_1\gamma_2 + r_4'^{(0)}\{\beta^2 + 2\beta\alpha_1 + 2\beta\gamma_1 + \alpha_1\gamma_1 - \alpha_2\gamma_2 + W_1^2 + (\Delta w)^2\},$$

$$b_{44} = -D_4\{\beta^2(\alpha_1 + \gamma_1) + 2\beta(\alpha_1\gamma_1 - \alpha_2\gamma_2) + (\Delta w)^2(\alpha_1 + \gamma_1) + W_1^2(\gamma_1 + \beta)\}$$
$$- r_1'^{(0)}\gamma_2 W_1 \Delta w - r_2'^{(0)}\gamma_2 W_1 \beta + r_3'^{(0)} W_1^2 \gamma_2$$
$$+ r_4'^{(0)}[\beta^2(\alpha_1 + \gamma_1) + 2\beta(\alpha_1\gamma_1 - \alpha_2\gamma_2) + W_1^2(\beta + \gamma_1) + (\Delta w)^2(\alpha_1 + \gamma_1)]$$

and

$$X = -(b^2+s^2)[c(a^2+c^2)+a^2(2b-a)-c^2(a+2b)+(c-a)(b^2+s^2)] + ac(c-a)[-ac+2b(c+a)-4b^2].$$

3. Results

A computer program was developed to calculate the values of $r_2'(\tau)$ in $\pi - \tau - \pi/2$ pulse experiment for a given system. Since eqs (6a) to (6d) could not be solved exactly, an iterative technique starting with initial values given by (7a) to (7d) was used. The results for the different systems are plotted in figures 1 to 4 along with the corresponding exponential decay as obtained by the following equation.

$$r_2'(\tau) = A\exp(-\alpha\tau) + B,$$

where A and B are constants. For all the systems studied here, deviations from the exponential decay have been found. These deviations are not so significant as to be observed by the presently available techniques. However this may be possible in future (Mehrotra and Mäder 1988).

4. Conclusions

The general solution for the four Bloch equations has been obtained and an additional exponential term has been found. The effect of this term has been calculated in a

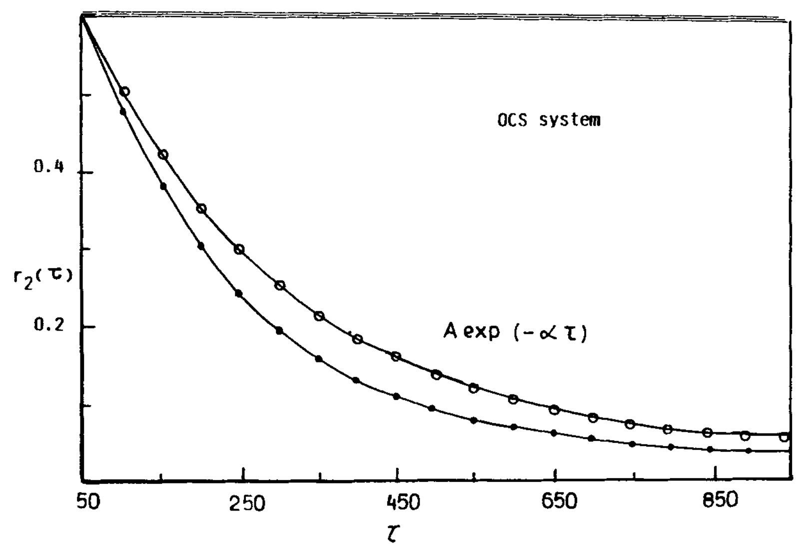

Figure 1. Plot of $r_2'(\tau)$ vs delay τ (ns) in a $\pi-\tau-\pi/2$ experiment for OCS system with $\beta = \alpha_1 = 600\,\mathrm{kHz}$, $\alpha_2 = \gamma_2 = \beta/20$ and $\gamma_1 = \beta/12$.

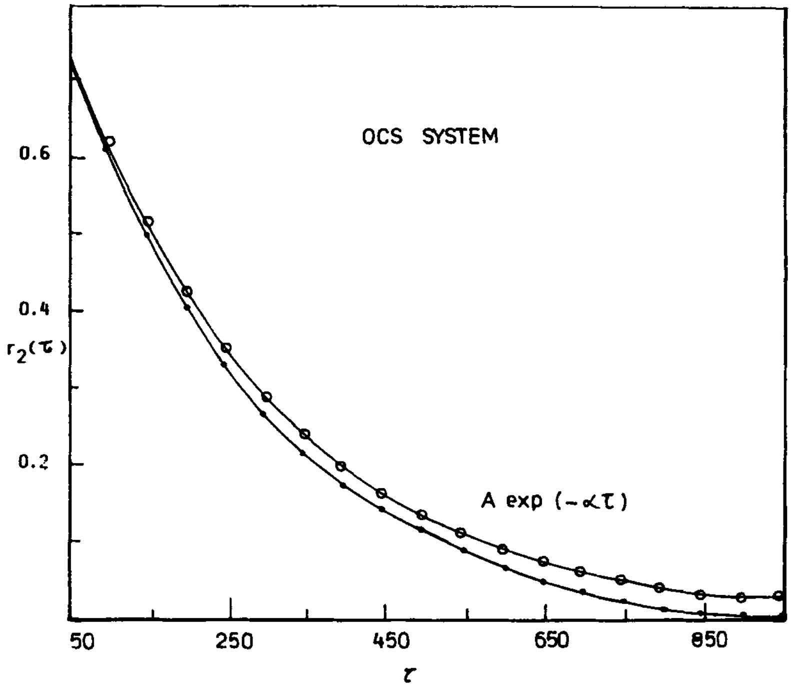

Figure 2. Plot of $r_2'(\tau)$ vs delay τ (ns) in a $\pi-\tau-\pi/2$ experiment for OCS system with $\beta=\alpha_1=600\,\mathrm{kHz}$, $\alpha_2=\gamma_2=\beta/20$ and $\gamma_1=\beta/8$.

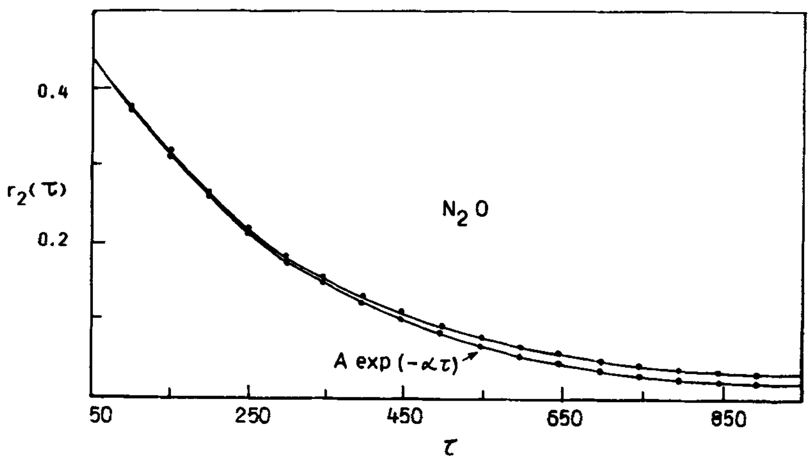

Figure 3. Plot of $r_2'(\tau)$ vs delay τ (ns) in a $\pi-\tau-\pi/2$ experiment for N_2O system with $\beta=\alpha_1=600\,\mathrm{kHz}$, $\alpha_2=\gamma_2=\beta/20$ and $\gamma_1=\beta/8$.

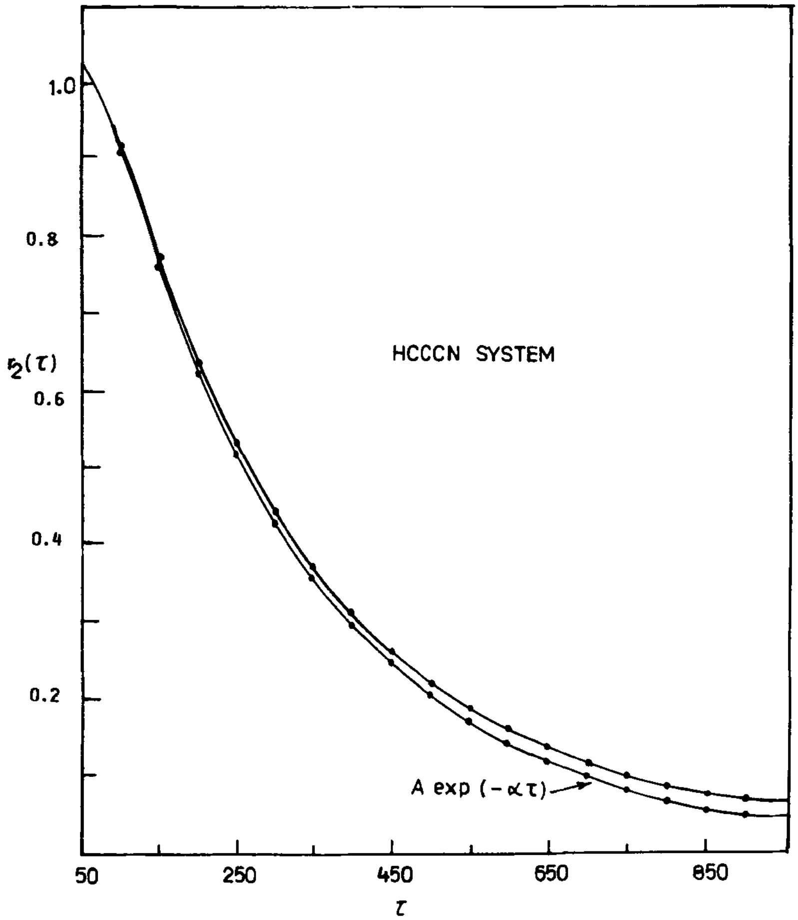

Figure 4. Plot of $r_2'(\tau)$ vs delay τ (ns) in a $\pi-\tau-\pi/2$ experiment for HCCCN system with $\beta=\alpha_1=600\,\mathrm{kHz}$, $\alpha_2=\gamma_2=\beta/20$ and $\gamma_1=\beta/8$.

$\pi-\tau-\pi/2$ experiment on many systems and compared with the corresponding exponential decay. It is seen that this effect is small, but should be observable in an experiment.

References

Liu W K and Marcus R A 1975 *J. Chem. Phys.* **63** 272
Feynman R P, Vernon F L Jr and Hellworth R W 1957 *J. Appl. Phys.* **28** 49
Mehrotra S C and Mäder H 1988 *Z. Naturforsch.* **A43** 454
Schmalz T G and Flygare W H 1978 *Laser and coherence spectroscopy* (New York: Plenum Press) p. 125
Tanaka K, Boggs J E and Mehrotra S C 1983 *Pramana – J. Phys.* **20** 439