Microwave Transient Phenomena of Symmetric Top Molecules. An Extended Bloch Type Description

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The Bloch equations for the macroscopic polarization components P_r and P_i and the population difference ΔN of a two-level system are derived with inclusion of diagonal elements of the electric dipole moment operator.

The influence of such elements on the solutions is discussed. The effect of Stark-switching technique on the observed transient emission signal is considered.

Introduction

In the last few years, a number of transient experiments in gas phase microwave spectroscopy have been performed on two-level systems by using the Stark-switching technique [1a–1l].

To our knowledge, this technique has been applied so far only to the quantitative investigation of two-level systems with vanishing diagonal matrix elements of the electric dipole operator, i.e. to transitions with a non-linear (quadratic) Stark-effect. Consequently, the interpretation of the experimental results in terms of the two-level relaxation parameters T_1 and T_2 could be based on a theoretical treatment which includes only the transition dipole matrix element. The basic differential equations for the induced macroscopic polarization components P_r and P_i and the two-level population difference ΔN (Bloch equations) are derived by treating the electric dipole interaction of the microwave radiation with the quantum-mechanical two-level system semiclassically [2].

In this paper we extend this treatment by allowing for non-vanishing diagonal dipole matrix elements which occur for degenerate eigenstates such as the rotational levels of symmetric top molecules ($K \cdot M \neq 0$) or the ro-torsional levels for degenerate torsional substates (E-species). The effect of resulting additional terms on the solutions of the Bloch equations and the observed transient signals will be discussed.

The Bloch Equations

The following treatment is closely related to the theoretical derivation in Reference [2].

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We shall briefly outline the basic equations which govern electric dipole transitions between rotational energy levels of molecules in a gas which are treated as an ensemble of two-level quantum systems. The effects of the translational motion of molecules will not be taken into account here, i.e. Doppler broadening will be neglected with respect to pressure broadening. We consider at first only the coherent perturbation of the two-level systems due to the electric dipole interaction with the microwave radiation, represented by a plane wave, polarized in Z-direction and propagating in X-direction, with the electric field component

$$E(X,t) = 2\,\varepsilon(X,t)\cos(\omega t - kX)\,. \tag{1}$$

With μ, the dipole operator with respect to the Z-axis, the Hamiltonian is

$$H = H_0 - 2\,\mu\,\varepsilon\cos(\omega t - kX)\,, \tag{2}$$

where H_0 is the time-independent Hamiltonian of the two-level system with eigenvalues E_a and E_b.

The dynamical behaviour of the system may be described by the density matrix σ whose equation of motion is given by

$$i\hbar\frac{\partial\sigma}{\partial t} = [H,\sigma] \tag{3}$$

with H given by Equation (2).

The electric field induces a polarization (macroscopic dipole moment per unit volume) into the sample which for N two-level systems per unit volume is given by

$$P = N\cdot\mathrm{Tr}\{\mu\,\sigma\}\,. \tag{4}$$

Explicitely,

$$P = N(\mu_{ab}\,\sigma_{ba} + \mu_{ba}\,\sigma_{ab} + \mu_{aa}\,\sigma_{aa} + \mu_{bb}\,\sigma_{bb}) \tag{5}$$

where $\mu_{gg'}$; $g, g' = a, b$ denote the dipole matrix elements.

By introducing the number densities of molecules in the states $|a\rangle$ and $|b\rangle$ respectively,

$$N_a = N\,\sigma_{aa}, \quad N_b = N\,\sigma_{bb} \tag{6}$$

and a real and imaginary time-dependent component of the polarization, P_r and P_i,

$$(P_\mathrm{r} - i\,P_\mathrm{i})\exp\{-i(\omega t - kX)\} = N\,\mu_{ab}\,\sigma_{ba} \tag{7}$$

we can rewrite Eq. (5)

$$\begin{aligned} P &= (P_\mathrm{r} + i\,P_\mathrm{i})\exp\{i(\omega t - kX)\} \\ &\quad + (P_\mathrm{r} - i\,P_\mathrm{i})\exp\{-i(\omega t - kX)\} \\ &\quad + \mu_{aa}\,N_a + \mu_{bb}\,N_b \\ &= 2\,P_\mathrm{r}\cos(\omega t - kX) - 2\,P_\mathrm{i}\sin(\omega t - kX) \\ &\quad + \mu_{aa}\,N_a + \mu_{bb}\,N_b\,. \end{aligned} \tag{8}$$

With the definitions (6), (7) and Eq. (3) we obtain three coupled differential equations for P_r, P_i and $\Delta N = N_a - N_b$, the two-level population difference

$$\begin{aligned} &\frac{\partial P_\mathrm{r}}{\partial t} + \left[\Delta\omega + \frac{2\varepsilon}{\hbar}(\mu_{aa} - \mu_{bb})\cos(\omega t - kX)\right] P_\mathrm{i} + \varkappa^2\,\varepsilon\,\frac{\hbar\,\Delta N}{4}\sin 2(\omega t - kX) = 0\,, \\ &\frac{\partial P_\mathrm{i}}{\partial t} - \left[\Delta\omega + \frac{2\varepsilon}{\hbar}(\mu_{aa} - \mu_{bb})\cos(\omega t - kX)\right] P_\mathrm{r} + \varkappa^2\,\varepsilon\,\frac{\hbar\,\Delta N}{4}[1 + \cos 2(\omega t - kX)] = 0\,, \\ &\frac{\hbar}{4}\frac{\partial \Delta N}{\partial t} - \varepsilon\,P_\mathrm{r}\sin 2(\omega t - kX) - \varepsilon\,P_\mathrm{i}[1 + \cos 2(\omega t - kX)] = 0\,. \end{aligned} \tag{9}$$

where

$$\varkappa = 2\,|\mu_{ab}|/\hbar$$

and

$$\Delta\omega = (E_b - E_a)/\hbar - \omega = \omega_0 - \omega$$

is the offset from resonance frequency.

Deriving Eq. (9) is equivalent to the transformation of Eq. (3) into the interaction representation with the additional terms for nonvanishing diagonal dipole matrix elements oscillating with frequency ω. We have also retained the oscillating (2ω)-terms which are usually assumed to the negligible (rotating wave approximation) [3]. It has been argued [4] that, on the average, the action of the high-frequency (2ω) terms is considerably smoothed over in the time which is characteristic for the rate of change of the variables P_r, P_i and ΔN. As result of averaging Eq. (9) over short time intervals ($\sim 1/2\omega$) such high frequency terms can be neglected. The same arguments may be used to justify the neglection of the high-frequency (ω) terms which are due to the diagonal dipole matrix elements.

To support the result of these considerations somewhat more quantitatively we have carried out for the special case of resonance $\Delta\omega = 0$ an iterative Picard-Lindelöf procedure [5] to approximately solve Equation (9). This procedure may also be used to give a justification of the rotating wave approximation which has not yet been given in the literature.

Being interested in the time development of P_r, P_i and ΔN describing the dynamical behaviour of the two-level systems which are switched from far off-resonance into resonance at time $t = 0$, the initial values for P_r, P_i and ΔN are

$$P_\mathrm{r}(0) = P_\mathrm{i}(0) = 0, \quad \Delta N(0) = \Delta N_0 \tag{10}$$

where ΔN_0 is the thermodynamical equilibrium value of ΔN.

Then in n-th iteration

$$\begin{aligned} P_\mathrm{r}^{(n)}(t) &= -\frac{2\varepsilon}{\hbar}(\mu_{aa} - \mu_{bb})\int_0^t P_\mathrm{i}^{(n-1)}(t')\cos(\omega t' - kX)\,\mathrm{d}t' - \varkappa^2\,\varepsilon\,\frac{\hbar}{4}\int_0^t \Delta N^{(n-1)}(t')\sin 2(\omega t' - kX)\,\mathrm{d}t', \\ P_\mathrm{i}^{(n)}(t) &= -\varkappa^2\,\varepsilon\,\frac{\hbar}{4}\int_0^t \Delta N^{(n-1)}(t')\,\mathrm{d}t' - \frac{2\varepsilon}{\hbar}(\mu_{aa} - \mu_{bb})\int_0^t P_\mathrm{r}^{(n-1)}(t')\cos(\omega t' - kX)\,\mathrm{d}t' \\ &\quad - \varkappa^2\,\varepsilon\,\frac{\hbar}{4}\int_0^t \Delta N^{(n-1)}(t')\cos 2(\omega t' - kX)\,\mathrm{d}t', \\ \frac{\hbar}{4}\Delta N^{(n)}(t) &= \frac{\hbar}{4}\Delta N_0 + \varepsilon\int_0^t P_\mathrm{i}^{(n-1)}(t')\,\mathrm{d}t' + \varepsilon\int_0^t P_\mathrm{i}^{(n-1)}(t')\cos 2(\omega t' - kX)\,\mathrm{d}t' \\ &\quad + \varepsilon\int_0^t P_\mathrm{r}^{(n-1)}(t')\sin 2(\omega t' - kX)\,\mathrm{d}t'\,. \end{aligned} \tag{11}$$

The solutions which are obtained from Eq. (9) when neglecting the rapidly varying terms [2], may be used in zero order approximation

$$\begin{aligned} P_r^{(0)}(t) &= 0\,, \\ P_i^{(0)}(t) &= -\frac{\hbar\varkappa}{4}\Delta N_0 \sin\varkappa\varepsilon t\,, \\ \Delta N^{(0)}(t) &= \Delta N_0 \cos\varkappa\varepsilon t\,. \end{aligned} \tag{12}$$

The iterative procedure (11) allows the expansion of the solutions of Eq. (9) in powers of $\varkappa\varepsilon/\omega$. By carrying through the iterations (11) up to first order in $\varkappa\varepsilon/\omega$ we get

$$\begin{aligned} P_r(t) = \frac{\varkappa\varepsilon}{\omega}\Bigg[& \frac{\mu_{aa}-\mu_{bb}}{\mu_{ab}}\cdot\frac{\hbar\varkappa}{4}\Delta N_0 \\ & \cdot\sin\varkappa\varepsilon t\sin(\omega t - kX) + \frac{\hbar\varkappa}{8}\Delta N_0\cos\varkappa\varepsilon t \\ & \cdot\{\cos 2(\omega t - kX) - \tfrac{1}{2}\} - \frac{\hbar\varkappa}{16}\Delta N_0\Bigg], \\ P_i(t) = P_i^{(0)}(t) & \\ & -\frac{\varkappa\varepsilon}{\omega}\left[\frac{\hbar\varkappa}{8}\Delta N_0\cos\varkappa\varepsilon t\sin 2(\omega t - kX)\right], \\ \Delta N(t) = \Delta N^{(0)}(t) & \\ & -\frac{\varkappa\varepsilon}{\omega}\left[\frac{\Delta N_0}{2}\sin\varkappa\varepsilon t\sin 2(\omega t - kX)\right]. \end{aligned} \tag{13}$$

+ higher order terms in $(\varkappa\varepsilon/\omega)$.

For the usual experimental conditions we have $\varkappa\varepsilon \ll \omega$ which makes the magnitude of the oscillating corrections in (13) negligibly small. For example, at a typical 5 mW/cm² microwave power density, we obtain for a $J, K, M = 1, 1, 1 \to 2, 1, 1$ transition of a symmetric top molecule with a dipole moment of 4 D:

$$\frac{\varkappa\varepsilon}{\omega} < 10^{-4}; \quad \left(\frac{\mu_{aa}-\mu_{bb}}{\mu_{ab}} \approx 1\right).$$

Thus, in most practical cases, the Eqs. (9) will be reducible to the Bloch-equations [2] with inclusion of relaxation terms to phenomenologically account for the random perturbation of the two-level system due to molecular collisions. Then

$$\begin{aligned} &\frac{\partial P_r}{\partial t} + \Delta\omega\, P_i + \frac{P_r}{T_2} = 0\,, \\ &\frac{\partial P_i}{\partial t} - \Delta\omega\, P_r + \frac{\hbar\varkappa^2}{4}\varepsilon\,\Delta N + \frac{P_i}{T_2} = 0\,, \\ &\frac{\hbar}{4}\frac{\partial\Delta N}{\partial t} - \varepsilon\, P_i + \frac{\hbar}{4}\frac{\Delta N - \Delta N_0}{T_1} = 0\,. \end{aligned} \tag{14}$$

The above conclusions on the influence of the oscillating terms in (9) should also hold with inclusion of the relaxation terms which do not drastically change the time scale for the variation of P_r, P_i and ΔN. The case of far-off resonance $\Delta\omega \gg \varkappa\varepsilon$ and $\Delta\omega \gg 1/T_1, 1/T_2$ which is of interest for the investigation of transient emission (optical free induction decay) is most easily solved by setting $\varepsilon = 0$ [2]. Then, Eqs. (14) and (9) (with inclusion of relaxation terms) are identical.

However, when calculating the polarization P, there remains still a difference to the case of non-vanishing diagonal dipole matrix elements. When analyzing the transient experiments we have to relate the solutions of the Bloch equations to the observed signal. This signal depends on the macroscopic polarization of the sample, which in (8) contains an additional "quasi-static" term

$$P_s(t) = \mu_{aa}\, N_a(t) + \mu_{bb}\, N_b(t)\,. \tag{15}$$

We may rewrite (15) in a form which is more adapted to the solution of (14):

$$P_s(t) = \frac{N(t)}{2}(\mu_{aa} + \mu_{bb}) + \frac{\Delta N(t)}{2}(\mu_{aa} - \mu_{bb}) \tag{16}$$

where the number density of two-level systems

$$N(t) = N_a(t) + N_b(t) \tag{17}$$

may be replaced by its equilibrium value N_0, if there is little net transfer of population out of the two-level system during the course of the experiment

$$N(t) \approx N_0 = N_{a_0} + N_{b_0}\,. \tag{18}$$

Theoretical considerations to justify (18) are given elsewhere [8].

The Transient Signal

We restrict ourselves to the discussion of the transient emission experiment to determine the relaxation time T_2 by using the Stark-switching technique (see, for instance, Reference [1d]).

By polarizing an ensemble of two-level systems consisting of the M-sublevels of a rotational transition ($\Delta M = 0$ selection rule assumed) we achieve maximum polarization by a $\pi/2$-pulse (time $t_{\pi/2} := 0$). For times $t > 0$, the system is brought far out of resonance and we may apply the solution of (14) for $\varepsilon = 0$ [2]. Then, with the

definitions (8) and Eqs. (16), (17), and (18), we obtain for the polarization

$$P(t) = -2P_i(0)\,e^{-t/T_2}\{\sin \Delta\omega t \cos(\omega t - kX) + \cos \Delta\omega t \sin(\omega t - kX)\} + \mu_{aa} N_{a_0} + \mu_{bb} N_{b_0} - \frac{\Delta N_0}{2}(\mu_{aa} - \mu_{bb})\,e^{-t/T_1} \quad (19)$$
$$= \tilde{P}(t) + P_s(t)$$

where $\tilde{P}(t)$ is standard solution, $P_i(0) = -\frac{\hbar\varkappa}{4}\Delta N_0$.

The additional terms

$$P_s(t) = \mu_{aa} N_{a_0} + \mu_{bb} N_{b_0} - \frac{\Delta N_0}{2}(\mu_{aa} - \mu_{bb})\,e^{-t/T_1} \quad (20)$$

which arise from diagonal dipole matrix elements represent an exponentially damped non-oscillating polarisation relaxing to a steady state value which gives rise to an electric field component

$$E_0 = 4\pi(\mu_{aa} N_{a_0} + \mu_{bb} N_{b_0}). \quad (21)$$

Of course, in the absence of an external field, such a constant molecular field cancels out to zero together with the corresponding (non-polarized) M-component with opposite sign ($\mu_{gg}(M) = -\mu_{gg}(-M)$; $g = a, b$).

The remaining time dependent decay term in (20) is comparable in magnitude with the amplitude of the oscillating terms $\tilde{P}(t)$ in Equation (19). However, its influence on the transient emission signal should be negligibly small as it contains only frequency components which are far below the cut-off frequency of the waveguides used in the experiments. Consequently this term may be dropped in the further analysis.

To derive the signal at the output of a nonlinear detector, one has to relate $\tilde{P}(t)$ in Eq. (19) to the electric field distribution by means of the wave equation

$$\frac{\partial^2 E_{em}}{\partial X^2} - \frac{1}{c^2}\frac{\partial^2 E_{em}}{\partial t^2} = \frac{4\pi}{c^2}\frac{\partial^2 \tilde{P}(t)}{\partial t^2} \quad (22)$$

where E_{em} is the emitted field due to $\tilde{P}(t)$. Separating this field from the source radiation (1) which — with constant amplitude — is used to calculate $\tilde{P}(t)$, implies the concept of an optically thin sample.

When integrating Eq. (22), the change of wave vektor k during the course of the Stark-switch experiment has to be considered. This change of k — mostly neglected in previous publications — affects the transient emission signal amplitude as may be seen by solving Eq. (22) under the slowly varying envelope assumption for P_r, P_i and ε [3].

With the trial solution

$$E_{em} = 2\varepsilon_r \cos(\omega_0 t - k_0 X) - 2\varepsilon_i \sin(\omega_0 t - k_0 X) \quad (23)$$

for the emitted field where

$$k_0 = \omega_0/c \quad \text{and} \quad \Delta k = k_0 - k = \Delta\omega/c$$

we may then rewrite Eq. (22)

$$\partial\varepsilon_r/\partial X = 2\pi k_0 P_i(0)\,e^{-t/T_2}\cos \Delta k X,$$
$$\partial\varepsilon_i/\partial X = 2\pi k_0 P_i(0)\,e^{-t/T_2}\sin \Delta k X. \quad (24)$$

With the boundary conditions

$$\varepsilon_r(X = 0) = \varepsilon_i(X = 0) = 0 \quad (25)$$

at the beginning of the absorption cell, we then have the solution

$$E_{em} = 8\pi k_0 P_i(0)\,e^{-t/T_2}\cdot\frac{1}{\Delta k}\sin\frac{\Delta k X}{2} \cdot\cos\left(\omega_0 t - k_0 X + \frac{\Delta k X}{2}\right). \quad (26)$$

For the usual Stark-switch experiment* the field at the detector ($X = L$) is then given by the superposition of source and emitted microwave fields (1) and (26)

$$E = 2\varepsilon\cos(\omega t - kL) + 8\pi\frac{\omega_0}{c}P_i(0)\frac{1}{\Delta k} \cdot\sin\frac{\Delta k L}{2}\,e^{-t/T_2}\cos\left(\omega_0 t - k_0 L + \frac{\Delta k L}{2}\right). \quad (27)$$

Then, for a square law diode detector the change in signal may be given as [6]

$$\Delta S(t) = \frac{8\pi\beta\omega L}{c}\left(\frac{\sin\frac{\Delta k L}{2}}{\frac{\Delta k L}{2}}\right)\varepsilon P_i(0)\,e^{-t/T_2} \cdot\cos\left(\Delta\omega t - \frac{\Delta k L}{2}\right) \quad (28)$$

where β is a constant, characterising the diode efficiency.

* or a bridge type experiment in the absorption mode [1h].

The solution (28) differs from previous results [6] by a damping factor

$$\eta = \frac{\sin \frac{\Delta k L}{2}}{\frac{\Delta k}{2} L}. \tag{29}$$

A similar expression for this loss of efficiency due to spatial incoherence (k-switch) has been derived by Glorieux [7], using a different theoretical approach. For the usual experimental conditions ($\Delta k L \ll 1$) the factor (29) is close to unity.

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