Some Theoretical Considerations on the Microwave Three-wave Mixing Experiments

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Patterson and Doyle demonstrated that optical isomers could be discriminated by using microwave three-wave mixing experiments [1]. Apparently their work was carried out, being stimulated by a theoretical work on microwave triple resonance by Hirota [2]. Subsequently their work was followed by several investigations performed by using similar techniques [3–8]. Grabow presented theoretical background on this microwave three-wave mixing experiments [9]. Also Lobsiger *et al.* gave similar theoretical explanations [8].

For C_1 enantiomers, all the dipole moment components along the principal moment of inertia axes are nonzero. The sign of the product of the three components should be different for the different enantiomers. This is the reason why the experiments are designed to observe the phenomena that depend on it; triple resonance or microwave three-wave mixing. In this investigation, we present some theoretical background of those experiments which is similar to that given by Grabow [9]. However, in the end, we will see a different factor which might evoke a different perspective on the experiments.

Consider a three level system depicted in Fig. 1. Assume, for simplicity, that a system is similar to that used in Patterson and Doyle; the transition between the levels 1 and 2 is a c-type transition and between the levels 2 and 3 an a-type, and between the levels 1 and 3 a b-type. The time evolution of the wave functions is generally described as a linear combination of the three eigenstates with time dependent coefficients such as

$$\Psi(t) = \sum_i a_i(t)\phi(i). \tag{1}$$

The density matrix ρ is defined to be $\rho_{ij} = a_i a_j^*$ as its matrix element. The time dependent density matrix equation is given by

$$i\hbar\frac{d\rho}{dt} = [\mathcal{H}, \rho], \tag{2}$$

where the Hamiltonian $\mathcal{H}$ consists of the zero-th order molecular Hamiltonian and the interaction with the applied external radiation field,

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'. \tag{3}$$

We assume two resonant microwave radiations are applied to excite the transitions between the levels 1 and 2 and the levels 2 and 3. Therefore

$$\begin{aligned} \mathcal{H}' &= -\mu\mathcal{E}(t) && (4)\\ \mathcal{E}(t) &= \mathcal{E}_0\cos\,\omega t + \mathcal{E}_0'\cos\,\omega' t && (5) \end{aligned}$$

where $\omega = (E_2 - E_1)/\hbar$ and $\omega' = (E_3 - E_2)/\hbar$. As the transition between the levels 1 and 2 is a c-type transition, the Rabi frequency $\Omega_{12}(=\mu_{12}\mathcal{E}_0/\hbar)$ can be written as $i\Omega$, and accordingly $\Omega_{21} = -i\Omega$ with Ω being a real quantity by adapting the phase convention used in microwave spectroscopy (see, for example, Townes and Schawlow). For the transition between the levels 2 and 3, $\Omega_{23} = \Omega_{32} = \Omega'$, and Ω' is real.

By using the rotating wave approximation,

$$\rho_{12} = \tilde{\rho}_{12}e^{i\omega t},\ \rho_{23} = \tilde{\rho}_{23}e^{i\omega' t},\ \rho_{13} = \tilde{\rho}_{13}e^{i\omega t}e^{i\omega' t},$$

and by defining three Bloch vector components for each of the three transitions,

$$\begin{aligned} u^c &= \tilde{\rho}_{12} + \tilde{\rho}_{21},\ v^c = i(\tilde{\rho}_{21} - \tilde{\rho}_{12}),\ w^c = \rho_{11} - \rho_{22}\\ u^a &= \tilde{\rho}_{23} + \tilde{\rho}_{32},\ v^a = i(\tilde{\rho}_{32} - \tilde{\rho}_{23}),\ w^a = \rho_{22} - \rho_{33}\\ u^b &= \tilde{\rho}_{13} + \tilde{\rho}_{31},\ v^b = i(\tilde{\rho}_{31} - \tilde{\rho}_{13}),\ w^b = \rho_{11} - \rho_{33} \end{aligned}$$

the equations of motion can be written as

$$\begin{aligned} \dot{u^c} &= \Omega w^c + \frac{\Omega'}{2}v^b,\ \dot{v^c} = -\frac{\Omega'}{2}u^b,\ \dot{w^c} = -\Omega u^c - \frac{\Omega'}{2}v^a\\ \dot{u^a} &= \frac{\Omega}{2}u^b,\ \dot{v^a} = -\Omega' w^a + \frac{\Omega}{2}v^b,\ \dot{w^a} = \frac{\Omega}{2}u^c + \Omega' v^a\\ \dot{u^b} &= \frac{\Omega'}{2}v^c - \frac{\Omega}{2}u^a,\ \dot{v^b} = -\frac{\Omega'}{2}u^c - \frac{\Omega}{2}v^a,\ \dot{w^b} = -\frac{\Omega}{2}u^c + \frac{\Omega'}{2}v^a. \end{aligned}$$

Suppose first we apply a pulse radiation field which is resonant to the c-type transition of the time duration of Δt to excite the transition between the levels 1 and 2. Then we obtain,

$$\begin{aligned} u^c(\Delta t) &= w^c(0)\sin(\Omega\Delta t)\\ v^c(\Delta t) &= w^c(0)\cos(\Omega\Delta t)\\ w^a(\Delta t) &= \frac{1}{2}w^c(0)[1 - \cos(\Omega\Delta t)] + w^a(0)\\ w^b(\Delta t) &= -\frac{1}{2}w^c(0)[1 - \cos(\Omega\Delta t)] + w^b(0), \end{aligned}$$

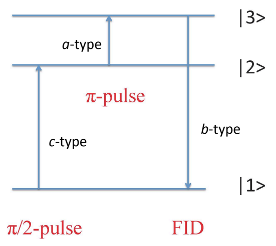

FIG. 1: First shine a pulse radiation which is resonant to the transition between the levels 1 and 2. Immediately after this pulse, we apply the second pulse to excite the transition between the levels 2 and 3. Following these preparation processes, observe free induction decay from the level 3 to 1.

with all other components to be zero. Following this pulse, we apply a resonant radiation to excite the a-type transition between the levels 2 and 3.

$$\begin{aligned}
u^a(t) &= 0\\
v^a(t) &= -(\frac{1}{2}w^c(0)[1-\cos(\Omega\Delta t)]+w^a(0))\sin\Omega'(t-\Delta t)\\
w^a(t) &= (\frac{1}{2}w^c(0)[1-\cos(\Omega\Delta t)]+w^a(0))\cos\Omega'(t-\Delta t)\\
u^b(t) &= 0\\
v^b(t) &= w^c(0)\sin(\Omega\Delta t)\sin\frac{\Omega'}{2}(t-\Delta t)\\
w^b(t) &= -\frac{1}{2}(w^a(0))(1-\cos\Omega'(t-\Delta t))+w^b(0)\\
u^c(t) &= w^c(\Delta t)\sin(\Omega\Delta t)\cos\frac{\Omega'}{2}(t-\Delta t)\\
v^c(t) &= 0\\
w^c(t) &= \frac{1}{2}w^c(0)\cos(\Omega\Delta t)(1-\cos\Omega'(t-\Delta t))\\
&+ w^c(0)\cos(\Omega\Delta t).
\end{aligned}$$

Now we see that the polarization of the b-type transition is induced through this “double resonance” process. The induced polarization is expressed for this transition as

$$\mathbf{P} = N\mathrm{Tr}(\mu\rho) \tag{6}$$

It can be written explicitly as

$$\begin{aligned}
\mathbf{P} &= N(\mu_{13}\rho_{31}+\mu_{31}\rho_{13})\\
&= N\bar{\mu}[(\tilde{\rho}_{31}+\tilde{\rho}_{13})\cos\omega''t - i(\tilde{\rho}_{31}-\tilde{\rho}_{13})\sin\omega''t]
\end{aligned} \tag{7}$$

where $\omega''=\omega+\omega'$. Here we assume the matrix elements of the dipole moment, μ_{13} and μ_{31}, are real and equal, and designated as $\bar{\mu}$, but the sign can be either positive or negative. This induced polarization generates the electric field and the relationship between the two is given by

$$\mathbf{P} = \frac{1}{2}\chi\mathcal{E}_0 e^{i\omega''t} + c.c. \tag{8}$$

where χ is complex susceptibility, $\chi=\chi'-i\chi''$. The susceptibility is related to the density matrix elements as follows;

$$\begin{aligned}
\chi'\mathcal{E}_0 &= N\bar{\mu}(\tilde{\rho}_{31}+\tilde{\rho}_{13}) = N\bar{\mu}u^b &(9)\\
\chi''\mathcal{E}_0 &= iN\bar{\mu}(\tilde{\rho}_{31}-\tilde{\rho}_{13}) = N\bar{\mu}v^b &(10)
\end{aligned}$$

Power emitted (or absorbed) is given by

$$W = \overline{\mathbf{E}\frac{\partial\mathbf{P}}{\partial t}} = \frac{\omega''}{2}\mathcal{E}_0^2\chi''$$

Therefore we obtain

$$\begin{aligned}
W &= N\frac{\omega''}{2}\mathcal{E}_0\bar{\mu}w^c(0)\sin(\Omega\Delta t)\sin\frac{\Omega'}{2}(t-\Delta t)\\
&= (N_1(0)-N_2(0))\frac{\omega''}{2}\mathcal{E}_0\bar{\mu}\sin(\Omega\Delta t)\sin\frac{\Omega'}{2}(t-\Delta t)
\end{aligned} \tag{11}$$

The emitted power is maximized by applying sequentially $\pi/2$- and π-pulses. As formulated above, the induced polarization from the two-step pumping process appears to depend on the product of the matrix elements of the three dipole moment components, μ_a, μ_b, and μ_c. In the treatment presented above, the Rabi frequencies are implicitly assumed to be the signed quantities. This assumption should be examined carefully. In all cases for two level systems, the sign of the dipole moment does not matter, and we automatically use the absolute value of the dipole moment in calculating the Rabi frequency. In general, the oscillation frequency of the polarization is given by $\bar{\Omega}=\pm\sqrt{(\omega-\omega_0)^2+\Omega^2}$, as the radiation frequency may not be in exact resonance. The sign of $\bar{\Omega}$ can be either positive or negative, but the sign has nothing to do with the sign of the dipole moment. It should be noted that, in the microwave three-wave mixing experiments done so far, the process was the three-step sequential two-level processes. If the sign of the product of the three dipole moment components really plays a role, the power given in eq.(11) indicates emission for one enantiomer, on the other hand the signal corresponds to absorption for the other enantiomer. This is not reasonable.

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