MULTIQUANTUM TRANSITIONS IN THE RADIO FREQUENCY RANGE

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Submitted to JETP editor January 18, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) 46, 2011-2016 (June, 1964)

An investigation is made of induced multiquantum transitions manifested in the resonance scattering of harmonics by a two-level system irradiated by a monochromatic signal. The DPPH free radical placed in a constant magnetic field was used as the two-level system in the experiments. The experimental results are in good agreement with an analysis based on the solutions of the modified Bloch equation.

1. INTRODUCTION

THE simplest experiment for the observation of induced multiquantum transitions consists of observing harmonics in the radiation scattered by some substance when it is irradiated by an intense monochromatic electromagnetic wave (frequency multiplication as a result of multiquantum transitions). Such experiments have been performed both in the optical [1] and in the UHF [2] frequency ranges. In the case of a two-level quantum system (i.e., in the case when interaction between the radiation and only two levels of a system is significant) the probability of an induced multiquantum transition of order n is smaller than the probability of transition of order $n-1$ by a factor of approximately $(V/\hbar\omega)^2$, where V is the energy of a monochromatic perturbation of frequency ω. Therefore, observation of induced multiquantum transitions can be easily carried out in the radiofrequency range.

Below we give results of observing radiation of the second and the third harmonics by the free radical of diphenyl picryl hydrazil (DPPH) placed in a constant magnetic field when it is irradiated by a signal of frequency 20 Mc/sec ("pumping"). The dependence of the polarization and the intensity of the harmonics on the polarization and the intensity of the pumping radiation and on the value of the constant magnetic field agrees well with results obtained with the aid of the modified Bloch equation (cf., for example, [3]). It is shown that the observed regularities can be conveniently interpreted from the point of view of the laws of conservation of energy and angular momentum in multiquantum transitions.

2. RADIATION OF HARMONICS BY A TWO-LEVEL SYSTEM

The electron paramagnetic resonance in DPPH at radiofrequencies is well described by means of the modified Bloch equation [3]:

$$dM/dt = \gamma[\mathbf{MH}] + \Omega(\chi_0\mathbf{H} - \mathbf{M}). \qquad (1)^*$$

Here $\mathbf{M}$ is the magnetization, γ is the gyromagnetic ratio (for DPPH $\gamma < 0$), $\mathbf{H}$ is the external magnetic field, $1/\Omega$ is the relaxation time, χ_0 is the static magnetic susceptibility. One might expect that with the aid of this equation one could also investigate induced multiquantum processes in DPPH.

Let the constant magnetic field H_0 be directed parallel to the z axis, while the variable pumping field is equal to $(\mathbf{H}_\omega e^{i\omega t} + \text{c.c.})/2$ [1)]; we seek the stationary solution of (1) in the form

$$\mathbf{M} = \sum_{\pm\infty} \mathfrak{M}_n e^{in\omega t} = \sum_{\pm\infty} [m_n(\mathbf{x} + i\mathbf{y}) + m_{-n}^*(\mathbf{x} - i\mathbf{y}) + M_n\mathbf{z}]\, e^{in\omega t}, \qquad (2)$$

where $\mathbf{x}, \mathbf{y}, \mathbf{z}$ are unit vectors. We adopt the following notation:

$$V_+ = -\gamma\mathbf{H}_\omega(\mathbf{x} - i\mathbf{y})/4, \quad V_-^* = -\gamma\mathbf{H}_\omega(\mathbf{x} + i\mathbf{y})/4,$$
$$W_+ = W_-^* = \gamma\mathbf{H}_\omega\mathbf{z}/2, \quad \omega_0 = \gamma H_0,$$
$$L_n = n\omega - \omega_0 - i\Omega, \quad 2D_n = n\omega - i\Omega. \qquad (3)$$

Taking into account saturation due only to single quantum transitions the constant z-component of magnetization is equal to

1)The effect of the "self" fields of frequency $n\omega$ (i.e., the effect of radiation reaction) is negligible under the conditions of our experiments.

*$[\mathbf{MH}] = \mathbf{M} \times \mathbf{H}$.

$$M_0 = \chi_0 H_0 \times \frac{1 + |2V_+/L_1|^2 (1 - \omega/\omega_0) + |2V_-/L_{-1}|^2 (1 + \omega/\omega_0)}{1 + |2V_+/L_1|^2 + |2V_-/L_{-1}|^2}. \quad (4)$$

The amplitudes of the harmonics of magnetization M_n $(n \neq 0)$ and m_n are obtained from (1) by the method of successive approximations (the expansion parameters are the ratios of V, W to L_n, D_n). In the first nonvanishing approximation the amplitudes of the harmonics are given by the following recurrence formulas:[2)]

$$m_{\pm 1} = \frac{V_\pm}{L_{\pm 1}} \left(M_0 + i\chi_0 H_0 \frac{\Omega}{\omega_0} \right),$$

$$M_{\pm 1} = -i \frac{W_\pm}{2D_{\pm 1}} \chi_0 H_0 \frac{\Omega}{\omega_0}; \quad (5)$$

$$m_{\pm(n+1)} = \frac{W_\pm m_{\pm n} + V_\pm M_{\pm n}}{L_{\pm(n+1)}},$$

$$M_{\pm(n+1)} = \frac{V_\mp^* m_{\pm n} - V_\pm m^*_{\mp n}}{D_{\pm(n+1)}} \quad (n > 0). \quad (6)$$

We note that in the case $V_- = W_\pm = 0$ (i.e., for left circular polarization of the pumping radiation in the xy plane) formulas (4) and (5) are equivalent to formulas (16) and (17) of the paper by Wangsness[4], while in the case $W = 0$, $V_+ = V_+^* = V_- = V_-^*$ (transverse linear polarization) they are equivalent to formula (5a) of the paper by Garstens and Kaplan.[5]

The amplitude of the radiation of the n-th harmonic by a sample placed in a resonator of characteristic frequency $n\omega$ is proportional to $\mathfrak{M}_n \mathbf{h} = U_n$, where $\mathbf{h}$ is the unit vector in the direction of the magnetic field of the resonator (the homogeneity of this field across the sample is assumed). From (2), (5), (6) it follows that U_n contains terms with resonance denominators $L_{\pm 1}, L_{\pm 2}, \ldots, L_{\pm n}$, and, therefore, the dependence of $|U_n|$ on ω_0 will have (in the case $\omega \gg \Omega$) 2n maxima at $\omega_0 \approx k\omega$ $(k = \pm 1, \ldots, \pm n)$.

Taking into account the approximations for m_n, M_n following the first nonvanishing one, the k-th order resonance occurs at $\omega_0 = k\omega - \delta\omega_k$, where

$$\delta\omega_k \approx \frac{2}{\omega} \left(\frac{|V_+|^2}{k-1} + \frac{|V_-|^2}{k+1} \right) \quad (7)$$

(the term which becomes infinite should be excluded). From (7) it follows, for example, that $\delta\omega_1 = |V_-|^2/\omega$, and in the case that the pumping radiation is linearly polarized this coincides with the expression for the Bloch-Siegert[6] shift; $\delta\omega_3 = (2|V_+|^2 + |V_-|^2)/2$, and in the case of linear polarization this coincides with the result of Fontana et al.[7].[3)]

3. QUANTUM INTERPRETATION OF FREQUENCY MULTIPLICATION

In this section it will be shown that if in (5) and (6) we leave out of consideration the nonresonant terms (which is permissible for $\omega \gg \Omega$), then the dependence given by these formulas [together with (2)] of the intensity and the polarization of the radiated harmonics on the intensity and the polarization of the pumping radiation and on ω_0 can be pictorially treated in terms of quantum language utilizing the laws of conservation of energy and of angular momentum in multiquantum transitions.

The radiation of the n-th harmonic by a two-level system can be represented (in accordance with the first nonvanishing order of perturbation theory) as a multiquantum process consisting of the absorption by a system in state 1 of n photons of energy $\hbar\omega$ and of the emission of a single photon of energy $\hbar n\omega$, with the process having a resonance character if one of the virtual states (k-th) coincides with the state 2. As an example Fig. 1 shows a system of levels for such a process for $n = 3$, $k = 2$.

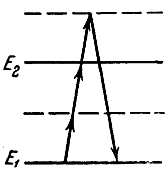

FIG. 1. Schematic representation of levels corresponding to the emission of the third harmonic ($\omega_0 \sim 2\omega$).

The conservation of energy and of angular momentum in quantum transitions can be conveniently checked by use of diagrams in which a displacement in the vertical direction corresponds to a change in the energy of the system, while a displacement in the horizontal direction corresponds to a change in the z-component M_z of the angular momentum of the particle (cf., Fig. 2a,b,c);[4)] the factors W in (5), (6) correspond in the diagrams to vertical arrows $(\Delta M_z = 0)$, and the factors V correspond to oblique arrows $(\Delta M_z = \pm\hbar)$. The virtual states are shown by circles, while filled circles correspond to real states.

[2)]These formulas are also valid in the case of the "usual" Bloch equations if in (5) we neglect terms of order Ω/ω_0 and in (3) take $D_n = (n\omega - i/T_1)/2$ where T_1 is the spin-lattice relaxation time ($1/\Omega$ in this case is the spin-spin relaxation time).

[3)]Errors occur in the paper of Voskanyan et al.[2] in formulas (6), (12) and (17) for the shift of resonance.

[4)]Fig. 2 corresponds to the case $\gamma > 0$, $H_0 > 0$.

For example, in the case $n+1 = 3$, $2\omega \sim \omega_0 > 0$ and $\omega_0 \gg \Omega \gg |V|$, $|W|$ it follows from (5) and (6) that $m_3 \sim V_+W_+W_+$, $m_{-3} \approx 0$, $M_3 \sim V_+W_+V_-^*$; in Fig. 2a are shown two processes corresponding to these polarizations of the radiation. The case $n+1 = 3$, $\omega_0 \sim \omega$ yields four types of polarization: $m_3 \sim V_+V_+V_-^* + V_+W_+W_+$, $m_{-3}^* \sim V_+V_-^*V_-^*$, $M_3 \sim V_+W_+V_-^*$ (Fig. 2b). For the given types of polarization other processes in addition to those shown in the diagrams are possible which differ by having other virtual states (among them states with negative energy), i.e., by exhibiting an alternative succession of emission and absorption.

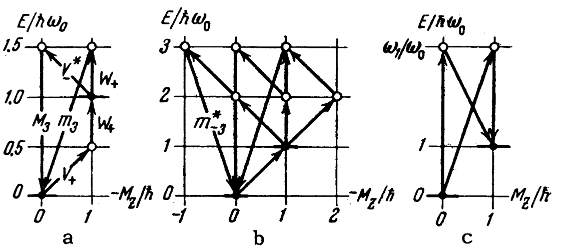

FIG. 2. Diagrams in terms of energy-angular momentum coordinates for the emission of the third harmonic in the cases: a – $\omega_0 \sim 2\omega$, b – $\omega_0 \sim \omega$, and c – for the induced radiation of the Stokes combination frequency.

With the aid of such diagrams one can also discuss the rules for polarization in the case of addition (or subtraction) of unequal quanta. For example, in Fig. 2c we have shown two possible types of polarization of quanta in the emission of the Stokes combination frequency (in the case when in the states 1 and 2 M_z differs by $\hbar$). The rules of correspondence between arrows showing transitions in the diagrams of Fig. 2 and the quantities V, W, m and M in formulas (5) and (6) can be explained in the following manner. In accordance with (3) the factor W_+ is proportional to the z-component of the pumping field, the angular momentum of which with respect to the z axis is equal to zero; the factor V_-^* is proportional to the component of the field with angular momentum parallel to the z axis, while the factor V_+ is proportional to the component with antiparallel angular momentum. Further, in the case of time reversal W_+, V_-^*, V_+ go over into W_-, V_+^*, V_-, and, therefore, if the former are made to correspond to the absorption by the particle of a quantum $\hbar\omega$ with a change in M_z respectively of 0, $+\hbar$, $-\hbar$, then the latter will correspond to the opposite direction of the process, i.e., to radiation of a quantum with a change in M_z of 0, $-\hbar$, $+\hbar$. Finally, in accordance with (2), m_n with $n > 0$ can be taken to correspond to the emission of a right circularly polarized quantum $\hbar n\omega$, m_{-n}^* can be taken to correspond to the emission of a left circularly polarized quantum (σ-quanta) and M_n can be taken to correspond to linear polarization (π-quantum).

4. DESCRIPTION OF THE EXPERIMENT

Approximately 3g of polycrystalline DPPH were placed inside two induction coils with mutually perpendicular axes: one of the coils, the transmitting coil, formed part of a circuit tuned to 20 Mc/sec, while the second coil, the receiving coil, was tuned to 40 (or 60) Mc/sec. The generator of the pumping signal connected to the transmitting coil produced in the sample a magnetic field oscillating at a frequency of 20 Mc/sec of amplitude H_1 up to 2.5 Oe. The field H_0 was produced by an electromagnet which could rotate in the plane containing the axes of the crossed coils. H_0 was varied in the range $\sim \pm 25$ Oe at a frequency of 0.15 or 50 cps and at the same time for synchronous detection the field H_0 was modulated at a frequency of 100 kc/sec with an amplitude ~ 0.5 Oe.

The voltage of frequency 40 (or 60) Mc/sec induced in the receiving coil by the precessing magnetization of the sample M(t) was amplified, detected and applied either to an oscillograph or to a synchronous amplifier and recorder.

The receiving coil also had induced in it a voltage due to the "self" harmonics of the generator of frequency 40 and 60 Mc/sec arising from the nonlinear distortion in the power amplifier of the pumping generator; the phase and the amplitude of this voltage could be regulated by means of "blocking" filters inserted between the generator and the transmitting coil, and this enabled us to select at will the real or the imaginary part of the amplitude of the harmonic $\mathfrak{M}_n$.

Figure 3 shows an example of the recorded de-

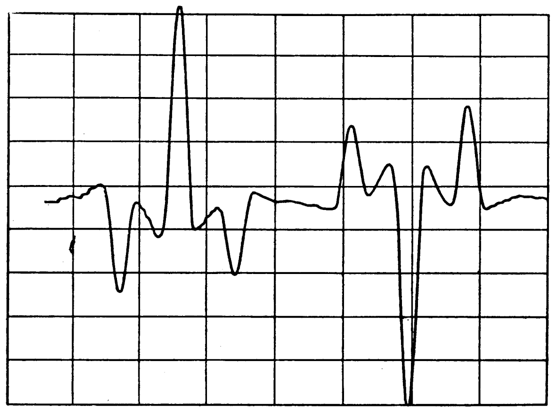

FIG. 3. A record of the dependence of H_0 of the derivative of the real part of the amplitude of the third harmonic for $\vartheta \sim 40°$, $H_1 = 2$ Oe.

pendence of $d(\mathrm{Re}\,\mathfrak{M}_3)/dH_0$ on H_0; the time constant of the synchronous detector was ~ 1 sec, the recording time was ~ 60 sec.

All the experiments were carried out at room temperature.

5. EXPERIMENTAL RESULTS

The experimental procedure consisted of the measurement of the dependence on H_0 of the voltage of the second or the third harmonic induced in the receiver coil. The parameters were the pumping amplitude H_1 and the angle ϑ between the directions of H_1 and H_0 (the angle between the axis of the receiver coil and the direction of H_0 was equal to $\vartheta + \pi/2$). The voltage of the n-th harmonic is proportional to the component of M_n along the axis of the receiving coil; we denote this component by $U_n(H_0, \vartheta, H_1)$ and choose the direction of the x-axis in the plane of the coil axes. We then obtain from (3) $V_+ = V_- = -\gamma H_1 \sin\vartheta/4$, $W_+ = W_- = \gamma H_1 \times \cos\vartheta/2$; if we neglect the nonresonance terms and the effect of saturation (i.e., if we assume that $\omega \gg \Omega \gg \gamma H_1$) it follows from (2)–(6) that the extremal amplitudes of the harmonics $U_{nk} = U_n(k\omega/\gamma, \vartheta, H_1)$ are equal to

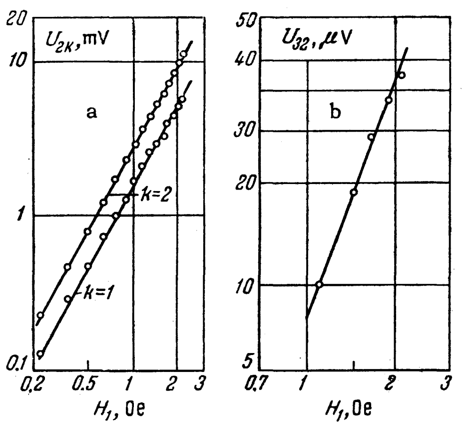

FIG. 4. Dependence on the pumping amplitude of the amplitudes of the second (a) and of the third (b) harmonics.

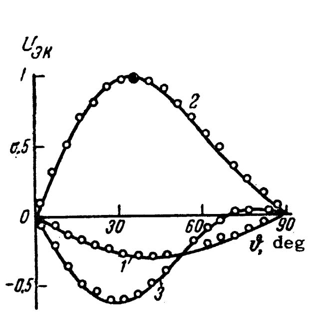

FIG. 5. Dependence of the amplitude of the third harmonic on the angle between the constant field and the pumping field for $\gamma H_0 = k\omega$, k = 1,2,3 ($H_1 \approx 1$ Oe).

$$U_{nk} = -i\frac{\chi_0}{\gamma}\left(\frac{\gamma H_1}{2}\right)^n \frac{1}{\Omega\omega^{n-2}} f_{nk}(\vartheta), \quad k = 1, \ldots, n, \tag{8}$$

where

$$f_{11} = \sin\vartheta\cos\vartheta/2; \tag{9}$$

$$f_{21} = \frac{1}{4}\sin\vartheta(1+\cos^2\vartheta), \qquad f_{22} = -\sin\vartheta\cos^2\vartheta;$$

$$f_{31} = \frac{1}{8}\left(\frac{86}{96}\sin 2\vartheta + \frac{5}{96}\sin 4\vartheta\right); \tag{10}$$

$$f_{32} = -\frac{2}{8}\left(\frac{4}{3}\sin 2\vartheta + \frac{1}{3}\sin 4\vartheta\right),$$

$$f_{33} = \frac{3}{8}\left(\frac{14}{32}\sin 2\vartheta + \frac{9}{32}\sin 4\vartheta\right). \tag{11}$$

The observed dependence on H_1 of U_{2k} (for $\vartheta \sim 35°$) and U_{32} (for $\vartheta \sim 45°$) is shown in Fig. 4, from which it can be seen that, indeed, $U_n \sim H_1^n$.

In Fig. 5 the solid curves are constructed in accordance with formula (11); the experimental data are normalized in such a way that the results of experiment and calculation coincide for $U_{32}(37°)$ (black dot). Figure 5 shows that the rules governing the polarization in the case of frequency tripling which are given for the conditions of the experiment by formulas (8) and (11) agree well with experiment. In the case of frequency doubling we have also obtained satisfactory agreement of experimental data with formulas (10).

6. CONCLUSION

The good agreement of experimental data with the results of calculations shows that it is possible to calculate with the aid of Bloch's equations nonlinear effects in magnetic resonance in substances exhibiting dynamic narrowing of the width of the resonance. The quantum interpretation of these effects is pictorially illustrated by diagrams in terms of energy and angular momentum used as coordinates.

The method utilized above for indicating resonance by means of harmonics may turn out to be convenient for certain radiospectroscopic measurements (for example, in measuring the time of spin-lattice relaxation).[5)]

The authors are grateful to V. S. Tumanov for useful discussions.

[5)]The detection of combination frequencies has already found application in NMR technique for the measurement of H_1[8], and in the so-called sideband method[9]. The method of detecting M_0 (cf., for example,[10]) can be regarded as belonging to the same type of experimental method.

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Translated by G. Volkoff
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