"PARAMETRIC RESONANCE" IN LUMINESCENCE AS A MULTI-PHOTON PROCESS

V. A. KHODOVOĬ

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A new qualitative and quantitative interpretation of the "parametric resonance" effect in luminescence is proposed. The effect consists in the appearance of modulated luminescence of atoms possessing in the excited state a system of closely spaced sublevels when the energy gap between them (the system "parameter") is modulated by an external field with a frequency which is equal to or is an integral multiple of the transition frequency between the sublevels. It is shown that the process can be described as a multi-photon process in which an optical photon is radiated or absorbed simultaneously with one or several photons of the modulating field.

1. INTRODUCTION

MULTI-PHOTON processes were considered theoretically as long as thirty years ago [1,2]; experimental work in this field, however, has only recently appeared, beginning in the radio region and then in the optical one, in connection with the advent of generators of stimulated emission (lasers). In the radio region there have been observed transitions of paramagnetic atoms between magnetic sublevels under the influence of fields at non-resonant frequencies.[3] Resonance maxima in the transition probabilities arose when the energy of several photons coincided with the difference in energy of the states in question. In the optical region transitions have been observed accompanied by the absorption of two photons from a ruby laser.[4,5] In both cases photons of closely similar frequencies participate in the elementary act and the operators of the transition are the same for all photons.

Aleksandrov et al.[6] recently described a phenomenon called "parametric resonance" in resonant luminescence. They observed a modulation of the luminescence of atoms possessing in the excited state a system of closely spaced sublevels when the interval between them (the system "parameter") is modulated by an external field at a frequency which is, for example, equal to the frequency of transition between the sublevels. We shall show in this paper that this phenomenon can be considered as a kind of multi-photon process.

The peculiarity of this multi-photon process resides in the fact that here one optical photon and one or several radiofrequency (rf) photons participate in one elementary act. In addition, the transition operators are different: an electrical dipole transition operator for absorption of optical photons and a magnetic dipole operator for absorption of the rf photons. Another feature of the considered experiment is such that the observed quantity is not associated with excitation of pure states, but with excitation of their coherent superposition. This leads to the condition that the probability of excitation involving n rf photons is not proportional to the n-th power of the intensity of the rf field, as has always been observed previously in multi-photon transitions. This dependence is determined both by the number of photons that participate in the elementary act and by the means of excitation of the coherent superposition of states.

2. QUALITATIVE TREATMENT

We shall present a brief description of an experiment for the observation of a "parametric" resonance in order to make clear the essence of the phenomenon. The resonant scattering of light by cadmium vapors in a weak magnetic field has been studied. The scheme of the resonance levels of cadmium is shown in Fig. 1. The exciting light was plane-polarized and was propagated along the magnetic field, so that the level with $m = 0$ was not excited and will not be considered further. The magnetic field that split the excited state was modulated according to the law

$$H = H_0 + H_1 \sin(\Omega t + \varphi). \quad (1)$$

It has been established that the intensity of the light scattered at a fixed angle turns out to be modulated at the frequency Ω and its multiples. At the same time there are resonant maxima in the intensity of the scattered light whenever the

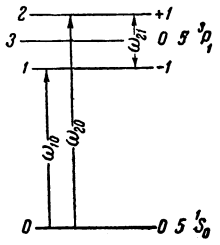

FIG. 1. Scheme of the resonance levels of cadmium.

frequency of the transition between the levels $m = \pm 1$ is a multiple of the frequency of the modulating magnetic field Ω.

The modulation of the luminescence has been interpreted as a consequence of the formation of a coherent superposition of the excited states in each scattering atom. Since the splitting of levels 1 and 2 was much less than the width of the exciting line, each atom in state 0 has a probability of excitation both to state 1 and to state 2 as the result of absorbing photons of the optical radiation only. In the general case, a superposition of states 1 and 2 arises, as a result of which each atom radiates two frequencies at once. These frequencies, by interference, give beats at the difference frequency. As a consequence of the incoherence of the exciting light, however, the phases of these beats are random for the different atoms, and are completely averaged over the ensemble of radiating atoms.[1)] Regular beats are obtained only if the difference of the phases of the excited states is the same for all atoms.

We shall show, in a qualitative way at first, how multi-photon transitions can lead to a constant difference in phase of the excited states. Consider some optical harmonic capable of exciting one of the sublevels, say level 1. The polarization of this harmonic is such that it can excite also level 2, but its energy is insufficient for this excitation. The atom can acquire additional energy by simultaneously absorbing one optical photon of just this harmonic and one radiofrequency photon at the frequency of the transition between sublevels 1 and 2. Now the phase of the optical harmonic enters in the same way into both the phase of state 1 and the phase of state 2, and the difference in phase of these states turns out to be the same for all atoms of the ensemble. The intensity of the emission from the entire assembly of atoms is found to be modulated at a frequency equal to the transition frequency between states 1 and 2.

Obviously, if not one but several rf photons are absorbed with every optical photon, then we observe multiple resonances. All the various phenomena observed in "parametric resonance" can be qualitatively described by similar simple considerations based on the model of multi-photon transitions. The possibility of such a qualitative treatment and the illustrative interpretation constitute the undoubted advantage of this means of analysis. We shall show below that it is possible to obtain not only a qualitative but also a quantitative description of these effects in terms of multi-photon transitions.

3. QUANTITATIVE THEORY

The theoretical examination of the effect from the point of view of multi-photon processes is greatly simplified if it is assumed that the radiation of the usually employed light sources has so low an intensity that the degree of its degeneracy, which is equal to the number of photons in one cell of phase space, is negligibly small (in the experiment described it is equal approximately to 10^{-4}). Then, because of the uncertainty relation between the number of photons in one cell of phase space and the phase of the field created by them, we can consider the phase of each harmonic of the incident optical radiation to be completely indeterminate.

The absence of a definite phase of the harmonics in the exciting light implies that there is no common dipole electric moment component of optical frequency for the ensemble (absence of "optical coherence" in the ground and excited states). The density matrix representing this ensemble then breaks up into two sub-matrices belonging to the ground and excited states. Neglecting induced emission compared to spontaneous emission, we can then consider the entire process of resonant scattering of light as consisting of two independent processes: excitation and subsequent spontaneous emission, separated by the lifetime of the excited state.

The agreement of the theoretical results predicted from such a model with experimental data [8] is an indication of the close approach of this model to reality. In addition, the absence of definite phase relations between the various harmonics means that the contributions of different frequency intervals to the excitation probability will be additive. [9] In this case it is possible to calculate the effect of excitation under the influence of an rf field $H_1 \sin(\Omega t + \varphi)$ and one harmonic of optical radiation $E(t) = E_\omega e^{-i\omega t}$, and then integrate the result obtained over ω.

[1)] Note that in contrast to double resonance experiments,[7] the alternating rf field, which is parallel to the dc field H_0, cannot cause transitions between the considered sublevels.

Let the atom be in the ground state ψ_0 at t = 0, and let the energy of the ground state be zero. The state of the atom at any later time is described by

$$\Psi = \sum_{m=0,1,2} a_m(t)\psi_m, \quad (2)$$

where ψ_m is an eigenfunction of the atom in the dc magnetic field H_0. According to [6], the intensity $I_s(t)$ of light scattered by one atom in a given direction is expressed via the density matrix of the atom in the following way:

$$I_s(t) = K[\rho_{11}(t)|d^{\mu}_{10}|^2 + \rho_{22}(t)|d^{\mu}_{20}|^2 + 2\mathrm{Re}\rho_{21}d^{\mu}_{10}d^{\mu}_{02}]. \quad (3)$$

Here K is a factor connecting the intensity of the radiation with the square of the dipole moment of the radiator, and d^{μ} is the operator of the atomic dipole moment component lying in a plane perpendicular to the direction of the radiation.

In order to obtain the total intensity of the scattered light, it is necessary to sum $I_s(t)$ over all atoms of the scatterer, taking the Doppler effect into account. However, if $\omega_{21}v/c \approx \gamma$, where v is the velocity of the scattering atom, c is the velocity of light, and γ is the natural line width, then this sum changes only the constant K.[6] Thus, the problem reduces to a calculation of the elements of the density matrix of one atom.

The Hamiltonian describing the density matrix has the form

$$\hat{\mathcal{H}} = \hat{H} + \hat{V};$$

$$\hat{H} = \hat{H}_0 - i\Gamma/2, \quad \hat{V} = -d^x E_\omega e^{-i\omega t} + g\mu_0 J_z H_1 \sin(\Omega t + \varphi). \quad (4)$$

Here g is the Lande factor, μ_0 is the Bohr magneton, J_z is the z component of the angular momentum operator. The remaining symbols are the same as those used by Aleksandrov et al.[6] The Schrödinger equation for the amplitude $a_m(t)$ has the form

$$i\hbar\dot{a}_0(t) = V_{10}e^{-i\omega t}a_1(t) + V_{20}e^{-i\omega t}a_2(t),$$

$$i\hbar\dot{a}_m(t) = \hbar(\omega_{m0} - i\gamma/2)a_m(t) + (V_{mm}e^{i\Omega t} + V^*_{mm}e^{-i\Omega t})a_m(t) + V_{0m}e^{-i\omega t}a_0(t), \quad m = 1,2. \quad (5)$$

Here

$$V_{m0} = -E_\omega d^x_{m0}, \quad V_{11} = \tfrac{1}{4}i\hbar\omega_1 e^{i\varphi},$$
$$V_{22} = -\tfrac{1}{4}i\hbar\omega_1 e^{i\varphi}, \quad \omega_1 = 2g\mu_0 H_1. \quad (6)$$

To solve the system (5) we make use of Winter's method,[3] which was successfully used for investigating multi-photon processes in the radio region. We will seek solutions of Eqs. (5) in the form of the following expansion

$$a_m(t) = \sum_{n,k=-\infty}^{+\infty} a_m^{(n)+(k)}(t), \quad m = 0, 1, 2. \quad (7)$$

In this we choose the system of equations for $a_m^{(n)+(k)}$ in such a way that $a_m^{(n)+(k)}$ is connected with $a_0^{(n-1)+(k)}$ or $a_m^{(n)+(k\pm1)}$ only through a single exponential term. The solution of this system should be such that if a summation is carried out over n and k, quantities satisfying (5) will be obtained.

Then the equation for the coefficients of the expansion $a_m^{(n)+(k)}$ (m = 1, 2) will have the form

$$i\hbar\dot{a}_m^{(n)+(k)} = \hbar(\omega_{m0} - i\gamma/2)a_m^{(n)+(k)} + V_{mm}e^{i\Omega t}a_m^{(n)+(k+1)} + V^*_{mm}e^{-i\Omega t}a_m^{(n)+(k-1)} + V_{0m}e^{-i\omega t}a_0^{(n-1)+(k)} \quad (8)$$

with initial conditions

$$t = 0, \quad a_0^{(0)+(0)} = 1, \text{ the remaining } a_m^{(n)+(k)} = 0. \quad (9)$$

Equation (8) is the equation of the change of state of the system, atom + optical field + rf field. It is very much like the equation obtained in the quantization of optical and rf fields.[10] The index n is equal to the number of optical photons absorbed with the initial state n = 0. Similarly the index k is the number of absorbed (+k) or stimulated-emitted (−k) photons for an initial state k = 0. The coefficients $a_m^{(n)+(k)}$ have in this treatment the significance of amplitudes of states in which the atom is in state m, having absorbed n optical and k rf photons.

The choice of this method of analysis is connected with the fact that we desire to account simultaneously for both the phase and the change in the number of photons of the optical and rf fields. In our chosen model of optical excitation we could have described its state by accurately giving the number of photons in each harmonic. In contrast, the rf field has a very high degree of degeneracy. The state of such a field is characterized practically also by specifying the phase and number of photons. A precise statement about the number of photons, however, leads to completely indeterminate phase. The method used here allows us, without determining precisely the number of photons of the rf field, to judge its variation, with the phase of the field kept definite.

An approximate solution to Eq. (8) can be obtained if elementary perturbation theory[10] is used. Its application is valid for the case of a very weak rf field $H_1 \ll H_0$. We limit ourselves here to calculating only those amplitudes $a_m^{(n)+(k)}$ which either do not contain H_1 or contain it in the first power. The only amplitudes that are significantly different from zero are $a_m^{(1)+(0)}$, $a_m^{(1)+(1)}$,

and $a_m^{(1)+(-1)}$. Omitting the simple calculations, we give directly the final expression for the amplitudes $a_m(t)$ in this approximation.

For intervals of time greater than the duration of the transient processes ($t \gg 1/\gamma$), we obtain

$$a_m(t) = \frac{V_{0m}}{\hbar}\frac{e^{-i\omega t}}{(\omega_{m0}-\omega-i\gamma/2)} \times\left\{-1+\frac{V^*_{mm}e^{-i\Omega t}}{\hbar(\omega_{m0}-\omega-\Omega-i\gamma/2)} + \frac{V_{mm}e^{i\Omega t}}{\hbar(\omega_{m0}-\omega+\Omega-i\gamma/2)}\right\}. \quad (10)$$

From this expression it is seen that the amplitude of the excited state $a_m(t)$ has three resonant terms, corresponding to different means of excitation (Fig. 2). The first term corresponds to direct optical excitation, the second to excitation with the simultaneous absorption of one optical and one rf photon, and the last to excitation with absorption of one optical photon and stimulated emission of one rf photon.

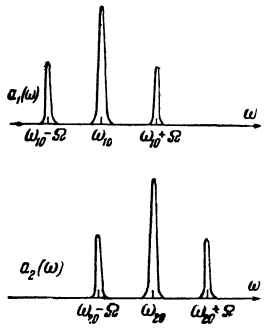

FIG. 2. Dependence of the state amplitudes a_m on the frequency of the optical radiation (case $\omega_{20} = \omega_{10} + \Omega$).

If the level splitting ω_{21} differs from Ω by more than the natural width of the level γ, then the excitation of levels 1 and 2 proceeds by optical photons of different harmonics, and consequently it does not bring about a coherent superposition of excited states. For $\omega_{21} = \Omega$ there are two possibilities for coherent excitation (Fig. 2): (1) level 1 is excited directly by a photon of frequency $\omega = \omega_{10}$ and level 2 by a photon of the same frequency with the simultaneous absorption of one rf photon; (2) level 2 is excited directly by a photon of frequency $\omega = \omega_{20}$ and level 1—with simultaneous stimulated emission of one rf photon.

The change of state of the rf field (a change in the number of photons or energy) depends on the ratio of the transition probabilities associated with the emission or absorption of rf photons. It is easy to see that for the case when the line of excitation is much wider than the absorption line, and the latter is completely within the first, the probabilities of these two processes are the same and the state of the rf field is not changed on the average. This is just the case realized experimentally.

Assuming that the spectral density of the optical radiation $E_\omega = E_0$ is constant within the line width of the excitation line, and integrating over ω from $-\infty$ to $+\infty$, we obtain the elements of the density matrix $\rho_{mm'}(t) = a^*_m(t)a_{m'}(t)$. Keeping only terms of first order in $\varepsilon = \omega_1/\Omega$, we obtain

$$\rho_{11} = 2\pi|E_0|^2|d^x_{10}|^2/\gamma\hbar^2, \quad \rho_{22} = 2\pi|E_0|^2|d^x_{20}|^2/\gamma\hbar^2, \quad (11)$$

$$\rho_{21} = \frac{2\pi|E_0|^2 d^x_{20}d^x_{01}}{\hbar^2}\left\{\frac{i}{\omega_{21}+i\gamma}+\frac{\omega_1}{2}\frac{e^{-i(\Omega t+\varphi)}}{(\omega_{21}+i\gamma)(\omega_{21}+\Omega+i\gamma)} - \frac{\omega_1}{2}\frac{e^{i(\Omega t+\varphi)}}{(\omega_{21}+i\gamma)(\omega_{21}-\Omega+i\gamma)}\right\}. \quad (12)$$

The intensity of the scattered light is related to the density matrix by Eq. (3). We see that modulation of the scattered light in this linear approximation is associated only with the off-diagonal element of the density matrix ρ_{21}. We are in fact interested only in this component (we denote it by $I_{21}(t)$). In ρ_{21} there are two resonant terms: the first when $\omega_{21} = \Omega$ and the second when $\omega_{21} = 0$.

We consider them separately, assuming that the resonances are well resolved:

1) $\omega_{21} = \Omega$, $\omega_{21} \gg \gamma$ (Fig. 2).

Substituting (12) into (3) and considering that (see [6])

$$d^x_{10} = d^x_{20} = d, \quad d^y_{10} = d^y_{20} = de^{-i(\psi-\pi/2)},$$

we obtain

$$I_{21}(t) = C\frac{\varepsilon}{2}\frac{\sin(\Omega t+\varphi+\chi)}{\sqrt{\gamma^2+(\Omega-\omega_{21})^2}};$$

$$\chi = -2\psi + \operatorname{arc\,tg}\frac{\omega_{21}-\Omega}{\gamma}, \quad C = \frac{4\pi}{\hbar^2}K|d|^4|E_0|^2, \quad (13)^*$$

where ψ is the angle between the direction of observation and the plane of polarization of the incident light.

From this formula it is seen that the light scattered by one atom is modulated at the frequency of the rf field, and the phase of this field enters into the phase of the modulation of the scattered light. Since the phase of the rf field is definite and constant, the modulation of all atoms is synchronized, i.e., the radiation of the entire ensemble is modulated.

2) $\omega_{21} = 0$, $\Omega \gg \gamma$. In this case all three terms in Eq. (12) are "in operation," which corresponds

*arc tg = $\tan^{-1}$

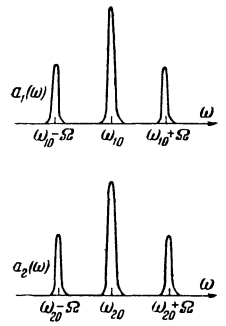

FIG. 3. Dependence of the state amplitudes a_m on the frequency of the optical radiation (case $\omega_{20} = \omega_{10}$).

to excitation of levels 1 and 2 by three optical harmonics (Fig. 3):

$$I_{21}(t) = -C\left\{\frac{\cos(-2\psi+\chi_0)}{\sqrt{\omega_{21}^2+\gamma^2}} + \varepsilon\frac{\sin(-2\psi+\chi_0)}{\sqrt{\omega_{21}^2+\gamma^2}}\cos(\Omega t+\varphi)\right\}$$

$$\chi_0 = \text{arc tg}\,(\omega_{21}/\gamma). \qquad (14)$$

Equations (13) and (14) agree precisely with the ones obtained by Aleksandrov et al.[6] for the limiting case $\varepsilon \ll 1$, which indicates the equivalence of both methods of analysis.

The treatment presented gives the result of a linear approximation. To describe the effect in higher orders requires, besides an assessment of possibility of multi-photon processes in absorption, a consideration of the possibility of multi-photon processes in emission as well. In fact, in analogy with excitation, it is possible to have spontaneous emission of an optical photon simultaneously with the absorption or emission of several rf photons. Thus, for example, a quadratic effect—a change in the average intensity of the scattered light upon coincidence of the modulation frequency with the frequency of the transition 1—2—can be explained in the following fashion. Let there be a coherent superposition of states 1 and 2 under excitation. The decomposition of this superposition from the classical point of view can be considered in the following way: one of the levels is decomposed with emission of only an optical harmonic, and the other with the emission of the same harmonic of optical radiation and the emission or absorption of an rf harmonic. The interference of these optical-frequency harmonics leads to a change in the spatial distribution of the intensity of the scattered light. Since the amplitude of the rf field enters linearly both in the excitation of the coherent superposition of the states and in its decomposition, the whole effect is proportional to the square of the amplitude of the rf field.

In conclusion, we wish to point out that multi-photon processes in emission constitute a related phenomenon discussed in the literature but not yet realized. We mean frequency modulation of the radiation of an atom by means of the Stark and Zeeman effects. As is known,[12] the spectrum of a frequency modulated oscillation is given by

$$U(\omega) = U_0\sum_{k=-\infty}^{+\infty} J_k\left(\frac{\Delta\omega}{\Omega}\right)\cos(\omega_0+k\Omega)t, \qquad (15)$$

where ω_0 is the mean frequency of the oscillation, Ω is the modulation frequency, and $\Delta\omega$ is the maximum deviation of the frequency upon modulation. Equation (15) can be applied to an excited atom if it is possible to ignore the decay of the excited state, i.e., if the period of modulation is much less than the lifetime of the atom in the excited state. In view of what has been said above, this spectrum can be considered as the superposition of multi-photon processes of different order with respect to the number of participating photons of the modulation field.

In order to observe experimentally the appearance of these additional lines in the spectrum of an atom in an alternating field, the frequency of the modulation should be greater than 10^9 cps, so that Doppler broadening will not mask the phenomenon. For a sufficiently large field intensity this constitutes a definite technical problem, still unsolved. ''Parametric resonance'' in luminescence allows one to perceive the elements of the effects considered under the Doppler shape, using the phase relations between the components of a complex spectrum.

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