Nonlinear phase resonance of quantum beats in the dimer ground state

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The nonlinear phase resonance of quantum beats for the ground state of dimers is treated theoretically. It is shown that during observation along an external magnetic field a resonance appears, under definite conditions, in the total intensity of the fluorescence averaged over time. There is no nonlinear shift of the resonance. Recording of such a resonance enables one to determine both the magnitude and sign of the Lande factor of a selected vibrational–rotational level of the ground electronic state of dimers.

Beginning in the first half of the Sixties and going up to our time, the phenomenom of quantum beats[1,2] has attracted the interest of spectroscopists. Investigation of this effect, on the one hand, enables one to understand more deeply the essence of the dynamics of a spectral transition and, on the other, to obtain concrete data about the energy interval between closely lying quantum levels.

Beats after a pulse of excitation are the most obvious manifestation of quantum beats. It requires for their observation, however, the recording of the kinetics of fluorescence with rather high time resolution.

The indirect manifestations of quantum beats are simpler to record: resonance of beats, parametric resonance, phase resonance, and the relaxation resonance of quantum beats.[3] In these cases, an increase of the amplitude of fluorescence or absorption modulation during the coincidence of the modulation frequency of some one of the parameters of the exciting radiation (amplitude, phase) with the frequency of the energy splitting of coherently excited atomic states is observed.

In the enumerated cases the value of the resonance signals depends linearly on the intensity of the exciting light. At the same time there exists a group of experiments[1] in which one and the same light field produces the coherence of nondegenerate states and probes these states. In this case the resonance signals are nonlinear. This leads, on the one hand, to different shifts of the absorption resonance and, on the other, to the possibility of recording resonance not only with respect to the depth of modulation of the induced fluorescence but also to the time-averaged modulation of the intensity of the radiation.[4,5]

For the ground state of dimers the nonlinear resonance of quantum beats is one of the few methods that enable one to determine directly the magnetic moment of a selected vibrational–rotational (VR) level. In the present paper we treat the prospects of applying the nonlinear phase resonance of beats to the ground state of dimers placed in an external magnetic field. We shall perform the analysis of nonlinear signals of phase resonance by applying the methods of polarization moments (PM).[6] We treat the cases of states, typical for dimers, with large values of the angular momentum J. We use the approach of exciting a line with a broad spectral contour.[7] An analysis of such an approach for laser excitation of dimers was carried out in Ref. 5. We treat the open cycle of absorption–emission,[8] where the molecule, finding itself in a definite VR level of the ground electronic state, absorbs light and makes a transition to a vibrational–rotational level of an excited state. After this, spontaneous deex-

citation takes place, and the molecule decays to the ground electronic state but to a VR level different from the initial one. In the case of dimers there is frequently a relationship in which the rate of light absorption $\Gamma_p < \gamma_x$, where γ_x is the relaxation rate of the PM φ_0^x of the ground state. In dimers the relaxation of the ground electronic state takes place through two channels. This is flight and collisional relaxation.[9] At the same time $\Gamma_p \ll \Gamma_K$, where Γ_K is the relaxation rate of the PM f_Q^K of the excited state. Frequently, radiative decay of the excited state makes the principal contribution to Γ_K.[10]

Traditionally, phase modulation of the exciting light is achieved by the harmonic modulation of the plane of polarization of linearly polarized light.[11] In the model assumed by us the PM arising in the ground state can be found by solving the equation[12]

$$\dot{\varphi}_q^x = -\Gamma_p \sum_{X'x'} {}^x A^{X'x'} \{\Phi^{(X)} \otimes f^{(x')}\}_q^x - (\gamma_x - iq\omega) + \lambda_q^x \delta_{x0}\delta_{q0}. \tag{1}$$

Here ω is the frequency of the Zeeman splitting of the neighboring magnetic sublevels of the VR level of the ground state of the molecule; Φ_ξ^x is a tensor introduced by Dyakonov for the characteristics of light polarization;[6] the coefficient

$$ {}^x A^{X'x'} = (-1)^\Delta \sqrt{\frac{(2X+1)(2x'+1)}{2x+1}} \; C_{1\Lambda1-\Delta}^{X0} C_{X0x0}^{x'0} , \tag{2}$$

where $C_{\alpha a b\beta}^{\gamma}$ are Clebsch-Gordan coefficients; $\Delta = J' - J''$ is the difference of the quantum numbers of the angular momentum of the excited and ground state; the constant λ_q^x indicates the rate of filling the state being investigated.

If the exciting light is linearly polarized in a plane perpendicular to the external magnetic field and its direction of polarization is determined by the angle $\psi = \Delta\psi \sin \omega_M t$ (see Fig. 1), where $\Delta\psi$ is the amplitude and ω_M the modula-
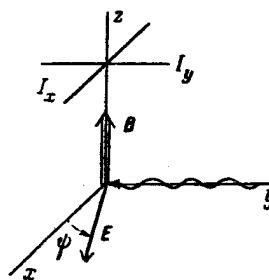

FIG. 1. Geometry for the computation of the nonlinear phase resonance signals of quantum beats.

tion frequency, then the nonzero components of the tensor Φ_ξ^κ equal

$$\Phi_0^0 = -\frac{1}{\sqrt{3}}, \quad \Phi_0^2 = -\frac{1}{\sqrt{30}}, \quad \Phi_{\pm2}^2 = \frac{1}{2\sqrt{5}} e^{\pm i2\psi}. \tag{3}$$

In this case, solving Eq. (1) in the first approximation with respect to the parameter Γ_p/γ_x for the absorption types $Q(\Delta = 0)$, $P(\Delta = -1)$, and $R(\Delta = +1)$, we obtain

$$\varphi_0^0(Q) = \varphi_0^0(P, R) = 1 - \frac{1}{3}\frac{\Gamma_p}{\gamma_0},$$

$$\varphi_0^2(Q) = -2\varphi_0^2(P, R) = \frac{1}{15}\frac{\Gamma_p}{\gamma_2},$$

$$\varphi_{\pm2}^2(Q) = -2\varphi_{\pm2}^2(P, R)$$

$$= -\frac{\Gamma_p}{5\sqrt{6}} \sum_{n=-\infty}^{\infty} J_n(2\Delta\psi) \frac{1}{\gamma_2 \mp i(2\omega - n\omega_M)} e^{\pm in\omega_M t}, \tag{4}$$

where $J_n(2\Delta\psi)$ is a Bessel function. The PM of the ground state are connected by the same exciting light with the PM f_Q^K that directly affect the fluorescence of the excited state[12]

$$f_Q^K = \frac{\Gamma_p}{\Gamma_K - i2\Omega} \sum_{x_1} {}^x A^{x_1} \{\Phi^{(x)} \otimes \varphi^{(x_1)}\}_Q^K, \tag{5}$$

where Ω is the Zeeman splitting of the excited state. Knowing the PM f_Q^K, one can compute the intensity of the fluorescence with a specific polarization e

$$I \sim (-1)^{\Delta'} \sum_K \sqrt{2K+1} \, C_{1-\Delta'1\Delta}^{K0} \sum_Q (-1)^Q f_Q^K \Phi_{-Q}^K(e). \tag{6}$$

where $\Delta' = J' - J''$ is the difference of the quantum numbers of the angular momentum of the initial and final state of the radiative transition.

Frequently, the difference of intensities of fluorescence with mutually orthogonal polarizations $\bar{I}_x - \bar{I}_y \sim \text{Re } \overline{f_2^2}$ (see Fig. 1) is chosen for observation. For phase resonance of beats this is not expedient, however, because one can show that $\overline{f_2^2} = 0$. In this case it is convenient to record the total intensity of the fluorescence in the direction of the z axis (see Fig. 1) integrated over the time without separation of any one component of polarization. In this case for the QQ cycle absorption–emission we obtain

$$\bar{I}_x + \bar{I}_y \sim \frac{2}{3}(\bar{f}_0^0 - 2\bar{f}_0^2)$$

$$= \frac{\Gamma_p}{\Gamma}\left(\frac{7}{15} - \frac{7}{45}\frac{\Gamma_p}{\gamma_0} - \frac{17}{315}\frac{\Gamma_p}{\gamma_2} - \frac{11}{105}\Gamma_p\gamma_2 \right.$$

$$\left. \times \sum_{n=-\infty}^{\infty} J_n^2(2\Delta\psi)\frac{1}{\gamma_2^2 + (2\omega - n\omega_M)^2}\right), \tag{7}$$

and for P or R absorption and P or R emission

$$\bar{I}_x + \bar{I}_y \sim \frac{1}{3}(2\bar{f}_0^0 + \bar{f}_0^2)$$

$$= \frac{1}{3}\frac{\Gamma_p}{\Gamma}\left(\frac{7}{10} - \frac{7}{30}\frac{\Gamma_p}{\gamma_0} - \frac{1}{15}\frac{\Gamma_p}{\gamma_2} - \frac{1}{7}\Gamma_p\gamma_2 \right.$$

$$\left. \times \sum_{n=-\infty}^{\infty} J_n^2(2\Delta\psi)\frac{1}{\gamma_2^2 + (2\omega - n\omega_M)^2}\right). \tag{8}$$

Here for brevity it is assumed that $\Gamma_0 = \Gamma_2 = \Gamma$. The dependence of the signal on Ω is absent in the expressions obtained. This means the absence of nonlinear shifts of the position of resonance connected with the magnetism of the excited state. Such shifts played an essential role in the method of resonance of quantum beats realized earlier for the molecules Te$_2$ (Ref. 4) and K$_2$ (Ref. 5) for amplitude modulated excitation. Nonlinear shifts of resonances as a result of partial overlapping of a series of resonances at frequencies $\omega_M = 2\omega/n$ continue to exist, however. The method of analysis also does not allow one to determine the sign of the frequency interval ω, i.e., the orientation of the magnetic moment of the molecule relative to its angular momentum J (the sign of the Lande factor).

A modulation of the exciting light for which the E vector of the wave rotates in the xy plane with constant angular frequency ω_M, i.e., $\psi = \omega_M t$ (see Fig. 1), gives essential advantages over the procedure considered. In this case, solving Eq. (1), we obtain

$$\varphi_0^0(Q) = \varphi_0^0(P, R) = 1 - \frac{1}{3}\frac{\Gamma_p}{\gamma_0}, \quad \varphi_0^2(Q) = -2\varphi_0^2(P, R) = \frac{1}{15}\frac{\Gamma_p}{\gamma_2},$$

$$\varphi_{\pm2}^2(Q) = -2\varphi_{\pm2}^2(P, R) = \frac{\Gamma_p}{5\sqrt{6}}\frac{\gamma_2 \pm 2i(\omega - \omega_M)}{\gamma_2^2 + 4(\omega - \omega_M)^2} e^{\pm i2\omega_M t}. \tag{9}$$

Analogously to the preceding case we find the total intensity of fluorescence averaged over the recording time and in the direction of the external magnetic field B. We obtain for the QQ type of transitions

$$\bar{I}_x + \bar{I}_y \sim \frac{2}{3}(\bar{f}_0^0 - 2\bar{f}_0^2)$$

$$= \frac{\Gamma_p}{\Gamma}\left(\frac{7}{15} - \frac{7}{45}\frac{\Gamma_p}{\gamma_0} - \frac{17}{315}\frac{\Gamma_p}{\gamma_2} - \frac{11}{105}\Gamma_p\gamma_2 \frac{1}{\gamma_2^2 + 4(\omega - \omega_M)^2}\right), \tag{10}$$

and for transitions PP, PR, RP, and RR

$$\bar{I}_x + \bar{I}_y \sim \frac{1}{3}(2\bar{f}_0^0 + \bar{f}_0^2)$$

$$= \frac{1}{3}\frac{\Gamma_p}{\Gamma}\left(\frac{7}{10} - \frac{7}{30}\frac{\Gamma_p}{\gamma_0} - \frac{1}{15}\frac{\Gamma_p}{\gamma_2} - \frac{1}{7}\Gamma_p\gamma_2 \frac{1}{\gamma_2^2 + 4(\omega - \omega_M)^2}\right). \tag{11}$$

An analysis of Eqs. (10) and (11) shows that in the recorded signal with changing ω_M or ω only one resonance is observed at $\omega = \omega_M$. It does not experience a shift either because of the effect of the excited state or because of resonances at other frequencies. The fact that it enables one to determine simultaneously also the sign of ω is the great advantage of the signal analysis.

It is necessary to note that the assertions about the nature of the of the observed resonance are also valid for a computation to a higher order of approximation. For example, for the QQ-type transitions considered, we obtain with an accuracy to second order of the expansion

$$\bar{I}_x + \bar{I}_y \sim \frac{2}{3}(\bar{f}_0^0 - 2\bar{f}_0^2)$$

$$= \frac{\Gamma_p}{315\Gamma}\left[98 - 44\frac{\Gamma_p}{\gamma} - 22\frac{\Gamma_p\gamma}{\gamma^2 + 4\Delta\omega^2} + 20\left(\frac{\Gamma_p}{\gamma}\right)^2 \right.$$

$$\left. + 10\frac{\Gamma_p^2}{\gamma^2 + 4\Delta\omega^2}\left(2 + \frac{\gamma^2 - 4\Delta\omega^2}{\gamma^2 + 4\Delta\omega^2}\right)\right].$$

In Eq. (12) we assume for brevity $\gamma_2 = \gamma_0 = \gamma$ and $\Delta\omega - \omega_M = \Delta\omega$. It is evident that for a computation in an approximation of higher than second order a distortion of the shape of the resonance takes place, but there is no shift of its position. The structure of the utilized equations enable one to conclude that a shift does not appear even for higher approximations. Of course, the conclusions are correct only to the extent that induced transitions can be excluded from consideration.

The results presented can be extended, for states with large values of angular momentum J, to states with arbitrary J. For this the coefficients $^xA^{Xx'}$ will have other numerical values and depend on J.[4] Equation (5) will also change. The changes indicated in the procedure of the computation do not change the structures of the expressions for the observed signals. All the conclusions relative to the character of the resonances remain valid for states with arbitrary values of the quantum numbers of the angular momentum J.

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