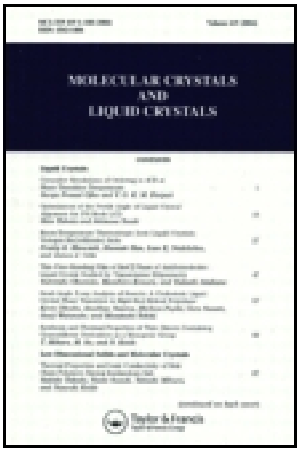

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Transformation of the Fourier Spectrum of Modulated Photoluminescence of Rubrene Due to the Non-Linearity of the Magnetic Field Spin Effect

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Transformation of the Fourier Spectrum of Modulated Photoluminescence of Rubrene Due to the Non-Linearity of the Magnetic Field Spin Effect

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Fourier analysis is applied for investigation of the magnetic field dependent photoluminescence in a polycrystalline film of rubrene. The sine-shaped external magnetic field results in oscillations of a rate constant at multiple harmonics. Action of a sum of two harmonic perturbations results in numerous harmonics at difference and summary frequencies. Possible kinetic applications of the bichromatic perturbation of the rate constant and subsequent frequency transformation by the non-linear system are discussed.

Keywords photoluminescence, magnetic field effect, nonlinearity

INTRODUCTION

There are numerous experimental techniques based on the modulation of some parameter (such as: temperature, pressure, magnetic or electric field intensity) of the system and simultaneous detection of the oscillations of the physical or chemical process yield. However, in most cases the complicated frequency transformation, which is due to the non-linear dependency of the system response on these parameters, is neglected.

This paper is to demonstrate such non-linear modulation effects and to discuss some promising applications of this frequency transformation. We show that sine-shaped influence induced several multiple harmonics in the system response. Besides, the use of two or more sine perturbations of different frequency results in formation of summary and difference frequencies.

Using fission of the singlet excited state of rubrene molecule into two triplet excitons[1,2] as an example, in the present work the magnetic field spin effect (MFSE) method[3] has been applied to demonstrate the non-linearity of photophysical processes.

The goals of the present work are:

1) to demonstrate the transformation of the modulation spectrum, revealed either as the appearance of several multiple frequencies in the case of harmonic modulation of the rate constant or as the appearance of several summary and difference frequencies when a non-linear system is subjected to the action of a sum of two harmonic modulations of different frequencies;
2) to propose and discuss novel opportunities for kinetic techniques based on these non-linear modulation effects.

EXPERIMENT AND DISCUSSION

The experimental technique of MFSE measurements on rubrene film photoluminescence is described elsewhere(3). Two magnetic fields (MF) were produced by Helmholtz coils: 1) a modulated one with the amplitude from 0.1 mT to 0.5 mT and a 2) constant one (from zero to 5 mT) to shift the central point of a modulated MF. The alternating MF was generated by means of the two identical audio frequency generators and summed by the mixer, and amplified by the power amplifier. Selective nanovoltmeter (40 dB/octave) was used for the analysis of the Fourier spectra of modulated photoluminescence intensity as well as of the MF applied.

When a sample is exposed to exciting light in absorption band of rubrene, the excited molecules S_1 can be deactivated in two competing processes: by prompt emission of fluorescence or by non-radiative formation of free triplet excitons T via the intermediate spin-correlated pair [T...T]:

$$S_0 \underset{\text{fluorescence}}{\overset{\text{excitation}}{\rightleftarrows}} S_1 \overset{\text{fission}}{\rightleftarrows} [T...T] \rightarrow 2T$$

External MF changes the spin states of the intermediate [T...T] complex and, subsequently, changes the fission rate. It is this quantum phenomenon to be responsible for the variation of fluorescence intensity of rubrene in an external MF. Theoretical descriptions of the MFSE in rubrene (2,3) predict the fluorescence intensity to be a non-linear function of the MF induction.

When an alternating MF is applied to the sample, the non-linear forced oscillations of the fluorescence intensity should be expected. They may have more complicated pattern when the frequency of the MF applied corresponds to the characteristic times of the spin system, namely the lifetime of paramagnetic species[4], the times of coherent spin interactions[5] and spin-lattice relaxation, all of them being of the order of 10^{-9} s in rubrene[4]. In the present work, however, we used relatively small frequencies of the alternating MF, so it is possible to describe the oscillations by the steady-state I(B) dependence.

Harmonic modulation of the MF leads to periodic modulation of fluorescence intensity with the same period. In general, these vibrations are no more sine-shaped. Or, in other words, their Fourier spectrum consists not only of the frequency of MF modulation (base harmonic) but as well contains a manifold of harmonics at multiple frequencies.

For example, if the modulation amplitude is low enough, then the I(B) in the vicinity of a constant field B_0 may be approximated by the second order polynomial and fluorescence intensity I consists of a constant term and two harmonic oscillations at frequencies ω and 2ω (α and β are constant parameters, b is the MF modulation amplitude and ω is its frequency):

$$I[B(t)] = I(B_0) + \alpha b \cos \omega t + \beta b^2/2 + \beta b^2/2 \cos 2\omega t. \qquad (1)$$

If the I(B) curve is well approximated by a polynomial including terms up to $(B-B_0)^n$, then similarly to (1) one should expect the harmonics up to $n\omega$.

Application of the bichromatic alternating MF, which is a sum of two harmonics at different frequencies ω_1 and ω_2 results in a further complication of spectrum of modulated fluorescence intensity (Fig. 1). This can be explained in terms of the simplest second-order I(B) approximation:

$$I[B(t)] = I(B_0) + \alpha b \cos \omega_1 t + \alpha b \cos \omega_2 t + \beta b^2 + \beta b^2/2 \cos 2\omega_1 t +$$
$$\beta b^2/2 \cos 2\omega_2 t + \beta b^2 \cos[(\omega_1+\omega_2)t] + \beta b^2 \cos[(\omega_1-\omega_2)t] \qquad (2)$$

All frequencies in the expression (2) correspond to the peaks of spectrum in Fig. 1. They are: basic harmonics ω_1 and ω_2; double harmonics: $2\omega_1$ and $2\omega_2$; difference and summary harmonics: $\omega = (\omega_2 - \omega_1)$ and $\Omega = (\omega_1 + \omega_2)$.

Modulation of the MF around the point B=0 is a very important case for observation of non-linear oscillations of the reaction yield. First, the MFSE dependence I(B) is an even function of B, so the spectrum of modulated fluorescence should contain only even harmonics, namely at frequencies 0, 2ω, 4ω, etc. Second, zero magnetic field is a singular point of the I(B) dependence. It is obvious that the most intensive harmonics $n\omega$ are expected at the regions of MF where there is a large derivative $\partial^n I/\partial B^n$. Good approximation for the I(B) in the vicinity of B=0 is a function proportional to the absolute value of the MF induction, $I = D|B|$, where $D = \left.\frac{\partial I}{\partial B}\right|_{B \to +0}$ is the derivative in right vicinity of zero MF. Supposed B = b sinωt, b>0, we see that the spectrum of modulated fluorescence is described by the Fourier series of sine modulus:

$$I[B(t)] = Db\left|\sin\omega t\right| = Db\left(\frac{2}{\pi} - \frac{4}{\pi}\left(\frac{\cos 2\omega t}{3} + \frac{\cos 4\omega t}{15} + \frac{\cos 6\omega t}{35} + \dots\right)\right) \tag{3}$$

In the case of bichromatically modulated MF around zero at frequencies, for example, $\omega_1/2\pi$=1008 Hz and $\omega_2/2\pi$= 1152 Hz and equal amplitudes b=0.5 mT the MFSE spectrum (Fig. 2) may be interpreted within this approximation. Simple calculation shows that the spectrum of MFSE consists of the terms:

$$\frac{\cos(n\Omega + m\omega)}{(4n^2 - 1)(4m^2 - 1)}, \text{ where n, m=0, } \pm 1, \pm 2, \dots \tag{4}$$

Therelative intensities of the first several harmonics of the MFSE spectrum calculated according to (4) are in satisfactory coincidence with the experimental spectrum in Fig. 2.

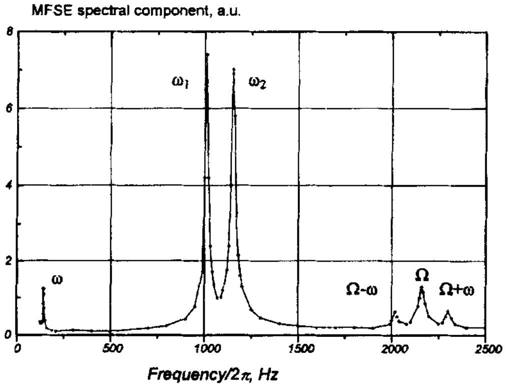

FIGURE 1. Appearance of summary and difference frequencies in the spectrum of modulated fluorescence under the action bichromatic modulation.

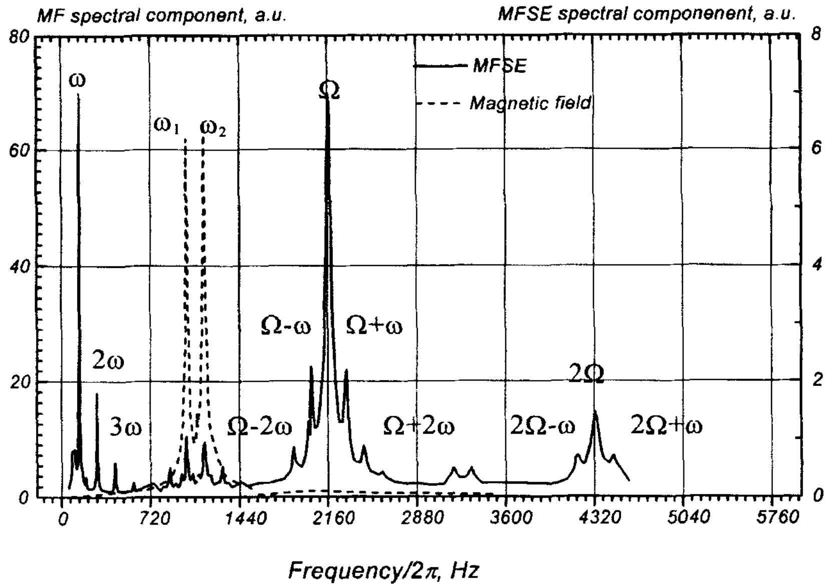

FIGURE 2. Spectrum of modulated fluorescence under the action of double modulation of the magnetic field around the singular point (zero MF).

SUMMARY AND PERSPECTIVES

This work demonstrates the possibility to observe the nonlinear system response at frequencies different from the those of the perturbation applied. This phenomenon can be extended to the case of different external agents, such as excitation light, electrical field and their combinations. The main opportunities for future development of new kinetic techniques based on this nonlinear effect are: possibility to avoid the action of scattered fields; to study systems with subsequent short- and long-lived stages; to measure dramatically different lifetimes of transient species in the same experiment; to derive the shape of field dependency, including local peculiarities, from the Fourier spectrum of the forced oscillations.

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