TWO-PHOTON-EXCITED EMISSION FROM SOLIDS

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Abstract

The characteristics of two-photon-excited emission from organic and inorganic crystals are studied and the results are presented. We used a copper-vapor laser in the pulse-repetition mode as a source of excitation radiation. This laser features an average power of 3 W, peak power of $10^4$ W, pulse-repetition rate of $10^4$ c$^{-1}$, and radiation wavelength of $\lambda = 510.5$ and $\lambda = 578.2$ nm. Also, a YAG:Nd laser operating in the Q-switched mode was employed in a number of experiments. We found that the two-photon-excited emission spectra are located within the wavelength range of 300-450 nm. The features of the spectra are observed to depend on the power of the excitation radiation and are essentially different from the resonance fluorescence spectra. Conditions for the transition from spontaneous fluorescence to stimulated one are analyzed; it is demonstrated that the coefficient of conversion of the excitation radiation into ultraviolet fluorescence reaches $\sim 1\%$ in certain crystals. The results obtained are of interest in the diagnostics of solid-state structures and also for the development of laser sources in the ultraviolet region of the spectrum.

1. General Description of Processes Involved in Two-Photon-Excited Emission. Statement of the Problem

When the power of excitation radiation is sufficiently high, nonlinear processes in crystalline materials become important. In this situation there is the possibility of initiating secondary radiation due to simultaneous absorption of two quanta of excitation light [1-5]. In what follows, emission of this radiation will be called two-photon-excited emission (TPEE). The energy diagram for the possible optical transitions for this case is shown in Fig. 1. The features of these processes depend on the energy of the excitation radiation quantum $h\nu$.

First we consider the case where the energy of two excitation-radiation quanta $2h\nu$ is close to the energy of the electron term characterized by even parity symmetry (see Fig. 1a). According to the selection rules, two-photon-induced transition from the ground state to this term is allowed. The exciton-vibrational levels, corresponding to a combination of polar excitons and polar phonons, can act as terms of this type (see Figs. 1a and 1b). At low temperatures, the one-particle bound state, the biexciton, can be formed [6-8].

As a rule, such states are short-lived; their lifetime ranges from $10^{-11}$ to $10^{-12}$ s. The de-excitation of these states is accompanied by radiative or nonradiative recombination and the transition of the system to the lowest excited state $E_n$ corresponding usually to the “long-lived” excitons ($\tau \sim 10^{-8} - 10^{-7}$ s) in the crystal. The transition of the crystal from the excited state to the crystal vibrational level of the ground state results in fluorescence radiation (Figs. 1a and 1b) as observed in optical experiments. Furthermore, hyper-Rayleigh scattering can occur in the crystal with consequent emission of double-energy photon $E = 2h\nu_0$ (see Figs. 1a and 1b).
Fig. 1. Schematic diagram of energy levels and radiative (straight arrows) and nonradiative (wavy arrows) transitions. $E_e$ is the energy of the lowest exciton state; the hatched zone in the upper part of the diagram corresponds to the biexciton states.

If the two-photon energy $2hv_0$ does not coincide with the actual energy states of the material medium (see Figs. 1a and 1b), the system comes to an excited virtual state. The relaxation from this state and the transition to the ground level can proceed by several pathways. The simplest process corresponds to hyper-Rayleigh scattering. Furthermore, hyper-Raman scattering is possible [4, 9, 10]; as a result, a photon with the energy $E' = hv' = 2hv_0 - E_e$ is emitted and the system goes over to the level $E_e$. At the final stage, as was in the resonance case, the fluorescent radiation is emitted concurrently with the transition from the exciton state to the ground state of the crystal. Moreover, a four-photon process can be feasible, in which case two quanta of excitation radiation are absorbed simultaneously and two quanta are emitted, one with the energy $E'$ and the other with the energy $E'' = E_e - h\Theta$, where $h\Theta$ is the energy of the corresponding phonon. In these processes the laws of conservation of energy and quasi-momentum should be observed; accordingly, we obtain for the hyper-Raman scattering

$$2hv_0 = E' + E_e, \quad 2k_0 = k' + k_e,$$  \hspace{1cm} (1)

and for the four-photon process

$$2hv_0 = E' + E'' + h\Theta, \quad 2k_0 = k' + k'' + q.$$  \hspace{1cm} (2)

Here $k_0, k', k'', q,$ and $k_e$ are the corresponding wave vectors. The polaritonic effects [9, 11-14] were ignored in the schematic diagram of transitions shown in Fig. 1.

A characteristic feature of TPEE from crystals is that it is possible (under certain excitation conditions) to obtain spectra collected from the rather large volume in the sample. With the estimated coefficient of two-photon absorption [3, 15], the effective depth of the emission zone ranges from 0.1 to 100 $\mu$m depending on the intensity of the exciting radiation.