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NONLINEAR OPTICAL PROPERTIES OF FLUORESCEIN IN BORIC-ACID GLASS†

Mark A. KRAMER, Wayne R. TOMPKIN, Jerzy KRASINSKI,* and Robert W. BOYD

The Institute of Optics, University of Rochester, Rochester, N. Y. 14627

Fluorescein in boric-acid glass has an extremely low saturation intensity measured in saturated absorption and phase conjugation experiments to be of the order of 10 mW/cm². The time evolution of the long-lived luminescence is highly nonexponential, leading to a nonlorentzian spectral hole of width ~750 millihertz in the absorption profile measured in a pump-probe experiment.

There is much current interest in the development of nonlinear optical materials displaying small saturation intensities, and hence large optical nonlinearities, for use in real-time holography, phase conjugation, and optical bistability. The long lifetimes of the triplet states of certain organic molecules in solid matrices can lead to exceptionally low saturation intensities. One such material is fluorescein in a glass matrix of boric-acid. In this paper we report the results of an experimental study of several of the nonlinear optical properties of this material.

The origin of the long luminescent decay time (~ 2 sec) at room temperature in the fluorescein-doped boric-acid glass is a process known as delayed fluorescence.[1] Following optical excitation from the ground singlet state to an excited singlet state, intersystem crossing may transfer population to a long-lived triplet state. Delayed fluorescence arises from intersytem crossing from excited vibrational states of the lowest lying triplet manifold back to the singlet excited state, which then fluoresces. In a solid matrix, a majority of the mechanisms that can quench the triplet state are removed, and the triplet state can remain populated for several seconds. Due to the longevity of the triplet state, significant population can be trapped in that state even by very weak optical fields, implying an exceptionally small value of the saturation intensity (see Fig. 1).

As a result of the pronounced polarization dependence of the absorption cross section of fluorescein molecules,[2] the absorption of the doped glass saturates with an intensity dependence that differs from that obeyed by typical saturable absorbers, in which the molecules are free to rotate. Due to random orientation within the glass, different dye molecules display differing degrees of saturation when exposed to a linearly polarized incident optical field. If we assume that the molecules absorb light polarized only along one

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molecular axis, the absorption coefficient experienced by an ensemble of randomly oriented molecules is given by

$$\alpha = \frac{\alpha_o}{4\pi}\int \frac{d\Omega}{1 + I/I_s(\theta)} = \frac{\alpha_o}{(I/I_{s,o})^{1/2}} \tan^{-1}[(I/I_{s,o})^{1/2}], \qquad (1)$$

where $I_s(\theta) = I_{s,o}/\cos^2(\theta)$ is the saturation intensity for molecules oriented at angle θ with respect to the electric field direction and α_o is the small field absorption coefficient. The saturation response of fluorescein in boric-acid glass is shown in Fig. 1 for a wavelength of 4579 Å. This data is in good agreement with the theoretical curve which is based on Eq. (1) with a saturation intensity of $I_{s,o} = 0.7$ mW cm^{-2}.

The low saturation intensity of fluorescein-doped boric acid glass allows four-wave mixing experiments to be performed at power levels easily obtainable with cw lasers. In Fig. 2 the results of the measurement of the phase-conjugate reflectivity at a wavelength of 4765 Å are shown for various fluorescein concentations. These results are obtained under the experimental conditions of equally intense, counter-propagating pump beams and a probe beam whose intensity is eight percent that of the pump beam. The measured values of the reflectivities are similar to those obtained in other studies.[2,3] We have observed a dramatic loss of diffraction efficiency when the pump and probe beams are separated by more than 20 degrees, due presumably to optical inhomogeneities of the boric acid host. We have also observed photochemical damage to the dye molecules at large pump intensities (~ 0.5 W cm^{-2}); this effect may be used to advantage if it is desired to write permanent holograms into the medium.

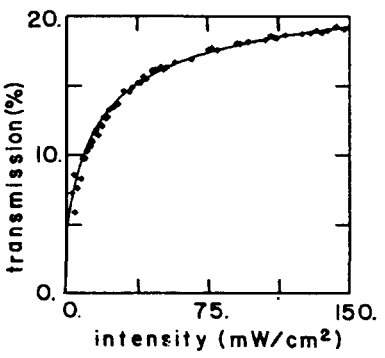

Fig. 1. Saturation behavior of fluorescein-doped glass.

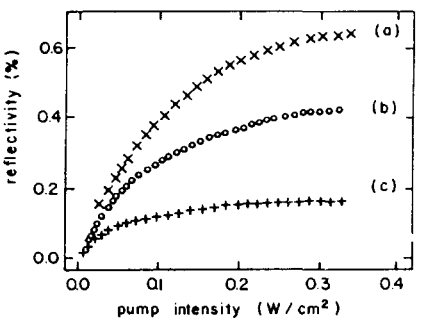

Fig. 2. Phase conjugate reflectivity versus laser intensity for several fluorescein concentrations (C): (a) $\alpha_o L = 0.66$, C=0.3 M; (b) $\alpha_o L = 0.48$, C = 0.02 M; (c) $\alpha_o L = 0.16$, C=0.003 M.

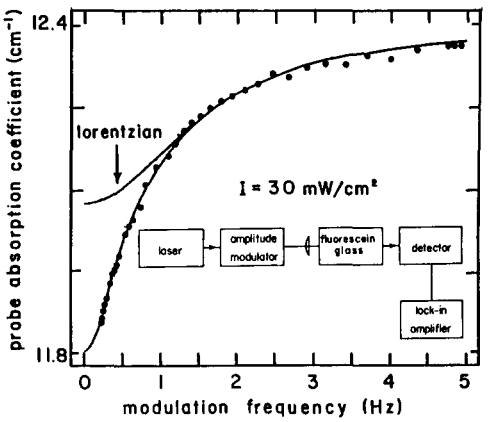

Fig. 3. Probe beam absorption spectrum of fluorescein-doped boric acid glass measured using modulation spectroscopy (see inset). An exceedingly narrow (~750 millihertz), markedly nonlorentzian hole is observed at low modulation frequencies.

The temporal evolution of the delayed fluorescence is notably nonexponential, and has been ascribed to variations in the environment of different dye molecule sites.[4,5] Although the nonlorentzian lineshape arising from this nonexponential decay is masked in spontaneous emission, a nonlorentzian feature due to this nonexponential decay does appear in the nonlinear response of the system, as measured in a pump-probe, saturated-absorption experiment. Through use of amplitude modulation (AM) spectroscopy,[6] we have observed a nonlorentzian spectral hole in the probe-beam absorption lineshape. The experimental setup is shown in the inset of Fig. 3. An AM beam is sent through the fluorescein-doped glass, and the depth of modulation at the output is monitored as a function of the modulation frequency. The resulting AM spectrum contains information regarding the dynamics of the relaxation processes occurring within the sample. Shown in Fig 3 is the AM spectrum of fluorescein in boric-acid glass. The spectral hole has a width of ~ 750 millihertz and owes its markedly cusped, nonlorentzian shape to the nonexponential decay of the excited state. In conclusion, fluorescein-doped boric acid glass has an extremely low saturation intensity and thus is useful as a nonlinear optical material for use with low power lasers.

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*Present address: Allied Corporation, Mt. Bethel, New Jersey 070601.

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