

PHOTON UP-CONVERSION IN RHODAMINE 6G-POLYURETHANE OPTICAL WAVEGUIDES

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ABSTRACT

For the first time photon up-conversion in Rhodamine 6G-polyurethane optical waveguides has been detected. Using a HeNe-laser (633 nm) for excitation, emission of luminescence at a wavelength of 570 nm has been detected. A linear relation between excitation and emission intensity was found. Two two-photon up-conversion schemes are proposed. Experiments can not exclude one of these schemes, but show that the emission is due to the $S_1 \rightarrow S_0$ transition of Rhodamine 6G, and that a long-lived energy state is present in the system.

INTRODUCTION

Rhodamine 6G is a well known organic dye, commonly used in liquid dye lasers. Its emission spectrum lies in the wavelength region between 560 and 620 nm. Emission of luminescence at 570 nm has been detected in Rhodamine 6G-polyurethane (Rh6G-PU) optical waveguides, due to excitation with a HeNe-laser (633 nm or 15800 cm^{-1}). This so-called up-conversion may be explained by a two-photon process, and could be used in integrated optics for solid state waveguide lasers and amplifiers [1] and in sensor applications [2]. In this paper two schemes for the up-conversion process are proposed. Furthermore results of experiments, carried out in order to exclude one of these two schemes, are presented.

THEORETICAL MODELS

The photon up-conversion must be caused by a two-photon process, because the energy separation between absorption and emission is too large to be explained by one-photon anti-Stokes luminescence. Two possible schemes, only differing from each other in the first absorption step, are proposed here.

1. 'Dimer'-scheme

In solutions with a high Rh6G-concentration dimers are formed, causing a shift in the absorption spectrum to higher wavelengths. It might be possible for these dimers to absorb HeNe-light. After this absorption step, energy transfer from a dimer to a monomer molecule is necessary to excite the monomer molecule to its triplet state. Then the monomer can easily be excited to its T_3 -state, by absorption of a second photon. A clear peak in $T_1 \rightarrow T_3$ absorption was found at 633 nm by Kuznetsov [4]. The complete up-conversion scheme is shown in fig. 1.a.

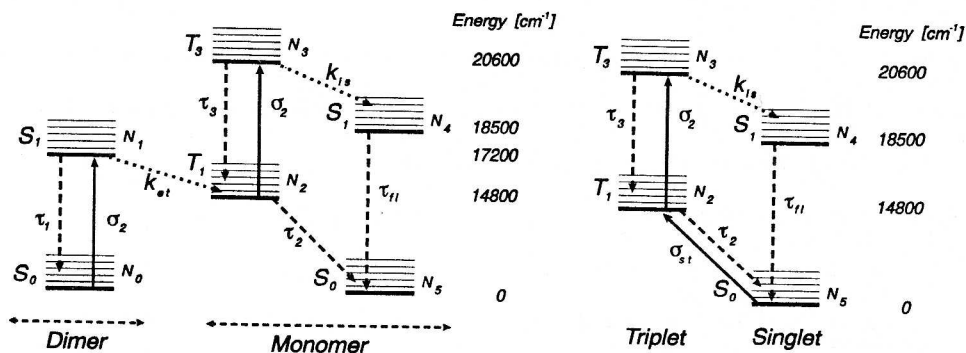


fig. 1 (a) 'dimer'-scheme

(b) 'triplet'-scheme

Used symbols: N =number of molecules in each state, τ =lifetime, σ =absorption cross section, k_{is}, k_{et} = rate constants.

Using rate equations for the transitions shown in fig. 1a, the following relation can be derived for the luminescence intensity in a steady state situation, neglecting back-transfer and quenching:

$$\frac{N_4}{\tau_{f1}} = \frac{k_{is}\tau_3}{1+k_{is}\tau_3} \cdot \frac{\sigma_2\tau_2 I_{ex}}{1+\sigma_2\tau_2 I_{ex}} \cdot \frac{k_{et}\tau_1}{1+k_{et}\tau_1} \cdot \sigma_1 N_0 I_{ex} \quad (1)$$

Under the condition that $\tau_2\sigma_2 I_{ex} \gg 1$, the luminescence intensity depends linearly on the excitation intensity, I_{ex} :

$$\frac{N_4}{\tau_{f1}} = \frac{k_{is}\tau_3}{1+k_{is}\tau_3} \cdot \frac{k_{et}\tau_1}{1+k_{et}\tau_1} \cdot \sigma_1 N_0 I_{ex} \quad (2)$$

2. 'Triplet'-scheme

This second scheme (fig. 1b) differs only in one aspect from the 'dimer'-scheme. Instead of absorption in the dimer, absorption straight to the monomer T_1 -state is proposed. This leads to the following equation for the luminescence intensity in a steady state situation:

$$\frac{N_4}{\tau_{f1}} = \frac{\sigma_2\sigma_{st}\tau_2 N_5 I_{ex}^2}{1 + \sigma_2\tau_2 I_{ex}} \quad (3)$$

Again, for $\tau_2\sigma_2 I_{ex} \gg 1$, the dependence on I_{ex} will become linear:

$$\frac{N_4}{\tau_{f1}} = \sigma_{st} N_5 I_{ex} \quad (4)$$

EXPERIMENTAL RESULTS

The Rh6G-PU optical waveguides were prepared on microscope slides with a dipping technique. The resulting layers had Rh6G-concentrations ranging

from $3.5\text{E-}5\text{ M}$ to $5.2\text{E-}2\text{ M}$, and a thickness of about $2\ \mu\text{m}$.

Optical absorption spectra of these layers were taken with a photo-spectrometer. No absorption at the HeNe-wavelength was observed (fig. 2). No deviation from the Lambert-Beer absorption law, due to possible dimerisation of Rh6G, is observed, as shown in fig. 3.

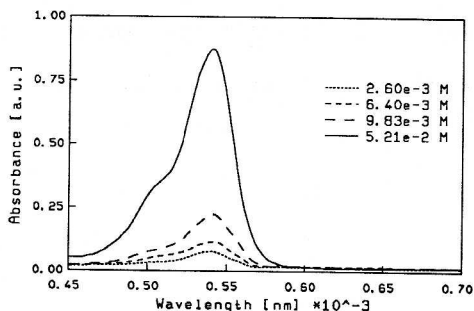


fig. 2 Absorption spectra of Rh6G-PU

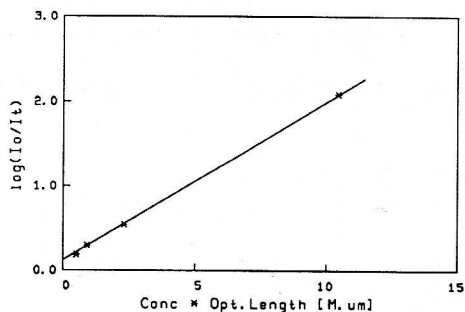


fig. 3 Concentration dependence of absorption peak

Emission spectra of the Rh6G-waveguides, excited with laser light coupled into the waveguide by end-fire technique, were measured with a modified Raman-microscope setup. Normalized emission spectra for two layers with different Rh6G-concentrations, excited with 633 and 514 nm, are given in fig. 4.

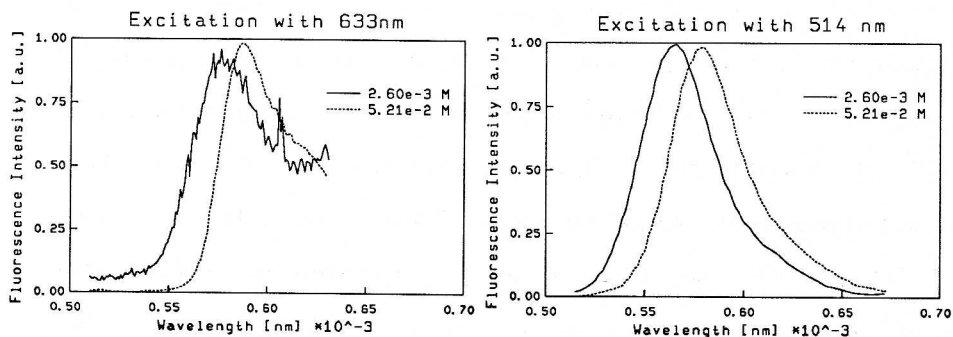


fig. 4

(a)

(b)

In both cases, emission is due to the $S_1 \rightarrow S_0$ transition of Rh6G. The apparant shift of the emission peaks towards higher wavelengths at higher concentrations, is caused by self-absorption in the low-wavelength region, and is seen for both excitation wavelengths.

With a prism-coupling experiment, the relation between the excitation and emission intensity was measured. The detected curve (fig. 5) clearly shows a quadratic relation for very low values of the excitation intensity, I_{ex} , but this relation becomes linear for higher values of I_{ex} .

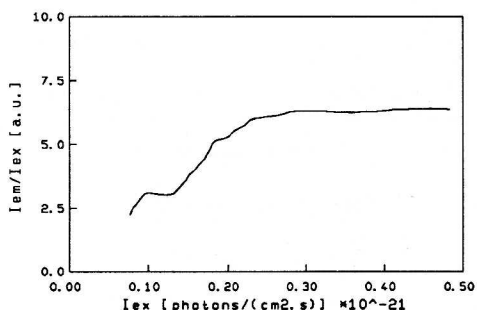


fig. 5 Relation between excitation and emission intensity.

DISCUSSION

The measured curves in fig. 2 show no absorption at 633 nm, which may be caused by the insufficient resolution of the photospectrometer. From the rate equations of both the 'dimer'-scheme and the 'triplet'-scheme it followed that a linear relation between excitation and emission intensity is only possible for $\sigma_2\tau_2I_{ex} \gg 1$, which means that T_1 has to be a relatively long-lived energy state. In fig. 5 the relation becomes linear for $I_{ex} > 2E20$ photons/cm².sec. In the literature it is found that $\sigma_2 = 4E-17$ cm² [5] and $\tau_2 = 1E-4$ sec [6] for Rh6G solvents, so $\sigma_2\tau_2I_{ex} = 8$. However, these parameter values might be even larger for the Rh6G-PU

waveguides. The condition for a linear relation is fulfilled, which is mainly due to the confinement of the light in the waveguide, which leads to very high photon intensities. Because no dimerisation is seen, the 'triplet'-scheme is the most likely one, but additional measurements are necessary to check this.

CONCLUSIONS

The Rh6G-PU optical waveguides show emission of luminescence at 570 nm, when HeNe-light of 633 nm is coupled into the waveguides. No absorption is detectable at 633 nm with the afore-mentioned method. The emission spectra coincide with the $S_1 \rightarrow S_0$ luminescent transition of Rh6G. A linear relation between excitation intensity, I_{ex} , and emission intensity, I_{em} , was found, above a certain threshold value of I_{ex} . The measurements could not exclude neither the 'dimer'-scheme nor the 'triplet'-scheme.

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