

# Anti-Stokes fluorescence of phenalemine 512 dye in polymeric matrix under low-intensity irradiation

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A He-Ne laser (632.8 nm), a laser diode (648 nm), and a light emitting diode (678 nm) have been used to obtain anti-Stokes fluorescence of phenalemine 512 in a polymeric matrix (PMMA) with concentrations of  $10^{-3} - 10^{-2}$  M. The existence of a "red limit" of excitation of anti-Stokes fluorescence is shown experimentally and theoretically. The temperature dependence demonstrates the decrease in the intensity of anti-Stokes fluorescence with the decrease of temperature. The energy of activation of anti-Stokes fluorescence of phenalemine 512 in PMMA for simple molecule was determined to be  $(2.52 \pm 0.09) \cdot 10^{-20}$  J.

## Introduction

The anti-Stokes fluorescence is understood as photoluminescence, whose wavelength is shorter than that of the exciting radiation. In this sense, the anti-Stokes fluorescence does not obey the Stokes rule, that is, the emitted quanta have higher energy than the quanta of the exciting radiation. The quanta energy increases at the expense of the atomic thermal-motion energy, as was noticed by Pringsheim yet in 1929 (Ref. 1).

The anti-Stokes fluorescence is one of the basic physical phenomena. It was investigated in numerous papers, which focused mostly on the decrease in the quantum yield of the anti-Stokes fluorescence with the increase of the wavelength of the exciting radiation. The causes of the decrease in the quantum yield of the anti-Stokes fluorescence and even the existence of this decrease are still under discussion.<sup>2</sup>

The anti-Stokes fluorescence is based on the transfer of the atomic kinetic energy to the radiation, which, at first glance, contradicts the second law of thermodynamics. At the same time, the cooling of molecules due to the transfer of the molecular kinetic thermal-motion energy to radiation has been demonstrated experimentally and was named "the effect of optical cooling." The increased interest in optical cooling in recent time has rekindled the investigations of the anti-Stokes fluorescence.

First solid-state anti-Stokes coolers have been made on the basis of a Yb:ZBLAN glass in 1995 (Ref. 4). At that time, a sample was cooled by more than 50 K below room temperature. In the first experiments with organic dyes, the radiation of a dye laser with the wavelength of 632 nm and the mean power of 350 mW was focused onto the

Rhodamine 101 dye solution in ethanol. For 4 hours of irradiation, its temperature decreased by 4° (Ref. 3).

The anti-Stokes cooling of a Tm<sup>3+</sup>:ZBLANP glass was demonstrated in Ref. 5. The anti-Stokes fluorescence was excited by a parametric oscillator based on a nonlinear lithium niobate crystal with synchronous excitation by radiation of a 20-W Nd:YAG Q-switched laser. The radiation beam with the wavelength  $\lambda = 1.75 - 2.05 \mu\text{m}$  was focused into a  $5 \times 5 \times 9 \text{ mm}^3$  sample, placed in a vacuum channel with the pressure of  $10^{-5}$  Torr. At the mean radiation power of 3 W, the sample was cooled to  $-1.2^\circ\text{C}$  below room temperature.

In the general case, the efficiency of laser cooling  $\gamma$  can be expressed as the ratio

$$\gamma = \frac{P_{\text{cool}}}{P_{\text{abs}}} = \frac{\lambda_{\text{exc}} - \lambda_{\text{fl}}}{\lambda_{\text{fl}}} = \frac{\nu_{\text{fl}} - \nu}{\nu} \approx \frac{kT}{h\nu}, \quad (1)$$

where  $P_{\text{cool}}$  is the power taken from an object,  $P_{\text{abs}}$  is the absorbed power.

In accordance with Eq. (1), the cooling will be efficient in materials upon the exposure to IR radiation, when the peak of the anti-Stokes fluorescence is significantly shifted to the shortwave region. At the same time, samples were exposed to the IR laser radiation with a rather high mean power. It is reasonable to assume the existence of a "red limit" of excitation beyond which radiation does not cause the anti-Stokes fluorescence.

Besides the optical cooling, there may be other practical applications of the anti-Stokes fluorescence. For example, it can be used to visualize high-power IR radiation.<sup>6</sup> The possibility of obtaining cell images in fluorescent microscopy upon the excitation of anti-Stokes fluorescence by longwave radiation has been demonstrated in Ref. 7.

Polymeric materials with dyes having the anti-Stokes fluorescence are of great interest both for the investigation of the effect of intermolecular interaction on this phenomenon and for creation of optical coolers, IR visualizers, and for other practical applications.

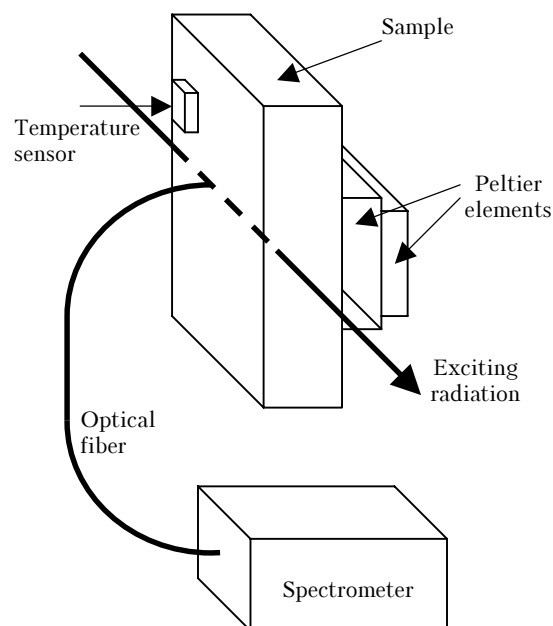
This paper is devoted to the study of the effect of the radiation wavelength (He–Ne laser (632.8 nm), laser diodes (648, 792 nm), light emitting diode (678 nm), and temperature (from  $-30$  to  $+50^{\circ}\text{C}$ ) on the anti-Stokes fluorescence of the phenalemine 512 dye in PMMA.

## Materials and methods

The investigations have been carried out with samples of phenalemine 512 laser dye in PMMA at concentrations of  $10^{-2}$ ,  $3.9 \cdot 10^{-3}$ , and  $10^{-3}$  M, synthesized in Alfa-Akonis (Dolgoprudnyi, Russia). Samples cut from the synthesized were rectangles of  $14.5 \times 28.5 \times 3.5 \text{ mm}^3$  size with polished sides. For comparison, samples with identical dimensions and the side treated in the same manner were also made of a PMMA matrix without dye.

The sources of radiation were an LGN-207B He–Ne laser, a laser diode (laser pointer), and LUR-2043 light emitting diodes with the mean power of 2, 0.5, and 0.8 mW, respectively.

The laser radiation was focused onto a polymer sample by a lens with the focal length  $F = 8 \text{ cm}$ . This resulted in an orange-red track of the anti-Stokes fluorescence observed in the longitudinal direction in the matrix. The fluorescence was recorded at an angle of  $90^{\circ}$  to the track with an optical fiber (200  $\mu\text{m}$ ) connected to an Angström optical analyzer on the basis of a linear photodiode array (wavelengths range from 330 to 900 nm, energy sensitivity of 1 pJ).



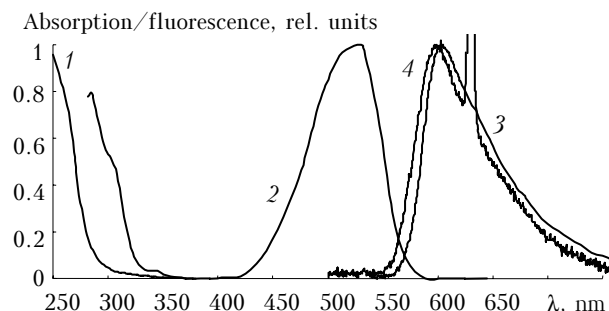
**Fig. 1.** Schematic of the setup for investigation of the temperature dependence of the anti-Stokes fluorescence.

The time for recording of an optical spectrum was determined by the exposure time and amounted to 150–300 ms. The optical spectrum was recorded simultaneously with the measurement of the sample temperature, which allowed the temperature drifts of the samples to be minimized.

The matrix with the dye was cooled by two frigidator-based Peltier elements (Fig. 1):  $40 \times 40$  (K1-127-1.4/1.1) and  $30 \times 30 \text{ mm}$  (K1-127-1.0/1.3). The first element was in contact with the polymeric sample, while the second one was used to cool the hot side of the first element. The hot side of the second element was cooled by running water. Such a design allowed the matrix temperature to be quickly decreased to  $-30^{\circ}\text{C}$ . Alternating the voltage polarity across the Peltier elements, it was possible to warm the object up to  $55^{\circ}\text{C}$ . A semiconductor temperature sensor was attached directly to the matrix surface, opposite to the cooled (warmed) surface, from the side of optical signal recording with an optical fiber. The temperature was measured with a digital thermometer accurate to  $0.5^{\circ}\text{C}$ .

## Results and discussion

Figure 2 shows the absorption spectra of PMMA and phenalemine 512 in PMMA. The spectra are recorded in a thin (1 mm) sample with the dye concentration of  $10^{-3}$  M. The peak of the phenalemine 512 absorption band lies at 526 nm.

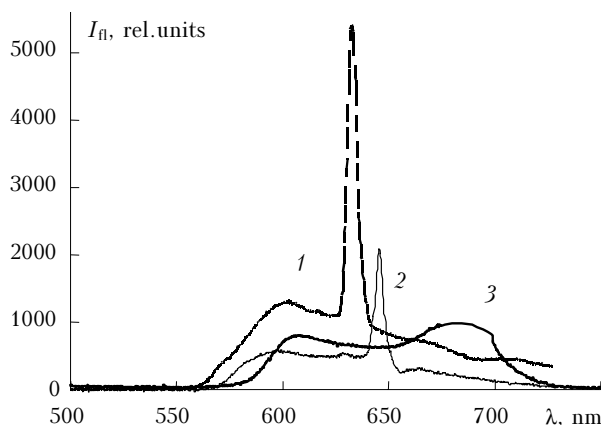


**Fig. 2.** Absorption (1, 2) and fluorescence (3, 4) spectra of PMMA (1), phenalemine 512 in PMMA (2–4). Ordinary fluorescence (3), anti-Stokes fluorescence excited by He–Ne laser radiation (4).

The PMMA absorption was observed in the spectral range shorter than 260 nm; at  $\lambda > 280 \text{ nm}$  the matrix was transparent. In addition, Fig. 2 shows the fluorescence spectra at the Stokes and anti-Stokes excitation of phenalemine 512. Besides the characteristic wide dye fluorescence band peaking at 604 nm, in the case of the anti-Stokes excitation, the signal of pump radiation (632.8 nm) scattered at an angle of  $90^{\circ}$  is recorded as a narrow intense line. At the same excitation geometry and the dye concentration, the anti-Stokes fluorescence spectrum coincides with the Stokes fluorescence spectrum.

Figure 3 shows the anti-Stokes fluorescence spectra of phenalemine 512 in PMMA upon the excitation by different sources: He–Ne laser (2 mW,  $\lambda = 632.8 \text{ nm}$ ) (curve 1), laser diode (0.5 mW,  $\lambda = 648 \text{ nm}$ ) (curve 2),

and light emitting diode (0.8 mW,  $\lambda = 678$  nm) (curve 3).

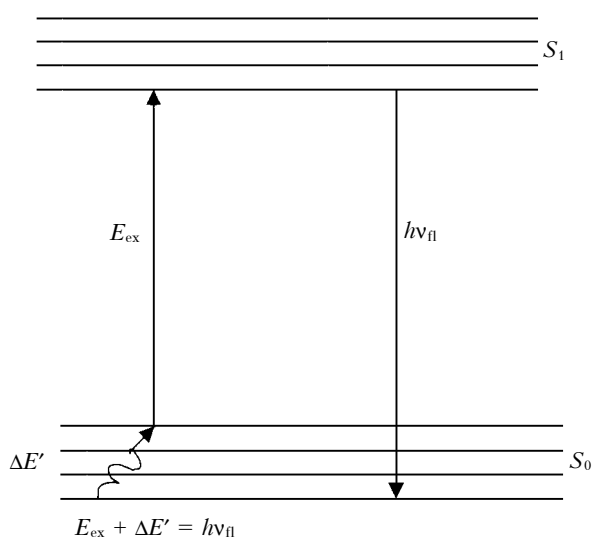


**Fig. 3.** Anti-Stokes fluorescence spectra of phenalemine 512 in PMMA upon the irradiation by different sources.

The mean energy, taken from the vibrational energy of the ground state of the molecule ( $\Delta E$ ) (Fig. 4), is determined as

$$\Delta E = E_{aS} - E_{ex}, \quad (2)$$

where  $E_{aS}$  is the mean energy of the anti-Stokes fluorescence of the molecule,  $E_{ex}$  is the energy of the exciting quanta.



**Fig. 4.** Physical nature of the anti-Stokes fluorescence.

Let the energy of the excitation quantum  $E_{ex} = h\nu_{ex}$  be converted into the energy of anti-Stokes fluorescence, taking into account the fact that a part of energy of anti-Stokes fluorescence is received from the vibrational energy of the ground state ( $\Delta E$ ):

$$h\nu_{ex} = h\nu_{aS} - h\nu_{vib}. \quad (3)$$

Determine the mean vibrational energy of the ground state ( $h\nu_{vib}$ ) as a difference between the energies of the upper and lower vibrational sublevels of this state at a certain temperature:

$$h\nu_{vib} = h\nu_{abs} - h\nu_{aS}, \quad (4)$$

where  $\nu_{abs}$  is the frequency of the fundamental absorption band of the dye.

Combining Eqs. (3) and (4), we obtain the condition for minimum frequency of excitation of the anti-Stokes fluorescence:

$$h\nu_{ex} \geq 2h\nu_{aS} - h\nu_{abs}. \quad (5)$$

From Eq. (5), we can find the wavelength of the red limit of the anti-Stokes fluorescence, neglecting the loss for heating of the matrix:

$$\lambda_{lim} \leq \frac{\lambda_{aS}\lambda_{abs}}{2\lambda_{abs} - \lambda_{aS}}. \quad (6)$$

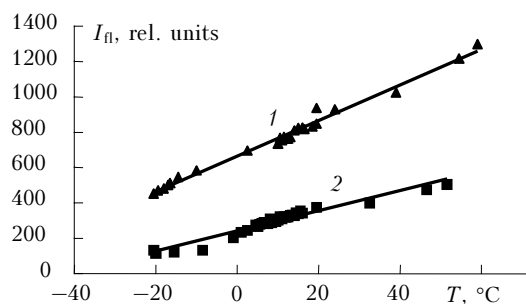
For phenalemine 512, we have the following spectral parameters:  $\lambda_{abs} = 526$  nm;  $\lambda_{aS} = 604$  nm, which gives

$$\lambda_{lim} = \frac{604 \times 526}{2 \times 526 - 604} \approx 709 \text{ nm}. \quad (7)$$

In the previous experiments, we did not observe the anti-Stokes fluorescence of phenalemine 512 upon the excitation by the semiconductor laser radiation with the wavelength of 792 nm, which can be regarded, to a certain extent, as a proof of the presence of the red limit for excitation of the anti-Stokes fluorescence.

It can be supposed that the red limit of excitation of the anti-Stokes fluorescence will increase with temperature. The experimental check of this dependence will be the subject of our further investigations.

As the sample temperature changed, we recorded the anti-Stokes fluorescence spectra and used them to draw the temperature dependence of the maximum intensity for the sample cooling down below the room temperature and its heating above the room temperature. The joined plot of the temperature dependence for the samples with two different concentrations is shown in Fig. 5.



**Fig. 5.** Temperature dependence of the intensity at the peak of the anti-Stokes fluorescence of phenalemine 512 in PMMA at the concentration:  $10^{-2}$  M (1),  $3.9 \cdot 10^{-3}$  M (2).

As the temperature decreased, the intensity of the anti-Stokes fluorescence decreased in all the samples. This fact confirms the nature of the anti-Stokes fluorescence. It is obvious that, with the

decrease of temperature, the population of vibrational sublevels of the main excited state of the dye decreases, and, consequently, the contribution of the vibrational energy to the anti-Stokes fluorescence decreases as well.

In the general case, the temperature dependence of the anti-Stokes fluorescence intensity can be presented in the following form<sup>8</sup>:

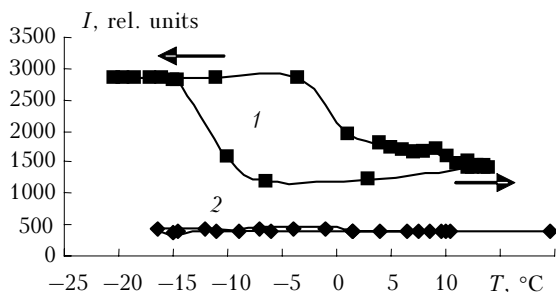
$$\frac{I}{I_0} = A \exp\left(-\frac{E_a}{kT}\right), \quad (8)$$

where  $E_a$  is the activation energy;  $A$  is some frequency coefficient;  $I_0$  is the intensity at  $T = 0$ .

The activation energy of the phenalemine 512 dye in PMMA, calculated on the basis of five temperature dependences for the sample with the concentration of  $10^{-2}$  M, was  $(2.52 \pm 0.09) \cdot 10^{-20}$  J. Earlier the activation energy of anti-Stokes fluorescence of Rhodamine 101 in ethanol was reported to have a close, by the order of magnitude, value  $(3.7 \pm 0.3) \cdot 10^{-20}$  J [Ref. 8].

The activation energy can be considered as one of the quantitative characteristics of the anti-Stokes fluorescence, which can be used in comparison of different dyes with the anti-Stokes fluorescence. The higher is the activation energy of the anti-Stokes fluorescence of a dye, the lower is the intensity of the anti-Stokes fluorescence.

The scattered excitation signal shows quite specific temperature dependence (Fig. 6).



**Fig. 6.** Temperature dependence of the intensity of the exciting (He-Ne laser) radiation scattered by the PMMA matrix: with (1) and without (2) phenalemine 512 dye.

As the temperature decreases, the intensity of the radiation scattered in the matrix with the dye increases significantly, while remaining almost unchanged in the matrix without the dye at the same recording geometry. In addition, the temperature dependence of the scattered exciting radiation demonstrates a significant hysteresis during heating. For the anti-Stokes fluorescence signal, no hysteresis was found (see Fig. 5).

The unusual behavior of the scattered signal is likely connected with the change in the dye mobility in the polymeric matrix, connected with the mobility of polymer chains. The discovered temperature dependences of the scattered signal are of undoubted interest and call for the further investigation.

## Conclusions

The anti-Stokes fluorescence of phenalemine 512 in PMMA upon the exposure to cw low-intensity radiation has been found and investigated.

It has been shown that the intensity of the anti-Stokes fluorescence decreases with the decrease of temperature, which confirms the supposed nature of the phenomenon observed. The Stokes fluorescence, on the contrary, is characterized by the increase of the intensity with the decrease of temperature.

The temperature dependences of the anti-Stokes fluorescence intensity have been used to calculate the activation energy of phenalemine 512 in PMMA, which amounted to  $(2.52 \pm 0.09) \cdot 10^{-20}$  J. The wavelength of the red limit of the anti-Stokes fluorescence for phenalemine 512 has been estimated to be  $\lambda_{\text{lim}} = 709$  nm.

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