

FLUORESCENCE SATURATION PHENOMENON FOR DISSOLVED ORGANIC COMPOUND

S. V. Patsaeva, V. V. Fadeev, E. M. Filippova, V. V. Chubarov, and V. I. Yuzhakov

Specific features of the effect of fluorescence saturation for an organic compound dissolved in water were studied after fluorescence was excited by an LGI-505 nitrogen laser ($\lambda = 337$ nm, $\tau = 8$ ns, photon flux density $F = 10^{26}$ cm⁻² s⁻¹). The experimental data obtained are discussed in terms of the model concepts of the origin of the fluorescence band for the dissolved natural organic compound.

Dissolved natural organic compounds (DOC) represent one of the most important components of water ecosystems, so the development of new methods of their monitoring is a rather urgent problem. Laser fluorometry using calibration by a signal of Raman scattering in water [1, 2] is one of such methods. But powerful laser irradiation may induce changes in the parameters of the DOC fluorescence bands that are caused by photochemical processes and fluorescence saturation effect [1-3]. These changes must be taken into account in a qualitative and a quantitative analysis of DOC, as well as other water contaminants (in particular, of petroleum origin), whose fluorescence bands may superimpose on the DOC fluorescence band.

We have studied and described the influence of photochemical reactions on the DOC fluorescence bands earlier [4, 5]. In this work, we study the phenomenon of DOC fluorescence saturation which is due to a finite lifetime of a molecule in the excited state and manifests itself as a nonlinear dependence of fluorescence intensity on the exciting radiation flux density. We have obtained fluorescence spectra and plotted fluorescence saturation curves for various DOC concentrations in water. The experimental data are discussed in terms of model concepts of the fluorescence band origin for the dissolved natural organic compound.

The DOC fluorescence spectra were excited and measured by a laser fluorometer described elsewhere [4] and comprising an LGI-505 nitrogen laser ($\tau = 8$ ns, $P = 20$ kW, beam cross section in the cell $S = 10^{-4}$ cm²), a quartz cell with a peristaltic pump, and a 500-channel Plasma Monitor optical analyzer (PARC, Model 1451, USA). The rate of pumping the solution through the cell and the repetition frequency of laser pulses were adjusted so that each new laser pulse should hit a new volume of the solution. In this way we could for the first time explore the saturation phenomenon under the conditions when the photochemical reactions induced minimal distortions in the spectral parameters of DOC [4]. The laser beam was focused into the cell by a quartz lens with a focal length of 10 cm, the maximal photon flux density F was 10^{26} cm⁻² s⁻¹.

DOC FLUORESCENCE SPECTRA AT VARIED EXCITATION INTENSITY

Figure 1 shows DOC fluorescence spectra normalized to their maximal peak heights at various exciting radiation flux densities F . The line at 381 nm belongs to Raman scattering of water. Such a behavior of the spectra points to the occurrence of fluorescence saturation. First of all, it should be noted that the shape of the spectra remains unchanged over the entire range of F . This is evidence for the occurrence of homogeneous broadening of the DOC fluorescence band [1, 3].

FLUORESCENCE SATURATION CURVES

For a quantitative characterization of saturation, let us introduce the following parameters [1, 2]: fluorescence parameter $\Phi = N_{fl}/N_{Rs}$, $\Phi_0 = \lim_{F \rightarrow 0} (N_{fl}/N_{Rs})$, saturation factor $\Gamma = \Phi_0/\Phi$, where N_{fl} is the number of detected fluorescence photons, and N_{Rs} is the number of photons Raman-scattered by water. The signal of Raman scattering by water, N_{Rs} , was used as a linear characteristic of the exciting radiation intensity F .

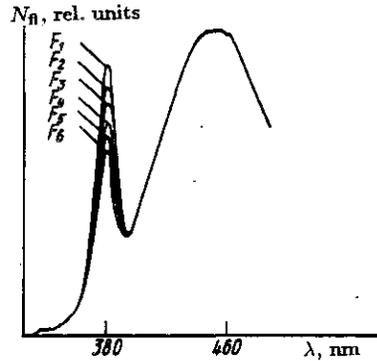


Fig. 1

DOC fluorescence spectra as excited by laser radiation of different photon flux density: $F_1 : F_2 : F_3 : F_4 : F_5 = 1 : 0.75 : 0.5 : 0.21 : 0.1$, where $F_1 = 10^{26} \text{ cm}^{-2} \text{ s}^{-1}$.

Fluorescence saturation curves $N_{fl}(F)/N(F=1)$ normalized to equal peak heights are given in Fig. 2 for samples with various DOC concentrations. The saturation is seen to be low, and the deviation from a straight line (i. e., the extent of fluorescence saturation) increases with decreasing concentration of DOC. For each fluorescence spectrum obtained at certain excitation intensity F , the Φ^{-1} values were found and the $\Phi^{-1}(F)$ dependencies were plotted for samples of varied DOC concentration (Fig. 3). All the dependencies are seen to fit a straight line. Since $\Phi^{-1} \rightarrow \Phi_0^{-1}$ at $F \rightarrow 0$, the Φ_0 value was found by extrapolating the straight line to intersect the ordinate. Having determined this parameter, we plotted the $\Gamma(F) = \Phi_0/\Phi$ dependencies, which were then approximated by straight lines of the form $\Gamma(F) = 1 + \beta F$.

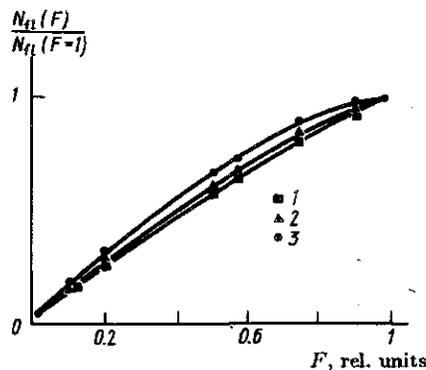


Fig. 2

DOC fluorescence saturation curves normalized to equal peak heights for water samples containing different amounts of DOC: C_1 (1) $>$ C_2 (2) $>$ C_3 (3).

Fluorescence saturation effect for dye molecules excited by laser pulses were studied in detail in [3, 6, 7]. The physical meaning of the nonlinearity parameter β is clear in the simplest case when the same molecules are both absorbing and fluorescent, there is a quasi-steady-state excitation (the laser pulse duration t_i is much greater than the lifetime of the molecule excited state, τ) by pulses with rectangular distribution of photon flux intensity in time and over the flux cross section, and conversion between Raman scattering events is absent. Then $\beta = \sigma\tau$, where σ is the cross section of absorption for fluorescent DOC molecules.

The nonlinearity parameter β tends to decrease with increasing concentration (Table 1)*, and the scatter of values is sufficiently large to consider β to be constant. Qualitatively, this effect is clear from Figs. 2 and 3. This feature will be used in the further discussion on the nature of the DOC fluorescence band.

* Here the parameter Φ_0 is merely a measure of concentration.

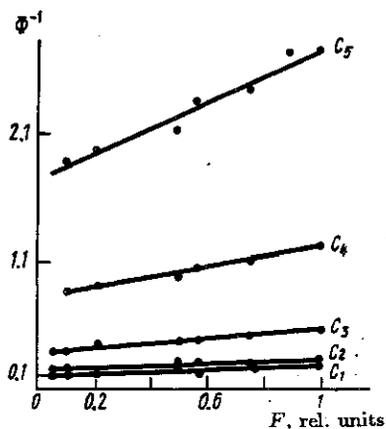


Fig. 3

Parameter Φ^{-1} as a function of excitation photon flux density for water samples containing different amounts of DOC: $C_1 > C_2 > C_3 > C_4 > C_5$.

Table 1

Nonlinearity Parameter β for Different DOC Concentrations and for Petroleum Contaminants in Water

	DOC					Libyan petroleum	Diesel fuel
	$\beta \times 10^{-26}, \text{cm}^2 \text{s}$	0.57	0.48	0.43	0.39	0.42	0.61
Φ_0	0.58	1.2	2.6	4.23	5	4	2.34

Earlier it was assumed [2, 8] that the parameter β is the same for DOC in any kind of water, is independent of concentration, and can be used for identification of other organic pollutants in water (in particular, petroleum derivatives) against the DOC background. Our studies carried out under above-described conditions of sample irradiation by a nitrogen laser, which excluded the influence of photochemical reactions on the DOC fluorescence spectra, showed that, as noted above, there is a concentration dependence of the parameter β and that its values for the Libyan petroleum and diesel fuel contaminants in water are close to those for DOC (see Table 1). This circumstance makes it difficult to utilize the method of nonlinear fluorometry for identification of various petroleum pollutants in water with the given excitation source. The situation may become more favorable if other excitation sources (e. g., the fourth harmonic of the YAG : Nd³⁺ laser with $\lambda_{\text{ex}} = 266 \text{ nm}$) and shorter pulses of excitation are used.

MODEL CONCEPTS OF THE ORIGIN OF FLUORESCENCE BAND FOR NATURAL DOC

Let us outline once more two important experimental results obtained in this work.

- (1) Invariance of the DOC fluorescence spectrum shape over the range of flux densities F and all the DOC concentrations studied.
- (2) A trend toward a decrease in the fluorescence saturation parameter β with increasing DOC concentration.

These data seem to add substantially to the earlier obtained information about specific spectral features of DOC luminescence and their dependence on various factors.

(3) Slight dependence of the fluorescence maximum wavelength λ_{\max} on the exciting radiation wavelength λ_{ex} over the spectral range of the latter from 200 to 340 nm [3].

(4) Nearly complete identity of fluorescence band shapes for different molecular fractions of DOC [3].

(5) Shift of the DOC fluorescence band maximum and deformation of the fluorescence excitation spectra caused by the ultraviolet radiation from pulsed and cw light sources [4, 5]. The largest changes in the fluorescence excitation spectra were observed within the spectral range of exciting radiation.

(6) Lack of correlation in the behavior of the DOC absorption and fluorescence spectra, i.e., not all molecules are capable of fluorescence and the fluorescing fraction of DOC seems to be very small [5, 9].

Therefore, the accumulated data on the spectral parameters of DOC make it possible to further develop the hypothesis suggested earlier [1, 2] that among natural organic compounds there are certain groups, fluorophors, which are responsible for fluorescence and constitute a very small part of DOC. This explains the remarkable (for a multicomponent system) invariance of the DOC fluorescence spectrum shape for all the types of water and all molecular fractions of DOC at various wavelengths of exciting radiation. The chemical composition of absorbing and fluorescing groups is complicated and nonuniform, and therefore the UV irradiation results in inhomogeneous structures of absorption and fluorescence excitation bands.

The concentration dependence of β found in this work suggests that intermolecular interactions and the probability of nonradiative intermolecular transfer of excitation energy grow with increasing DOC concentration.

However, these suggestions, based on experimental data, so far remain model and approximate. A strict substantiation of this hypothesis requires specially designed comprehensive studies using lasers of varied wavelength and pulse duration.

REFERENCES

1. V. V. Fadeev, Sc. D. (Phys.-Math.) Thesis, Moscow University, Moscow, 1983.
2. V. V. Chubarov, Ph. D. (Phys.-Math.) Thesis, Moscow University, Moscow, 1984.
3. V. V. Fadeev, A. M. Chekalyuk, and V. V. Chubarov, *Dokl. AN SSSR*, vol. 262, p. 338, 1982.
4. S. V. Patsaeva, E. M. Filippova, V. V. Chubarov, and V. I. Yuzhakov, *Vest. Mosk. Univ. Fiz. Astron.*, vol. 32, no. 4, p. 76, 1991.
5. S. V. Patsaeva, V. V. Fadeev, E. M. Filippova, V. V. Chubarov, and V. I. Yuzhakov, *Vest. Mosk. Univ. Fiz. Astron.*, vol. 32, no. 6, p. 71, 1991.
6. A. M. Chekalyuk, Ph. D. (Phys.-Math.) Thesis, Moscow University, Moscow, 1982.
7. S. Ya. Dzhasim, Ph. D. (Phys.-Math.) Thesis, Moscow University, Moscow, 1991.
8. V. A. Sivovolov, V. V. Fadeev, and V. V. Chubarov, *Proc. 4th International Conference on Luminescence*, Szeged (Hungary), p. 229, 1982.
9. K. S. Shifrin, *Introduction to the Ocean Optics* (in Russian), Leningrad, 1983.

18 November 1991

Department of General Physics