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Solvent Polarity and Microenvironment Effects on the Excited-State Properties and UV Photolysis of Serotonin (5-Hydroxytryptamine)

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Abstract

The photophysical behavior and UV-induced photochemical degradation of serotonin (5-hydroxytryptamine, 5-HT) were studied in aqueous, organic, and micellar media using UV–visible absorption and fluorescence spectroscopy. Solvent polarity, pH, and microenvironment exert a decisive influence on the spectral response and photochemical reactivity of 5-HT under UV irradiation. Solvatochromic analysis reveals a marked increase in dipole moment upon excitation ($\mu_e \approx 7.8$ D vs. $\mu g \approx 3.0$ D), consistent with π–π* transitions accompanied by a significant redistribution of π electron density in the excited state.

Keywords: Serotonin; UV photolysis; Solvatochromism; Fluorescence; Micelles.

1. Introduction

The electronic properties of aromatic and heteroaromatic molecules are highly sensitive to their environment. Solvent polarity, pH, and hydrogen-bonding ability affect electronic distribution and solvation dynamics, resulting in marked changes in absorption and fluorescence spectra between the ground and excited states [1–4]. Solvatochromic analysis is therefore a valuable approach for probing solvent–solute interactions and estimating excited-state dipole moments, which are essential parameters for understanding molecular reactivity and intermolecular interactions [2,3,5]. For indole derivatives such as serotonin, electronic excitation is commonly associated with a redistribution of π-electron density and an increase in molecular polarity, often accompanied by structural relaxation [6–8]. Quantifying these changes is crucial not only for interpreting fluorescence behavior but also for elucidating photochemical pathways. Several solvatochromic models, including the Lippert–Mataga, Bakhshiev, Kawski–Chamma–Viallet, and Reichardt approaches, have been widely applied to characterize excited-state properties of fluorescent molecules [2,3,5]. However, comparative studies integrating multiple solvatochromic models for serotonin remain scarce.

In parallel, serotonin is susceptible to photodegradation under ultraviolet irradiation. This phenomenon is particularly relevant in spectrofluorimetric analyses, where prolonged exposure may induce photobleaching or the formation of secondary fluorescent photoproducts [9–11]. More broadly, the UV photodegradation of biologically active molecules is a central issue in environmental and biomedical photochemistry [10,12]. Photolysis kinetics strongly depend on experimental parameters such as pH, solvent polarity, dissolved oxygen, and the surrounding microenvironment [12,13]. Organized media, including micellar systems, may significantly alter photochemical behavior by modifying local polarity, molecular mobility, and access to reactive species [14–16]. Nevertheless, a systematic and comparative investigation of serotonin photolysis in aqueous, organic, ionic, and micellar media is still lacking.

In this work, we address this gap through an integrated study of the solvent-dependent photophysical properties and UV photolysis kinetics of serotonin. The influence of solvent polarity and pH on absorption and fluorescence spectra is examined, and the singlet excited-state (S_1) dipole moment is determined using multiple solvatochromic models. In addition, the kinetics and mechanisms of serotonin photodegradation are investigated in aqueous, organic, and micellar environments. This combined approach provides a coherent framework for correlating solvation effects, excited-state properties, and photochemical reactivity, and offers practical insight for the interpretation of spectrofluorimetric data and the assessment of serotonin photostability.

2. Materials and Methods

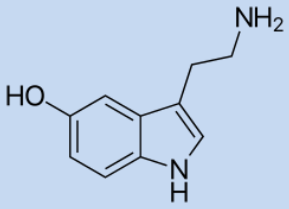
2.1. Chemicals

5 hydroxytryptamine (5 HT, serotonin, purity ≥ 99%, analytical grade) was purchased from Alfa Aesar (France) and used as received, without further purification. To evaluate possible interference effects, other biogenic amines commonly found in physiological environments, namely histamine and putrescine (purity ≥ 99%, analytical grade), supplied by Sigma Aldrich, were also studied. The main physicochemical properties of serotonin are summarized in Table 1.

Distilled water and a series of spectroscopic grade solvents were used to minimize background absorption and stray fluorescence contributions, in accordance with recommended practices for solvatochromic and fluorescence studies. These studies consistently use high purity solvents to avoid spurious signals arising from impurities, solvent stabilizers, or trace moisture that can quench or shift emission spectra [18,19]. The polar protic solvents used were methanol (MeOH, 99.8%), ethanol (EtOH, 99.99%), propan 2 ol (2 PrOH, 99.99%), and propan 1 ol (PrOH, 99.99%). Polar aprotic solvents with non zero dipole moments included acetonitrile (MeCN), dimethyl sulfoxide (DMSO), and dimethylformamide (DMF). The nonpolar aprotic solvents used were dichloromethane (CH_2Cl_2), ethyl acetate (CH_3CO_2Et), diethyl ether (Et–O–Et), chloroform ($CHCl_3$), cyclohexane (C_6H_{12}), and hexane (Hex), all of spectroscopic quality and with purity ≥ 99%, chosen to span a wide range of polarity parameters relevant for solvatochromic and fluorescence measurements [17-19].

Four surfactants were used to study the influence of micellar environments: sodium dodecyl sulfate (SDS, 99%), Brij 700, cetyl trimethyl ammonium chloride (CTAC, 25 % m/m in aqueous solution) and hexadecyltrimethyl ammonium hydroxide (CTAOH, 99 % m/m in aqueous solution), all supplied by Aldrich. Surfactants were selected to form micellar systems with distinct charge and micelle structure, which are known to influence local solvation, molecular mobility, and spectroscopic response of solutes [14,20,21].

Table 1. Chemical Properties of Serotonin

	Chemical Properties		Formula
Serotonin	Formula	$C_{10}H_{12}N_2O$	
	Molecular	176.22 $g.mol^{-1}$	
	Water solubility (25°C)	25.5 $g.L^{-1}$	
	Melting point	167-168 °C	
	pKa (23.5°C)	10,16	
	Log Kow (25°C)	1.34	

2.2. Preparation of the Solution and pH Control

The aqueous solutions were prepared using distilled water. The pH was adjusted using appropriate buffer systems, chosen to cover acidic, neutral, and basic conditions while ensuring the chemical stability of the 5-HT molecule. This pH control was essential for studying the influence of protonation–deprotonation equilibria on spectral properties. The concentration of 5-HT was optimized to satisfy the linearity conditions of Beer–Lambert's law and to avoid internal filter and self-quenching effects in fluorescence measurements [22,23]. Typical absorbance values were kept below 0.1 at the excitation wavelength.

2.3. UV–Visible Absorption and Fluorescence Measurements

UV–Visible absorption spectra were recorded at room temperature using quartz cuves with a fixed optical path length. Fluorescence emission spectra were acquired by exciting the samples at their corresponding absorption maxima**.** All spectra were corrected to account for solvent background noise and instrumental response. These

measurements served as the basis for analyzing the effects of solvent and pH on the electronic transitions of 5-HT. Similar experimental protocols have been widely applied in fluorescence studies of biologically relevant indole derivatives, including tryptophan and serotonin, to characterize their excited-state properties and solvent-dependent behavior [6,24–26].

2.4. Estimation of Dipole Moments in the Excited State

The Stokes shifts obtained from the absorption and emission maxima were analyzed as a function of the solvent polarity parameters using the Lippert–Mataga formalism and related solvatochromic models [27–31]. This approach allows the estimation of the dipole moment of 5 HT in its first singlet excited state (S_1), assuming a spherical Onsager cavity and negligible specific solute–solvent interactions [2,29].

In these analyses, the Lippert–Mataga equation correlates the Stokes shift ($\Delta\nu$) with the orientation polarizability of the solvent, while the Bakhshiev and Kawski–Chamma–Viallet formalisms provide complementary approaches for accounting for the refractive index and solvent response. The validity and limitations of these assumptions are discussed by comparing the results obtained with different solvatochromic models and evaluating potential deviations arising from specific hydrogen bonding or other solute–solvent interactions [23, 32,33].

This combined approach provides a robust framework to derive the excited-state dipole moment, which is a key parameter for understanding solvation dynamics, fluorescence behavior, and photochemical reactivity of serotonin in

various media.Bakhshiev equation : $$\bar{\nu} = \frac{\nu_A+\nu_F}{2} = \frac{2(\mu_e-\mu_g)^2}{hca^3}\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right) + cste \quad (1)$$

Kawsi-Chamma-Viallet equation: $$\frac{\bar{\nu}_A+\bar{\nu}_F}{2} = -\frac{2(\mu_e{}^2-\mu_g{}^2)}{hca^3}\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right) + cste \quad (2)$$

Lippert-Mataga equation: $$\Delta\nu = \nu_A - \nu_F = \frac{2(\mu_e{}^2-\mu_g{}^2)^2}{hca^3}\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right) + cste \quad (3)$$

Combination of the Bakhshiev and Kawski-Chamma-Viallet equations: $$\frac{\mu_e}{\mu_g} = \left|\frac{m_1-m_2}{m_1+m_2}\right| \quad (4)$$

Dimroth-Reichardt equation: $$\bar{\nu}_A - \bar{\nu}_F = 11307.6\left[\left(\frac{\mu_e-\mu_g}{\mu_{eB}-\mu_{gB}}\right)^2\left(\frac{a_B}{a}\right)^3\right]\frac{E_T(30)_{solvant}-30,7}{32,4} + cste \quad (5)$$

2.5. Photolysis and Kinetic Analysis

Photodegradation experiments were conducted by irradiating 5 HT solutions with UV light at a fixed wavelength. The change in fluorescence intensity as a function of irradiation time was monitored in situ. Under the experimental conditions used, the observed decrease in fluorescence intensity was attributed primarily to molecular photodegradation rather than photophysical quenching effects [6,7,34].

The kinetic data were analyzed assuming pseudo-first-order behavior, a common approximation for dilute solutions where the solvent and oxygen concentrations remain effectively constant [35,36]. This approach allowed the determination of the apparent photolysis rate constants (kobs) for serotonin under different experimental conditions.

These kinetic parameters were then compared between aqueous, organic, and micellar environments to elucidate the influence of the medium on the photostability of 5 HT. Differences in photodegradation rates were interpreted in terms of solvent polarity, hydrogen bonding, microviscosity, and local dielectric environment, which are known to modulate the accessibility of reactive excited states and the generation of reactive intermediates [14,18,37].

This methodology provides a systematic framework for assessing the photostability of serotonin and understanding how organized media such as micelles can modulate its photochemical behavior, a critical aspect for both environmental photochemistry and in vitro fluorescence studies.

3. Results and Discussion

3.1. UV–Visible Absorption Properties of 5-hydroxytryptamine

The UV–Visible absorption spectra of 5 HT are dominated by several intense bands attributed to allowed π–π* electronic transitions of the indole chromophore. These bands show a marked dependence on pH and solvent environment, reflecting the amphoteric nature of the molecule and the high sensitivity of its electronic structure to medium–solute interactions. In experimental studies, the broad UV absorption spectrum of serotonin spans approximately from 200 to 320 nm, with major peaks near 220 nm, 275 nm and 295 nm under physiological conditions, consistent with π–π* transitions of the indole chromophore [38].

In aqueous solution, the spectra recorded at different concentrations strictly obey Beer–Lambert's law in the range studied, with excellent linear correlation coefficients ($r^2 \approx 0.999$), confirming the absence of aggregation and the chemical stability of 5 HT under the experimental conditions. The strong UV absorption ($\varepsilon > 10^3$ L.mol^{-1}.cm^{-1}) is characteristic of allowed π–π* transitions for indole derivatives [38].

The influence of pH on the absorption properties of 5 HT is significant because protonation state affects the electronic distribution on the chromophore. Under strongly acidic conditions, protonation of the indole ring and side chain functionalities alters π conjugation and can affect the positions and intensities of UV bands [31,38]. At neutral pH (7.4), bands corresponding to π–π* transitions remain prominent and align with previously reported spectra that show absorption maxima around 220 nm and 275 nm [38].

Changes in pH induce shifts in the absorption spectra due to changes in protonation of the amino and hydroxyl groups that modulate the distribution of electron density in the indole chromophore. For indole and closely related compounds, pH dependent optical spectra have been documented, showing that changes in protonation can lead to wavelength shifts and altered band intensities [39].

In addition to pH, solvent type strongly influences absorption maxima and band intensities. In a series of organic solvents spanning a wide range of polarity, the spectra generally retain similar overall shapes, indicative of the preserved electronic structure of the indole core, yet with notable solvent dependent shifts. In nonpolar and aprotic polar solvents such as hexane, acetonitrile and dimethyl sulfoxide (DMSO), absorption maxima exhibit limited shifts consistent with weak specific solute–solvent interactions [38]. However, polar solvents with high dielectric constants and hydrogen bonding ability (methanol, ethanol) can induce moderate bathochromic shifts because of stabilization of excited states via dipole–dipole interactions and specific hydrogen bonding [40–45].

This distinction between protic and aprotic solvents reflects differences in how solvent molecules interact with the indole chromophore. Protic solvents, capable of hydrogen bonding, often more effectively stabilize excited states relative to ground states, leading to solvent dependent spectral shifts, whereas aprotic solvents primarily engage in nonspecific dipolar solvation [43–45].

Overall, the combined influence of pH and solvent type highlights the strong coupling between the electronic structure of 5 HT and its environment. These parameters are determining factors in interpreting its fluorescent behavior, excited state dynamics and photochemical reactivity.

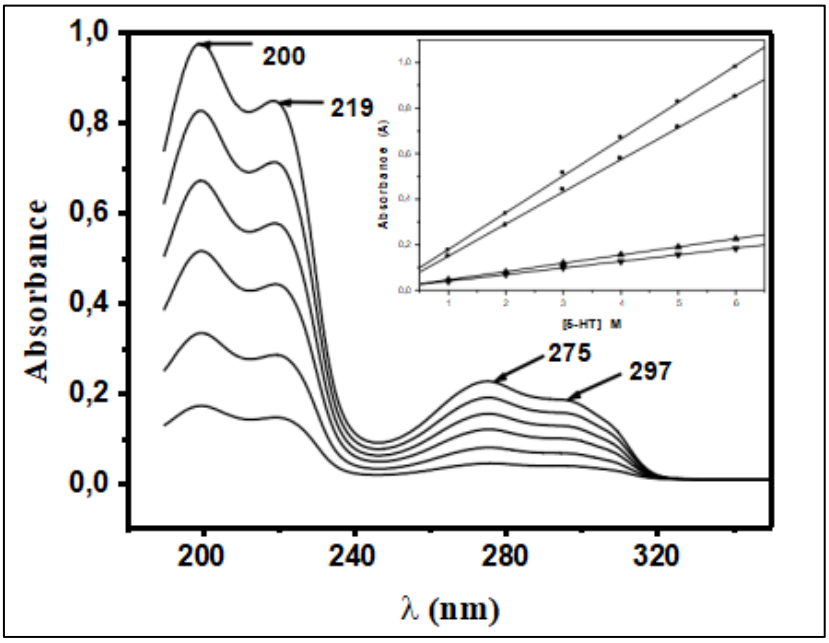


Figure-1. Absorption spectra of 5-HT in water at different concentrations (2-12 µg.mL^{-1})

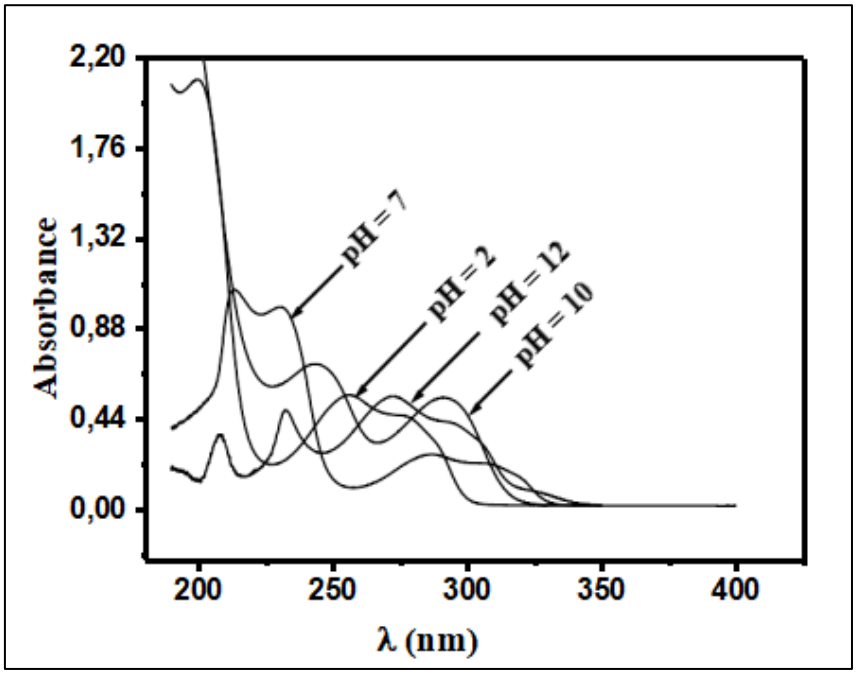


Figure-2. Absorption spectra of 5-HT (4 µg.mL^{-1}) in water at different pH values.

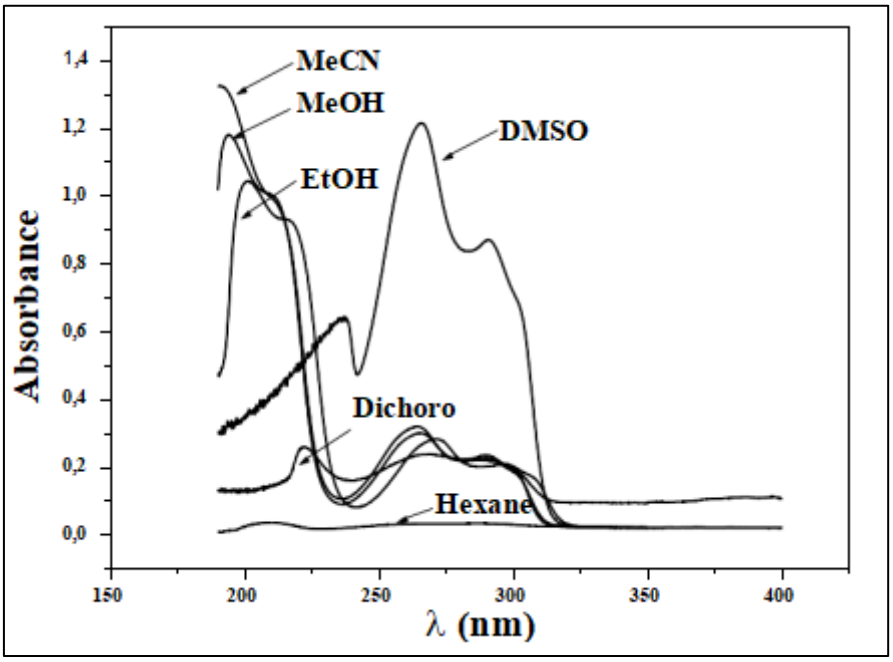


Figure-3. Absorption spectra of 5-HT (4 µg.mL^{-1}) in various organic solvents.

3.2. Fluorescence and Determination of the Dipole Moment in the Excited State S_1

5 HT exhibits marked fluorescent behavior in all solvents studied, confirming its strong analytical potential by fluorescence. The excitation and emission spectra recorded at 25 °C (Figure 4) reveal a similar overall pattern regardless of the solvent, indicating that the electronic skeleton of the indole chromophore is generally preserved. Fluorescence of indole derivatives such as serotonin typically arises from π–π* transitions within the indole ring and is sensitive to solvent environment without gross changes in spectral profile [6,24].

In an aqueous medium, the excitation spectrum shows two maxima around 223 nm and 275 nm, while the emission spectrum is dominated by a main band centered at 340 nm, consistent with previously reported fluorescence behavior of serotonin. In organic solvents, the emission spectra often reveal two main spectral regions, located around 290–300 nm and 340–350 nm, reflecting the existence of different excited states or contributions from distinct conformations of the indole moiety [19,20]. The relative population of these emissive states depends heavily on solvent polarity and its ability to stabilize excited configurations [15,25].

Despite these variations, the fluorescence of 5 HT remains robust across solvents, highlighting its photophysical stability. Studies on analogous indole compounds show that aqueous and organic environments can both support intense fluorescence, with minor shifts in spectral maxima attributed to solvent polarity and hydrogen bonding interactions [16,17]. In an aqueous medium at neutral pH, a 30 minute kinetic study shows that the fluorescence intensity remains constant, with similar behavior observed in organic solvents, consistent with observations that ground state absorption and emission profiles of indoles are stable over moderate irradiation times in the absence of photodegradation [16,17].

To determine the dipole moment in the excited state (S_1), the measured Stokes shifts were correlated with solvent polarity functions using solvatochromic models such as Lippert–Mataga, Bakhshiev, and related formalisms [2,18]. These models assume that the excited state dipole moment can be estimated by analyzing how the emission maximum shifts relative to the absorption maximum as solvent polarity changes, provided specific solute–solvent interactions are minimal [8,18].

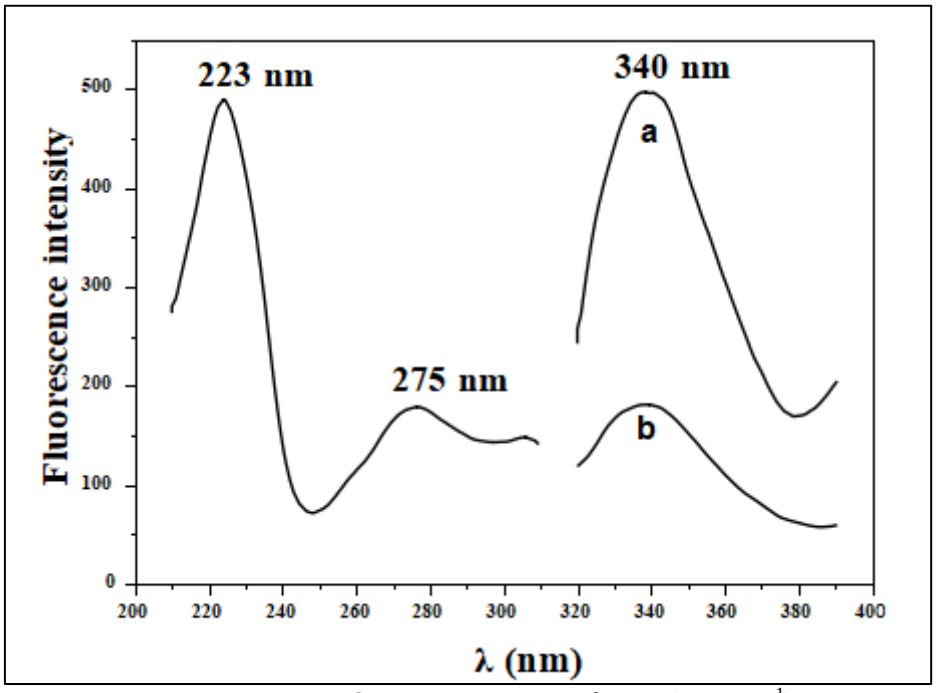


Figure-4. Excitation and emission spectrum of 5-HT (4 µg.mL^{-1}) in water
(a) emission spectrum at λ = 223 nm **(b)** emission spectrum at λ = 275 nm)

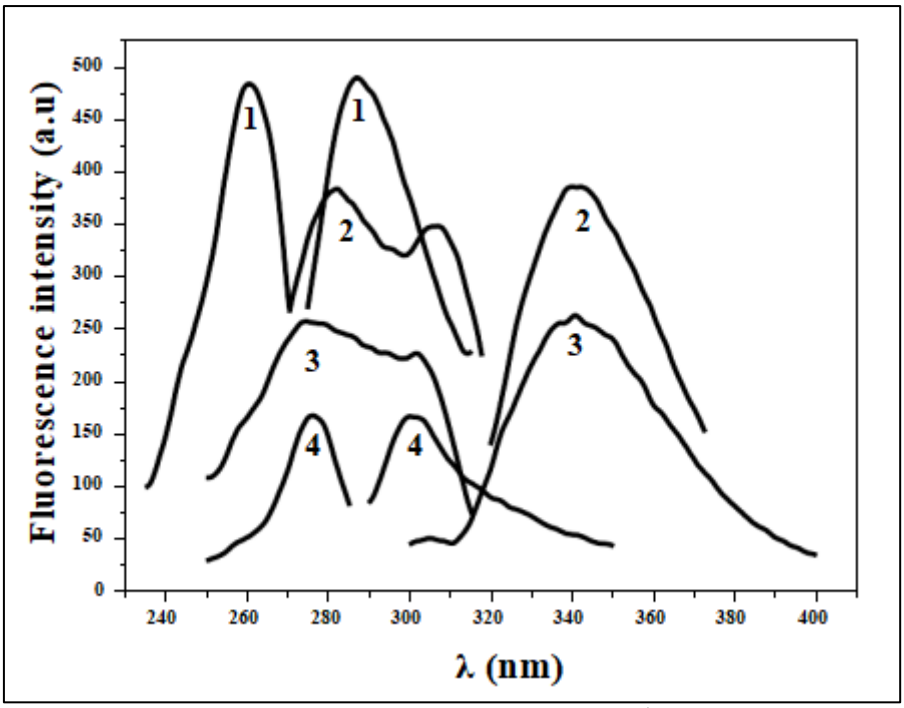


Figure-5. Excitation and emission spectra of 5-HT (4 µg.mL^{-1}) in different organic solvents
(1: Acetonitrile, 2: Dimethyl sulfoxide, 3: Water, 4: Hexane).

Analysis of Stokes shifts ($\nu_A - \nu_F$, Table 2) reveals a strong dependence on the nature of the solvent. Small shifts are observed in nonpolar or aprotic polar solvents such as hexane and DMSO, whereas significantly larger shifts occur in protic polar solvents such as methanol and ethanol. This trend reflects the ability of protic solvents to stabilize the relaxed excited state (S_1R) via specific solute–solvent interactions, particularly hydrogen bonding with the –OH and –NH_2 groups of 5 HT. In contrast, aprotic solvents primarily provide nonspecific dipolar stabilization, leading to relatively more intense fluorescence but reduced Stokes shifts [6, 16,21,22].

The influence of solvation is also evident in binary solvent mixtures, such as water/methanol and water/ethanol. Maximum fluorescence intensity is typically observed at intermediate compositions (50/50 v/v for water/methanol; 70/30 v/v for water/ethanol), whereas higher water fractions reduce intensity, likely due to enhanced solvation favoring non-radiative relaxation pathways [6,22].

These observations can be interpreted in the context of the Franck–Condon principle, whereby the unrelaxed excited state (S_1NR) rapidly reorganizes into the relaxed excited state (S_1R) via reorientation of solvent molecules before emission occurs [8,24]. The magnitude of the Stokes shift thus provides a quantitative indicator of solvent–

solute interactions and the degree of stabilization of the excited state, consistent with the general behavior of indole derivatives in protic versus aprotic media [20–23].

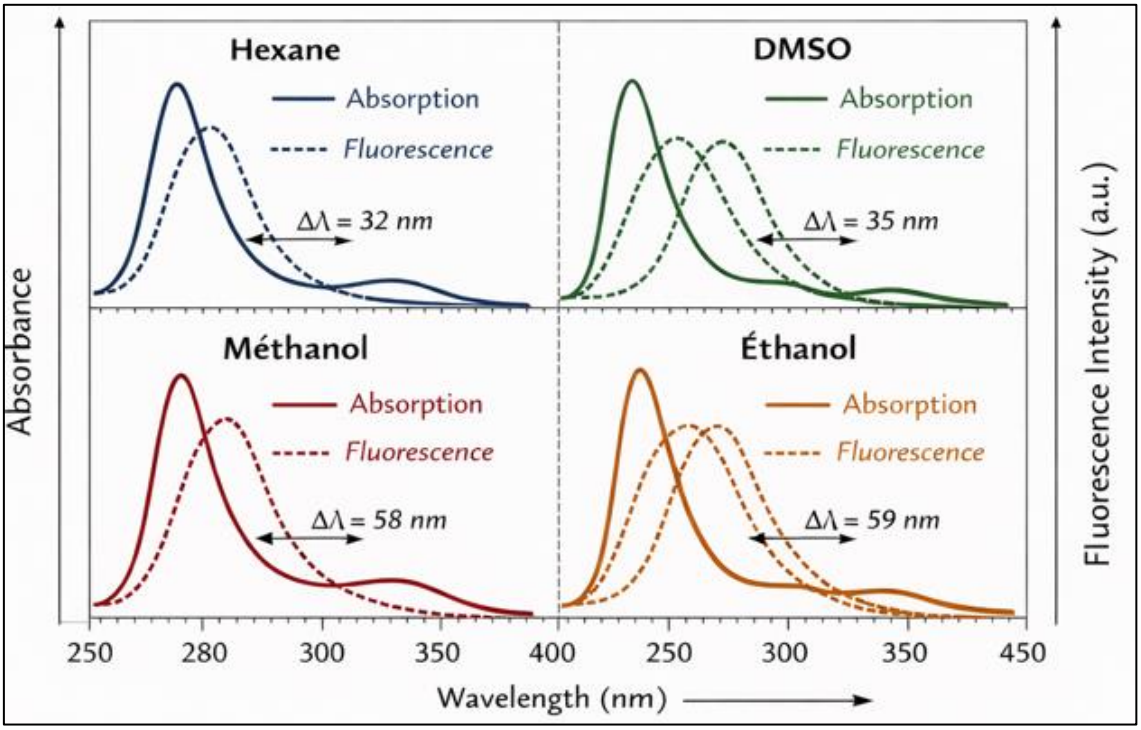


Figure-6. Absorption and fluorescence spectra of 5-HT in various solvents, highlighting Stokes shifts (Δλ) in hexane, DMSO, methanol, and ethanol.

Table-2. Spectroscopic parameters of 5-HT in different solvents

Solvent	λ_{max} (absorption) (nm)	λ_{max} (emission) (nm)	Stokes shift Δλ (nm)	Ground-state dipole moment μ_g(D)	Excited-state dipole moment μ_e(D)
Hexane	278	310	32	3.0	7.8
DMSO	280	315	35	3.0	7.8
Methanol	282	340	58	3.0	7.8
Ethanol	283	342	59	3.0	7.8

To quantify these effects, the absorption and fluorescence spectra of 5 HT were analyzed using established solvatochromic models, including Bakhshiev, Kawski–Chamma–Viallet, Lippert–Mataga, and Reichardt correlations. These formalisms relate the Stokes shift to solvent polarity parameters, allowing the dipole moment in the excited state (S_1) to be estimated [6, 8, 15, 20]. Such analyses provide insights into electronic redistribution during π–π transitions, which is critical for understanding the photophysics of indole derivatives like serotonin.

The results show a significant increase in dipole moment upon excitation, from μg ≈ 3.0 D (ground state) to μe ≈ 7.8 D (excited state), indicating enhanced polarization in S_1 [22,24,28]. Comparison of protic versus aprotic solvents reveals a clear correlation between Stokes shifts and excited-state polarization: protic solvents efficiently stabilize the S_1 state via hydrogen bonding and dipolar interactions, leading to larger Stokes shifts and increased sensitivity to photolysis. In contrast, aprotic solvents provide weaker stabilization, resulting in smaller shifts and more intense fluorescence that is less sensitive to solvatochromic effects (Figure 6) [24,28,30-38].

These findings demonstrate that the photophysics and photostability of 5 HT depend not only on solvent polarity but also on the ability of the solvent to form specific interactions with the –OH and –NH_2 groups. This understanding is crucial for predicting the behavior of serotonin in chemical and biological systems and for selecting appropriate solvents in analytical, spectroscopic, and photophysical applications.

Table-3. Results of the characteristics of the Bakhshiev, Kawski-Chamma-Viallet, Lippert-Mataga, and Reichardt correlations of 5-HT.

Correlations	Slope [a]	(r^2) [b]	n [c]
Bakhshiev (m_1)	7729	0,99	6
Kawski-Chama-Viallet (m_2)	-8048	0,97	6
Lippert-Mataga (m_3)	24829	0,96	6
Dimroth-Reichardt (m_4)	12022	0,98	6

[a] slope values; [b] correlation coefficients; [c] n : number of points.

Table-4. Solvathochromic data for 5-HT in various solvents.

Solvant	λ_A^a	λ_F^b	$\bar{\nu}_A^c$	$\bar{\nu}_F^d$	$\bar{\nu}_A^c - \bar{\nu}_F^d$	$\frac{\bar{\nu}_A + \bar{\nu}_F}{2}$
Hexane	208	301	48077	33223	14854	40650
Dichloromethane	223	367	44843	27248	17595	36045
Ethanol	202	342	49505	29240	20267	39372
Methanol	194	341	51546	29326	22220	40436
Acetonitrile	191	286	52356	34965	17391	37338
DMSO	266	341	37594	29326	8268	33460

Table-5. Results of experimental dipole moments at the first excited singlet state μe (Debye) of 5-HT.

a[(a)](Å)	μ_g[(b)] (D)	μ_e(I) [(c)] (D)	μ_e(II) [(d)] (D)	μ_e(III) [(e)] (D)	μ_e/μ_g(IV) [(f)] (D)	μ_e(V) [(g)] (D)
4	3,015	10,023	7,761	15,580	49,458	7,824

[(a)] Theoretical radius of the Onsager cavity calculated using the AM1 method.
[(b)] Theoretical dipole moment in the ground state, in Debye, calculated using the AM1 method.
[(c)] Calculated from Bakhshiev's formula (Eq. 1).
[(d)] Calculated using the Kawski-Chamma-Viallet formula (Eq. 2).
[(e)] Calculated using the Lippert-Mataga formula (Eq. 3).
[(f)] Calculated by combining the Bakhshiev and Kawski-Chamma-Viallet formulas (Eq. 4).
[(g)] Calculated using the Reichardt formula (Eq. 5).

3.3. Photolysis Kinetics of 5-HT in Various Media

The photolytic behavior of 5-HT was investigated by irradiating its solutions with a mercury lamp under conditions representative of spectrofluorimetric analyses. It is well established that light exposure can induce chemical transformations or degradation of organic analytes, leading to the formation of by-products that may fluoresce within the same spectral region as the target compound, thereby interfering with quantitative measurements [19,39].

To evaluate the sensitivity of 5-HT to UV irradiation, the temporal evolution of its characteristic fluorescence was monitored in various solvents. Continuous irradiation over exposure times ranging from 5 s to 300 s resulted in a progressive decrease in fluorescence intensity, underscoring the necessity of accounting for photostability and photodegradation in kinetic studies. For many organic molecules that absorb in the UV, direct photolysis follows first-order kinetics, with a decline in analyte concentration and the concomitant formation of photoproducts over time [40,41].

These findings are consistent with previous reports indicating that biogenic amines and pharmaceutical compounds can be susceptible to light-induced degradation, especially in polar media where solvent-mediated processes such as radical formation or excited-state reactions facilitate decomposition [38, 42-48]. Such photolysis behavior must be taken into account when interpreting fluorescence measurements, as loss of fluorescence signal may reflect chemical degradation rather than simple photophysical quenching.

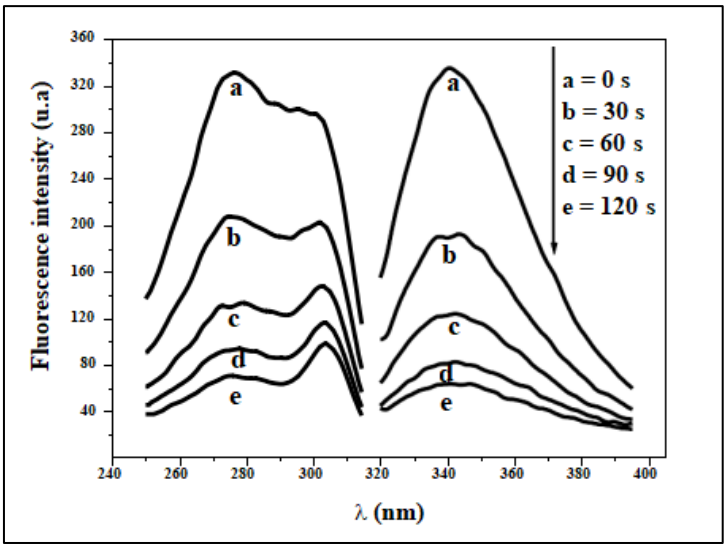


Figure-7. Evolution of the excitation and emission spectra of 5-HT (4 μg.mL^{-1}) as a function of irradiation time (seconds).

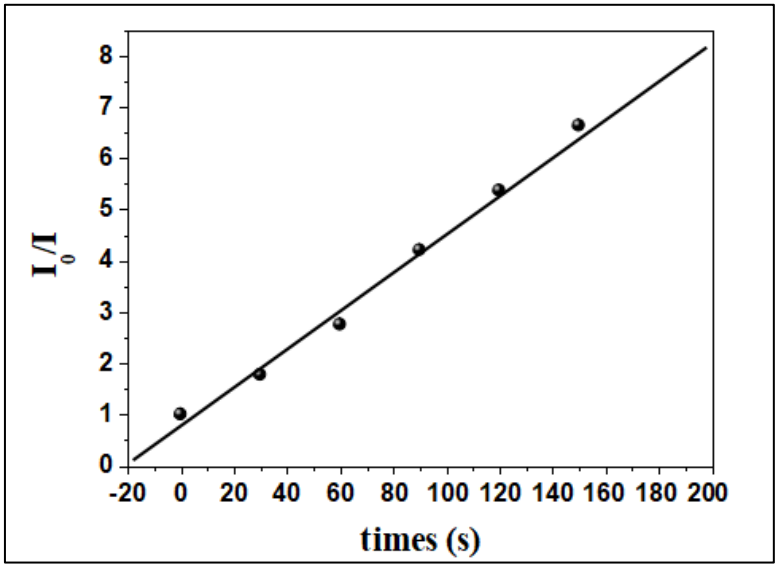


Figure-8. Photodegradation kinetics of 5-HT (4 µg.mL^{-1}) in water (λ_{ex} = 275 nm; λ_{em} = 340 nm)

The decrease in fluorescence intensity under UV irradiation reflects the photochemical degradation of serotonin (5-HT) through a radical-mediated pathway. Upon absorption of UV light, 5-HT is excited to its singlet state (S_1), which can generate indole-centered radicals that react with molecular oxygen to form oxidized products such as quinones and carbonyl derivatives:

$$5-\mathrm{HT}\,(S_0) + h\nu(\mathrm{UV}) \rightarrow 5-\mathrm{HT}\,(S_1)$$

$$5-\mathrm{HT}\,(S_1) \rightarrow 5-\mathrm{HT}^{\bullet}$$

$$5-\mathrm{HT}^{\bullet} + O_2 \rightarrow \text{Oxidized products (quinones, carbonyls)}$$

3.4. Photolysis Kinetics of 5-HT in Various Media

The photolytic behavior of 5-HT is strongly influenced by the chemical nature of the medium. Under neutral aqueous conditions, light absorption can induce direct photodegradation of the indole chromophore, often involving photoionization and radical-mediated pathways, which lead to a rapid loss of fluorescence intensity and the formation of reactive intermediates that may further react or degrade [41,43]. In contrast, organic solvents that stabilise the excited state tend to slow degradation, consistent with observations for other photoactive indole derivatives [44,47].

Neutral aqueous solutions favor faster kinetics that can deviate from simple first-order decay due to competing photochemical pathways and reactive species formation [38,42,43]. By contrast, organic solvents tend to promote slower, first-order degradation due to reduced interaction with water-mediated radical processes and increased stabilization of the excited state. Furthermore, micellar systems such as those formed by CTAOH and SDS can enhance the photostability of 5-HT by restricting molecular mobility, altering local polarity and solvation microenvironments, and attenuating the accessibility of reactive oxygen species or excited-state ionization channels [47,48].

In pure aqueous solution at pH 7, 5-HT (4 µg.mL^{-1}) exhibited a marked decrease in fluorescence intensity at λ_{em} = 340 nm upon irradiation. Kinetic analysis revealed that the degradation follows second-order kinetics, suggesting involvement of bimolecular photochemical processes or reactive intermediates whose concentrations influence the rate [49]. The half-life ($t_{1/2}$) was short (24 s), confirming rapid photodegradation under neutral aqueous conditions, consistent with the high susceptibility of tryptophan-like chromophores to UV-induced reactions in water [43,46].

The pH sensitivity of photolysis kinetics was also evident: neutral media promoted faster degradation, while acidic or basic conditions provided partial protection, likely through protonation or deprotonation of the indole ring, which modifies electron density and shifts the balance of competing excited-state processes [42,43]. Similar pH effects have been observed in the photodegradation pathways of amino acid chromophores like tryptophan, where pH alters the relative importance of photoionization and excited-state proton transfer channels [43,49].

In organic solvents, the photodegradation of 5-HT monitored at λ_{em} = 340 nm followed a first-order rate law, with significantly longer half-lives in nonpolar media than in protic solvents. For example, in ethyl acetate the half-life was substantially longer than that in methanol, reflecting greater stabilization of the excited state and reduced propensity for radical-mediated or water-assisted photochemistry. This observation aligns with literature showing that solvent polarity and the ability to form hydrogen bonds strongly influence photolytic stability of UV-absorbing compounds [34-36].

The potential influence of inorganic ions (Cl^-, SO_4^{2-}, NO_3^-, Na^+, Ca^{2+}, Mg^{2+}) common in natural waters was also evaluated. At typical environmental concentrations (10^{-3} M), these ions did not exert a significant catalytic effect on 5-HT photodegradation, suggesting that for this class of compounds direct photolysis pathways dominate under the studied conditions rather than indirect, ion-mediated oxidative processes [49].

Photodegradation of 5-HT in micellar media (Brij 700, SDS, CTAC, CTAOH) showed a gradual decrease in fluorescence intensity under irradiation at $\lambda_{ex} = 275$ nm and $\lambda_{em} = 340$ nm. The kinetic behavior depended markedly on the nature of the micelle: Brij 700, CTAOH, and SDS systems followed second-order behavior likely reflecting micelle-facilitated interactions between excited states and photoproducts whereas CTAC exhibited kinetics close to zero order, possibly due to saturation of reactive sites or micellar phase constraints on molecular encounters. The range of observed half-lives (26 s to >1900 s) demonstrates the strong impact of micellar encapsulation on photostability, consistent with studies showing that surfactant assemblies can significantly modify the photochemistry of indole and related chromophores [47,48].

Table-3. Photolysis kinetics of 5-HT in various media

Sovent		Order [a]	r^2 [b]	$t_{1/2}$ [c] (s)	K_{obs} [d]
Water	pH = 2	1	0.9998	78	1.512 s^{-1} s^{-1}
	pH = 3	2	0.9965	82	1.216×10^5 $L.mol^{-1}.s^{-1}$
	pH = 7	2	0.9989	24	4.093×10^5 $L.mol^{-1}.s^{-1}$
	pH = 10	0	0.9978	98	5.12×10^{-10} $s^{-1}.mol.L^{-1}$
	pH = 11	0	0.9998	42	1.2×10^{-9} $s^{-1}.mol.L^{-1}$
Organics media	MeOH	1	0.9997	47	1.476×10^2 s^{-1}
	EtOH	1	0.9969	76	0.92×10^2 s^{-1}
	DCM	1	0.9987	98	7.09×10^2 s^{-1}
	Ethyl acetate	1	0.9978	316	0.22×10^2 s^{-1}
	MeOH/EtOH/H_2O (2/2/1)	1	0.9978	84	0.82×10^2 s^{-1}
	MeOH/DCM/H_2O (2/2/1)	1	0.9997	23	3.05×10^2 s^{-1}
Salts	$2K^+$, SO_4^{2-}	1	0.9968	44	1.56×10^2 s^{-1}
	Ca^{2+}, PO_4^{3-}	1	0.9989	39	1.78×10^2 s^{-1}
	Na^+, $H_2PO_4^-$	1	0.9988	21	0.33×10^2 s^{-1}
Micelle	Brij 700	2	0.9998	80	1.25×10^5 $L.mol^{-1}.s^{-1}$
	SDS	2	0.9987	26	3.93×10^5 $L.mol^{-1}.s^{-1}$
	CTAC	0	0.9997	44	1.126×10^{-9} $s^{-1}.mol.L^{-1}$
	CTAOH	2	0.9986	1932	3.01×10^5 $L.mol^{-1}.s^{-1}$

[a] order of kinetics; [b] correlation coefficient; [c] half-reaction time; [d] rate constant

The investigation of 5-HT photolysis in various media demonstrates that this biogenic amine is highly photosensitive, with its degradation rate strongly dependent on the nature of the solvent, the pH, and the micellar environment. Nonpolar organic solvents and micellar systems significantly prolong the half-life of 5-HT, most likely due to excited-state stabilization and restricted molecular mobility. The degradation kinetics also exhibit a pronounced pH dependence: rapid photolysis occurs under neutral conditions, whereas acidic and basic media provide relative protection, probably as a result of protonation or deprotonation of the indole ring [20,22,25,26]. The presence of metal ions and common salts at the investigated concentrations does not significantly affect the photodegradation rate [27].

These findings highlight the necessity of carefully controlling experimental conditions during spectrofluorimetric analyses of 5-HT and provide a solid basis for modeling its photochemical stability in biological and environmental contexts. The observed trends regarding solvent and pH effects are consistent with literature data on aromatic amines and neurotransmitters [19,20].

4. Conclusion

This study demonstrates that the photophysics and photostability of serotonin (5-HT) are strongly governed by solvent polarity and the surrounding microenvironment. Absorption and fluorescence spectra indicate that π–π* electronic transitions are accompanied by significant charge redistribution and an increase in the dipole moment in the first singlet excited state (S_1). UV-induced photolysis of 5-HT is rapid in neutral aqueous solutions, following second-order kinetics, slower in organic solvents with first-order kinetics, and strongly inhibited in CTAOH micelles, while inorganic ions exert only a marginal effect. These results emphasize the crucial role of solute–solvent interactions and supramolecular organization in controlling radiative and nonradiative relaxation pathways. Overall, this work provides a robust framework for the spectrofluorimetric interpretation and for understanding the photostability of 5-HT in biological and environmental media.

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Author Contributions

Abdourahmane Konté, Diégane Sarr, and Pape Abdoulaye Diaw were responsible for conceptualization, methodology, investigation, data curation, formal analysis, and drafting of the manuscript.
Dène Diégane Thiaré, Jean Pierre Bakhoum, and Ndeye Arame Diop contributed to methodology, validation, formal analysis, and manuscript review and editing.
Philippe Giamarchi and Atanasse Coly contributed to supervision, resources, project administration, and manuscript review and editing. All authors have read and approved the final version of the manuscript.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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