Self-absorption Effect on Quantum Yield of (1-Naphtylamine) Molecule in Different Solvents

Article *in* International Journal of Scientific Research · May 2012

CITATIONS
0

READS
35

3 authors:

Seetha Khartini Abdul Wahab
Cell Therapy Catapult
3 PUBLICATIONS **7** CITATIONS
SEE PROFILE

Yaqoob M. Jawad
University of Diyala
13 PUBLICATIONS **9** CITATIONS
SEE PROFILE

Ali Obies Muhsen Almayyali
University of Babylon
23 PUBLICATIONS **255** CITATIONS
SEE PROFILE

ВЛИЯНИЕ САМОПОГЛОЩЕНИЯ НА КВАНТОВЫЙ ВЫХОД (1-НАФТИЛАМИН) МОЛЕКУЛЫ В РАЗЛИЧНЫХ РАСТВОРИТЕЛЯХ

Валид С. Абдул Вахаб, Якуб М. Джавад,
кафедра физики факультета естественных наук Университета Аль-Мустансирии, Ирак,
Али О. Мухсен,
кафедра физики педагогического факультета Ибн Хайан Университета Вавилона, Ирак,
Мохаммед Идаан,
кафедра химии факультета Науки для девочек Университета Вавилона, Ирак

Аннотация

Спектры флуоресценции для 1-нафтиламинового раствора измеряли и исследовали в зависимости от концентрации гексана и этанола (которые являются растворителями) при длине волны возбуждения (λ_{ex}= 313nm), а также был рассчитан квантовый выход (Φ_{FM}). Квантовый выход равен (Φ_{FM} =0.35) и (Φ_{FM} =0.29) для раствора 1-нафтиламина в гексане и этаноле при концентрации (10^{-5}M) , (Φ_{FM} =0.37) и (Φ_{FM} =0.31) при концентрации (10^{-4}M), (Φ_{FM} =0.36) и (Φ_{FM} =0.30) при концентрации (10^{-3}M), соответственно. Значения квантового выхода различны, что связано с эффектом самопоглощения явлений. В дополнение, значение квантового выхода было рассчитано по сравнению со стандартными соединениями антрацена с квантовой эффективностью (q_{FM} =0.27) при той же длине волны возбуждения. Все измерения были проведены при комнатной температуре.

Keywords: fluorescence spectra, Naphtyl amine derivaties, absorption.

Many of researchers used this method such as J.B. Birks and J.B. Aladekoman [1], calculated the quantum efficiency of aromatic compound. T.S. Ahn [2] and et.al. in 2007, study self-absorption correction for solid-state photoluminescence quantum yield obtained from integrating sphere measurements. A.K. Gaigalas and Lili Wang [3], in 2008, study the measurement of the fluorescence quantum yield using a spectrometer with an integrating sphere detector. Ryszard Misiak [4] and et.al., in 2011 study self-absorption correction and efficiency calibration for radioactivity measurement of environmental samples by gamma-ray spectrometry.

Fluorescence is a radiative process when molecules transition between states of the same multiplicity (S_1>S_o). But when molecules transition between states of different multiplicity is described as phosphorescence (T_1>S_o). While non-radiative processes occur when molecules transition between isoenergetic vibrational levels of different electronic states. A radiationless transition between states of the same multiplicity is described as internal conversion.[5] One between states of different multiplicity is described as intersystem crossing as shown in figure[1].

A photophysical processes is defined as a physical processes (i.e. one which does not involve a chemical change) resulting from the electronic excitation of a molecule or system[7], and the photophysical processes are divided into two types non – radiative processes and radiative processes. The radiative processes is the process of transitions of the molecule from a higher to a lower electronic state by the emission of a photon. When a radiative transition between states of same multiplicity is described as fluorescence, a radiative transition between states of different multiplicity is described phosphorescence [5]. the fluorescence is a radiative process resulting from the transition of molecules between two electronic states having the same multiplicity with short lifetime are typically (10^{-8} sec) which a spin-allowed process[8]. There are many processes bimolecular which commonly compete with fluorescence

emission (and internal quenching) in solutions, and thereby modify the fluorescence characteristics. This processes are collision impurity quenching, concentration quenching, energy transfer quenching and self-absorption quenching[9].The self-absorption quenching is in principle, an increase in the concentration of the fluorescence solute in a given material should be accompanied by an increase in the emitted light intensity. This is due to the corresponding increase in the absorption efficiency. This is due to the corresponding increase in the absorption efficiency. However, such behavior only occurs up to a certain critical concentration of the fluorescence solute. Above this concentration, the fluorescence intensity starts to decrease. This process is known as concentration quenching of fluorescence.[10]

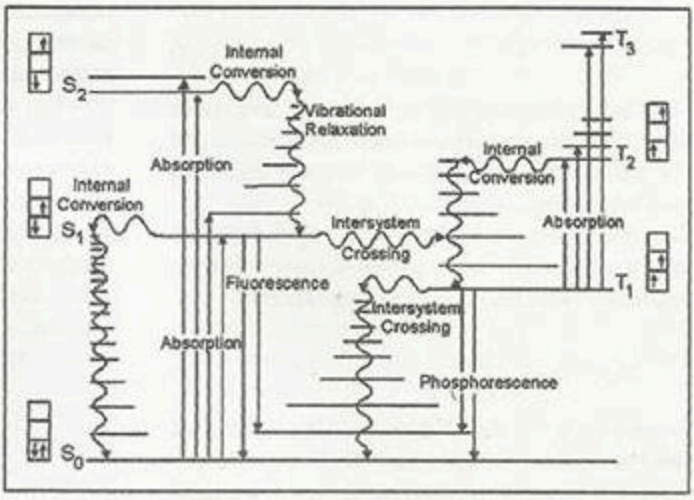


Fig.(1): Jablonski diagram.[6]

There is commonly an overlap of the (0-0) bands of the fluorescence and absorption spectra. The spectral overlap may be considerable and lead to self-absorption of part of the fluorescence emission.[7,10]

The molecular fluorescence quantum efficiency (q_{FM}) is defined as the ratio of the number of fluorescence photons emitted by a system of molecules in dilute solution to the number of molecules excited into S_1(the number of absorbed photons). Where K_{FM}, K_{IM} the rate parameters of radiative emission and non-radiative by internal quenching respectively. The quantum efficiency equal to:[7]

$$q_{FM} = \frac{k_{FM}}{k_{FM} + k_{IM}} = \frac{\tau_M}{\tau_{FM}} \qquad (1)$$

τ_M: the molecular fluorescence lifetime of the excited state is defined by the average time that molecule spends in the excited state prior to return to the ground state is equal to:

$$\tau_M = \frac{1}{k_{FM} + K_{IM}} \cdots \qquad (2)$$

the lifetime of the fluorescence in the absence of non-radiative processes is called the intrinsic or natural lifetime and is defined as the reciprocal of the radiative transition probability k_{FM} (in S^{-1}) is given by:[10]

$$\tau_{FM} = \frac{1}{k_{FM}} \qquad (3)$$

The quantum efficiency (q_{fm}) is called quantum yield Φ_{FM} at quantum efficiency in higher concentration for solute, overlap of the (0-0) bands of the fluorescence and absorption spectra, availability of a impurity in solution, occurrence energy transfer if the solution contains a molar concentration of an aromatic impurity and availability of any parameters effect on quantum efficiency as in (§2.8).[11] The equation (1) becomes,

$$\Phi_{FM} = \frac{K_{FM}}{K_{FM} + K_{IM} + K_{EM}} \qquad (4)$$

Where K_{EM} : represented any rate parameters effect on quantum efficiency.

Consider a fluorescence system with fluorescence quantum efficiency q_{FM} and lifetime $[(\tau)]_M$), in which (a) is the probability of self-absorption of an emitted photon, so that (1-a) is the photon escape probability. Photons which are absorbed are re-emitted with quantum efficiency (q_{FM}) and lifetime (τ_M). The quantum yield $[(\Phi)]_{FM}$) of the escape of the fluorescence is given by:[7]

$$\Phi_{FM} = \frac{q_{FM(1-a)}}{1 - a\,q_{FM}} \qquad (5)$$

$$\tau = \frac{1}{(1-a)K_{FM} + K_{IM}} = \frac{\tau_M}{1 - a\,q_{FM}} \qquad (6)$$

$$a = \frac{A_m^T}{A_m} \quad (7)$$

Where A^T_m and A_m represent the area under the fluorescence spectrum of the concentrated and diluted solution, respectively. Are normalized in the low fluorescence spectrum.[12]

The quantum yield calculated by the method of comparison with compounds of known quantum yield from using this equation:[9]

$$\Phi_{Fx} = \Phi_{Fr}\left(\frac{I(\lambda r)}{I(\lambda x)}\right) \quad (8)$$

where: n_r, n_x : is the refractive index for standard and unknown compound , Φ_{Fx}, Φ_{Fr} : is the quantum yield of unknown and stander compound, A_r, A_x : is the absorbance of standerd and unknown compound, $I(\lambda_x)$, $I(\lambda_r)$: is the wavelength excitation of unknown and stander compound and D_x, D_r: is the area under the curve of fluorescence spectrum of unknown and stander compound, respectively.

Experimental section

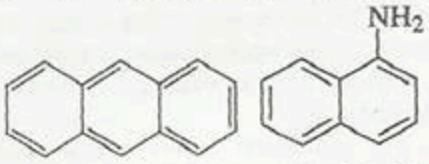
The solution of 1-Naphthylamine in (hexane and ethanol) prepared at concentration [1×10^{-3},1×10^{-4},1×10^{-5} and 1×10^{-6}]M. (1NA) purchased from Uma Company imported from India.

Fluorescence spectra were recorded on a (JASCO- model-FP-770) spectrofluorometer; samples were mounted in cubic cell of quartz dimensions (1×1×5) cm^3 at right angle 90° with incident beam. The fluorometry has dedicated computer which control instrumental operating (excitation and emission wavelength, scan, monochromator slit width, detector parameter) and the acquisition of spectral data.

The exciting wavelength (λ_{ex}= 313nm) is used in the measurements and there slit width of excitation (S_{ex}=1.5 nm) and of emission (S_{em}= 3 nm). The measurements were made in the same sensitivity of photomultiplier. The anthracene was used as a standard compound dissolved in ethanol with concentration [10^{-4}]M and quantum efficiency equal to (q_{FM} = 0.27), measurements were at room temperature.

Results and Discussions

The fluorescence spectra of anthracene solution is used as a standard compound dissolved in ethanol with concentration [1×10^{-4} M]. Thus, the solutions of (1NA)dissolved in hexane and ethanol are studied as be shown in figure(2), with concentration [1×10^{-3},1×10^{-4},1×10^{-5}and1×10^{-6}]M and observation the effect of increasing concentration in the form of the fluorescence spectrum as well as calculation of quantum yield.



Anthracene ($C_{14}H_{10}$) 1-Naphthylamine ($C_{10}H_9N$)
Fig. (2): Chemical formula of compounds.

In the figure (3-a and 3-b) the peak of the fluorescence spectrum located at wavelength (λ_{max}=378 nm) in hexane and (λ_{max}= 426 nm) in ethanol.

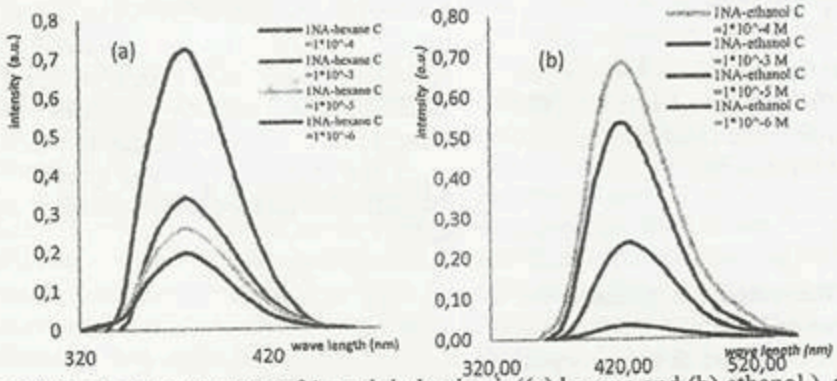


Fig.(3): fluorescence spectra of 1-naphthylamine in((a) hexane and (b) ethanol) at concentration (1×10^{-3}M, 1×10^{-4}M, 1×10^{-5}M and 1×10^{-6}M), (λ_{ex}=313 nm).

The table (1) shows the values of quantum yield (Φ_{FM}) with concentration of (1NA) solution in hexane and ethanol, by using the relation (8).

Table (1): The quantum yield of (1NA) solutions in hexane and ethanol

[M] mol	The Solvent	Φ_{FM}
1×10^{-6}	hexane	0.345
	ethanol	0.28
1×10^{-5}	hexane	0.35
	ethanol	0. 29
1×10^{-4}	hexane	0.37
	ethanol	0.31
1×10^{-3}	hexane	0.36
	ethanol	0.30

The figure (3) and table (1) shows the relative fluorescence intensity increase with increasing the molar concentration, but at the concentration equal to [1×10^{-3}M], the relative fluorescence intensity decreases. The decreasing in the relative fluorescence intensity and quantum yield are caused by the phenomenon of the self-absorption.

The self-absorption leads to the decrease in the value of quantum yield which is equal to (Φ_{FM} =0.37) of (1NA) dissolved in hexane and (Φ_{FM} =0.31) of (1NA) dissolved in ethanol at concentration [1×10^{-4} M], by using the relation (8), and correcting the value of quantum yield by calculating the probability of self-absorption (a) by using the relation (7), where (a) equal (0.778) and (0.475) in hexane and ethanol, respectively . where the fluorescence spectrum at concentration [1×10^{-3}M], calibrated with fluorescence spectrum at a concentration [1×10^{-4} M] at wavelength (410 nm) of (1NA) dissolved in hexane and (475 nm) of (1NA) dissolved in ethanol , which is far from the region of overlap under constant conditions of excitation wavelength, geometry, slit width and other instrumental setting. After compensation for the value of (a) and value of quantum yield in equation (5) where the resulting is the corrected quantum yield. Whereas value of quantum yield at non-correction the fluorescence spectrum of (1NA) solution in hexane at concentration [1×10^{-3} M] are equal to (Φ_{FM}= 0.35) in hexane and (Φ_{FM}= 0.29) in ethanol.

When comparing between (1NA) solution in hexane and ethanol, the quantum yield and the relative fluorescence intensity in hexane is greater than of the ethanol solvent because the polarity of hexane is less than of ethanol, but the self-absorption phenomenon of solution in ethanol is less than of the hexane solvent, whereas the Self-absorption decreases (the probability of self-absorption (*a*)) with the increase of solvent polarity because of the shift result of the fluorescence spectra toward the longer wavelength. When the shift of the fluorescence spectra increased, the overlap between the absorption and fluorescence spectra decreases. This decrease in overlap leads to decrease in the Self-absorption, as shown in figure (4).

Conclusions

Reduced intensity of fluorescence spectrum and the quantum yield with increased an molar concentration for 1-naphthylamine because of the

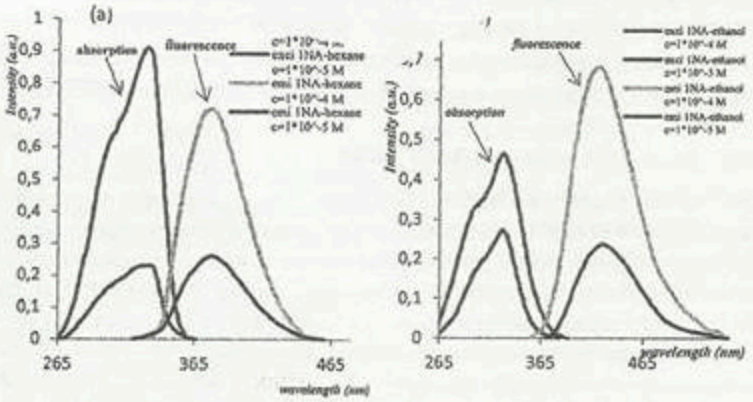


Fig. (4):absorption and fluorescence spectra of 1-naphthylamine in a)hexane and b)ethanol at concentration (1×10^{-4}M and 1×10^{-5}M), (λ_{ex}=313 nm).

phenomenon of self-absorption of emitted photons before leaving the solution by the molecules as a result that increase in radiationless processes and decrease radiation processes

REFERENCES

1. *Previtali C.M.* «Solvent effects on intermolecular electron transfer processes», Appl. Chem., , Vol. 67, p.p. 127-134, (1995).
2. *Ahn T.S.* «Self-absorption correction for solid-state photoluminescence quantum yields obtained from integrating sphere measurements», Review of Scientific Instruments, Vol. 78, p.p.(086105), (2007).
3. *Gaigalas AK. and Lili Wang,* J. Res. Natl. Inst. Stand. Technol. 113, 17-28, (2008).
4. *Misiak R. and et al.,* Nukleonika, 56(1), 23-28, (2011).
5. *Berlman I.B.* «Handbook of fluorescence spectrum of Aromatic molecules», Academic press, New York, 1st edition (1965), 2nd edition (1971).
6. *Undenfriend S.* «Development of spectro photofluorometer and its commercialization», Pro. Sci., Vol. 4, 542-551, (1995).
7. *Birks J.B.* «Photophysics Aromatic molecules», (1970), Wiley and Sons, London.
8. *Birks J.B., Conte J. C. and Walker,* «The Florescence Excitation of Aromatic Liquids and Solution», J. Phys. B (Proc. Phys. Soc.), Vol. 1, p.p.(934-945), (1968).
9. *Demas J.N. and Crosby G.A.,* «The measurement of photoluminescence quantum yields», J. Phys. Chem., Vol.75, PP(991-1031), (1971).
10. *Valeur B.*, «Molecular fluorescence: principles and applications», Wiley-VcH Verlag GmbH, (2001).
11. *Baum R.D.,* «Introduction to instrument analysis», Mc. Graw-Hill, New York, (1987).
12. *Peter T.S.,* «Fluorescence spectrophotometry», Macmillan publishers Ltd, Nature, Nature publishing group, (2002).

Поступила в редакцию 21.03.2013.

МЕТОД ВОЛЬТАМПЕРОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ МАРГАНЦА В ВОДЕ И ИССЛЕДОВАНИЕ ФИЗИЧЕСКИХ И ХИМИЧЕСКИХ СВОЙСТВ МАРГАНЦА

Ахмед Мохаммед Абдулла, Джухайна Муатасем Баллах Таха,
магистр химических наук , магистр физическихнаук
факультета наук Университета Мустансирия,
Технологический университет Ирака, г. Багдад, Ирак,
соискатели Московского государственного университета
тонких химических технологий им. М.В. Ломоносова (МИТХТ)

Аннотация

Марганец широко используется в промышленности. Он незаменим в производстве стали. В низких концентрациях он также необходим для нормального функционирования живых организмов. В тоже время марганец, как и все тяжелые металлы, является токсичным ядом. Из-за его широкого применения в промышленности возможны случаи отравления. Для слежения за концентрациями марганца в окружающей среде необходим точный и надежный метод его количественного определения. В настоящее время используют два метода количественного определения марганца: комплексонометрия и атомно-абсорбционный метод. Первый из перечисленных методов является титриметрическим и не может определять следовые количества, определение марганца вторым методом сопряжено со многими трудностями и является весьма