Experimental study on the fluorescence lifetime of ethanol-water mixtures

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The ethanol-water mixtures can emit fluorescence when excited by the ultraviolet (UV) light, which is different from pure ethanol and water. There are three emission bands of the mixtures and the center bands are located at 290, 305, and 330 nm, respectively. The fluorescence lifetimes of different emission bands are tested respectively: the average lifetime of 330-nm fluorescence band is about $\tau = 26.5$ ns, for the 305-nm emission band $\tau = 2.5$ ns and for the 290-nm band $\tau = 11$ ns. By the spectral characteristic and the time-resolved spectroscopy one can conclude that there are several components in the solution of ethanol-water mixture.

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Once a molecule is promoted to an excited electronic state, it may return to the ground state either radiatively or nonradiatively. The former pathway leads to emission spectroscopy. The second decay path includes all ways that the excited state may lose energy without emitting, such as collisions. If nonradiative decay is negligible, then for every photon that is absorbed in order to create the excited state, one is emitted. The emission spectroscopy comprises two types of information, one is the frequency domain (spectral characteristic) and the other is time domain (fluorescence lifetime). The fluorescence lifetime is the average time of the photon staying in the single excited state. It is related not only to the molecular structure but also to the surrounding microenvironment, such as the polarity, the viscosity and so on. So it can be used to study the change of the system by measuring the fluorescence time. The fluorescence emission takes place in nanoseconds which is within the time scale of molecular motion. Many complicated interaction processes between molecules can be "seen" by this fluorescent technique, such as supermolecule system cluster[1]. So in research of molecular structure and molecule clusters the time-resolved spectrum has been extensively used.

A great number of studies have been reported on the solute effect of ethanol on other molecules' optical properties such as fluorescence spectral characteristic, fluorescence lifetime and quantum yield[2−5]. After the pioneering work on emission spectra of the ethanol-water mixtures solutions[6−8], the mixture can emit fluorescence and it was more or less recognized that not all the energy acquired by optical excitation was emitted as light. In molecular structure and some clusters structure research, the fluorometric analysis has been extensively used for high sensitivity. About the structure of liquid ethanol, solid ethanol, and ethanol-water mixture, a great deal of effort spanned for several decades, but no general viewpoint has reached concerning the structure properties of liquid alcohols and their solutions with water[9−14].

Absolute quantum yield measurements gave evidence for the occurrence of radiationless processes; these were classified as either internal conversions (no change in multiplicity of the participating electronic states) or intersystem crossings (a change in multiplicity). Time-resolved single-photon counting is the most efficient method to detect emission with a time resolution of some tens of picoseconds. With this technique, every emitted photon that can be collected by the optics and photomultiplier will be used as data. That is not the case with, for instance, optical gating techniques, which have superior time resolution, but degraded detection efficiency since only the fraction of photons within the gate out of all available emitted photons are used as data. In this paper, the steady-state and time-resolved fluorescence spectroscopy are used to study the cluster molecular structure of the ethanol-water mixtures. The instrument is FLS900 combined fluorescence lifetime and steady state spectrometer (Edinburgh Instruments Ltd., UK). The spectrometer is based on the technique of time correlated single photon counting (TCSPC).

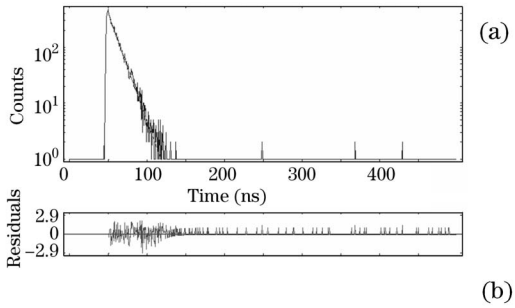
One can measure fluorescence lifetimes using time-resolved detection of fluorescence intensity. This gives the total rate of decay $1/\tau_{\rm f}$ ($\tau_{\rm f}$ the fluorescence lifetime) of the excited electronic state. In general, a state may decay by both radiative and nonradiative pathways, thus the total decay rate is

$$\frac{1}{\tau_{\rm f}} = \frac{1}{\tau_{\rm rad}} + \frac{1}{\tau_{\rm nonrad}},$$

where $1/\tau_{\rm rad}$ and $1/\tau_{\rm nonrad}$ are the decay rates of radiative and nonradiative pathways.

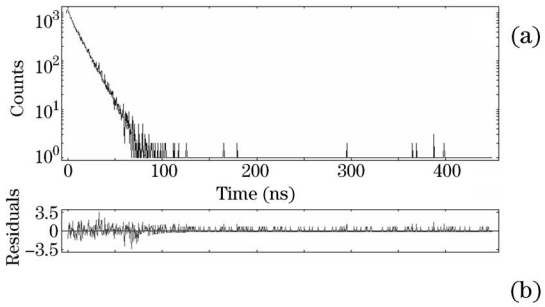
Fluorescence decay process of ethanol-water mixtures has been obtained by the TCSPC method. Firstly, the excited light wavelength is selected as 250 nm to irradiate the ethanol-water solution and the emission wavelength is 290 nm (see Fig. 1). The decay process is shown in Fig. 1(a), and the data is fitted to single exponential function and constants are obtained respectively. This component lifetime is $\tau = 11$ ns. Secondly, the excited light wavelength is 250 nm and the emission band centre is 305 nm. The decay process and the fitted curve are shown in Fig. 2. In this case the decay process is fitted to double exponential function. That is to say, when we detect the fluorescence counts of the 305-nm emission band, the counts are composed of two parts, one lifetime is longer ($\tau = 11.8491$ ns) and the other is shorter (τ=2.5003 ns). From the fitted decay value one can conclude that the longer fluorescence lifetime is corresponding to the emission bands of 290 nm, and the shorter one is 305 nm.

Lastly, the excited light wavelength is about 236 nm and the emission bands center is 330 nm (see Fig. 3). The data are well fitted to triple exponential function, which suggests either different locations or different emitting forms of the clusters molecules or a combination of these two molecules. There are several components in the solution of ethanol-water mixture, the lifetime of each fluorescence photons is different and the emission bands are overlapped to each other. The lifetime of the mixture is different from each components and the logarithm decay curve of the lifetime is bend accordingly. The curve is divided into several parts and each part is linearly fitted line respectively. So the linear logarithm decay curves of different lifetimes are present. The lifetimes of different components are $\tau_3 = 27.4265$ ns, $\tau_2 = 2.5588$ ns, and $\tau_1 = 12.9968$ ns, respectively. In this case τ_1 and τ_2 are longer than in Fig. 2. The method can be used to do proximate analysis in the solution.



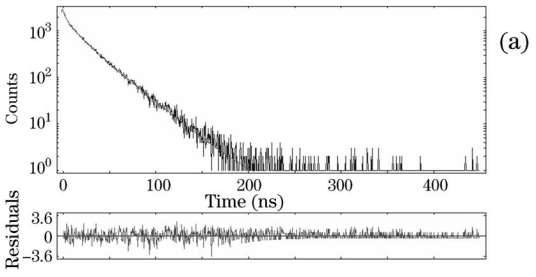
Fit = $A + B_1 e^{(-t/\tau_1)} + B_2 e^{(-t/\tau_2)} + B_3 e^{(-t/\tau_3)} + B_4 e^{(-t/\tau_4)}$						
	Value	Std. Dev.		Value	Std. Dev.	Rel. (%)
τ_1 (s)	1.122×10^{-8}	1.244×10^{-10}	B_1	3.956×10^{2}	6.083	100.00
τ_2 (s)	—	—	B_2	—	—	—
τ_3 (s)	—	—	B_3	—	—	—
τ_4 (s)	—	—	B_4	—	—	—
χ^2	2.368×10^{-1}		A	7.700×10^{-2}		
Shift (s)	—					

Fig. 1. Exponential fit time scan of the decay process, the excitation light wavelength is 250 nm and the emission light wavelength is 290 nm, (a) The fit curve and the actual decay curve; (b) the exponential fit values.



Fit = $A + B_1 e^{(-t/\tau_1)} + B_2 e^{(-t/\tau_2)} + B_3 e^{(-t/\tau_3)} + B_4 e^{(-t/\tau_4)}$						
	Value	Std. Dev.		Value	Std. Dev.	Rel. (%)
τ_1 (s)	11.8491	0.13079	B_1	967.442	23.4350	94.14
τ_2 (s)	2.5003	0.53436	B_2	285.649	35.6340	5.86
τ_3 (s)	—	—	B_3	—	—	—
τ_4 (s)	—	—	B_4	—	—	—
χ^2	0.351		A	0.169		

Fig. 2. Exponential fit time scan of the decay process, the excitation light wavelength is 250 nm and the emission light wavelength is 305 nm. (a) The fit curve and the actual decay curve; (b) the exponential fit values.



Fit = $A + B_1 e^{(-t/\tau_1)} + B_2 e^{(-t/\tau_2)} + B_3 e^{(-t/\tau_3)} + B_4 e^{(-t/\tau_4)}$						
	Value	Std. Dev.		Value	Std. Dev.	Rel. (%)
τ_1 (s)	12.9968	1.61597	B_1	843.295	73.4249	24.29
τ_2 (s)	2.5588	0.32331	B_2	1034.803	73.9830	5.87
τ_3 (s)	27.4265	0.60621	B_3	1148.927	105.7824	69.84
τ_4 (s)	—	—	B_4	—	—	—
χ^2	0.622		A	0.337		

Fig. 3. Exponential fit time scan of the decay process, the excitation light wavelength is 236 nm and the emission light wavelength is 330 nm. (a) The fit curve and the actual decay curve; (b) the exponential fit values.

The original experiment data are calculated by the formulas as follows: relative concentrations of different components:

$$c_1 = \frac{B_1}{B_1 + B_2 + B_3},\ c_2 = \frac{B_2}{B_1 + B_2 + B_3},$$

$$c_3 = \frac{B_3}{B_1 + B_2 + B_3};$$

relative fluorescence intensities of different components, as a percentage:

$$\phi_1 = \frac{B_1\tau_1}{B_1\tau_1 + B_2\tau_2 + B_3\tau_3} \cdot 100\%,$$

$$\phi_2 = \frac{B_2\tau_2}{B_1\tau_1 + B_2\tau_2 + B_3\tau_3} \cdot 100\%,$$

$$\phi_3 = \frac{B_3\tau_3}{B_1\tau_1 + B_2\tau_2 + B_3\tau_3} \cdot 100\%;$$

average lifetime of the entire decay process:

$$< \tau >= \frac{B_1\tau_1^2 + B_2\tau_2^2 + B_3\tau_3^2}{B_1\tau_1 + B_2\tau_2 + B_3\tau_3}.$$

In the case when excitation light wavelength is 250 nm and emission center band is 305 nm, the fitted decay curve is composed of two components, and the relative concentrations of different components, relative fluorescence intensities and average lifetime of the entire decay process are calculated respectively: $c_1 = 77.2\%$, $c_2 = 22.8\%$, $\phi_1 = 94.14\%$, $\phi_2 = 5.86\%$, and $< \tau >= 11.3$ ns.

That is to say, when we detect the fluorescence counts in this case, 94.14% of the emission is due to the first component and 5.86% is due to the second component. In the solution the concentration of the first component is 77.2% and the second component is 22.8%. The average lifetime of the entire decay process is $< \tau >= 11.3$ ns, which is longer than that in the first case.

In the case of the excitation light wavelength being 236 nm and the emission center band 330 nm, relative concentrations of different components, relative fluorescence intensities and average lifetime of the entire decay process are calculated respectively: $c_1 = 27.9\%$, $c_2 = 34.2\%$, $c_3 = 37.9\%$, $\phi_1 = 24.29\%$, $\phi_2 = 5.87\%$, $\phi_3 = 69.84\%$, and $< \tau >= 22.5$ ns.

From the fitted decay curve, one can conclude that the detected fluorescence counts are composed of three parts. The first is $\tau_1 = 12.9968$ ns and the percent of counts is 24.29%, the second is $\tau_2 = 2.5588$ ns corresponding to the counts percent of 5.87%; and the third is $\tau_3 = 27.4265$ ns, the corresponding counts percent is 69.84%. There are three emission components contributing to the general counts and the component concentrations are $c_1 = 27.9\%$, $c_2 = 34.2\%$, $c_3 = 37.9\%$. The average lifetime of the entire decay process, $< \tau >= 22.5$ ns is longer than the first two cases. Different lifetimes correspond to different molecules, so when detecting fluorescence counts of the emission band with wavelength 330 nm, there are three different molecule clusters.

To summarize, we have tested, by time-resolved fluorescence spectroscopy, different emission bands have different average lifetimes of the entire decay process. Three molecule clusters are associated with different fluorescence lifetimes. As the system of ethanol and water mixture with three different components, the average relaxation times $< \tau >$ indicates the average lifetime of the entire decay process.

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