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Fluorescence spectrum characteristic of ethanol–water excimer and mechanism of resonance energy transfer*

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The steady-state fluorescence spectrum characteristic of ethanol–water excimer has been studied in this paper. By analysing the features of the sharp emission spectrum with fine structures in a shortwave band and the characteristics of the broad and featureless fluorescence peaks in the longwave band, one can conclude that the excimers are formed between the new ethanol–water cluster molecules in the excited state and the ground state through the interaction among different chromophores. The excitation spectra in the two fluorescence bands have been studied, and their emission mechanisms have been ascertained based on the energy transfer theory. Furthermore, the critical distance of the resonance energy transfer has been calculated.

Keywords: fluorescence spectrum, energy transfer, ethanol–water cluster, excimer
PACC: 3350D, 3640

1. Introduction

The structural features of ethanol molecules in different phase states and the characteristics of the associated cluster molecule groups, generated by ethanol and water molecules through hydrogen bond, have aroused great interest in the last decade.[1−9] Nevertheless, there have not yet been any well accepted conclusions about structures of ethanol molecules in liquid, in solid, and especially in ethanol–water solution. Some investigators have suggested that ethanol molecules connected with water molecules through hydrogen bond are easy to form cluster molecule groups of ring or open chain structures, but the conclusion is distinct from experiment to experiment.[10,11] Owing to the unknown effect of the hydrogen bond, the proposed structures of the new cluster molecules have not been widely accepted, whereas a contrary opinion is presented that the interaction between ethanol and water molecules is generated by hydration rather than hydrogen bonding, because there is no interlinkage of hydrogen bonding, and molecules are connected together by hydration like a bridge.[12] On account of the cluster structure being uncertain, it is still under study now. Moreover, what has been reported in the literature is only about the cluster style, the combined numbers of the cluster molecule groups, the ring or open chain characteristic, etc, but no perspective on the planar structure features of the cluster molecules has been mentioned. In our previous study, the combined numbers of the ethanol–water cluster molecule groups, which were calculated by the theories of analytical chemistry and organic chemistry, were investigated by light-induced steady-state fluorescence spectra.[13] We presented the three possible clusters, whose spectrum characteristic corresponded to different frequency-domain and time-domain parameters, but the spacial framework of the ring or chain cluster, whether they are planar or not, has not been discussed yet. In a further experiment, a broad and featureless fluorescent peak changing obviously with intensity has been observed in a long wave range of the steady spectrum, which has the prominent characteristic of excimer. The formation of an excimer can be characterized experimentally by the observation of the intensity quenching of the sharp emission spectrum, and of a broad and red-shifted fluorescent spectrum appearing at the same time. Some researchers

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have also inferred that the energy exchange or the exciton resonance interaction between two molecules in a mixed dimer is a key factor in the formation of excimers.[14] The aim of this paper is to investigate the excimer formation and the spectrum characteristic by fluorescent spectrometry,[15] and to ascertain the emission mechanism through the energy transfer theory.[16] Furthermore, the critical distance of the resonance energy transfer is to be calculated. The obtained results may offer experimental and theoretical reference to the study of the planar structural features on the cluster molecules. The detailed structural information of the new cluster molecule groups formed by the ethanol and water molecules, is under investigation.

2. The experimental setup and sample

The Lifetime and Steady State Fluorimeter 900 (FLS900) combined with fluorescence lifetime and steady-state spectrometers, made by Edinburgh Instruments Ltd, UK, were used in our experiments. The light source for steady-state excitation was the Xe 900, 450W Xenon arc lamp with continuous spectral distribution from 190 nm to 2600 nm. In our experiment, the wavelength of the excited-light was selected by the grating from 230 nm to 300 nm and the scan range of the emission spectrum was from 300 nm to 500 nm.

The samples were tri-distilled water and HPLC ethanol with a concentration of no less than 99.5%, which was produced by TEDIA Co. of USA. Ten aqueous solutions of ethanol were prepared with volume percentages ranging from 100% to 10% in 10% increment.

3. The experimental results

When ethanol–water solutions are excited by an ultraviolet light with a shorter wavelength ($\lambda <$ 250 nm), the emission bands are centred in a range of 290–350 nm and the spectral characteristic has been discussed in detail in Ref.[13]. With the increasing of the excited light (250 nm $< \lambda <$ 300 nm), the sharp fine emission band with a peak located at 305 nm shown in Fig.1(a) dies away. At the same time, a broadened emission band (350 nm–500 nm) with a peak around at 418 nm, a FWHM of 100 nm, and the Stokes shift of about 150 nm, is obtained and shown in Fig.1(b).

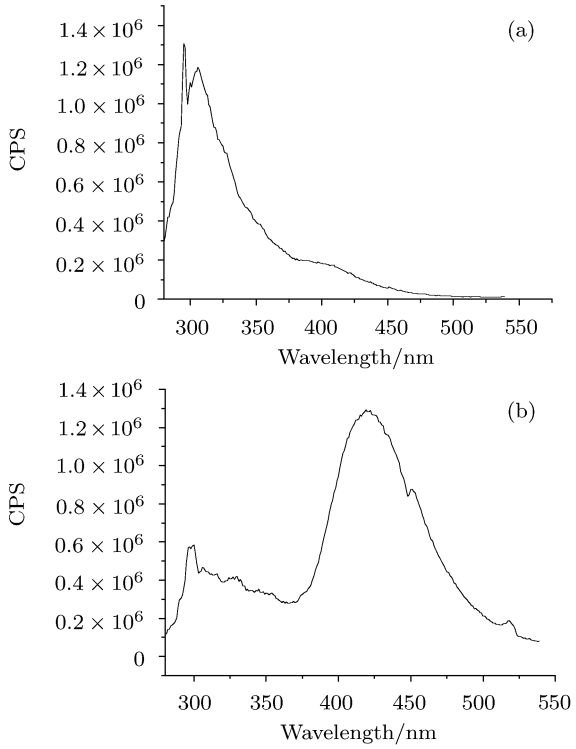


Fig.1. The steady-state fluorescence spectra of ethanol–water solution excited by the UV-light.

As the wavelength of the excitation light increases from 240 to 280 nm, the fluorescent intensity of the sharp fine structure at 305 nm decreases gradually as shown in Fig.2(a). Meantime, a broad and featureless fluorescence peak at 418 nm appears, whose fluorescent intensity is enhanced with the excitation wavelength, and reaches a maximum at a wavelength of 268 nm. The important characteristic in this experiment is that all the emission spectra pass through the same emission point at 360 nm. From Fig.2(a), we can see that the incident light with a wavelength of 268 nm has the highest quantum production rate of emitting fluorescence. So a fixed excitation wavelength of 268 nm was selected to irradiate ethanol–water solutions with different concentrations. It is observed that the peak intensities of sharp emission at 305 nm monotonically increase with the increasing of ethanol concentration and the intensities of the broad and featureless fluorescence peaks at 418 nm change their simultaneity (shown in Fig.2(b). In those spectra all the emission spectra pass though the same emission point at 360 nm too. And the broad and featureless fluorescence spectrum, which is centred at 418 nm, reaches a maximum fluorescent intensity when the ethanol–

water ratio is 6:4.

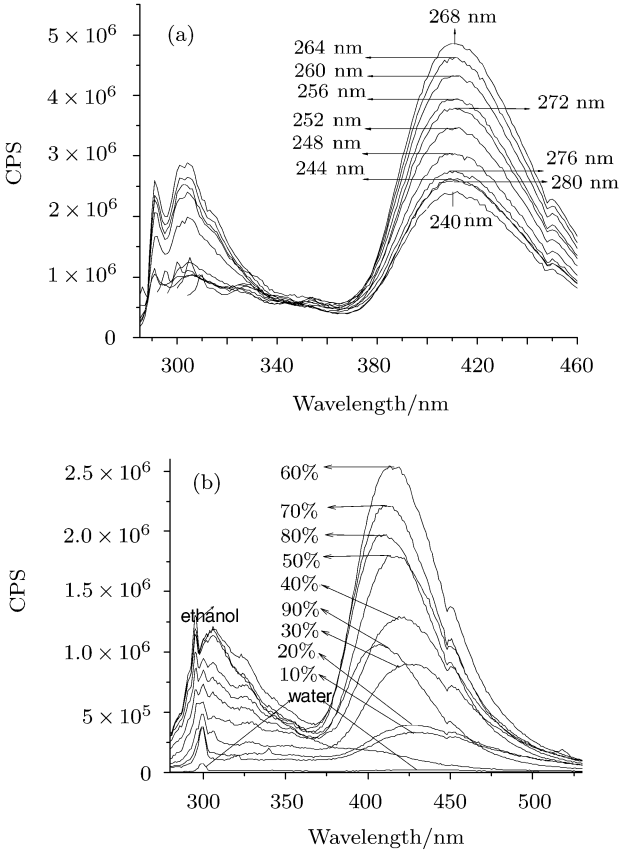


Fig.2. The fluorescence spectra of ethanol–water solution excited by incident light (a) Incident light varies in wavelength from 240 to 280 nm, and the solution concentration fixed at 60%. (b) Incident light in wavelength is fixed at 268 nm, and the solution concentration varies from 10% to 99.5%

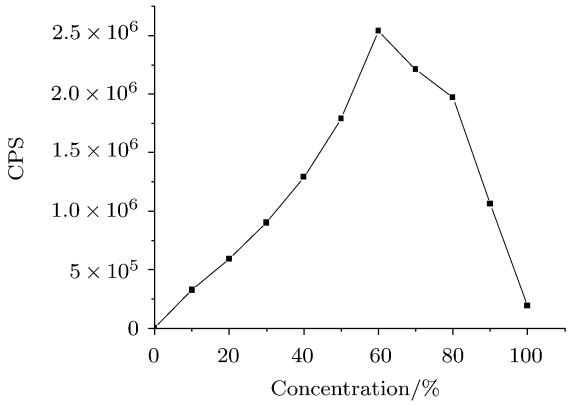


Fig.3. The relationship between the intensity of the broad emission peak and ethanol volume percent.

Figure 3 shows the relation between the peak of fluorescence intensity at 418 nm and the volume percentage of ethanol in its water solutions. The relation is nearly linear when the volume percentage of ethanol is lower than 60%, and then it sharply declines. Decreasing the ethanol proportion leads the broad and featureless fluorescence peak to a red shift as shown in Fig.4.

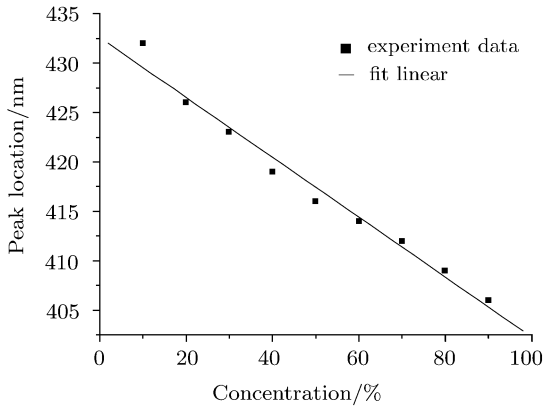


Fig.4. The relationship of the peak location of the broad emission band and ethanol volume percent.

Summarizing the above steady-state fluorescence spectra of ethanol–water solutions obtained experimentally, the fluorescent spectrum of ethanol–water solution has all the characteristics of the excimer.[17] The sharp peak at a higher energy, a fine structure with a small Stokes shift, is the fluorescent peak emitted by the unimolecules which are the clusters generated by ethanol and water molecules. The fluorescent intensity of the sharp peak quenches when the excited light wavelength increases or ethanol volume percentage decreases. Meanwhile, a broad and featureless fluorescence peak, which is emitted by the excimer, is observed with a large Stokes shift, in which a dimer is bound in the excited state but unbound in the ground state. Moreover, the change of two peak intensities is anti-correlated. This fluorescent peak emitted by the excimer has a red shift with the ethanol portion declining. These spectra have all those fluorescence characteristics of excimers, indicating that the new intermolecular or intramolecular excimers are formed by ethanol–water cluster molecules through hydrogen bonding or hydration.

After the excimers are formed, the absorption spectra of monomer and excimers become the same. As the profiles of absorption spectra are the same as those of their excitation spectra, the excitation spectra of the two fluorescent peaks are measured in this paper instead of the absorption spectra, and the absorption intensity is normalized as plotted in Fig.5. A comparison between these two excitation spectra, although

the two plots look quite different and the normalized excitation spectrum of the emission peaks of 305 nm has quite a bit sharper line than the 418 nm one, shows that they have the same absorption peak approximately at 270 nm, which implies that the peaks at 305 nm and 418 nm originate from the absorptions at the same wavelength 270 nm. This is an important characteristic of the excitation spectrum of an excimer. That is to say, the peak at 305 nm (Fig.1(a)) is emitted by the unimolecules and the peak at 418 nm (Fig.1(b)) by the excimers. This experimental result verifies the early suggestion again that the broad and featureless peak is emitted by excimers.

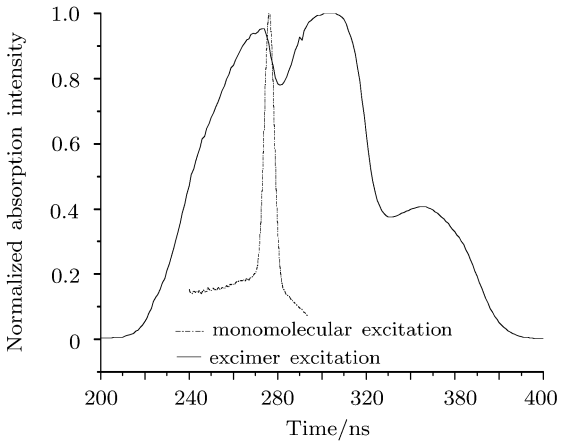


Fig.5. The normalized excitation spectra of the emission peaks of 305 nm and 418 nm.

The fluorescent lifetime of the excimer is obtained from the experimental result shown in Fig.6. The decay process at 418 nm fits a di-exponential curve, implying that there are two objects which can emit fluorescent photons and their lifetimes are $\tau_1 = 11.36$ ns and $\tau_2 = 2.6$ ns, respectively. In other words there exist mixing emissions from both the excited monomers and the excimers. In this decay process, there is a fast fluorescent relaxation with an exponential decay of $\tau_2 = 2.6$ ns for monomers and a subsequent slow decay of $\tau_1 = 11.36$ ns for excimers.

The strong luminescence of the clusters in a long wavelength range arouses a suspicion whether the fluorescence emitting results from the energy transfer. The fluorescence of 305 nm emitted by the unimolecules is located at the absorption peak of the excimer. Thus, according to the energy viewpoint, it could cause the energy to transfer between the cluster and the excimer. But the contribution of the exciton resonance interaction in the quenching process cannot be excluded. On the other hand, between two molecules in a mixed dimer the energy exchange or the exciton resonance interaction is coexistent. But the contribution of the energy transfer is likely predominant. The emission spectrum of the unimolecule and the excitation spectrum of the excimer are normalized respectively and plotted together in the Fig.7. From this figure we can see that the fluorescence emission domain of the unimolecules is nearly in the absorption domain of the excimer. It is obvious that the fluorescent quenching at the small Stokes shift is due to the emission at the large Stokes shift. The overlapping area of the emission band of the unimolecule and the absorption band of the excimer is larger and the energy transfer probability is bigger. In this experiment, we think that the broad emission band with the peak at 418 nm originates from the energy transfer. Thereinafter, these experimental results will be discussed from the angle of the mechanism of the energy transfer and transfer efficiency.

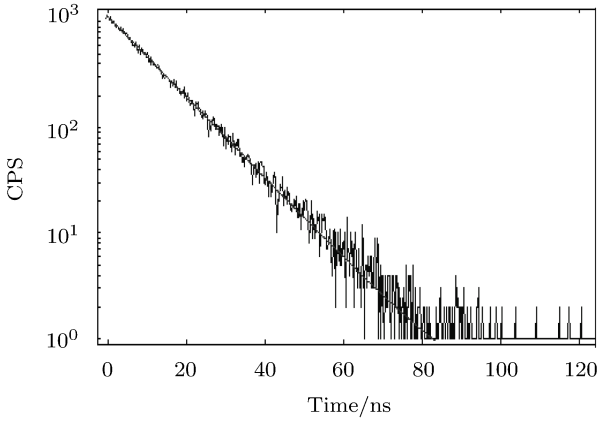


Fig.6. The decay process of the emission intensity of an excimer.

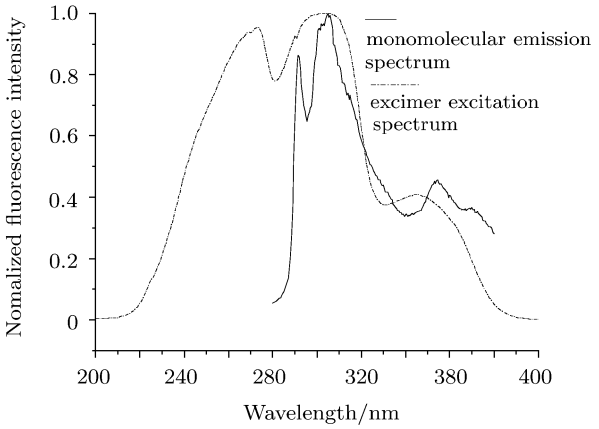


Fig.7. The normalized spectra of the unimolecule emission and the excimer excitation.

4. The energy transfer between the unimolecules and the excimers in ethanol–water solution

According to the resonant energy transfer theory of dipole–dipole coupling, when the two identical dipoles generate a resonant vibration in the distance of r, the benefactor in the excited states will transfer the energy to the acceptor in the ground state. Then the acceptor jumps to the excited state and at the same time the benefactor returns to the ground state by the nonradiative transition. The energy transfer efficiency is expressed as follows:[18]

$$K_{\mathrm{T}} = \frac{9000(\ln 10)K^2\phi_{\mathrm{D}}}{128\pi^5 n^4 N r^6 \tau_{\mathrm{D}}} \int_0^{\infty} \frac{F_{\mathrm{D}}(\bar{\nu})\varepsilon_A(\bar{\nu})}{\bar{\nu}^4}\mathrm{d}\bar{\nu}, \quad (1)$$

where K_{T} is the energy transfer efficiency; ϕ_{D} is the emission quantum yield rate of the benefactor when there is not any acceptor; n is the refractive index of the medium; N is Avogadro's number; r is the average central distance between the benefactor and the acceptor; τ_{D} is the emission lifetime of the benefactor when there exists no acceptor; $F_{\mathrm{D}}(\bar{\nu})$ is the correction fluorescence intensity of the benefactor within the wave-numbers ranging from $\bar{\nu}$ to $\bar{\nu}+\mathrm{d}\bar{\nu}$ and the overall fluorescence intensity is normalized to 1; $\varepsilon_{\mathrm{A}}(\bar{\nu})$ is the molar absorption coefficient of the acceptor at a wave number $\bar{\nu}$; $\lambda_{\mathrm{D}}(=\phi_{\mathrm{D}}/\tau_{\mathrm{D}})$ is the emission rate of the benefactor; K^2 is the directional coefficient to describe the spatial relative direction of the transition dipoles of the benefactor and the acceptor. The integral variable of $\int_0^{\infty}\frac{F_{\mathrm{D}}(\bar{\nu})\varepsilon_{\mathrm{A}}(\bar{\nu})}{\bar{\nu}^4}\mathrm{d}\bar{\nu}$ distributes all over the overlapping area of the emission spectrum of the benefactor and the excitation spectrum of the acceptor and shows the overlapping degree of the benefactor emission and the acceptor absorption.

The transpositional form of the above formula is

$$K_{\mathrm{T}} = \left(\frac{r_0}{r}\right)^6 \times \frac{1}{\tau_{\mathrm{D}}},$$

$$r_0^6 = \frac{9000(\ln 10)K^2\phi_{\mathrm{D}}}{128\pi^5 n^4 N} \int_0^{\infty} \frac{F_{\mathrm{D}}(\bar{\nu})\varepsilon_{\mathrm{A}}(\bar{\nu})}{\bar{\nu}^4}\mathrm{d}\bar{\nu}, \quad (2)$$

where r_0 is the critical distance when there exist the energy resonance and energy transfer. When $r = r_0$, then $K_{\mathrm{T}}\tau_{\mathrm{D}} = 1$, which implies that within the lifetime τ_{D}, the molecule in the excited state will achieve the energy transfer by resonance, and generate nonradiative transition. When $r < r_0$, the probability of energy transfer is larger than that of the decay of the benefactor; when $r > r_0$, most excited-state molecules would decay and return to the ground state, moreover the probability of the energy transfer is very small.

The efficiency of the energy transfer can be given as follows:

$$\omega = \frac{K_{\mathrm{T}}}{\tau_{\mathrm{D}}^{-1} + K_{\mathrm{T}}} = \frac{1}{1+(r/r_0)^6}. \quad (3)$$

When the intermolecular distance is r_0, the probability of energy transfer is equal to that of the decay of the benefactor.

By using energy E to replace the wave number $\bar{\nu}$, Eq.(2) is described as follows:[19]

$$r_0^6 = \frac{3h^4c^4}{64\pi^5 n^4} Q_{\mathrm{A}} \int \frac{F_{\mathrm{A}}(E)F_{\mathrm{E}}(E)}{E^4}\mathrm{d}E, \quad (4)$$

where Q_{A} is the absorption cross section of the integrated energy, E is the energy value, the integration variable spreads over the overlapping area of the emission spectrum of the benefactor and the excitation spectrum of the acceptor, $E_{\mathrm{A}}(E)$ and $E_{\mathrm{E}}(E)$ denote the normalized linear functions of absorption and emission respectively.

As shown by the experimental results in Fig.6, the benefactor, which is the unimolecule, and the acceptor, which is the excimer, have the biggest overlapping area of their emission band and absorption band, and at the same time the fluorescence emission domain of the unimolecules is nearly in the absorption domain of the excimer. So there is the biggest energy-transfer coefficient. For convenience, E^4 is denoted as an approximate expression $E^4 = h^4c^4/\lambda^4$. According to the definition, $E_{\mathrm{A}}(E)$ and $E_{\mathrm{E}}(E)$ are expressed as

$$F_{\mathrm{E}}(E) = A\tau_{\mathrm{D}},$$

$$F_{\mathrm{A}}(E) = \frac{\sigma_{\mathrm{A}}(E)}{Q_{\mathrm{A}}} = \frac{\sigma_{\mathrm{A}}(E)}{\int \sigma_{\mathrm{A}}(E)\mathrm{d}E}, \quad (5)$$

where A is the transition probability, which can be substituted by the reciprocal of the experimental fluorescence lifetime. And the integration range is the overlapping area of the two spectra. We replace $F_{\mathrm{A}}(E)$ and $F_{\mathrm{E}}(E)$ with Eq.(5) and solve Eq.(4), the critical distance is calculated as follows:

$$\begin{aligned} r_0'^6 &= \frac{3h^4c^4}{64\pi^5 n^4} Q_{\mathrm{A}} \int \frac{F_{\mathrm{A}}(E)F_{\mathrm{E}}(E)}{E^4}\mathrm{d}E \\ &= \frac{3h^4c^4}{64\pi^5 n^4} Q_{\mathrm{A}} \int \frac{F_{\mathrm{A}}(E)}{E^4}\mathrm{d}E \\ &= \frac{3h^4c^4}{64\pi^5 n^4} Q_{\mathrm{A}} \int \frac{\sigma_{\mathrm{A}}(E)/\int \sigma_{\mathrm{A}}(E)\mathrm{d}E}{E^4}\mathrm{d}E \end{aligned}$$

$$= \frac{3h^4c^4}{64\pi^5 n^4} Q_{\mathrm{A}} \times \frac{\int \sigma_{\mathrm{A}}(E)\mathrm{d}E}{E^4 \int \sigma_{\mathrm{A}}(E)\mathrm{d}E}$$
$$= \frac{3h^4c^4}{64\pi^5 n^4 E^4} Q_{\mathrm{A}} = \frac{3Q_{\mathrm{A}}\lambda^4}{64\pi^5 n^4}. \quad (6)$$

With Eq.(6), we can calculate the critical distance between the benefactor and the acceptor when the resonance energy transfer takes place between them. The refractive indices of water and pure ethanol are $n_{\mathrm{w}} = 1.333$ and $n_{\mathrm{E}} = 1.361$ respectively. When the ethanol and water are mixed together and the volume percentage of ethanol is 6:4, the refractive index of the solution can be calculated to be $n = 1.35$ by weighted average. Because the emission band is very narrow, we can regard $\lambda = 305$ nm as constant for convenience. Q_{A} is calculated all over the overlapping area of the absorption and the emission spectra. As shown in Fig.5, the absorption cross section Q_{A} of the acceptor is equal to the emission cross section of the benefactor $Q'_{\mathrm{E}} = \int \sigma_{\mathrm{E}}(E)\mathrm{d}E$. But calculating the emission cross section is very difficult and complex. We can use the relation between the absorption cross section and the emission cross section as follows:[20]

$$\sigma_{\mathrm{E}} = \sigma_{\mathrm{A}}(\nu)\exp[(\varepsilon - h\nu)/kT], \quad (7)$$

where ε is the excitation energy, which is related to the temperature. It is the free energy for the molecule to be excited from a lower level to a higher level. k is Boltzmann constant, and T is thermodynamic temperature. According to the density functional theory (DFT), we have calculated the energy interval of the unimolecule to be $\varepsilon = 6.75$ eV and the experiment temperature to be $T = 290$ K.

When the wavelength of incident light is 270 nm, the emission spectrum has two bands with the peaks located at 290 nm and 305 nm respectively. As shown in Ref.[13], the two emission bands correspond to the two optimal incident light beams with wavelengths being $\lambda_1 = 265$ nm, and $\lambda_2 = 280$ nm. And the two excitation spectra of the two emission bands are displayed by the sharp absorption curves. So we can take

$$\sigma_{\mathrm{A}}(\nu) = \sigma(\nu_1) + \sigma(\nu_2), \text{ and } \sigma(\nu) = \sigma(\lambda) = \frac{A(\lambda)}{nl}, \quad (8)$$

where $A(\lambda)$ is the transition probability of absorbing the excited light, which we can take as the reciprocal of the fluorescent lifetime in the experiment, i.e. $A(\lambda_1) = 1/\tau_1$, $\tau_1 = 3$ ns, and $A(\lambda_2) = 1/\tau_2, \tau_2 = 10$ ns. n is the molecular number density absorbing the incident light and its unit is molecules/cm^3. l is the optical path length of light crossing the absorbing medium and its unit is cm. By using all the parameters we can calculate out $\sigma_{\mathrm{A}}(\nu) = 2.69 \times 10^{-21}$ cm^2. And substituting this result into Eq.(7) yields $Q_{\mathrm{A}} = 1.26 \times 10^{-20}$ cm^2. Then inserting it into Eq.(6), the critical distance can be calculated to be $r_0 = 1.08$ nm. So when the intermolecular distance between the benefactor and the acceptor is less than the critical distance ($r < r_0 = 1.08$ nm), the energy transfer probability is maximal and the fluorescent intensity of the excimer reaches a peak.

5. Conclusion

When ethanol and water molecules are mixed together to form an ethanol–water solution, the cluster molecule may be generated by the hydrogen bonding. The spectrum characteristics of the clusters have been shown in detail in Ref.[13]. Using the excited light with a longer wavelength to irradiate the solution, the sharp fine emission band with a small Stokes shift, which is emitted by the unimolecules of the ethanol–water clusters, exists as shown in Ref.[13]. With the decrease of the ethanol volume percentage or the increase of the excited light wavelength, the fluorescence intensity of the sharp emission peak dies away, at the same time, a broadened emission band without any structural characteristic but with a large Stokes shift appears, and this fluorescence band has all the spectral characteristics of the excimer. That is to say, the cluster molecules, of which some are in the excited state and some in the ground state, form the intermolecular excimers. By comparing the fluorescence spectrum of the unimolecules with the excitation spectrum of the excimer, one can conclude that there is energy transfer between the cluster and the excimer, and the fluorescent quenching of the sharp emission bands results from the appearance of the broad emission band. According to the resonant energy transfer theory of dipole-dipole coupling, we have calculated the critical distance between the benefactor and the acceptor to be $r_0 = 1.08$ nm. Owing to the intermolecular distance in the ethanol–water solutions being less than the critical distance, the probability of resonant energy transfer reaches a peak value and the fluorescence intensity of the broad emission band arrives at a maximum.

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