

# Formation mechanism of ethanol-water excimer

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The fluorescent spectrum and the excitation spectrum were used to present the cluster molecular structure feature in ethanol-water solutions. Through analyzing the fluorescent characteristics of an excimer, it is proposed that the excimers are formed between the ethanol-water cluster molecules in the excited state and in the ground state. The fluorescent lifetime and the fluorescent intensity decay process give information about the photo-physical and photo-chemical processes of the formation and the dissociation of an excimer. The theoretical calculation and physical analysis coincide with the experimental results. The preliminary conclusion about the structure feature of ethanol-water cluster molecule is that it has a planar one like a sandwich.

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It has attracted great interests in the last decade about the structure features of ethanol molecules in different phases and the characteristics of the associated cluster molecules which are generated by ethanol and water through hydrogen bonding (HB)<sup>[1-9]</sup>. Nevertheless, there are still not well accepted conclusions about the structures of ethanol molecules in liquid, solid, especially in ethanol-water solutions. Some investigators suggested that the HB of methanol with water molecules might form cluster molecule with ring or open chain structures<sup>[10-12]</sup>. But the proposed structures of the new cluster molecules have not been widely accepted due to the unknown effects of the HB. There is no proof about the planar structure features of the cluster molecules. The cluster molecules feature in ethanol aqueous solution has not been discussed yet. Because the hydrogen bonding in ethanol molecule is more complex than in methanol, and the interaction of hydrogen bonding between ethanol and water is also more complex. In those studies, some methods have been used, such as X-ray absorption spectroscopy, X-ray emission spectroscopy and neutron diffraction analysis<sup>[12]</sup>, but there is no report about the fluorescence techniques. The fluorescence spectrum technology is a keen analysis method to study the molecular structure. Especially, the time resolved fluorescence spectrum is independent of the path of detecting rays, and it is only affected by the micro-environment, some information of molecular structure, steric and electronic environment and so on<sup>[13]</sup>. In our previous studies, the combination numbers of the ethanol-water cluster molecule were counted according to light-induced steady-state fluorescence spectroscopy<sup>[14,15]</sup>. The fluorescence spectrum characteristic of ethanol-water excimer and the energy transferring between the excimer and the cluster have been discussed in detail<sup>[16]</sup>. However, the formation and dissociation mechanism of an excimer, and the photophysical and photochemical process of the excimer formation have not been studied. Especially, it has not been discussed yet whether the array framework of the ring chain clusters is planar or nonplanar. The two molecules to form

an excimer are necessarily parallel as the structure of a sandwich<sup>[17]</sup>. Therefore, it can be concluded that the cluster molecules have the planar structure. This paper investigates the excimers formed in the ethanol-water solution, and gives the structures of the new cluster molecules formed by the ethanol and water molecules.

There are two types of excimer formations: intermolecular and intramolecular excimers. In general, it is easy to form intra-molecular excimer in dilute solutions. The criterion of intramolecular excimer formation is that the fluorescent intensity ratio of the excimer to the monomolecule (the molecule in ground state) does not depend on the concentration of monomolecules; otherwise, it is an intermolecular excimer. To determine the type of the excimer in ethanol-water solutions, the variation of fluorescent intensity emitted by excimers along with the monomolecular concentration was studied. In the ethanol solution, the monomolecule is neither ethanol nor water molecule, but the cluster in the solution. The sharp fine structure in the fluorescent spectrum is emitted by the new cluster molecules formed by ethanol and water molecules through HB whose details of combination have not been discussed<sup>[16]</sup>. The new cluster molecules are formed by one ethanol and two water molecules, and the molecular formula is MR<sub>2</sub>, where M and R represent the ethanol and the water molecule, respectively. The concentration of MR<sub>2</sub> has been studied and will be discussed in the following sections. The theoretical molar concentration could be calculated as  $\frac{V_{\text{eth}} \times 3 \times 0.78}{46 \times 3}$  when  $V_{\text{eth}} \leq 60\%$  and  $\frac{V_{\text{w}} \times 3 \times 1}{18 \times 3 \times 2}$  when  $V_{\text{eth}} > 60\%$ , where  $V_{\text{eth}}$  and  $V_{\text{w}}$  denote the volume of ethanol and water, respectively. In the ethanol-water solution, the monomolecule, which emits the sharp fluorescent peak, is MR<sub>2</sub>. The fluorescent intensity ratio of excimer to monomolecule depends on the concentration of monomolecules (Fig. 1). Therefore, it is intermolecular excimer formed here.

A time-resolved spectrometer can directly trace the photophysical processes of the formation and the dissociation of excimers. The decay process of the fluorescent intensity can be studied by time correlated single photon counting technique. Generally, the emission process can

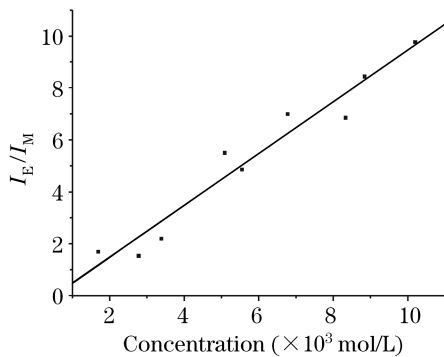


Fig. 1. Relation between  $I_E/I_M$  and the monomolecular concentration.  $I_E$ : the fluorescence intensity of excimer;  $I_M$ : the fluorescence intensity of monomolecule.

be fitted by the exponential decay curve defined as  $I_t = I_0 \cdot e^{-t/\tau}$ , where  $I_0$  is the initial fluorescent intensity and  $\tau$  is the fluorescent lifetime. If the decay process can be fitted with multi-exponential curves, there are several lifetimes and the variation of the fluorescence intensity with time can be represented by a sum of multi-exponential functions  $I_t = \sum a_i \cdot e^{-t/\tau_i}$ , where  $a_i$  represents the weight of the component whose lifetime is  $\tau_i$ .

The fluorescent lifetimes of both ethanol-water excimer and monomolecule were measured. The fluorescent emission at 305nm was fitted to a single-exponential curve with  $\tau = 7.86$  ns, demonstrating that there is only the cluster which can emit this fluorescent photon. However, the decay process at 418 nm fits a di-exponential curve, indicating that there are two objects that can emit fluorescent photon. In other words, there is a mixing emission from both the excited molecules and those dissociated excimers.

When the ethanol-water solution was excited by an ultraviolet light at 270 nm, the decay process of the fluorescent intensity at 418 nm is fitted to be a di-exponential curve. In this decay process, there is a fast fluorescent relaxation with exponential decay of monomolecules with  $\tau_2 = 2.6$  ns and a subsequent slower decay of excimers with  $\tau_1 = 11.36$  ns. To verify that the excimer formed by monomolecules is an intermolecular excimer, the curves of fluorescent intensity decay in the various ethanol-water solutions were measured, and the dependence of the reciprocal sum of these two fluorescent lifetimes on the concentration of  $MR_2$  was also measured as shown in Fig. 2. The reciprocal sum of the two

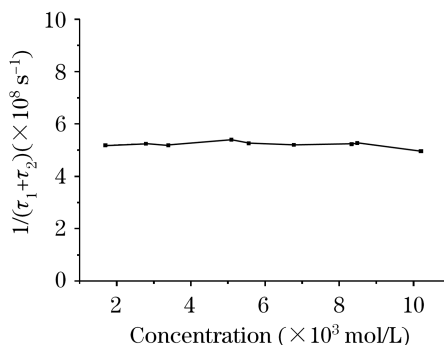
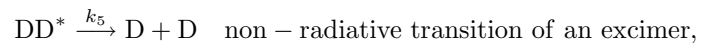
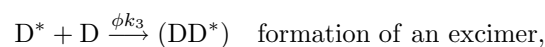
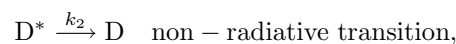
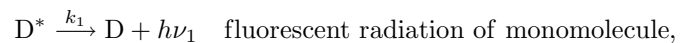
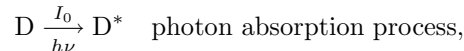


Fig. 2. Relation between  $1/(\tau_1 + \tau_2)$  and monomolecular concentration.

fluorescent lifetimes does not depend on the concentration of  $MR_2$ , which is the characteristic of an intermolecular excimer.

The excimer formation theory founded by Briks can be used to explain the formation mechanism of a micro-molecular system. The ethanol and water molecules as well as the new cluster molecules belong to small molecular system, which can be well explained using the Briks' theory. Based on the steady state and time resolved fluorescent spectra of the ethanol-water solutions, one can conclude that the new cluster molecules  $MR_2$ , which are in the ground state and the excited state, are easy to form excimers emitting a broad spectrum with a long Stokes shift. The possible photophysical mechanisms of the excimer are listed below as described in Ref. [18]:



where  $D$  is the ground state molecule of  $MR_2$ ,  $D^*$  is the excited state molecule of  $MR_2$ , and  $(DD^*)$  is the excimer.  $h\nu_1$  and  $h\nu_2$  are the fluorescence photons energies of the monomolecules and the excimer, respectively, and  $\phi$  is the quantum yield of the intermolecular excimer formation.  $k_1, k_2, k_3, k_4, k_5, k_6$  are the fluorescent radiation rates of monomolecule, non-radiative transition, formation of an excimer, dissociation of an excimer, non-radiative transition of an excimer, fluorescent radiation of excimer, respectively. Differential equations of the concentrations of the excited molecule  $D^*$  and the excimer  $(DD^*)$  in the solution can be derived as

$$\frac{d[D^*]}{dt} = k_4[(DD^*)] - (k_1 + k_2 + \phi k_3)[D^*],$$

$$\frac{d[(DD^*)]}{dt} = \phi k_3[D^*] - (k_4 + k_5 + k_6)[(DD^*)], \quad (1)$$

where  $[D^*]$ ,  $[(DD^*)]$  are the concentrations of the excited molecule  $D^*$  and the excimer  $(DD^*)$  in the solution. When  $t \rightarrow 0$ ,  $[(DD^*)] \rightarrow 0$ . Solve Eq. (1)

$$\lambda_{1,2} = \frac{1}{2} (k_1 + k_2 + \phi k_3 + k_4 + k_5 + k_6)$$

$$\mp \frac{1}{2} [(k_1 + k_2 + \phi k_3 + k_4 + k_5 + k_6)^2$$

$$-4((k_1 + k_2 + \phi k_3)(k_4 + k_5 + k_6) - \phi k_3 k_4)]^{1/2}. \quad (2)$$

It can be inferred that there are two lifetimes in this decay process, and the eigenvalues are the reciprocal of

these lifetimes, namely  $\lambda_1 = 1/\tau_1$ ,  $\lambda_2 = 1/\tau_2$ .

From Eq. (2), it can be obtained that

$$\lambda_1 + \lambda_2 = k_1 + k_2 + \phi k_3 + k_4 + k_5 + k_6. \quad (3)$$

If the values of  $k_3$  and  $\phi$  are the same, the value of  $\lambda_1 + \lambda_2$ , namely the reciprocal sum of lifetimes, are the same certainly, where

$$\begin{aligned} \tau_1 &= \frac{1}{\lambda_1} = \frac{1}{k_4 + k_5 + k_6}, \\ \tau_2 &= \frac{1}{\lambda_2} = \frac{1}{k_1 + k_2 + \phi k_3}, \end{aligned} \quad (4)$$

where  $\tau_1$  and  $\tau_2$  are the fluorescent lifetimes of excimer and monomolecule, respectively. The experimental results fit with this theory as shown in Fig. 2. It demonstrates that new cluster molecules  $MR_2$  in ethanol-water solution form intermolecular excimers. The possible formation mechanism is that the new cluster molecules in excited states are easy to form excimer through hydrogen bond or elastic carbon bond. The structure of  $MR_2$  is always a ring or an open chain. The chains of homogeneous polymers are getting closer and contracting under the force between them when the concentration increases, leading to increase in segment density in chains and the overlapping possibility of molecular rings. As chains maintain contracting, different segments in homogeneous polymers begin to transfix, the possibility of excimer formation obviously increases with an enhancement in excimer fluorescent intensity. When the ethanol-water proportion is 6:4, both the concentration of new cluster molecule  $MR_2$  and the fluorescent intensity of excimers reach their maximum. Experimental results fit well with calculation and theoretical analysis.

Based on the steady state spectra of ethanol-water solutions excited with the ultraviolet light<sup>[16]</sup>, we find that the cluster molecules of  $MR_2$  are easy to form the excimer. A sharp peak at 305 nm, whose fluorescent intensity obviously depends on the ethanol-water ratio, corresponds to the fine structure of new cluster molecule  $MR_2$ . A broad and featureless fluorescent spectrum at long Stokes shift has all the fluorescent characteristics of an excimer and all spectra passing a constant emitting point at 360 nm. For the fluorescent intensity ratio of the excimer and the monomolecule depending on the concentration of the new cluster molecules, it can be proved that intermolecular excimers are formed in the ethanol-water solution. The fluorescent lifetimes measured in the experiments consist of two components, a shorter lifetime of the monomolecule and a longer one of the excimer. The reciprocal sum of the two lifetimes depends on the concentration of the monomolecules, which proves that it is intermolecular excimer again. The possible photophys-

ical process of the excimer formation is analyzed theoretically. The two eigenvalues of the differential equation of the fluorescence decay demonstrate that the excimer has two different lifetimes.

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