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Rapid internal conversion in a symmetric molecule LD 700 studied by means of femtosecond fluorescence depletion*

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The rapid internal conversion dynamics at room temperature is determined by using the femtosecond time-resolved fluorescence depletion measurements of a complex solvated molecule of LD 700 (rhodamine 700) combined with steady-state absorption and fluorescence spectroscopy, as well as quantum chemical calculation. The molecule is excited by a 50 fs laser pulse at 400 nm which directly populated the highly excited singlet state, the rapid internal conversions (ICs) are observed, which leads to the directional changes of the emission transition moment following photoexcitation to the highly excited singlet state S_5 of LD 700.

Keywords: femtosecond fluorescence depletion, internal conversion (IC), solvation
PACC: 3250, 3350H, 3300

1. Introduction

Ultrafast dark processes such as internal conversion (IC), intramolecular vibrational relaxation (IVR) and solvation are the most common phenomena in physics, chemistry and biology, and they have been intensively studied over the past ten years.[1−29] With few exceptions as predicted by Kasha in 1950,[30−32] for a polyatomic molecule, the fluorescence is emitted only from the lowest excited singlet state no matter which stable electronic state it is excited from. When the molecule is initially excited to the highly excited singlet state S_n ($n \geq 2$), the difference in electronic energy between S_n and S_1 is converted into excess vibrational energy in IC and other dark processes, where these dark processes often highly compete with each other, and they take place simultaneously on an ultrafast time scale.[16] The IC, a typical ultrafast dark process, is a true nonadiabatic transition. Study of the IC is of special interest in that it opens up possibilities for observing the transfer of the electronic energy into vibrational excitation of molecule.[3,33,34] Although much effort has been made with various ultrafast spectral techniques,[1−22,35−37] a major practical problem in studying the large-sized polyatomic molecules in condensed matter is still challenging experimentalists to determine these ultrafast dark processes.[14,16]

We have studied the specific population transfer along the reaction coordinate through the higher vibrational energy levels of excited states of a complex solvated molecule of LDS 751 by employing a powerful pump-dump technique of femtosecond time-resolved stimulated emission pumping fluorescence depletion (FSTRSEPFD).[12−14] The dynamics of the formation of the dark states corresponding to the complex excited-state isomerization was investigated as a function of solvent viscosity and solvent polarity, where a cooperative two-step isomerization process was clearly identified within LDS 751 upon excitation.[14] In the present paper, we report on our new results about

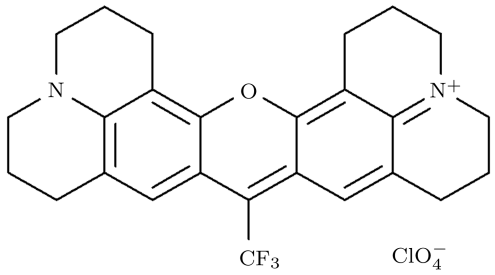
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the anisotropic femtosecond fluorescence depletion dynamics from a rigid symmetric molecule of LD 700 (rhodamine 700) to provide the detailed information of the change in direction of the emission transition moment corresponding to the ultrafast intramolecular IC from highly excited singlet state (S_n) to lowest excited singlet state S_1, while solvation will not contribute to the observed ultrafast anisotropic changes.

2. Material and methods

2.1. Materials

The laser dye LD 700 (rhodamine 700) is purchased from Lambda Physik GmbH (German). Scheme 1 shows the molecular structure of LD 700. All solvents used are of analytical reagent (A.R.) or even higher grade.



Scheme 1 Molecular structure of LD 700 (rhodamine 700).

2.2. Steady-state spectroscopy

The UV/V absorption spectra and the fluorescence spectra are recorded on a spectrophotometer (UV1601, Shimadzu, Japan) and a fluorescence spectrometer (F4500, Hitachi, Japan), respectively. Anisotropic fluorescence excitation spectrum is measured by using two polarizers and calculated from

$$r = \big(I_{||} - G \cdot I_{\perp}\big)/\big(I_{||} + 2G \cdot I_{\perp}\big), \qquad (1)$$

where $I_{||}$ and $I_{\perp}$ are the parallel and the perpendicular fluorescence intensities to the excitation polarization, respectively; $G(G = I_{\perp}/I_{||})$ is the geometrical factor of fluorescence spectrometer when the excitation is vertically polarized. To avoid the fast rotation of molecule in solution, LD 700 is dissolved in an ethanol/glycerol mixture with a volume ratio of about 4/1 during anisotropic fluorescence excitation spectral measurement.

2.3. Femtosecond fluorescence depletion measurements

Femtosecond fluorescence depletion from LD 700 is measured by using the femtosecond time-resolved simulated emission pumping fluorescence depletion (FS TR SEP FD) technique based on the principle of so-called 'pump–probe' technology described elsewhere.[12,14,36]

To pump the molecule of LD 700 at 400 nm, a CW laser with a wavelength of 532 nm (Verdi-V5, Coherent, USA) is used to pump a Ti:sapphire laser (Mira 900S, Coherent, USA), thereby producing a pulse train at 800 nm with a duration of 50 fs at a repetition of 76 MHz. The power output is about 650 mW. This fundamental beam was led into a 0.5 mm thick BBO crystal to produce a second harmonic beam at 400 nm. The second harmonic beam and the residual fundamental beam are split by a dichromic mirror. The ultrafast double-frequency beam at 400 nm (80 MW/cm^2) is used for pumping the sample solution to generate the Franck–Condon state, then the residual ultrafast fundamental pulses at 800 nm (1.7 GW/cm^2) with a specific polarization (modulated by rotating a zero-order half-wave plate) are introduced as a probe beam to 'dump' the population of dye molecules from excited states after a variable delay time. The spontaneous fluorescence emission is perturbed due to compulsive stimulated emission depletion (STED), i.e. the fluorescence is depleted in the presence of 'dumping' pulse. The relative fluorescence intensity depletion at the monitored fluorescence wavelength as a response to delay time is detected via a photomultiplier tube (PMT) coupled monochromator. A lock-in amplifier is employed to extract the depletion signal correlated with the 'dumping' beam. To avoid the possible thermal effects and photobleaching upon intense femtosecond pulse, the sample solution is stirred up with a high speed rotor in the sample cell to increase the S/N ratio of detection. In order to obtain the full information about the ultrafast dynamics, we have performed the measurements on isotropic (54.7°) and anisotropic (parallel and vertical) femtosecond fluorescence depletion, where the polarization of dumping beams with respect to that of pumping beam is selected by rotating a zero-order half-wave plate to obtain isotropic (54.7°) and anisotropic (parallel and vertical) results, separately. The time-resolved anisotropic decay $r(t)$ is calculated from the decay curves under the condition

of parallel polarizations ($I_{||}$) and perpendicular polarizations ($I_{\perp}$) of dumping beam relative to the polarization of pumping beam according to expression (1),[38−40] where the factor G accounts for the difference in sensitivity to the detection of signals between in the perpendicular-configuration and in the parallel-polarized configuration, where $G(G = I_{\perp}/I_{||}$, when the excitation is vertically polarized) is estimated to be about 1.02 in the case of the excitation of 400 nm. The instrument response function is determined according to the 1+1' two-photon excited fluorescence method as described in Refs.[12, 13, 41], in which the instrumental response function (IRF) was achieved to be up to 90 fs.

All the temporal evolution profiles are fitted by the convolution between the IRF with a multiexponential function according to iterative deconvolution by using the FluoFit software based on the Levenberg–Marquardt and Simplex algorithms (Version 3.3, PicoQuant, Germany). The fitting quality is judged by weighted residual and reduced χ^2 value.

All the experiments are carried out at ambient temperature.

2.4. Computational methods

The ground state stationary configuration of LD 700 is fully optimized by using the density functional theory (DFT) method under B3LYP/6-31+g** level for the gas phase and the polarized continuum mode (PCM) method. Calculations for the vertically excited state have also been carried out by using the corresponding ground state configuration of LD 700 and the time-dependent DFT (TD-DFT) method under the same level as that by using the relative ground state configurations. All the calculations are carried out by using the Gaussian 03 package.[42]

3. Results and discussion

3.1. Steady-state absorption and fluorescence spectra

Figure 1 shows the steady state absorption and emission spectra of LD 700 in an ethanol/glycerol mixture with a volume ratio of about 4/1, separately. It is found that there are three main absorption bands at around 395 nm, 460 nm and 560–670 nm. Taking a close look at the absorption spectrum, six absorption peaks could be identified, and they are around at 395, 435 (shoulder), 463, 547 nm (shoulder), 594 (shoulder) and 654 nm. The fluorescence of LD 700 is located around at 684 nm, which is close to the mirror image of the $S_1 \leftarrow S_0$ absorption. The emission position and spectral shape are less dependent on excitation wavelength and solvent. The absorption bands around at 395, 463 and 547 nm mainly originate from the higher excited states ($S_2 - S_n$), where the broad absorption band ranging from 570 to 670 nm is assigned to the lowest excited state (S_1). The peaks around at 547 and 594 nm come from highly vibrational states of S_1 state, which are proved from steady fluorescence excitation anisotropic spectrum monitored at a fluorescence wavelength of 684 nm as shown in Fig.1.

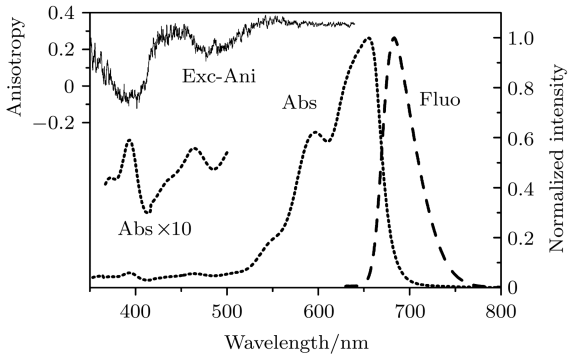


Fig.1. Steady-state absorption, emission and fluorescence excitation anisotropy spectra of LD 700 in an ethanol/glycerol mixture with a volume ratio of about 4/1. The excitation wavelength of fluorescence spectra is 620 nm. The fluorescence excitation anisotropy spectrum is monitored at 684 nm. The 10-time magnified absorption spectrum in a region of 350–520 nm is also shown in the inset.

The fluorescence excitation anisotropic measurement could give the relative orientations of various absorption transition dipole moments from S_0 to S_n. Several different anisotropy values, indicating several distinct excited states, are found in different excitation regions, where the anisotropy value is about −0.1 around at 395 nm, about 0.3 ranging from 420 to 450 nm, and about 0.2 ranging from 460 to 530 nm, as well as 0.35 ranging from 560 to 650 nm. The constant anisotropy value around 0.35 in a low-energy region from 560 to 650 nm indicates that the shoulders around at 560 and 594 nm source from the higher vibrational states of S_1 state. The negative anisotropy value of about −0.1 around at 395 nm suggests that the absorption transition dipole moment for 395 nm has a large angle relative to that of $S_1 \leftarrow S_0$, where the fluorescence comes only from the lowest excited

state S_1 according to the Kasha's rule.[30,40] The relative angle between the transition dipole moments of S_n (at 395 nm) and S_1 (at 654 nm) could be calculated from the observed fluorescence excitation anisotropic spectrum as shown in the inset of Fig.1 according to the following expression:[40]

$$r = (2/5)\left[\left(3\cos^2\theta - 1\right)/2\right], \qquad (2)$$

where, θ is the displacement angle between the absorption and emission dipole moments. Here, we simply assume that both the absorption and the emission transition dipole moments of the lowest excited state S_1 are nearly parallel to each other. Therefore, by taking $r = -0.1$, the relative angle between the absorption transition dipole moments of $S_n \leftarrow S_0$ (at 395 nm) and $S_1 \leftarrow S_0$ (654 nm) is obtained as 115°. As shown in Fig.1, the anisotropy in fluorescence excitation anisotropy spectrum increasing from −0.1 to 0.2 and finally up to 0.35 indicates the radiationless IC from S_n (around 395 nm) to S_1 (about 654 nm), which is followed by a large change in transition dipole moment. Accordingly, we also obtain the various orientations of transition dipole moments of $S_n \leftarrow S_0$ relative to that of $S_1 \leftarrow S_0$, estimated from the anisotropic fluorescence excitation spectrum of LD 700 as listed in Table 1.

To have a deeper insight into the nature of spectra and various orientations of the absorption transition dipole moments of the excited states of LD 700, the quantum chemical calculations are performed by using DFT and TD-DFT methods as implemented in the Gaussian 03 package.[42] The ground state geometry of LD 700 is fully optimized under B3LYP/6-31g* level, and the calculation of the vertical excited state is also carried out by using the corresponding ground state configuration of LD 700 and the TD-DFT method under the same level. Listed in Table 1 are various calculated and measured absorption transition dipole moments, energy gaps and oscillation strengths of the first five excited states of LD 700 in gas phase. It is found that all the calculated energy gaps of LD 700 are about 100 nm blue-shifted compared with the experimental values obtained from the UV–vis absorption spectra (see Fig.1). The difference between the calculated and experimental values results from the solvation effects for experiments and the gas-phase for calculations. The calculated results show that the lowest absorption transition dipole moment of $S_1 \leftarrow S_0$ is almost along the long-axis of LD 700; whereas the high absorption transition dipole moment of $S_5 \leftarrow S_0$ is along the short-axis. This means that the well-separated $S_1 \leftarrow S_0$ and $S_5 \leftarrow S_0$ transitions are oriented along the long and short axes of LD 700, respectively, where the relative angle between transition dipole moments of these two transitions is nearly a rectangle, in other words, the two transition dipole moments are almost orthogonal to each other.

Table 1. Highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energy gaps, oscillation strengths and relative orientations of various transition moments, respective energy gaps and relative orientations of transition moments obtained from absorption and anisotropic spectra of LD 700 in an ethanol/glycerol mixture with a volume ratio of about 4/1.

transition	orbital	calculated energy gap/(eV/nm)	oscillation strength	observed absorption/ nm	relative orientation[b]
$S_1 \leftarrow S_0$	LUMO←HOMO	2.4575/504	0.8120	654	
$S_2 \leftarrow S_0$	LUMO←$HOMO_{-1}$	2.6773/463	0.0081	547 or 594 (s)[a]	156.1° (138°)
$S_3 \leftarrow S_0$	LUMO←$HOMO_{-3}$	3.5896/345	0.0257	463	174.4° (163°)
$S_4 \leftarrow S_0$	LUMO← $HOMO_{-2}$	3.6168/342	0.0452	435 (s)[a]	102° (132°)
$S_5 \leftarrow S_0$	$LUMO_{+1}$ ←HOMO	4.2696/290	0.1203	395	93.7° (115°)

Superscript [a] represents shoulder peak.
Superscript [b] refers to the calculated orientation of the transition dipole moments of $S_n \leftarrow S_0$ ($n = 2 - 5$) relative to that of $S_1 \leftarrow S_0$. The respective orientations observed from anisotropic fluorescence excitation spectrum are also listed in bracket for comparison. The calculated orientation of all the transition dipole moments in the Table is projected on the $x - y$ plane of the molecule.

The transition dipole moments of $S_n \leftarrow S_0$ ($n = 2 - 5$) vary from 93.7 to 174.4° relative to that of $S_1 \leftarrow S_0$. For the $S_1 \leftarrow S_0$ excitation, the anisotropy value is obtained experimentally to be as high as 0.35 (0.4 could be expected theoretically) for LD 700; whereas, for the $S_5 \leftarrow S_0$ excitation, rapid IC from S_5 to S_1 yields a fluorescence from S_1 according to the Kasha's rule with the transition dipole moment ori-

ented along the long axis rather than along the short axis of LD 700. A negative anisotropy value is obtained experimentally upon $S_5 \leftarrow S_0$ excitation to be as low as about -0.1 (-0.2 could be expected theoretically). The anisotropic fluorescence excitation spectra accord with the calculated results of the relative orientations of transition dipole moments for various highly excited states.

Obviously, the relaxation processes such as IC from the excited singlet states (S_n) to lowest excited singlet state (S_1) lead to a large change in the transition dipole moment direction of the excited states corresponding to the fluorescence. To determine these spectral properties, femtosecond fluorescence depletion measurements could be employed to further provide the excited state dynamics and rapid internal conversional information within LD 700.[12,14,36,43]

3.2. Femtosecond fluorescence depletion dynamics of LD 700

To determine the ultrafast internal conversional dynamics of LD 700 from the highly excited singlet state S_5, the femtosecond fluorescence depletion measurements of LD 700 are performed in polar aprotic acetone and DMSO. The highly excited state S_5 is directly populated by 400 nm excitation. It is known that there is no obvious excited state absorption for LD 700 at 800 nm, the fluorescence depletion signals under the depletion at 800 nm are monitored at a fluorescence wavelength of 680 nm. Figure 2 shows the typical fluorescence depletion of LD 700 in acetone and DMSO monitored at 680 nm under a 400 nm femtosecond pulse excitation.

The isotropic depletion decays are well fitted with a double-exponential function. The fitted results of LD 700 are all listed in Table 2. The values of slow decay (τ_2) which are about 1.03 ps in acetone and about 2.43 ps in DMSO, are mainly contributed by the solvation of the excited solutes,[12,14,36] whereas the values of initial ultrafast decay (τ_1) which are about 171 fs in acetone and about 215 fs in DMSO is attributed to IC and IVR processes in the monitored fluorescence state pumped at 400 nm. Furthermore, it is found that amplitude of the initial ultrafast decay (τ_1) component is about 99%，and that of the slow component is about 1% when LD 700 is pumped at 400 nm, indicating that the IC dominates when highly excited singlet state S_5 is populated.

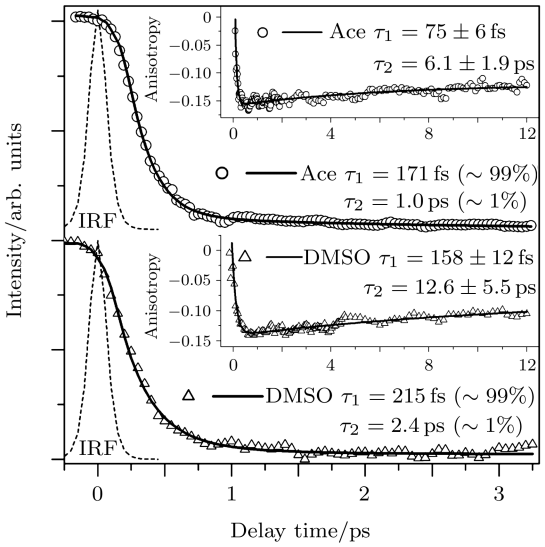


Fig.2. Isotropic and anisotropic (inset) fluorescence depletion signals of LD 700 in acetone (circle) and dimethylsulfoxide (DMSO) (triangle) monitored at 680 nm, where lines represents the fitted results. The pumping wavelength is 400 nm, and the dumping wavelength is 800 nm. The IRF about 90 fs is also shown at time zero.

Table 2. Fitted results of the isotropic and anisotropic decays of LD 700 under the excitation of 400 nm.

solvent	η/cP	τ_1/fs[a]	τ_2/ps[a]	τ_1/fs[b]	τ_2/ps[b]
acetone	0.308	171(99%)	1.0(≈1%)[c]	75 ± 6[d]	6.1 ± 1.9
DMSO	1.968	215(99%)	2.4(≈1%)[c]	158 ± 12	12.6 ± 5.5

[a] Time constant in isotropic experiments;

[b] Time constant in anisotropic experiments;

[c] The relative amplitude about 1% implies a typical fast IC process from S_5 to S_1, this value may have a slight deviation because this process is very fast around the IRF;

[d] This value is slightly smaller than the IRF, which is expected to have a large error.

To further explore the dynamics of the IC and solvation of LD 700, we perform the anisotropic depletion measurements with a pump at a wavelength of 400 nm as shown in the inset of Fig.2. The anisotropic depletion decays of LD 700 excited at 400 nm in both acetone and DMSO are fitted satisfactorily with a double-exponential function. The fitted results are also listed in Table 2. It is found that the anisotropic decay of LD 700 shows that the values of fast time constant ($\tau_{\rm ani}$) are about 80 fs in acetone and about 160 fs in DMSO, and the values of slow time constant are about 6.1 ps in acetone and about 12.6 ps in DMSO. The anisotropy value reaches a negative value about -0.13 before 1 ps and then recovers to about -0.11 with a time constant of about 6–12 ps within a detection time range. The negative anisotropy indicates a large displacement angle between the excitation ($S_0 \rightarrow S_5$) and emission ($S_1 \rightarrow S_0$) transition dipole moments in the fast IC process. Because solvation has little contribution to changing the anisotropic dynamics, the intramolecular ultrafast IC mainly causes the fast anisotropic decay. The fast anisotropic time constant ($\tau_{\rm ani}$) about 160 fs represents the fast IC process from S_5 to S_1 through various intermediate excited states (S_4, S_3 and S_2). It should be mentioned that the fast anisotropic time constants are slightly different, for example about 80 fs in acetone and 160 fs in DMSO, indicating that the IC could be complicated in LD 700, where there are many intermediate states between S_5 and S_1, the radiationless decays among these intermediate states from S_5 to S_1 could be solvent viscosity-dependent. The more viscous solvent could keep the molecule more rigid, reducing the radiationless possibility. Meanwhile, the slow anisotropic time constants result from the rotation diffusion of LD 700, showing the viscosity-dependent feature: about 12.6 ps in higher viscous DMSO ($\eta = 1.968$ cP) and about 6.1 ps in less viscous acetone ($\eta = 0.308$ cP).

Finally, it should be mentioned here that we cannot observe the fluorescence depletion signal of LD 700 by monitoring the fluorescence from S_5 (or S_4) because the ultrafast IC from S_4 and S_3 followed by vibrational cooling leads to very weak fluorescence from highly excited singlet states.[5,43] Furthermore, the IC from S_5 may not directly populate the lowest excited state S_1, for there appears a large angle between transition dipole moments of $S_5 \leftarrow S_0$ and $S_n \leftarrow S_0$ ($n = 1 - 3$) as shown in Table 1. A detailed comparison among the relative energy levels and orientations of transition dipole moments of various excited states indicates that the energies of excited states S_4 and S_3 are almost the same but the transition dipole moments are almost orthogonal to each other. The electronic relaxation from S_4 to S_3 could be regarded as an isoenergetic IC and/or conical intersection process. Because of the difficulties in searching the conical intersection point, we have not obtained the information about the possible conical intersection by quantum chemical calculation. On the other hand, there is a small energy separation between S_4- and S_3-states (about 0.027eV according to the theoretical calculation), therefore, the radiationless decay is expected to be much fast due to the high density of vibronic states involved in the radiationless process, leading to the very weak fluorescence from highly excited states. The very fast changes in the negative fluorescence anisotropy observed in the initial delay time are mainly caused by the IC from S_4 to S_3, where the strong vibrational coupling or conical intersection between them may be expected even the difference in angle between the transition dipole moments of $S_4 \leftarrow S_0$ and $S_3 \leftarrow S_0$ is as large as 72°.

4. Conclusions

The IC of LD 700 is investigated by steady-state absorption and fluorescence spectroscopy, quantum chemical calculation and femtosecond fluorescence depletion spectroscopy. The change in direction of the emission transition moment, caused by the ultrafast intramolecular IC, is observed to be followed by the photoexcitation to the highly excited singlet state S_5 of LD 700 by anisotropic femtosecond fluorescence depletion measurements. The time-constants of the ultrafast IC from S_5 to S_1 are determined to be about 80 fs in less viscous acetone ($\eta = 0.308$ cP) and about 160 fs in higher viscous DMSO($\eta = 1.968$ cP). The detailed information of directional changes of the emission transition moments corresponding to the ultrafast intramolecular IC from highly excited singlet state (S_n) to lowest excited singlet state S_1 is also given in this work.

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