Photo-induced intramolecular electron transfer and intramolecular vibrational relaxation of rhodamine 6G in DMSO revealed by multiplex transient grating spectroscopy*

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Photo-induced intramolecular electron transfer (PIET) and intramolecular vibrational relaxation (IVR) dynamics of the excited state of rhodamine 6G ($Rh6G^+$) in DMSO are investigated by multiplex transient grating. Two major components are resolved in the dynamics of $Rh6G^+$. The first component, with a lifetime $\tau_{PIET} = 140$ fs–260 fs, is attributed to PIET from the phenyl ring to the xanthene plane. The IVR process occurring in the range $\tau_{IVR} = 3.3$ ps–5.2 ps is much slower than the first component. The PIET and IVR processes occurring in the excited state of $Rh6G^+$ are quantitatively determined, and a better understanding of the relationship between these processes is obtained.

Keywords: photo-induced intramolecular electron transfer, intramolecular vibrational relaxation, excited state, multiplex transient grating

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1. Introduction

The excited-state intramolecular vibrational relaxation (IVR) and photo-induced intramolecular electron transfer (PIET) processes in molecules are strongly related to each other, and play significant roles in the ultrafast photoreaction dynamics in a wide range of chemical, biological, and physical systems.[1–7] Information about the dynamics of IVR and PIET on excited-state molecules in solution is essential for understanding the rates, pathways, and efficiencies of chemical reactions because many chemically relevant reactions take place in solution.[4–11] IVR is an intramolecular process where the excess excitation energy initially populating Franck–Condon active state(s) is distributed over the other dark states within the molecule. IVR dynamics occurs on a timescale ranging from hundreds of femtoseconds (fs) to a few picoseconds (ps), depending on solute–solvent interactions, chemical substitution of solute, and whether the system is in the gas or condensed phase.[2,7,10–14] Simultaneously, energy transfer is a very important pathway of nonradiative deactivation of the excited-state molecules in the reactive system.[15–17] The traditional Marcus theory assumes that the timescales of solvation dynamics or thermal equilibration are very much faster than those of ET.[15] However, considering a system with strong electronic coupling between donor and acceptor, ET takes place on a 5-fs dynamics of the excited state to several picoseconds dynamics of the excited state timescale.[18,19] Owing to such an ultrafast ET process, the system does not have time to reach its thermal equilibration, and it has been verified that IVR plays a significant role in the ultrafast charge transfer process.[18,20] Therefore, it is beneficial to investigate the relationship between the PIET and IVR processes occurring from the excited state of the molecule.

As is well known, photo-excitation of a molecule seldom results in the immediate population of the lowest-lying vibrational state (0–0 transition) of the excited electronic state, but rather leads to the population of an upper vibrational state.[2,7,21] The early fluorescence kinetics of an organic molecule is significantly affected by the IVR process, and the fluorescence spectrum is narrower than that observed in the steady-state fluorescence spectra.[7] Furthermore, the photophysical and photochemical properties of rhodamines have been widely investigated during recent decades.[22–27] For example, both the radiative and nonradiative properties associated with structural arrangements of rhodamines have been discussed in detail,[22,27–29] and the results revealed that the PIET process occurring in the excited state of rhodamines is a very important nonradiative pathway,[22–24] It should be noted that Savarese *et al.* have studied several common rhodamine and pyronine dyes through the combination of quantum chemical calculations and fluorescence lifetime imaging microscopy.[22] Their results indicated that the radiative lifetime of rhodamines can be considerably correlated to PIET

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from the phenyl toward the xanthene moiety occurring in the first singlet excited state (S_1) along the $S_0 \leftarrow S_1$ de-excitation pathway.[22] However, very little information can be currently obtained concerning the timescales of the PIET and IVR processes, and the significant relationship between the two processes from the excited state of rhodamines.

Rhodamine 6G dye ($Rh6G^+$) is a xanthene derivative, which has been recently used as a modern optical sensor in the areas of fluorescence signaling and encoding.[22,30–33] However, the competitive mechanism between IVR and PIET in $Rh6G^+$ has not been determined in detail, owing to the lack of knowledge of the quantitatively determined timescales for the IVR and PIET processes. Knowledge of excited-state dynamics of $Rh6G^+$ obtained in this work will be helpful to design molecular structures or solvent environments to enhance or minimize special electron-transfer pathways, depending on the desired application. Femtosecond time-resolved multiplex transient grating (TG) spectroscopy is a powerful tool to investigate the ultrafast dynamical processes, and it has been used to study photo-induced electron transfer reactions,[34–37] excited-state relaxation dynamics,[38,39] and IVR dynamics[40–43] for biological and chemical systems. Furthermore, TG has an advantage over transient absorption techniques in its superior sensitivity because of its background-free nature.[35–37]

2. Experiment

2.1. Apparatus and methods

The experimental apparatus and method of multiplex TG have been described in detail previously.[38,39,44] As shown in Figs. 1(a) and 1(b), the two equal beams ($\boldsymbol{k}_{pu1}$ and $\boldsymbol{k}_{pu2}$) with a wavelength centered at 530 nm are used to create the transient grating. A white light continuum (430 nm–750 nm), generated by focusing an 800 nm femtosecond pulse on the Al_2O_3 crystal, is used as the probe pulse ($\boldsymbol{k}_{pr}$). The TG signal appears in the direction of the phase matching condition ($\boldsymbol{k}_s = \boldsymbol{k}_{pr} + \boldsymbol{k}_{pu2} - \boldsymbol{k}_{pu1}$). The polarization of the pump pulse was set to be at the magic angle (54.7°) relative to that of the probe pulse. In order to avoid the destruction of the sample, the cuvette, with an optical pathlength of 1 mm, was mounted on a linear translation stage with an appropriate speed. The full widths at half-maximum (FWHMs) of the pump and probe pulse cross-correlation at the samples were both around 100 fs. The multiplex TG signal of MeOH was also measured to calibrate the effect of the group velocity dispersion of the probe light in the present experiment by using the same method as presented previously.[45]

The absorption spectra were measured with a UV–vis spectrophotometer (720PC, Shanghai). The fluorescence spectra were recorded with an imaging spectrograph (Chromex 500IS/SM, Bruker) and CCD (DU440, Andor), by using a 400 nm femtosecond laser for excitation. Fluorescence lifetimes were measured by the time-correlated single photon counting (TCSPC, laser source BDL-375-SMC; detector ID-100-20; TCSPC module SPC-130, Germany) method with an excitation wavelength of 375 nm. The instrument response function (IRF) of the system was observed to be about 60 ps.

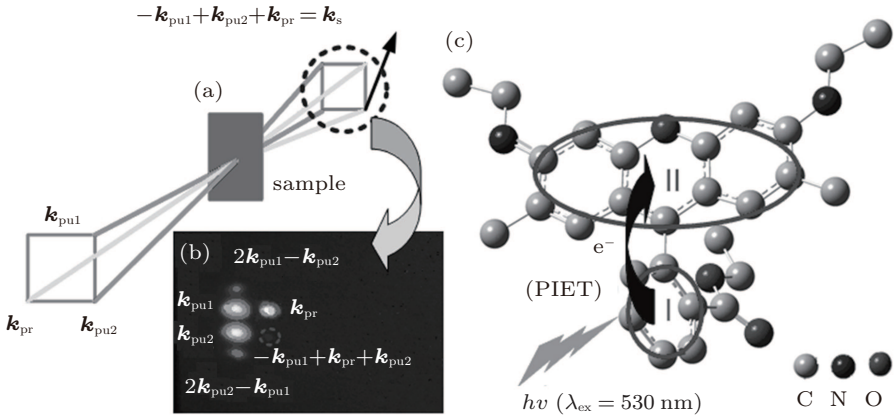


Fig. 1. The BOXCARS configuration (a) and real signal image (b) of the multiplex TG experiment. (c) Molecular structure of $Rh6G^+$ and schematic plot of PIET on the excited state potential energy surface after photo-excitation at 530 nm.

2.2. Materials

$Rh6G^+$ and dimethyl sulfoxide (DMSO) were purchased from Sigma–Aldrich. The chemical structure of $Rh6G^+$ and a schematic diagram of PIET on the excited state potential energy surface (vide post) are shown in Fig. 1(c). The solvent was directly used without further purification. The absorbance of the samples ($Rh6G^+$/DMSO) at 530 nm in a 1 mm pathlength cell was around 0.3. All experiments were carried out at room temperature.

3. Results and discussion

3.1. Steady-state measurements

Figure 2(a) shows the steady-state absorption and fluorescence spectra of the $Rh6G^+$/DMSO system. Symmetric Gaus-

sian functions are used to reproduce the spectra.[46] It can be clearly seen that these spectra are characterized by an absorption maximum centered at 540 nm and a vibronic shoulder band centered at 520 nm. The energy difference between the absorption maximum and vibronic shoulder band is around 675 cm^{-1}, which corresponds to an in-plane deformation of the xanthene ring.[4,47,48] The fluorescence of $Rh6G^+$ has a maximum centered at 568 nm and a shoulder at 596 nm, which can be ascribed to spontaneous emission of the first singlet excited state S_1 ($Rh6G^+$*) of $Rh6G^+$. The time-resolved fluorescence decay dynamics of $Rh6G^+$ in DMSO measured at 568 nm with an excitation wavelength of 375 nm is shown in Fig. 2(b). The fluorescence exhibits a single exponential decay with time constant $\tau = 4.34$ ns that can be assigned to the lifetime of the S_1 state of $Rh6G^+$. This assignment can also be confirmed by the fact that the time constants measured at other wavelengths (555 nm and 610 nm) in the fluorescence spectrum region are identical with that recorded at 568 nm.

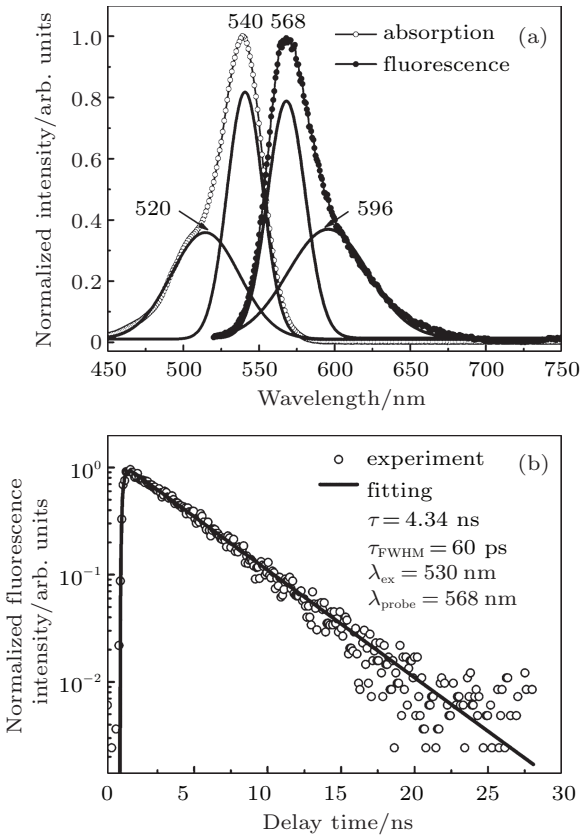


Fig. 2. (a) Steady-state absorption and fluorescence spectra of $Rh6G^+$ in DMSO. Symmetric Gaussian functions (solid lines) are used to reproduce the spectra. (b) Time-resolved fluorescence dynamics of $Rh6G^+$ in DMSO.

3.2. Multiplex TG measurements

As described in the introduction, PIET and IVR are important processes reflecting dynamic properties of the excited state of molecules. In order to further understand the electronic behaviors following photo-induced intramolecular electron transfer, it is very important to study the IVR process involved in many ultrafast photoreactions on an excited state potential energy surface.[2,7,11] TG is one of the four-wave mixing techniques, which are powerful tools for the study of ultrafast intramolecular dynamics.[43] The TG diffracted signals of the $Rh6G^+$/DMSO system are shown in Fig. 3. Figure 3(a) shows the diffraction spectra measured at various time delays. After a few hundred femtoseconds (so as to avoid any contribution of the optical Kerr effect to the signal), the square root of the TG diffracted intensity reflects the time evolution of the transient population.[35,36] The TG spectrum is composed of a peak centered at 568 nm and a shoulder localized at

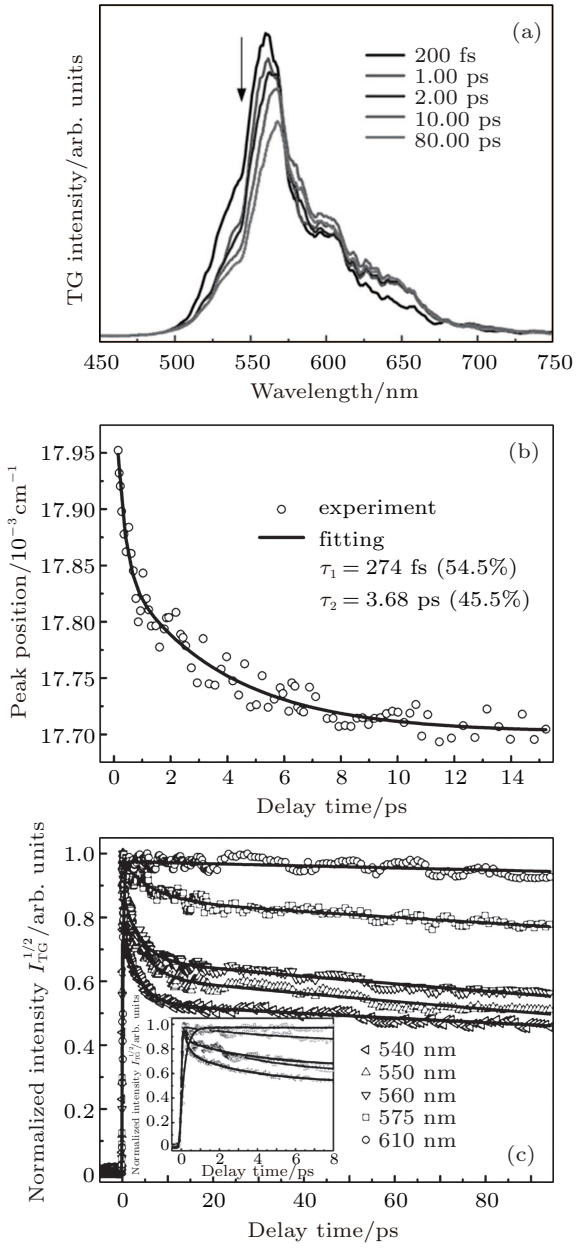


Fig. 3. (color online) (a) Representative TG signals of $Rh6G^+$ in DMSO. (b) Peak-shift of the diffracted spectra each with a central wavelength around 568 nm. (c) Time profiles of the square root of the diffracted intensity at different wavelengths.

610 nm, which are similar to those observed from the steady-state fluorescence spectrum, and is ascribed to the stimulated emission from the excited state S_1 ($Rh6G^+$*). It is clearly seen in Fig. 3(a) that the peak positions of the multiplex TG spectra are red-shifted significantly with increasing time delay. This can be ascribed to the structural change of $Rh6G^+$ introduced by PIET from the phenyl ring (I) to the xanthene plane (II) occurring on the excited state potential energy surface. The red-shift of the multiplex TG spectrum is shown in Fig. 3(b). The energy difference of the red-shift is about 250 cm^{-1}. The time evolution of the red-shift is characterized by a biexponential function with the time constants of 270 fs (54.5%) and 3.7 ps (45.5%). The biphasic dynamics originates from an interaction between the PIET and IVR processes. The fast component is attributed to PIET from the phenyl ring (I) to the xanthene plane (II), which leads to the formation of the intramolecular charge transfer (ICT) state,[22] while the slow component, with a lifetime of 3.7 ps, is ascribed to the excited-state IVR process. The time constant of IVR is in good agreement with previously reported values of 1.5 ps–4.9 ps obtained from the analysis of fluorescence up-conversion decay kinetics,[2,7,9,21] which cannot be observed in our TCSPC experiment, owing to the limitation of the experimental response function.

Figure 3(c) shows that TG intensity decay dynamics at different wavelengths can be reasonably reproduced with at least two exponential functions. The best-fit time constants and amplitudes are summarized in Table 1. It is notable that the dynamic behaviors below and above 568 nm present very distinct features. The dynamics in a wavelength range of 540 nm–560 nm, corresponding to the blue side of the fluorescence spectrum, has three different decay components: τ_1 = 140 fs–260 fs, τ_2 = 3.3 ps–3.9 ps, and τ_3 = 510 ps–680 ps. The ultrafast lifetime of 140 fs–260 fs is expected to be the time constant of ICT from the phenyl ring (I) to the xanthene plane (II) corresponding to the transition from the locally excited state to the ICT state. In previous investigations, it has been revealed theoretically and experimentally that the ultrafast PIET reaction occurs on a timescale as fast as 200 fs originating from charge transfer from the locally excited state to the ICT state, which is much faster than the diffusive solvation process,[18,19] and even considerably faster than the IVR processes of OX750 and coumarin chromophores.[18,19,49,50] The intermediate component, with a lifetime of 3.3 ps–3.9 ps, is attributed to the IVR process which follows the PIET process, and agrees well with the timescales reported previously.[2,7,11,12] The slowest component, with a time constant of 510 ps–680 ps, reflects the decay of the singlet excited state (S_1) of $Rh6G^+$. It should be noted that, within our experimental time window, this component is identical to the fluorescence lifetime occurring on a nanosecond timescale for $Rh6G^+$. However, the PIET process does not appear in the dynamics observed at 575 nm because the IVR and stimulated emission processes dominate the decay. Within the experimental uncertainty, a time of 5.2 ps should be assigned as the time constant of the IVR process, and the longer component corresponds to the fluorescence lifetime of the $Rh6G^+$. For the multiplex TG signal above 610 nm, the ultrafast rise time (250 fs) corresponds to the time constant of PIET from the locally excited state to the ICT state. In this wavelength range, the longest lifetime is close to the fluorescence lifetime, occurring on a nanosecond timescale for $Rh6G^+$.

Table 1. Values of best-fit time constant (τ) and amplitude obtained from the analysis of the TG intensity time profiles of the $Rh6G^+$/DMSO system.

Wavelength/nm	τ_1/fs	τ_2/ps	τ_3/ps
540	260 (26.9%)	3.3 (23.4%)	680 (49.7%)
550	180 (33.1%)	3.9 (23.6%)	610 (43.3%)
560	140 (27.1%)	3.8 (17.3%)	510 (55.6%)
575	–	5.2 (12.7%)	920 (82.3%)
610	250 (-Amp)	–	2950

The energy states and the kinetics of IVR following PIET for the $Rh6G^+$/DMSO system after photo-excitation at 530 nm are schematically shown in Fig. 4. First, the $Rh6G^+$/DMSO system is photo-excited to the locally excited state, which has an ultrashort lifetime, and then undergoes rapid PIET to the ICT state. Subsequently, this system relaxes to the lowest ICT state through IVR with a time constant in a range of 3.3 ps–5.2 ps. Finally, the system returns to the ground state (S_0) with a rate of $1/\tau$, where τ = 4.34 ns and is the fluorescence lifetime of $Rh6G^+$. In particular, the deactivation pathways at 575 nm are IVR and spontaneous emission without PIET. Thus, the PIET is found to be extremely fast with time constants in the range τ_{PIET} = 140 fs–260 fs. The PIET process leads to the formation of the ICT state, owing to charge transfer from the phenyl ring (I) to the xanthene plane (II) occurring on the potential energy surface of the first singlet excited state (S_1) of $Rh6G^+$. The deactivation of the excited vibrational state is much slower, with the time constant τ_{IVR} in a range of 3.3 ps–5.2 ps, which is attributed to the IVR process in the excited state. The longest lifetime (τ = 4.34 ns) corresponds to the steady-state fluorescence emission. The timescales of PIET and IVR processes obtained from the TG intensities are in good agreement with those resolved from the red-shift of the TG spectra. This confirms that the explanation of PIET and the IVR processes is reasonable.

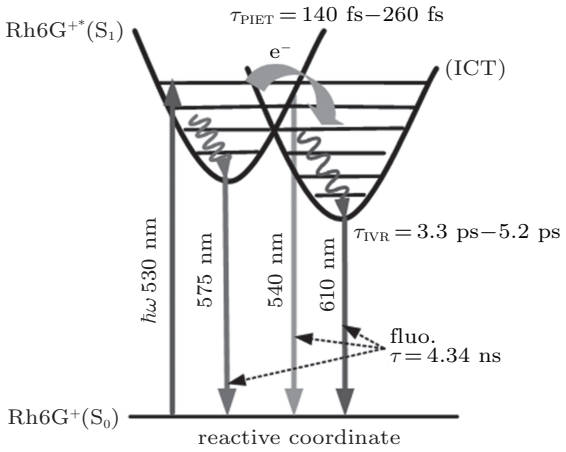


Fig. 4. (color online) Schematic diagram of the energy states and the kinetics of the Rh6G$^+$/DMSO system after photo-excitation at 530 nm.

4. Conclusion

In this paper, photo-induced intramolecular electron transfer (PIET) and intramolecular vibrational relaxation (IVR) of rhodamine 6G (Rh6G$^+$) in DMSO are investigated by multiplex transient grating spectroscopy. The results indicate that the excited state of Rh6G$^+$ has two deactivation pathways. One pathway is IVR and spontaneous emission with PIET, and the other is a similar process but without PIET. PIET originating from intramolecular charge transfer from the phenyl ring (I) to the xanthene plane (II) on the first singlet excited state (S_1) of Rh6G$^+$ takes place on a timescale $\tau_{\rm PIET}$ in a range of 140 fs–260 fs. The IVR following PIET is much slower, with time constant $\tau_{\rm IVR}$ in a range of 3.3 ps–5.2 ps. The longest time constant ($\tau = 4.34$ ns), obtained by the TCSPC experiment, corresponds to the lifetime of the spontaneous emission of Rh6G$^+$. The timescales achieved from multiplex TG intensities are consistent with those observed from the red-shifts of the multiplex TG spectra. The timescales of IVR and PIET taking place in the excited state of Rh6G$^+$ are quantitatively determined, and therefore the relationship between the PIET and IVR processes is clearly revealed. This work sheds light on the design of the molecular structures or solvent environments to enhance special electron-transfer pathways for application in photovoltaic devices.

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