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Spectrum Correction in Study of Solvation Dynamics by Fluorescence Non-collinear Optical Parametric Amplification Spectroscopy†

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Femtosecond time-resolved fluorescence non-collinear optical parametric amplification spectroscopy can extract the curve of spectral gain from its parametric superfluorescence. This unique spectrum correction method enables fluorescence non-collinear optical parametric amplification spectroscopy acquiring the genuine transient fluorescence spectrum of the studied system. In this work we employ fluorescence non-collinear optical parametric amplification spectroscopy technique to study the solvation dynamics of DCM dye in ethanol solution, and confirm that genuine solvation correlation function and shift of peak frequency can be derived from transient fluorescence spectra after the spectral gain correction. It demonstrates that fluorescence non-collinear optical parametric amplification spectroscopy can benefit the research fields, which focuses on both fluorescence intensity dynamics and fluorescence spectral shape evolution.

Key words: Transient fluorescence spectrum, Solvation dynamics, Non-collinear optical parametric amplification, Spectrum correction

I. INTRODUCTION

Time-resolved fluorescence spectroscopy is one of most popular tools in the fields of chemistry, biology, and physics. The time resolution of fluorescence spectroscopy is determined by its gate duration. To achieve a subpicosecond time resolution, the gate of spectroscopy should be implemented by nonlinear optical processes, including optical kerr effect, sum-frequency generation, and optical parametric amplification. The corresponding time-resolved fluorescence spectroscopy are fluorescence kerr-gating technique [1], fluorescence up conversion technique [2] and fluorescence non-collinear optical parametric amplification spectroscopy (FNOPAS) [3], respectively. The main advantage of fluorescence kerr-gating technique is broadband operation, but the time resolution is usually beyond one picosecond due to its slow response of kerr medium [4]. The time resolution of fluorescence up conversion technique is determined by the laser pulse duration, and can usually reach up to 100 fs, even higher. The spectrum coverage of this technique is limited by the acceptance bandwidth of sum-frequency mixing between fluorescence beam and gate pulse. Typically, the value of spectrum coverage is 10−20 nm in the condition of collinear sum-frequency [5]. Thus broadband operation of fluorescence up conversion technique resorts to the continuous rotation of nonlinear optical crystal [6], which makes the procedure of measurement very complex. FNOPAS can obtain a comparable time resolution with that of fluorescence up conversion technique. It gates fluorescence photons and amplifies them in energy by a non-collinear optical parametric amplification process, which can support a broadband phase match [7]. The gain bandwidth of 2500 cm^{-1} has been reported by means of a β-barium borate (BBO) crystal of 2 mm thickness [8]. Another advantage of FNOPAS is its intrinsic curve of spectral gain, which can be calculated from the spectrum of parametric superfluorescence. These outstanding properties of FNOPAS are favorable to the research fields, where spectral shape evolution is required, *i.e.* solvation dynamics [9].

In this work, FNOPAS was employed to study the solvation dynamics of DCM dye in ethanol solution. Transient fluorescence spectra of high quality were acquired for further analyses of solvation dynamics. The shift of peak frequency and solvation correlation function, derived from transient fluorescence spectra after spectral gain correction, were compared with those from uncorrected transient fluorescence spectra. Results show that the intrinsic curve of spectral gain can assist FNOPAS to probe genuine information of solvation dynamics.

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II. EXPERIMENTS

The DCM ethanol solution (0.3 mmol/L) was excited by the second harmonic generation of the fundamental beam from a Ti:sapphire femtosecond laser. The fluorescence photons from the DCM solution were gated and amplified in energy by another second harmonic beam in a BBO crystal of 2 mm thickness. Transient fluorescence spectra of DCM solution were recorded by a CCD spectrograph. The setup of FNOPAS is schematically presented in Fig.S1 (in supplementary materials).

For the FNOPAS technique, its curve of spectral gain can be expressed as a function of wavelength $G(\lambda;\alpha,\theta)$, where α is the angle between the second harmonic gate beam and the fluorescence beam in the BBO crystal, and θ is the angle between the second harmonic gate beam and the optical axis direction of the BBO crystal [8]. During the measurement, the θ should be adjusted carefully by rotating the BBO crystal till obtaining an optimum parametric superfluorescence generation. Here the optimum parametric superfluorescence satisfies two preconditions. First, its spectrum should be broad enough to cover the steady fluorescence spectrum of DCM. Second, its spectral peak should be close to that of steady fluorescence spectrum of DCM. The parametric superfluorescence can be regarded as the stimulated parametric amplification seeded by the quantum noise [10].

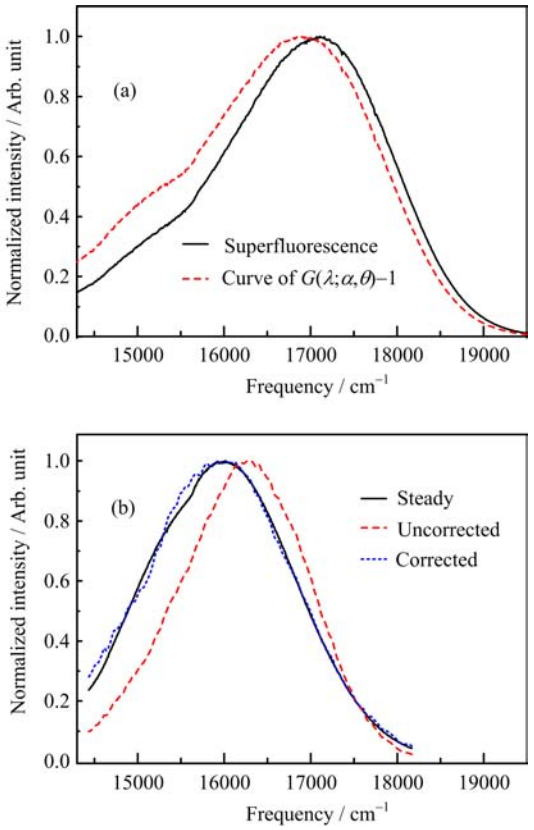

FIG. 1 (a) Normalized spectrum of parametric superfluorescence and normalized curve of $(G(\lambda;\alpha,\theta)-1)$. (b) Comparisons between the DCM molecule steady fluorescence spectrum, corrected and uncorrected transient fluorescence spectrum at time delay of 36 ps.

III. RESULTS AND DISCUSSION

It is well known that the parametric superfluorescence always accompanies the amplification of fluorescence photons. When they undergo the same angle α, *i.e.*, the same exiting direction with respect to the second harmonic gate beam, they would share the same curve of spectral gain $G(\lambda;\alpha,\theta)$.

The spectrum of parametric superfluorescence can be written in the form

$$\varphi_{\rm sp}(\lambda;\alpha,\theta)=\varphi_{\rm zp}(\lambda)[G(\lambda;\alpha,\theta))-1] \qquad (1)$$

where $\varphi_{\rm zp}(\lambda)$ is the equivalent noise spectrum due to the zero-point fluctuations, and its power can be treated as $h\nu{\rm d}\nu$ in the bandwidth dν, or $(hc^2/\lambda^3){\rm d}\lambda$ in the bandwidth dλ. According to the Eq.(1), the curve of spectral gain $G(\lambda;\alpha,\theta)$ can be calculated with known spectrum of parametric superfluorescence. We measured the spectrum of the parametric superfluorescence (Fig.1(a)), which shares the same curve of spectral gain $G(\lambda;\alpha,\theta)$ with that of DCM fluorescence, and calculated the curve of $G(\lambda;\alpha,\theta)-1$ (Fig.1(a)). From the curve of $G(\lambda;\alpha,\theta)-1$, we can know that the setup of FNOPAS provides the max gain at about 16782 cm^{-1} and bandwidth (full width half maximum) 2700 cm^{-1} .

Using the curve $G(\lambda;\alpha,\theta)-1$, we corrected transient fluorescence spectra of DCM ethanol solution. The validity of this spectrum correction is confirmed by the comparability of transient fluorescence spectrum at the time delay of 36 ps with the steady fluorescence spectrum (Fig.1(b)). The solvation lifetime of DCM ethanol solution has been reported as about 10 ps [11]. It is reasonable to believe that transient fluorescence spectrum at 36 ps does not suffer from the solvation process, and generally resembles the steady fluorescence spectrum of DCM. As shown in Fig.1(b), after the spectral gain correction, transient fluorescence spectrum at 36 ps displays good agreements with the steady spectrum in both spectral shape and peak frequency. This proves that our spectrum correction is valid. For the uncorrected transient fluorescence spectrum, its spectral shape is also similar to that of steady fluorescence spectrum, while the peak frequency has an about 340 cm^{-1} blue shift.

Solvation is defined as the response of surrounding solvent molecules to an instantaneous perturbation on the solute molecule. After the solute molecule is excited, a dynamic stokes shift occurs to its transient fluorescence spectra. The magnitude and rate of stokes shift are related with characteristics of the solvent, and can be described by a solvation correlation function

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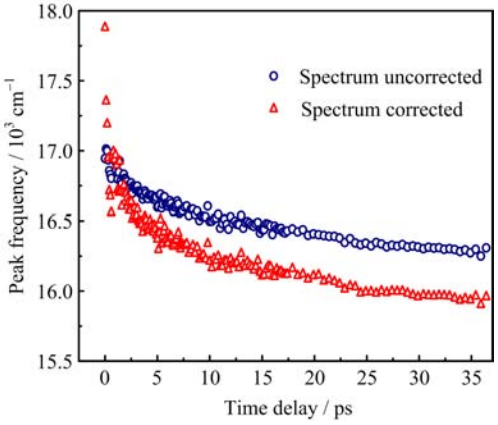

FIG. 2 Solvation induced dynamic Stokes shift obtained from transient fluorescence spectra with spectrum correction and without spectrum correction, respectively.

$C(t)$ [12].

$$t = \nu t - \nu(\infty)\nu_0 - \nu(\infty) \tag{2}$$

where $\nu(t)$ is the peak frequency (cm^{-1}) of transient fluorescence spectrum at time delay t. The $\nu(t)$ is available from time-resolved fluorescence spectra, then $C(t)$ can be constructed.

After spectral gain correction, the transient fluorescence spectra do not display standard Gaussian line shapes, but asymmetric. In order to quantify their peak frequencies $\nu(t)$, a log-normal function is used to fit the transient fluorescence spectra after spectral gain correction [13], as shown in Fig.S2 (in supplementary materials). The shifts of peak frequency $\nu(t)$, being derived from the corrected and uncorrected transient fluorescence spectra, respectively, are compared in Fig.2. In the case of spectral gain correction, the shift of peak frequency is more notable, which starts from about 17880 cm^{-1}, and reaches 15960 cm^{-1}. Whereas for the uncorrected transient fluorescence spectra, their peak frequencies are in the range of 17000−16250 cm^{-1}. The obvious mismatch between these two cases results from spectral gain correction. After the excitation of DCM, transient fluorescence spectra overlap with the higher frequency part of the curve $G(\lambda;\alpha,\theta)-1$ (Fig.1(a)) at first, and move to the lower frequency part of the curve $G(\lambda;\alpha,\theta)-1$ in the end. Consequently, the scope of peak frequency shift is enlarged by the spectral gain correction. The decay of peak frequency is faster in the first 10 ps (Fig.2) for the corrected transient fluorescence spectra. Afterwards, decay rates of peak frequency are nearly the same for the transient fluorescence spectra in both cases. According to the Eq.(2), we calculated the solvation correlation function $C(t)$ for both cases, and fit them with a double exponential decay model. The fitting parameters are listed in Table I.

According to the parameters in Table I, we can conclude that solvation correlation function, calculated from the transient fluorescence spectra without spectral gain correction, has a slower decay. For the corrected transient fluorescence spectra, lifetime constants of solvation correlation function are generally consistent with the reported values (0.47 and 10.2 ps) in Ding's work [11]. In Ding's work, transient fluorescence spectra of DCM were also acquired by FNOPAS technique, but without spectral gain correction. For their setup of FNOPAS, the curve of spectral gain might be relatively flat in the range of DCM fluorescence spectrum, which gives rise to a genuine solvation correlation function. Herein, we calculated the total shift of peak frequency, which is about 1900 cm^{-1} and larger than their reported value (1050 cm^{-1}) [11]. This discrepancy is probably induced by different methods of data processing.

TABLE I Fitting parameters of solvation correlation function $C(t)$.

Case	a_1/ps	τ_1/ps	a_2/ps	τ_2/ps	Total shift[a]/cm^{-1}
Corrected	0.55	0.15	0.45	9.7	1900
Uncorrected	0.22	1.8	0.78	14.9	690

[a] The total shift is calculated by the difference between $\nu(0)$ and $\nu(\infty)$. In the case of corrected spectra, the $\nu(\infty)$ is 15975 cm^{-1}, calculated from the fitting of steady-state fluorescence spectrum by the log-normal function. In the case of uncorrected spectra, the $\nu(\infty)$ is 16250 cm^{-1}, calculated from the fitting of the transient fluorescence spectrum (36 ps) by the log-normal function.

IV. CONCLUSION

Solvation dynamics of DCM ethanol solution was studied by fluorescence non-collinear optical parametric amplification spectroscopy technique. Transient fluorescence spectra of DCM were corrected with the intrinsic curve of spectral gain. Furthermore, the genuine shift of peak frequency and solvation correlation function were extracted from the transient fluorescence spectra after spectral gain correction. For FNOPAS, the curve of spectral gain can be derived from the spectrum of parametric superfluorescence. This intrinsic curve of spectral gain is favorable to obtain the genuine transient fluorescence spectrum of the studied system, and benefits the study of solvation dynamics.

Supplementary materials: Spectrum correction in the study of solvation dynamics by fluorescence non-collinear optical parametric amplification spectroscopy is given.

V. ACKNOWLEDGMENTS

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