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Ultra-fast dynamics in Coumarin 153 obtained by differential fluorescence

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Abstract

We present measurements of the molecular rotational diffusion dynamics in the picosecond scale in a Coumarin 153 ethylene-glycol solution. A novel technique is used in which the fluorescent sample is excited with two femtosecond laser pulses in a pump and probe scheme. The spatial anisotropy generated by the first pulse excitation is sampled as a function of delay time through the fluorescence produced by the delayed pulse. The rotational time is obtained from the change in the fluorescence produced as a function of the delay time.

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1. Introduction

The study of molecular rotational dynamics is an active research area that provides useful information to understand the basis of the physical interactions between a molecule and the media in which it is immersed. These studies provide new insight in many aspects for example to get a better understanding of the chemical reactivity in the condensed phase at the molecular level [1]. Absorption and emission spectroscopies are also commonly used to study this dynamics and are performed mainly in pump and probe schemes with different experimental setups. With the advent of ultra-short laser pulses, time-resolved studies of these interactions became possible through the development of fast measurement techniques that allow resolution in the order of tens of femtoseconds. Among them we can mention two techniques that had proved to give very good time resolution: anisotropic absorption [2–4] and fluorescence up conversion [5]. In the first method the sample is excited with a pump and probe scheme. The first pulse is linearly polarized and modifies the distribution of molecules in the ground state.

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The absorption of the second pulse is measured as a function of the delay time between pulses. Time resolved absorption had proved a great versatility and is used in different applications such as diffusion movement, optical bleaching [6], photo-dissociation, charge transfer [7,8] including electron transfer, surface electron transfer and proton transfer. In the up-conversion technique an ultrashort pulse is used to excite the sample, then the fluorescence produced is collected and focused in a non-linear crystal where a cross-correlation with the excitation pulse is used to obtain time-resolved fluorescence anisotropy with subpicosecond resolution. It has been used in a variety of chemical dynamics studies in particular those related with solvation dynamics [1], rotational diffusion and electron transfer [1].

In recent papers [9,10] we presented a new method to obtain this dynamic information. This new technique allows the measurement of rotational diffusion times based on the study of the fluorescence produced when two linearly polarized laser pulses excite a fluorescent sample. This new method is a correlation technique and the information is obtained from the total time-integrated fluorescence signal. In consequence no high temporal resolution detection is needed. The experimental setup is a conventional pump and probe scheme with equal intensity in both arms. After the first pulse excites the sample, it induces a non-homogeneous spatial distribution in the population of excited molecules. This effect is produced by the anisotropy introduced in the ensemble of absorbing molecules by the electric field of the light and can be followed in its temporal evolution analyzing the fluorescence signal. After a certain delay, a second identical pulse interacts with the sample. This interaction occurs when some molecules are still in the excited state. Under this condition, the second excitation pulse finds a non-homogeneous spatial distribution of ground state absorbing molecules. Then, the induced anisotropy changes the total fluorescence produced by the double pulse excitation.

We measure this anisotropy with a new parameter defined as "differential fluorescence" [9, 10], obtained as the difference between the total fluorescence signal produced by the double pulse excitation and twice the fluorescence obtained only with the first excitation pulse. The analysis of the differential fluorescence as a function of the delay time between pulses allows the calculation of the molecular rotational times.

Recently we measured rotational diffusion times in a rhodamine 101 ethylene-glycol solution applying this technique [11], using a 500 ps dye laser to excite the sample, and we obtained results in the nanosecond time scale. In the present work we show results with better temporal resolution extending the method to the picosecond scale.

2. Differential fluorescence for oblate molecules

The detailed calculation to obtain the analytical expression for the differential fluorescence was published in previous papers [9–11] and will not be reviewed here. We assume that the sample is a diluted solution of fluorescent molecules interacting only with the surrounding solvent and this interaction is considered using the diffusing tensor in the equations. This approach means that the interaction between fluorescent molecules is considered negligible and that the solvent is considered as a continuum medium.

We assume that the absorbing molecules have a defined dipole moment interacting with the electric field of the incident light beam. The laser pulse excites the molecules, they can rotate and decay by fluorescence. To describe these processes we solved a diffusion equation including the fluorescence decay. This equation gives the orientation distribution of excited molecules as a function of time and determines the initial condition of the sample for the second pulse allowing the calculation of the fluorescence signal.

The differential fluorescence is calculated as the difference between the total fluorescence signal at different delay times and that fluorescence produced when the delay time is infinite. In the first situation the second pulse evaluates the anisotropy induced by the first pulse and this difference is compared with the case when both pulses find a non-disturbed sample (delay infinite). From this difference it is possible to calculate the characteristic rotational diffusion time.

In the case of oblate molecules, there are two different times ϕ_1 and ϕ_2, corresponding to the rotations around the two principal axis of the molecule. The de-excitation by fluorescence relaxation is also included in the diffusion equation giving the following expression for the differential fluorescence signal [11]

$$E_d = A\exp\left(-\frac{t_0}{\tau}\right)\left(B + C\exp\left(-\frac{t_0}{\phi_1}\right) + D\exp\left(-\frac{t_0}{\phi_2}\right)\right) \quad (1)$$

In this expression A is a constant that depends on the pulse energy and the initial population of fluorophores, B, C and D are geometrical constants, t_0 is the delay time between pulses, and τ is the fluorescence time.

3. Experiment and results

The sample used for the experimental test was Coumarin 153. This molecule can be considered as an oblate ellipsoid with axis of 2, 4.8 and 6.1 μm [5].

We used the second harmonic beam of a mode-locked Ti:sapphire laser (Mira 900 – coherent) to excite a diluted solution of Coumarin 153 (exciton) in ethylene glycol.

Fig. 1 shows the setup used in the experiment. The laser pulses are centered at 400 nm with a repetition rate of 76 MHz and a pulse width of 200 fs. A special effort was dedicated in the second harmonic system to control the divergence at the output. We used a telescope with two plane-convex lens (Newport SPX) with $f = 5$ cm combined with a LBO crystal 1.5 mm thick. With this scheme we obtained 300 mW (28% efficiency) at 400 nm.

The pulse is divided in two branches of similar energy in a Michelson scheme, where a controlled delay is introduced. The average power in each excitation beam is 20 mW. The delay line is implemented with an optical rail that assures accuracy in the lateral alignment better than 0.3 μm when the branch length is changed in 30 cm. At the

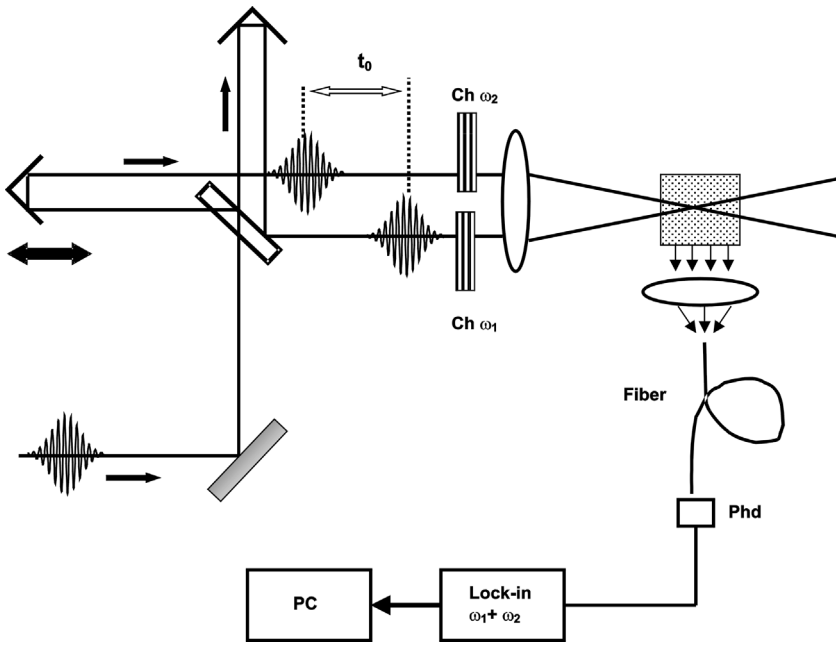

Fig. 1. Experimental setup, the two branches are chopped at frequencies ω_1 and ω_2 respectively. Fluorescence is collected through an optical fiber for spatial filtering. The excitation pulse is 200 fs Ti:sapphire laser at second harmonic. Ch_{ω_2}: chopper at ω_2 frequency, Ch_{ω_1}: chopper at ω_1 frequency, Phd: photodiode, PC: personal computer.

end of this delay line we used hollow retro-reflectors 1 in. in diameter with a tolerance of 1″.

The differential fluorescence signal expected represents a change less than 0.1% of the total fluorescence emitted by the sample when the two exciting pulses interact with the same volume. Consequently, it is very critical that the volumes excited by the first and second pulse coincide. This fact makes necessary a rigorous control of the beam divergence to assure that a change in the divergence of the beam would not produce a change in the excited volume after the focusing lens when the delay branch is changed.

To check the variation of the beam characteristics (divergence and alignment) for different delays, we measured the position and the waist diameter of the beam before the lens used to focus in the sample. The measurement was made with a CCD (Coherent-Cohu 48). With this system we measured, for delays between 0 and 1 ns, a maximum variation in the waist size of 1.5% and no measurable variation position of the center of the spot.

After the line delay the two beams are focused in the sample with a 7.5 cm focal length lens, assuring a variation in the superposition volume $\Delta V/V < 10^{-5}$.

The total fluorescence produced after the double excitation is collected at 90° from the excitation beam direction through an optical fiber to spatially filter the signal and assure that the light gathered corresponds only to the small volume where the two pulses coincide.

A slow photodiode is used to measure the fluorescence energy as a function of the delay between pulses, so the fluorescence is integrated for each double pulse excitation. The total fluorescence intensity is measured as a function of the delay time. From these data we then obtain the differential fluorescence signal (E_d). After fitting the experimental results we derived the rotation diffusion time.

As we showed in Refs. [6,7] the fraction of excited molecules after the excitation is a critical parameter of this measurement, since the maximum value obtained for E_d is proportional to this magnitude. In our case, we focused the beam to 100 μm with excitation energy of 200 pJ and a peak power of 10 MW/cm^2. With these parameters we calculate a fraction of excited molecules of 10^{-4}. This small fraction of excited molecules produces a weak differential signal and makes necessary the use of a lock-in amplifier before the photodiode. We modulate the pump at a frequency ω_1 (720 Hz) and the probe beam at a frequency ω_2 (600 Hz), and we measured the component of the fluorescence at the frequency $\omega_1 + \omega_2$. We integrated the total fluorescence produced during a time equal to the repetition rate of the excitation laser, 13 ns in our system.

In the experiment we used a solution of Coumarin 153 (exciton) and ethylene glycol. We tested the sample measuring the absorption spectrum and obtained the maximum absorption at 440 nm and a value of 0.05 for the absorbance. A circulation system was connected to the cell to refresh with new solution the excited zone and the fluorescence energy was measured. With these precautions, for typical measuring times, we observed a constant signal assuring that the sample is not degrading.

We measured the total fluorescence $E_{tot}(t_0)$ (modulated at $\omega_1 + \omega_2$) and the fluorescence produced with the probe pulse $E_2(t_0)$ (modulated at ω_2). Then we calculated the differential energy at this delay with the following expression:

$$E_d(t_0) = -\frac{E_{tot}(t_0)}{E_2(t_0)} + \frac{E_{tot}(t_0 = \infty)}{E_2(t_0 = \infty)} \tag{2}$$

$E_d(t_0)$ is obtained as the difference between the total fluorescence with long delay ($t_0 = \infty$) and total difference with a fixed delay (t_0). Both terms are normalized to the second pulse signal E_2 to compensate changes in the total fluorescence produced by laser fluctuations or small variations in the dimension of the excited volume.

A typical signal acquired with this setup is shown in Fig. 2. The plot corresponds to the differential fluorescence energy (E_d) obtained as a function of the delay time between pulses. The maximum value for E_d occurs for small delays when the photoinduced anisotropy produced by the first pulse is higher. At large delays, when the rotational diffusion process homogenizes the sample, this difference drops to zero.

The experimental data points show a decrement in the signal as the delay between pulses increase as

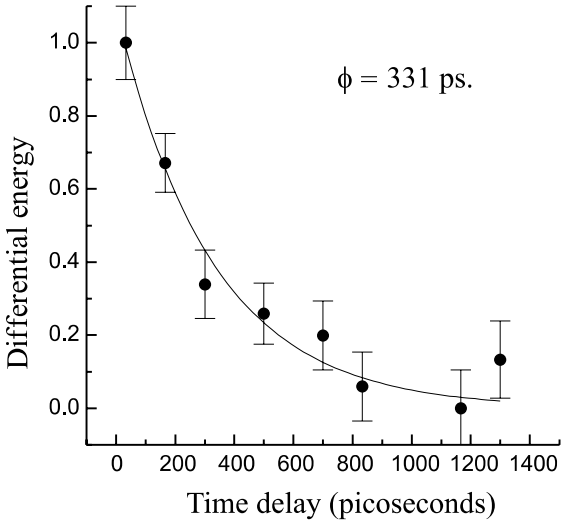

Fig. 2. Experimental results: differential fluorescence energy as a function of time delay between pulses. The exponential fit corresponds to a rotational diffusion time Φ_a of 331 ps.

expected. The data can be fitted with a mono-exponential decay with a typical time $\phi_a = 331$ ps. This value is obtained with the best fit to the data points shown in Fig. 2 and corresponds to a $\chi^2 = 5 \times 10^{-3}$. The typical dispersion obtained in the value ϕ_a when we repeat the measurement in the same experimental conditions is 30%. In consequence, we assume this criterion to determine an estimation of the ϕ_a error.

As stated by Horng et al. [5], Coumarine 153 presents a bi-exponential decay in some solvents like ethylene glycol. In this work they measured, using frequency up-conversion, a combined decay time $\phi_a = a_1\phi_1 + a_2\phi_2$, with parameters $\phi_1 = 44$ ps, $a_1 = 0.055$, $\phi_2 = 880$ ps and $a_2 = 0.945$. The two components of this bi-exponential decay may not have particular significance because the parameters a_1 and a_2 are related through $a_1 = (1 - a_2)$. However, as concluded in Ref. [5], it is preferable to use as a measure of the rotation time this combined decay time ϕ_a whose value is close to the value we obtained in our experiment. The measurement performed in Ref. [5] gives a combined decay time $\phi_a = 398$ ps which is in good agreement with the decay $\phi_a = 331 \pm 50$ ps observed in our experiment.

4. Conclusions

We presented experimental evidence showing that the differential fluorescence energy technique can be used in the picosecond time scale to evaluate molecular rotational diffusion times. The small change in the fluorescence produced when the sample is illuminated with two excitation pulses as the delay between pulses is changed produces a signal that we associate with a combined rotational diffusion time decay. This decay time is in good agreement with measurements made with an independent method in the same sample using the same excitation laser. These results show that the differential fluorescence technique is an alternative correlation method capable to achieve picosecond temporal resolution.

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References

[1] J. Simon (Ed.), Ultrafast Dynamics of Chemical Systems, Kluwer, Dordretcht, 1994.
[2] A. Kawski, Critical reviews in analytical chemistry, Fluorescence Anisotropy 23 (6) (1993) 459–529.
[3] D. Waldeck, A.J. Cross Jr., D.B. McDonald, G.R. Fleming, J. Chem. Phys. 74 (6) (1981) 3381–3387.
[4] D.S. Alavi, R.S. Hartman, D.H. Waldeck, J. Chem. Phys. 92 (7) (1990) 4055–4066.
[5] M. Horng, J. Gardecki, M. Maroncelli, J. Phys. Chem. A 101 (1997) 1030–1047.
[6] R.A. Engh, J.W. Petrich, G.R. Fleming, J. Phys. Chem. 89 (1985) 618.
[7] P.F. Barbara, G.C. Walker, T.P. Smith, Science 256 (1992) 975.
[8] M. Marroncelli, J. MacInnis, G.R. Fleming, Science 243 (1989) 1674.
[9] J. Torga, J. Etcheverry, M. Marconi, Opt. Commun. 143 (1997) 230–234.
[10] J. Torga, J. Etcheverry, M. Marconi, Proc. Int. Conf. Laser 96 (1996) 252–255.
[11] J. Torga, M. Marconi, M. Negri, P. Aramendia, Chem. Phys. 253 (2000) 249–257.