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Picosecond Polarization Grating Study of the Effect of Excess Excitation Energy on the Rotational Dynamics of Rhodamine 6G in Different Electronic States

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The effect of excess excitation energy on the rotational dynamics of rhodamine 6G in the ground and the first singlet excited state has been investigated in series of *n*-alcohols and alkanenitriles using the picosecond polarization grating technique. In nitriles, the reorientation times are the same for excitation at the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions, and no state dependence could be detected. In alcohols, the rotational dynamics of rhodamine 6G in the excited state is about 25% faster when formed with 1.15 eV excess excitation energy. This effect is ascribed to a decrease of the hydrodynamic volume due to dissociation of solute/solvent hydrogen bond following intramolecular vibrational redistribution. An accompanying perturbation of the solvent shell structure caused by the fast local temperature jump is not excluded.

Introduction

The role of the solvent in a chemical reaction can be of primary importance. It is well-known that many exergonic reactions taking place in condensed phase do not occur in the gas phase due to the lack of energy dissipation channels. For a better understanding of chemical reactions in condensed phase, it is therefore important to know the dynamics and the pathways of heat dissipation. In the case of photoinduced processes, there has been several discussions on whether or not the energy released in a nonradiative deactivation could cause a transient local heating, large and long enough to influence substantially the local properties of the environment. Experimental results have lead to contradictory conclusions. Using polarized phase fluorescence spectroscopy, Heiss et al. have determined the rotational diffusion time of rhodamine 6G and perylene in high-viscosity alcohols as a function of the excitation energy.¹ The rotational time of both molecules was found to decrease substantially as the excess vibrational energy was increased. This effect was attributed to a local heating lasting long enough to influence the rotational dynamics in the nanosecond range. In another investigation, Labhart and Pantke measured the rotational diffusion time of four aromatic hydrocarbons in ethanol using steady state polarized fluorescence spectroscopy by exciting the molecules in the first and second singlet excited states, putting in the latter case excess energy ranging from 0.9 to 2 eV.² An effect was only observed for the hydrocarbons with the higher excess energy. However, this was attributed to a different effective volume of rotation when exciting the $S_1 \leftarrow S_0$ or the $S_2 \leftarrow S_0$ transitions. Using a classical model of thermal diffusion, the authors concluded that the duration of a local heating was too short to observe an effect on the time scale of rotational diffusion. This conclusion has been recently reinforced by femtosecond IR spectroscopy measurement carried out by Hochstrasser and co-workers,³ where the 1800 cm^{-1} region of D_2O (the solvent) vibration spectrum was monitored after excitation of malachite green. Occurrence of local heating has also been searched for by investigating the excitation frequency dependence of the fluorescence spectra of dipolar molecules (1-naphthylamine and 4-aminophthalimide) in polar rigid matrices (DMF, ethanol).⁴ In an aprotic matrix (DMF), no excitation energy dependence could be detected. In a protic

matrix (ethanol), however, a red shift of the fluorescence maxima of both molecules was observed as the excitation frequency was increased. It was concluded that the effect of excess excitation energy on the environment of a solute was a rearrangement of the solvent shell, taking place with hydrogen-bonding systems only.

We report here on an investigation of the rotational dynamics of rhodamine 6G (R6G) in the ground state and in the first excited singlet state formed by direct excitation ($\lambda_{\text{ex}} = 532 \text{ nm}$) and by radiationless decay from the S_2 state generated by excitation at 355 nm. This system is studied in series of *n*-alcohols and *n*-alkanenitriles of increasing viscosity using the transient polarization grating technique.

The principles and advantages of this method have been described in detail by Myers and Hochstrasser⁵ and are summarized only briefly. Polarization gratings are produced by the interference of two fields linearly polarized at 0 and 90°, respectively. The light intensity remains constant throughout the overlap region, and therefore absorption by the sample will also be uniform and no population grating is formed. However, the polarization of the field is spatially modulated (see Figure 1A), and this polarization grating can be decomposed into four intensity gratings as shown by Fayer and co-workers.⁶ Two of these gratings have circular polarization and are not relevant for molecular reorientation studies. The other two intensity gratings have linear polarization at -45° and $+45^\circ$, respectively, and are π radian out of phase (see Figure 1B). A probe beam polarized at 0° can be decomposed into two components polarized at -45° and $+45^\circ$, respectively (see Figure 1C). Each of these components probes one of the two intensity gratings. As the intensity gratings are π radian out of phase, the relative phase of the two components in the diffracted signal will experience a π radian phase shift. Therefore, the polarization of the diffracted signal is rotated by 90° relative to the probe beam. The decay of a polarization grating is due to reorientation and to population relaxation, and the time dependence of the diffracted intensity, I_d , has the following functional form:

$$I_d(t) = I_d(0) \exp[-2(\tau_r^{-1} + \tau_{\text{ex}}^{-1})t] \quad (1)$$

where τ_r is the rotational diffusion time and τ_{ex} the excited state lifetime. This technique is very sensitive and has a very high signal-to-noise ratio, but the anisotropy at time zero, r_0 , cannot be obtained. The latter can be determined from a more

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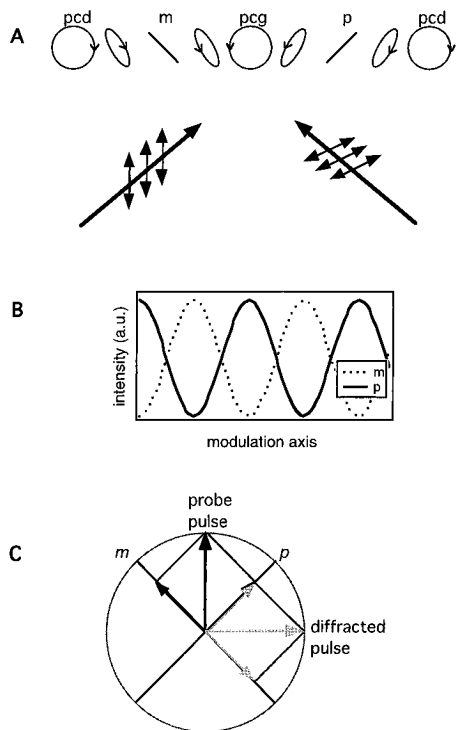


Figure 1. Principles of the polarization grating technique: (A) spatial dependence of electric field for one fringe of a linear polarization grating; (B) spatial dependence of electric field with linear polarization at -45° (m) and 45° (p); (C) probing of a polarization grating with linearly polarized light.

conventional transient grating method, where both pump pulses have parallel polarization, the probe beam being polarized at 45° , and the parallel and perpendicular components of the diffracted beam are measured separately.⁷

$$r(t) = \frac{[I_d^{\parallel}(t)]^{1/2} - [I_d^{\perp}(t)]^{1/2}}{[I_d^{\parallel}(t)]^{1/2} + 2[I_d^{\perp}(t)]^{1/2}} = r_0 \exp\left(-\frac{t}{\tau_r}\right) \quad (2)$$

where r is the anisotropy, $I_d^{\parallel}(t)$ and $I_d^{\perp}(t)$ the parallel and perpendicular components of the diffracted intensity. The excited lifetime can be obtained from $[I_d^{\parallel}(t)]^{1/2} + 2[I_d^{\perp}(t)]^{1/2} = I_0 \exp(-t/\tau_{ex})$. The use of this method requires the normalisation of the intensity of the time profiles recorded in the two measurements, which is not always straightforward and can be a serious source of error.

Experimental Section

Apparatus. The picosecond transient grating setup has been described in detail elsewhere.⁸ It is based on a active/passive mode-locked Q-switched Nd:YAG laser (Continuum model PY61-10), generating pulses of 30 ps duration at 10 Hz. The configuration of the beams on the sample is depicted in Figure 2. The two pump pulses at either 532 nm ($S_1 \leftarrow S_0$ excitation) or 355 nm ($S_2 \leftarrow S_0$ excitation) were crossed on the sample with an angle of incidence of 1° . The resulting polarization gratings were probed with the light obtained by Raman shifting the 532 nm pulse in benzene. The ensuing output contained light at 532, 562, 595, and 632 nm and was focused on the sample with an angle of incidence of 1.6° . Each wavelength component of the probe pulse was Bragg diffracted at different angles. The diffracted pulse at a wavelength corresponding to the absorption of the state investigated was spatially and spectrally separated from the others and directed to an analyser and to the detector. The polarization of the pump and probe

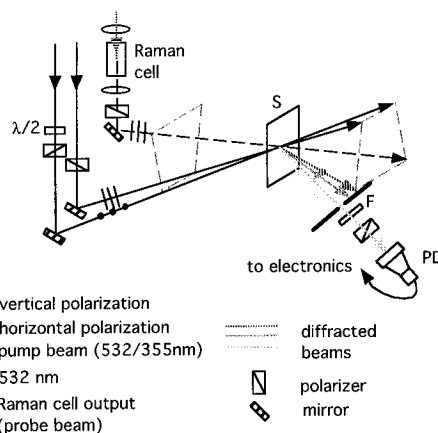


Figure 2. Experimental arrangement for the polarization grating measurements.

TABLE 1: Parameters of the Four Types of Experiments Performed^a

experiment	λ_{pump} (nm)	λ_{probe} (nm)	excited transition	probed state
S_0^{532}	532	532	$S_1 \leftarrow S_0$	S_0
S_0^{355}	355	532	$S_2 \leftarrow S_0$	S_0
S_1^{532}	532	595	$S_1 \leftarrow S_0$	S_1
S_1^{355}	355	595	$S_2 \leftarrow S_0$	S_1

^a The experiments are designated according to the probed state and the excitation wavelength.

pulses was controlled by a combination of half-waveplates and polarizers. The total pump intensity on the sample was around 1 mJ/cm², and the probe intensity was 5–10 times smaller. With these conditions, the magnitude of the signal depended linearly on the probe pulse intensity and quadratically on the total pump intensity. The diameter of the pump and probe spots on the sample were 3 and 1 mm, respectively. Each measurement was repeated three times, and the average value was used.

Samples. Rhodamine 6G (R6G, Exciton) was used as received. Methanol (MeOH), ethanol (EtOH), butanol (BuOH), and pentanol (PeOH) as well as acetonitrile (MeCN) were of spectroscopic grade and used without further purification. Butyronitrile (BuCN), valeronitrile (PeCN), hexanenitrile (HxCN), octanenitrile (OcCN), and decanenitrile (DeCN) were washed twice with half volume of concentrated HCl, then washed with saturated aqueous NaHCO₃, dried with MgSO₄, and distilled.⁹ The concentration of R6G was adjusted to obtain an optical density at the pump wavelength of about 0.15 on 1 mm, the sample thickness. This corresponds to concentrations of about 1.5×10^{-5} and 1.5×10^{-4} M at 532 and 355 nm, respectively. All experiments were carried out at $20 \pm 1^\circ\text{C}$.

Results and Discussion

The four different types of measurements performed are summarized in Table 1. When excited at 532 nm, the S_1 state of R6G is formed without excess energy. On the other hand, excitation at 355 nm populates first the S_2 state, which then deactivates rapidly to S_1 by internal conversion. In this process, about 1.15 eV of the excitation energy is converted into heat, and the environment of the excited molecule becomes warmer. The temperature of an adiabatically closed sphere of 10 Å with the heat capacity of acetonitrile would rise by 28 K after dissipation of 1.15 eV as heat. With the weak light power used for excitation (<1 mW), the average temperature of the sample is almost unaffected. Consequently, if this heat stays localized around the excited solute molecule for a few tens of picosecond, the rotational diffusion time measured in the S_1^{355} experiment

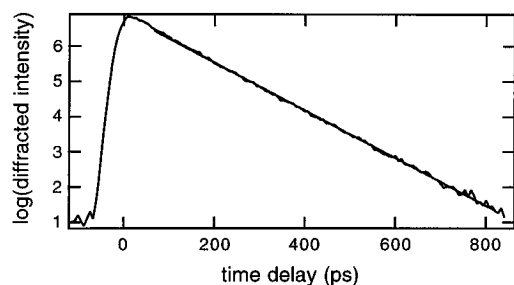


Figure 3. Logarithmic plot of the time evolution of the diffracted intensity at 595 nm after excitation at 355 nm (S_1^{355} experiment) of R6G in EtOH.

can be expected to be shorter than that determined in the S_1^{532} experiment. When exciting at 532 nm, the local temperature must be the same as the equilibrium temperature, which is also experienced by the molecules in the ground state.

To ensure that any difference detected in these two experiments is not due to the perpendicular orientation of the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transition dipoles¹⁰ as invoked by Pantke and Labhart,² the rotational diffusion time of the ground state has also been measured using both wavelengths to deplete the S_0 population (experiments S_0^{532} and S_0^{355}).

At 532 nm, the extinction coefficient of S_0 is more than 8 times larger than the extinction coefficient of S_1 ,^{11,12} and therefore the measured polarization anisotropy is due to the orientational distribution of R6G in the ground state. On the other hand, light at 595 nm is absorbed by S_1 only,^{11,12} and the S_1^{532} and S_1^{355} experiments monitor the excited state only.

The four types of polarization grating experiments have been performed in series of *n*-alcohols going from MeOH to PeOH and of alkanenitriles from MeCN to DeCN.

The initial anisotropy, r_0 , was obtained from transient grating experiments with pump pulses polarized parallel and probe pulse polarized at 45° and using eq 2. It was measured in a single solvent (MeOH) for the four types of experiments and was close to 0.4 for the S_0^{532} and S_1^{532} experiments and about -0.2 for the S_0^{355} and S_1^{355} experiments. These values are consistent with a perpendicular orientation of $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transition dipoles as predicted for R6G by von Jena and Lessing.¹⁰ Moreover, they also indicate that the direction of the transition dipole related to the absorption at 595 nm and ascribed to the $S_3 \leftarrow S_1$ transition¹³ is parallel to the $S_1 \leftarrow S_0$ transition dipole. The rotational reorientation times and the excited state lifetimes obtained from these experiments were consistent with those found by polarization grating and fluorescence lifetime measurements.

In all cases, the decay of the diffracted intensity could be well fitted with a single exponential as shown in Figure 3. The rotational reorientation times, τ_r , were obtained from eq 1 using a value of 3.9 ns for the lifetime of R6G S_1 state, τ_{ex} . Fluorescence lifetime measurements, using the same excitation intensity as in the polarization grating experiments, confirmed that τ_{ex} does not depend on the excitation wavelength and lies between 3.8 and 4 ns in all the solvents used in this investigation. The rotational times are listed in Table 2 and displayed as a function of viscosity in Figure 4. These values are in good agreements with those already reported in the literature.^{14–18} In the four types of experiments and in the two classes of solvents, the rotational time increases linearly with solvent viscosity. The slopes and intercept obtained from linear regression with these data are listed in Table 3. This table as well as Figure 4A shows that, in nitriles, the rotational times obtained from the four sets of experiments almost fit on the same line. The same is true in the *n*-alcohols except for the

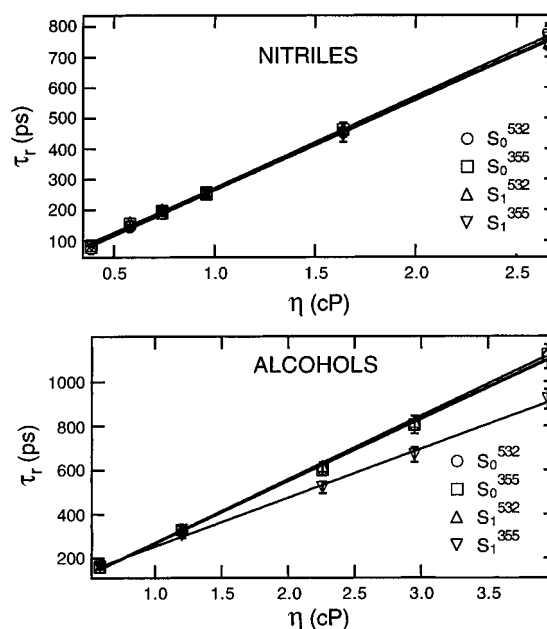


Figure 4. Viscosity dependence of the reorientation time of R6G in nitriles and alcohols in the four types of experiments.

TABLE 2: Rotational Diffusion Times of R6G in the Ground State after Depletion at 532 nm, $\tau_r(S_0^{532})$, and 355 nm, $\tau_r(S_0^{355})$, and in the Excited State after Excitation at 532 nm, $\tau_r(S_1^{532})$, and 355 nm, $\tau_r(S_1^{355})$ (Limits of Error $\pm 5\%$)

solvent	η (cP)	$\tau_r(S_0^{532})$ (ps)	$\tau_r(S_0^{355})$ (ps)	$\tau_r(S_1^{532})$ (ps)	$\tau_r(S_1^{355})$ (ps)
MeCN	0.39	73	85	78	87
BuCN	0.58	144	156	160	168
PeCN	0.74	189	190	201	207
HxCN	0.96	253	251	252	257
OcCN	1.64	454	463	467	444
DeCN	2.66	751	745	770	762
MeOH	0.59	160	161	158	164
EtOH	1.20	329	331	330	306
PrOH	2.26	600	617	604	522
BuOH	2.95	806	818	806	669
PeOH	3.95	1162	1138	1105	922

rotational times measured in the S_1^{355} experiment for which the slope is 25% smaller as shown in Figure 4B.

The linear dependence of τ_r on viscosity is predicted by the Debye–Stokes–Einstein expression, which assumes hydrodynamic friction:¹⁹

$$\tau_r = \frac{1}{6D_s} = \frac{\eta V}{k_B T} \quad (3)$$

where D_s is the diffusion coefficient for a spherical molecule of volume V in a solvent of viscosity η . R6G can be approximated to an oblate spheroid with an axis ratio of 1:3. As the transition dipoles involved in the probing processes are perpendicular to the symmetry axis, the anisotropy decay should be in principle biexponential²⁰ with rate constants equal to $6D_{\perp}$ and $2D_{\perp} + 4D_{\parallel}$, D_{\perp} and D_{\parallel} being the diffusion coefficients for motion perpendicular and parallel to the symmetry axis, respectively. In many cases, single-exponential decay is observed as in the present investigation, and the rotational diffusion time can be approximated to

$$\tau_r = \frac{1}{3D_{\perp} + 3D_{\parallel}} = \frac{f}{6D_s} = \frac{\eta f V}{k_B T} \quad (4)$$

where f is a shape factor which depends on the axis ratio of the

ellipsoid and which has been calculated as 1.65 for R6G. This equation is valid for stick boundary condition. In the case of slip boundary condition, the right-hand side of eq 4 should be multiplied by a shape-dependent coefficient C that should be of the order of 0.5 for R6G.²¹ However, the rotational motion of a charged molecule like R6G in polar solvents can be expected to follow stick hydrodynamics.⁷

According to eq 4, the slope of a τ_r vs η plot corresponds to $fV/k_B T$. Using a molecular volume for R6G of 410 Å³, as calculated with van der Waals increments,²² this slope should amount to 167 ps/cP. In alcohols, the slope is larger than the calculated one by a factor 1.8 in the first three experiments. This behavior has already been reported by Jena and Lessing and has been ascribed to solvent attachment through H bonds.²³

In nitriles, the slope is larger than the calculated one by about the same factor in all four experiments. In this case, H bonding cannot be invoked. Anomalous large rotational times in nitriles have already been observed.^{7,24,25} They have been ascribed to dielectric friction²⁴ or to the formation of a micelle-like solvation structure around the solute in longer nitriles.⁷ Independently of the origin of this behavior, it is important to observe that excess excitation energy has no influence on the rotational dynamics of R6G in alkanenitriles.

In alcohols, however, the rotational dynamics of R6G is influenced by the excess excitation energy. Indeed, the slope measured in the S_1^{355} experiment is larger than the calculated one by a factor 1.3 only.

Excess energy could affect the slope of a τ_r vs η plot in two different ways:

(i) **Local Change of Viscosity.** Excess energy will result in a temporary local heating. As a consequence of this temperature elevation, local viscosity will decrease. However, this change can be effective only if its duration is on the order of the rotational diffusion time. In a classical diffusion picture, the temperature after deposition at time $t = 0$, of an amount of energy, E , as heat is given by³

$$T(r,t) = \frac{E}{8\rho C(\pi\chi t)^{3/2}} \exp\left(-\frac{r^2}{4\chi t}\right) \quad (5)$$

where r is the distance from the source, ρ the density of the medium, C the heat capacity, and χ the thermal diffusivity.

In the present case, the heat source, R6G, can be modeled as a sphere of radius r_0 , and its cooling rate described as $F(t) = 1/\tau \exp(-t/\tau)$, τ being the cooling time. For a sufficiently short cooling time, the temperature distribution can be described approximately by³

$$T(r,t) = \frac{E}{\rho C} \int_0^t dt' F(t') \frac{1}{8\pi r r_0 (\pi\chi(t-t'))^{1/2}} \times \left[\exp\left(-\frac{(r-r_0)^2}{4\chi(t-t')}\right) - \exp\left(-\frac{(r+r_0)^2}{4\chi(t-t')}\right) \right] \quad (6)$$

where r is the distance from the centre of the heat source. Figure 5A shows the average temperature rise of a 5 Å thick solvent layer around a heat source of 4.6 Å radius and with a cooling times of 1 ps calculated using eq 6. In this case, the maximum temperature difference does not exceed 12 K. With a longer cooling time, this temperature difference is even smaller. For a similar dye, oxazine 1, Laermer et al. have observed that the cooling time depends on the amount of excess excitation energy.²⁶ It varies from 1 ps with excess energy of about 0.12 eV to 6 ps when the excess energy amounts to 2.1 eV. This time dependence of the local temperature allows the instantaneous local viscosity and instantaneous rotational diffusion time

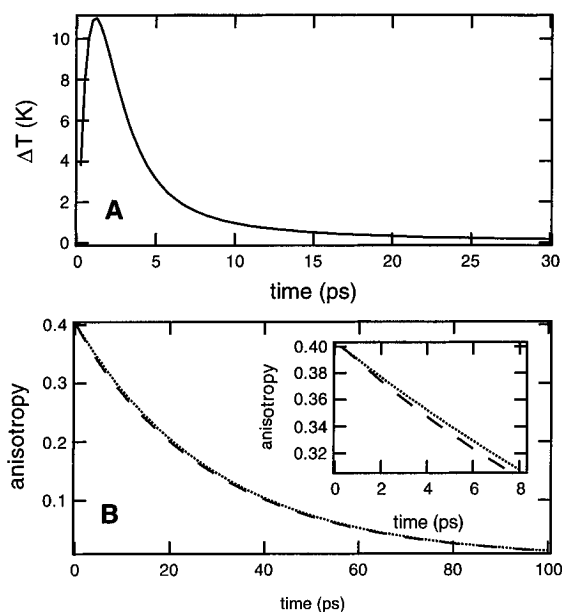


Figure 5. (A) Time dependence of the temperature rise in the first solvent shell after release of 1.15 eV excess energy calculated using eq 6 assuming a delta excitation function. (B) Simulation of the anisotropy decay of R6G in MeCN with (dashed line) and without (dotted lines) excess excitation energy. Insert: details of the first 8 ps after excitation.

TABLE 3: Slope and Intercept of the Best Line Fitting the Viscosity Dependence of R6G Rotational Diffusion Time for the Four Types of Experiments in Alkanenitriles (CN) and in *n*-Alcohols (OH)

experiment/ class of solvent	slope (ps/cP)	intercept (ps)	V (Å ³)
S_0^{532} /CN	296 ± 3	-32 ± 4	742
S_0^{355} /CN	290 ± 6	-19 ± 9	750
S_1^{532} /CN	300 ± 3	-29 ± 4	746
S_1^{355} /CN	295 ± 4	-28 ± 5	670
S_0^{532} /OH	284 ± 8	-18 ± 15	764
S_0^{355} /OH	288 ± 6	-19 ± 15	712
S_1^{532} /OH	282 ± 6	-15 ± 15	677
S_1^{355} /OH	221 ± 5	30 ± 14	548

to be calculated. Figure 5B shows the anisotropy decays calculated by assuming a constant temperature and by taking the local variation of temperature into account. It is immediately clear that, within this classical model of heat diffusion, the transient heating is too short to have any detectable influence on the reorientational dynamics of a molecule like R6G in any of the solvents used in this investigation. In order to detect the effect of local heating, one should choose a solute/solvent system such that the rotational time is of the order of 10 ps at most.

(ii) **Change of Hydrodynamic Volume.** In protic solvents, R6G is known to form H bonds of medium strength compared with those occurring with fluorescein.²³ The values listed in Table 3 suggest that excess excitation energy results in the dissociation of a H bond between R6G and solvent and to a decrease of the hydrodynamic volume. After excitation at S_2 , only the vibrational modes coupled to the chromophore are excited and H bond dissociation can take place after intramolecular vibrational redistribution. Laubereau and co-workers have shown that excitation at the CH stretching frequency of ethanol in CCl₄ leads to H bond dissociation with a time constant of 15 ps and an efficiency equal to 70% of that obtained by direct excitation at the OH frequency.²⁷ It was also found that a partial reassociation takes place with a time constant of about 20 ps.

If after dissociation the groups involved in the H bond move slightly apart, reassociation will require substantial reorientation of both solvent and solute molecules. Consequently, the reassociation time could be of the same order of magnitude or even slower than the rotational time of the solute. This reassociation time depends on the probability of finding a solvent H-donating group in the vicinity of the H-accepting site of the solute. This probability decreases as the length of the *n*-alcohol increases. This can explain why excess energy has no apparent influence on the rotational diffusion in MeOH. In this solvent, the density of H-donating groups around the solute is so large that only small reorientation is required to form a new bond. In longer alcohols like PeOH, a much more substantial reorientation of both solute and solvent must be necessary.

This observation of the perturbation of H-bonding upon excitation with excess energy is in accordance with the previous studies on transient local heating (see Introduction). Effects due to excess excitation energy were observed in protic solvents or in H-accepting solvents only. Some of the systems studied could form solute/solvent H bonds, such as for example oxazine-4 in 2-methyltetrahydrofuran, for which the solvation time appears to be faster with vibrational excess energy.²⁸ In two other investigations,^{1,2} however, association through H-bonds was only possible between the solvent molecules and an effect was observed with large excess energy only (about 2 eV). In this case, the accelerated depolarization might be due to bond breaking in the solvation shell. The most obvious mechanism would be resonant energy transfer from the solute to form vibrationally hot solvent molecules. However, according to an investigation carried out with oxazine 1 in various solvents, this energy pathway seems not to be very efficient.²⁹ In the same study, it was concluded that intermolecular energy dissipation via translational and rotational motions (phonons) is prevailing. In this case, the first solvent shell experiences a temperature rise of about 20 K for a few picosecond according to eq 6 for an excess energy of 2 eV. This temperature jump could somehow cause a perturbation and a loosening of the structure of the solvation layer, which would then relax back to its initial state after partial reorganization on the time scale of rotational motion or longer. This might explain why an effect is only observed with a large excess energy.

The results summarized in Table 3 show that the rotational dynamics of R6G does not exhibit a measurable state dependence when excited without excess energy. This contrasts with oxazines³⁰ and thiazines³¹ in alcohols which show faster rotational times in the ground state than in the first singlet excited state. This effect was ascribed to the change of electron density at the nitrogen heteroatom upon excitation, inducing an increase of Lewis basicity. This effect cannot be effective with xanthene dye, as there is no ring-bound nitrogen atom.

Finally, Table 3 also shows that the rotational dynamics of R6G in the ground state is independent of the depletion wavelength although the dipoles for the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transition are orthogonal. Contrarily to the assertion of Pantke et al., the measured polarization anisotropy dynamics is not dependent on the orientation of the excitation transition dipole in the molecular frame, but on the direction of the transition dipole involved in the probing process.¹⁰ For R6G in the ground state, the transition involved in the detection is the same for both depletion wavelengths, and therefore the rotational times have to be the same, and this is indeed observed.

Summary and Conclusions

We have shown that the rotational times of R6G in the excited state and in alcohols are about 25% faster with an excess

excitation energy of 1.15 eV. In alkanenitriles, however, this excess energy has no detectable influence on the rotational dynamics of R6G. In nonassociating solvents, any transient heating of the first solvation shell is too short-lived to accelerate the rotational diffusion of R6G. In alcohols, the shortening of the rotational time seems to be due mainly to a decrease of the hydrodynamic volume, caused by H-bond dissociation. This bond breaking could also be accompanied by a partial rearrangement of the solvent shell. The main difference between associating and nonassociating solvents is the recovery time after a temperature jump. Although equilibrium temperature is quickly reestablished in both types of solvents, the restoration of the initial solvation structure might need much more time for associating solvents.

These studies show that rotational diffusion of a dye molecule like R6G can be used as a probe for specific association. However, the rotational dynamics of this molecule is too slow for application as a "thermometer". A solute/solvent system, for which the rotational time is smaller than 10 ps, could possibly be used for this purpose.

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