

## Photoinduced random molecular reorientation by nonradiative energy relaxation: An experimental test

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By measuring the time-resolved fluorescence depolarization as a function of light excitation wavelength we address the question of a possible photoinduced orientational randomization of amino-anthraquinone dyes in liquid solutions. We find no significant dependence within the experimental uncertainties of both the initial molecule anisotropy and of the subsequent rotational diffusion dynamics on the photon energy. This indicates that this effect, if present, must be very small. A simple model of photoinduced local heating and corresponding enhanced rotational diffusion is in accordance with this result. This null result rules out some recent proposals that photoinduced local heating may contribute significantly to molecular reorientation effects in different materials. A small but statistically significant effect of photon energy is instead found in the excited-state lifetime of the dye.

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### I. INTRODUCTION

The intense light of a laser beam may affect the average molecular orientation of a material in many different ways. When a material is transparent, the main mechanism for light-induced molecular reorientation is the electric torque acting on the optical dipoles induced in the molecules, which gives rise to well-understood phenomena such as the optical Kerr effect and the correlated molecular reorientation of liquid crystals [1]. However, the strongest effects are seen when the light can be absorbed by the molecules, so that the photon energy can be fully exploited: a range of photoinduced molecular reorientation (PMR) phenomena becomes then possible, in some cases at very small light intensities. Many of these PMR phenomena are still not fully understood and are currently the subject of intensive research, owing to their potential for applications in optical data storage and processing [2].

Many PMR phenomena are ultimately driven by a *reversible modification of molecular properties* taking place in molecules that have absorbed a photon. A simple example is photoinduced isomerization, as that occurring in many azodyes. Many materials containing azo compounds are indeed known to exhibit effective PMR. But a significant change of molecular properties does not necessarily require a conformational transformation. The sole electronic excitation can also drive an effective PMR, if associated with a significant variation of intermolecular forces. This was demonstrated, for example, in liquids and liquid crystals containing amino-anthraquinone dyes [3–6], which exhibit a significant strengthening of polar interactions in the excited state [7–9].

Besides electronic excitation, another general consequence of photon absorption is a relatively large vibrational excitation of the molecule. This occurs already when the molecule is in its photoexcited electronic state, due to the Franck-Condon effect: a significant fraction of the photon energy is immediately converted to vibrational energy. However, the vibrational excitation may become even stronger

when the molecule relaxes back nonradiatively to its electronic ground state: in this case the photon energy is entirely converted into vibrational energy. The latter is then rapidly redistributed among many different degrees of freedom of the molecule and of its neighbor molecules, approaching a Boltzmann distribution. One can then approximately describe this process as a “local heating,” heating which may be very large (in the order of several hundreds kelvins, as estimated by dividing the photon energy by the heat capacity of a molecular volume of material), although also very short lived in condensed materials, due to rapid heat diffusion (typically, a few picoseconds) [10].

The possibility of PMR driven by this local heating effect was first proposed, in our knowledge, by Albrecht in the mid-1950s [11]. Albrecht’s idea was that local heating may strongly enhance rotational diffusion, thus leading to a partial or total orientational randomization. This randomization occurs preferentially for molecules oriented with their transition dipole more parallel to the optical electric field. Therefore, molecules are more often reoriented *away* from the field direction and a net orientation in the plane perpendicular to it can be achieved by cumulating many randomization events.

To our knowledge Albrecht’s effect, although theoretically possible, has never been demonstrated experimentally. This is probably because the rapidity of heat diffusion makes it highly ineffective in most materials, as discussed, for example, in Ref. [12]. However, the idea that a significant contribution to PMR can be due to photoinduced local heating keeps surfacing in the scientific literature whenever other models seem to fail or to leave room for doubts. For example many azodyes and some related materials, in certain conditions, are not capable at all of photoinduced isomerization, but nevertheless exhibit a significant PMR. This has been tentatively attributed to photon-induced local heating and consequent orientational randomization (see, for example, Refs. [13–15]). In some works, this randomization mechanism has been proposed *in combination* with other PMR effects. For example, in amino-anthraquinone dye solutions,

the possibility of a large sudden random reorientation of photoexcited molecules relaxing back to the ground state has been recently considered in Ref. [16]. The extent of this orientational randomization was parametrized by a constant  $F$  ranging from 0 to 1, with  $F=1$  meaning no randomization and  $F=0$  complete randomization. However, the data reported in Ref. [16] did not allow a good estimate of  $F$  (on this issue, see in particular the related erratum). A similar idea was put forward also in Ref. [17] to explain a peculiar excitation wavelength dependence of the photoinduced reorientation of certain azodye-doped liquid crystals. In this case, the assumption was that a partial random molecular reorientation occurs directly in the excited electronic state, due to the fast release of vibrational energy. The magnitude of this effect was then thought to depend on the amount of photon energy (hence the wavelength dependence) in excess of the minimum required for electronic excitation, which is converted to vibrational energy.

In this work we measured directly the orientational randomization taking place in the excited state of aminoanthraquinone molecules after photon absorption, by means of time-resolved fluorescence depolarization. In particular, our data allowed us to distinguish the ordinary (equilibrium) process of orientational Brownian motion that leads to a full randomization on a nanosecond time scale and the reorientation processes occurring on a much shorter time scale, which may be due, for example, to a fast release of vibrational energy or to other effects. The orientational dynamics was studied as a function of the photon energy—i.e., of the excitation wavelength. Any “local-heating”-like contribution to orientational randomization would depend on the photon energy (in particular, on the energy excess with respect to the minimum required for absorption), allowing us to single out this effect from others. Our experiment is described in Sec. II and our main results are reported in Sec. III. As will be shown there, we actually find a *null result*; i.e., no measurable photon-energy-dependent random reorientation takes place in our molecules, although the photon extra energy reaches values as large as 0.6 eV, theoretically capable of inducing a local heating of more than 100 K. An upper limit to the possible extent of the randomization is deduced from our data. In Sec. IV we then calculate by means of a simple phenomenological model the expected randomization due to local heating and find that only a very small effect is expected, consistent with our experimentally determined upper limit. Section V contains our conclusions and a brief discussion about the generality of our findings.

## II. EXPERIMENT

In our time-resolved fluorescence apparatus, 20-ps pulses from an optical parametric generator pumped by a frequency-tripled Nd:YAG laser were used as tunable excitation light. The transient fluorescence was detected by means of a fast photodiode (about 100 ps rise time) and sampled by 2-GHz analog bandwidth electronics. A polarizer was used to select parallel ( $\parallel$ ), perpendicular ( $\perp$ ), or “magic-angle” (i.e.,  $54.7^\circ$ ) linear polarizations of the detected fluorescence light with respect to that of the excitation light. As

the detection apparatus has a finite response time, the signal  $S(t)$  we measure is actually the convolution of the fluorescence intensity  $I(t)$  with the instrumental response function  $R(t)$ . To measure this response function, we replaced the sample with an opaque plate and collected the scattered light, which has essentially the same time duration as the laser pulse and therefore can be considered as a  $\delta$ -function input to the detection system. We measured the response function at wavelengths ranging within the whole fluorescence spectrum of our dye and found that its shape and temporal parameters [e.g., rise time, full width at half maximum (FWHM)] remained approximately constant. Therefore, we used the response function averaged over all detected wavelengths for our subsequent data analysis.

In the data analysis, the parallel and perpendicular signals  $S_{\parallel}(t)$  and  $S_{\perp}(t)$  were first combined into  $S_e(t)=S_{\parallel}+2S_{\perp}$  and  $S_d(t)=S_{\parallel}-S_{\perp}$ . We verified that  $S_e(t)=3S_{\text{magic}}(t)$  as expected, thus confirming that the detection efficiency of our apparatus was independent of light polarization. Each of the two combinations  $S_e(t)$  and  $S_d(t)$  was then best fitted by a single-exponential decay of the form  $I_i(t)=c_i \exp(-t/\tau_i)$ , with  $i=e, d$ , convoluted with the measured response function  $R(t)$ . The fit parameters are the excited-state lifetime  $\tau_e$ , the effective time  $\tau_d=(\tau_e^{-1}+\tau_r^{-1})^{-1}$ , where  $\tau_r$  is the rotational diffusion time, and the two preexponential factors  $c_e$  and  $c_d$ . The ratio  $r_0=c_d/c_e$ , hereafter called the *initial degree of anisotropy*, gauges the degree of excited-state dye orientational anisotropy (or “order parameter”) immediately after the laser pulse absorption—i.e., at the beginning of the fluorescence signal. More precisely, it can be shown that  $r_0=\langle(3 \cos^2 \theta - 1)/2\rangle$ , where  $\theta$  is the angle between the direction of the molecule fluorescence transition dipole and that of the excitation light electric field and where the angular brackets denote an average over the ensemble of excited dye molecules, sampled at a time of the order of our temporal resolution ( $\approx 50$  ps) after the excitation.

The sample cell had a thickness  $1.0 \pm 0.1$  mm and was placed into an oven allowing temperature control to within 0.1 K. All the fluorescence measurements reported in this paper refer to a sample temperature of  $45^\circ\text{C}$ . As dye, we used the 1,8-dihydroxy 4,5-diamino 2,7-diisopentyl anthraquinone derivative (HK271), provided by Nematel, Mainz, Germany. Its  $S_1$ - $S_0$  transition dipole is known to be along the longest geometrical axis of the molecule [18]. We also made control measurements on Rhodamine 6G and Rhodamine B (respectively Rh6G and RhB, Lambda Physik). As liquid-crystalline host, we used 4'-n-pentyl-4-cyanobiphenyl (5CB). Although 5CB is a liquid-crystalline material having a nematic phase between 297 and 308 K, in order to avoid the complications associated with an anisotropic host, our experiments were limited to the temperature range 311–368 K in which 5CB is in its ordinary isotropic liquid phase. The solutions were prepared at several concentrations ranging from  $10^{-6}$  to  $10^{-3}$  mol/l. In all measurements, we identified the concentration below which nonlinear effects were negligible, and in our discussion we consider only results obtained in this range.

We tested the setup and the analysis procedure by measuring the fluorescence lifetime  $\tau_e$  of Rh6G at  $10^{-4}$  mol/l in

ethylene glycol and in ethanol, finding in both cases  $\tau_e = 3.6 \pm 0.1$  ns, in agreement with values reported in the literature for the case of negligible energy transfer [19,20]. This ensured that energy transfer effects could be neglected for our experimental geometry [20]. As a further test, we verified that the fluorescence lifetime of HK271 was independent of dye concentration in the range  $10^{-4}$ – $10^{-3}$  mol/l and that the value of  $r_0$  is independent of dye concentration and laser intensity.

### III. EXPERIMENTAL RESULTS

We varied the excitation wavelength in the range 480–630 nm, corresponding to photons having an energy in the range 2.0–2.6 eV. In HK271 dissolved in 5CB, the absorption peak is at 633 nm, so that our photons had an excess energy with respect to the absorption peak ranging from 0 up to approximately 0.62 eV. When a photon having excess energy is absorbed, its excess energy is very quickly converted into internal vibrational energy, which is then rapidly dissipated. Within a time typically of several picoseconds or less, the excited molecule reaches the vibrational ground state of the first-excited electronic state  $S_1$ . Then it will remain there for a much longer time, dictated by electronic relaxation processes and whose average is  $\tau_e \approx 1$  ns for HK271.

At all times after the excitation, the dye molecule will have a certain probability of emitting a fluorescence photon. The degree of polarization of the fluorescence decreases over time, due to the random Brownian motion of the dye molecule orientation. As discussed in the previous section, by following the decay of the fluorescence polarization one gets information on the characteristic time  $\tau_r$  of this orientational Brownian motion, which in our case is about 2 ns. If the dye molecule orientation is not suddenly changed at excitation and if one may assume the  $S_0$ - $S_1$  transition dipole moment to remain constant relative to the molecule axes, then one expects a well-defined initial degree of polarization in the fluorescence dictated only by the usual cosine-square dependence of the cross sections for absorption and emission. This ideal degree of polarization corresponds to the initial anisotropy  $r_0 = 0.4$ . However, several effects may contribute to reducing this initial degree of polarization, including possible distortions of the molecule in its excited state, vibronic effects, fast oscillatory motion of the whole molecule within the “cage” set by nearest neighbors, etc. None of these effects should, however, depend critically on the excitation wavelength.

A very fast random reorientation of the molecule after excitation due to the local heating (or more generally nonradiative vibrational energy dissipation) effect discussed in the Introduction may also reduce the initial anisotropy  $r_0$ . Such a reduction should, however, depend strongly on the amount of dissipated heat, which in turn depends on the photon extra energy. Therefore this heating effect may be distinguished from the others by its expected strong dependence on excitation wavelength. If one models the orientational randomization as a diffusional process in angular space with root-mean-square (rms) angular rotation  $\Delta\theta$ , the  $r_0$  after the randomization  $r_0(\Delta\theta)$  is given by the following equation:

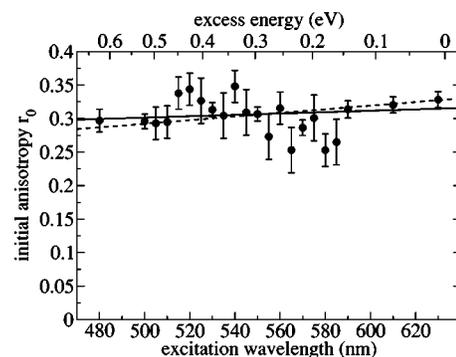


FIG. 1. Initial anisotropy factor  $r_0$  versus excitation wavelength or photon excess energy. The solid line is a linear best fit, whose slope (with respect to photon energy) is  $dr_0/dE = -0.024 \pm 0.021$  eV $^{-1}$ . The dashed line shows the best-fit line having the maximum slope compatible with our data, at a confidence level of 95%.

$$r_0(\Delta\theta) = r_0(0)e^{-3\Delta\theta^2/2}, \quad (1)$$

where  $r_0(0)$  is the anisotropy before the randomization.

In Fig. 1, we plot our results for the initial anisotropy factor  $r_0$  versus excitation wavelength and photon excess energy. In this and the following figures, error bars correspond to one standard deviation. It can be seen that  $r_0$  is indeed smaller than the ideal value 0.4, confirming that some of the aforementioned mechanisms is operating. Its average value is  $r_0 = 0.31 \pm 0.01$  (here and in the following all quoted uncertainties are standard deviations), which corresponds to a rms  $\Delta\theta = 24^\circ$  randomization of the transition dipole direction with respect to the ideal case. However, it is also seen in the figure that no significant dependence of  $r_0$  on the photon excess energy is present. A linear fit yields a slope  $dr_0/dE = -0.024 \pm 0.021$  eV $^{-1}$ , fully compatible with zero. The best-fit slope corresponds to a further rms angular randomization of  $10^\circ$  at  $E = 0.6$  eV or, if combined (by adding the angular variances) with the energy-independent rms angle  $24^\circ$ , a total rms angle of  $26^\circ$ . The maximum negative slope that is compatible with our data is  $-(dr_0/dE) = 0.065$  eV $^{-1}$ , at a 95% confidence level. This corresponds to an experimental upper limit for the rms angular randomization due to radiationless energy relaxation of  $17^\circ$  at  $E = 0.6$  eV or, equivalently, to an upper limit for the angular variance per unit energy of about  $0.15$  rad $^2$ /eV.

Actually a small “dip” in  $r_0$  is perhaps seen for wavelengths close to 570 nm, although it is not statistically very significant. Roughly at this wavelength, in the absorption spectrum of HK271 one finds a secondary peak. Moreover, in a narrow range of wavelengths between 570 and 590 nm, the fluorescence was also found to exhibit an additional fast-decaying component (decay time shorter than 100 ps). This additional fluorescence was superposed onto the normal one and fully unpolarized. We could not identify its origin. In the data analysis, we could, however, separate the two components by fitting our  $S_e(t)$  signal with a double-exponential decay, one of which is almost instantaneous; the anisotropic signal  $S_d(t)$  did not show this second component at all, indi-

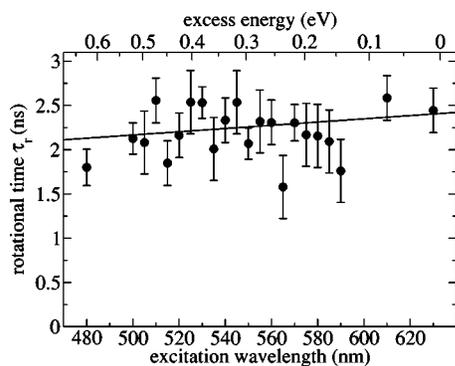


FIG. 2. Rotational time  $\tau_r$  versus excitation wavelength or photon excess energy (at a temperature of 45 °C). The solid line is a linear best fit. Its slope is  $1.8 \pm 1.5$  ps/nm, compatible with zero.

cating that it is fully unpolarized. The value of  $r_0$  reported in Fig. 1 only refers to the ordinary “slow”-decay signal.

Next, we investigated the possibility that some randomization mechanism somehow associated with excess energy (i.e., depending on the excitation wavelength) could be present also on a slower time scale, such that instead of being considered “sudden” and thus affecting the initial degree of polarization, it could act continuously during the fluorescence decay. In this case, one should, however, see it as a change of rotational time  $\tau_r$  as a function of photon excess energy. Figure 2 shows that a small effect could indeed be present in the form of a small reduction of  $\tau_r$  with increasing photon energy. However, the magnitude of this effect is compatible with zero within two standard deviations, so no definite conclusion can be drawn.

Finally, we verified if some excitation wavelength dependence could be seen in the excited-electronic-state lifetime  $\tau_e$ . Figure 3 shows that in this case a small but statistically significant wavelength dependence is actually found. Its physical meaning is not clear. It could be related just to the nature of the excited electronic state. However, since the excited-state lifetime in amino-anthraquinones is known to be very sensitive to intermolecular interactions [21], one might also speculate that the photon excess energy may cause some relatively long-lived modifications of these interactions—e.g., breaking a hydrogen bond—which in turn

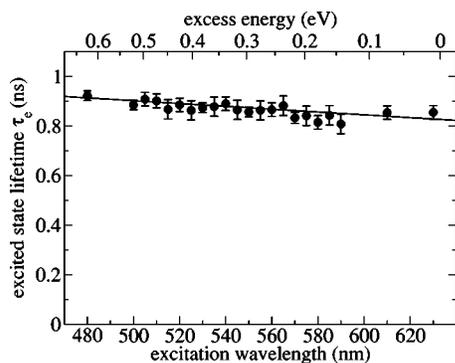


FIG. 3. Excited-state lifetime  $\tau_e$  versus excitation wavelength or photon excess energy. The solid line is a linear best fit. Its slope is  $-0.57 \pm 0.15$  ps/nm.

would be reflected in an increase of  $\tau_e$ . This would indeed be an important side effect of the nonradiative energy relaxation. A long-lived modification of intermolecular interactions should, however, be visible also in the wavelength dependence of the rotational time  $\tau_r$ , most likely as a reduction of  $\tau_r$  with increasing photon energy. In our case we cannot exclude that such an effect is indeed present, but our signal-to-noise ratio does not allow reaching a definite conclusion about this point.

#### IV. ENHANCED ROTATIONAL DIFFUSION INDUCED BY LOCAL HEATING

To estimate the expected orientational randomization effect of the nonradiative energy relaxation we combined a simple continuum model of heat diffusion to estimate the temperature dynamics (i.e., the local heating versus time) around the molecule with the measured dependence of the molecular rotational diffusion constant on temperature. Our approach is very similar to that outlined in the Appendix of Ref. [12].

Let us consider a spherical molecule of radius  $R_0$  surrounded by an infinite continuous medium having thermal conductivity  $\lambda$ , specific heat  $c$  (we neglect here the small difference between constant-volume and constant-pressure heat capacity), and mass density  $\rho$ . At time  $t=0$  an excess energy  $\Delta E$ , corresponding to the photon excess energy, suddenly appears on the external surface of the molecule and starts diffusing in the medium. This is a classic heat diffusion problem that has a simple closed solution. The temperature variation  $\Delta T(t)$  at a distance  $R$  from the center of the molecule is the following:

$$\Delta T = \frac{\Delta E}{4\pi^{2/3}R_0\rho c\sqrt{at}R} \left[ \exp\left\{-\frac{(R-R_0)^2}{at}\right\} - \exp\left\{-\frac{(R+R_0)^2}{at}\right\} \right], \quad (2)$$

where  $a=4\lambda/c\rho$ . Inserting in this expression the parameters characterizing our system (i.e.,  $R_0=7.3$  Å, obtained as the cube root of the HK271 molecule volume estimated in Ref. [21],  $c=1.8$  J/g K [22],  $\lambda=0.15$  W/K m [23], and  $\rho=1.0024$  g/cm<sup>3</sup> [24], for 5CB in the isotropic phase), we obtain the results shown in Fig. 4, where an excess energy excitation  $\Delta E=0.6$  eV has been used. It is seen that at any distance from the molecule the temperature increase becomes essentially negligible (i.e., below few degrees) within 10 ps, a time much shorter than both the fluorescence lifetime  $\tau_e$  and the diffusion rotational time  $\tau_r$ .

The time-dependent temperature increase  $\Delta T(t)$  leads to a corresponding time-dependent increase of the rotational diffusion constant  $\Delta D(t)$ . To estimate the latter we used the results of Ref. [21], where the temperature dependence of the rotational diffusion  $D$  for our system in the range 313–368 K was found to be well described by an Arrhenius behavior—i.e.,  $D=D_0 \exp(E_a/kT)$ , where  $E_a=28.6 \pm 0.3$  kJ/mol is an activation energy,  $D_0=(3.6 \pm 0.2) \times 10^{12}$  s<sup>-1</sup>, and  $k$  is the Boltzmann constant. We assumed

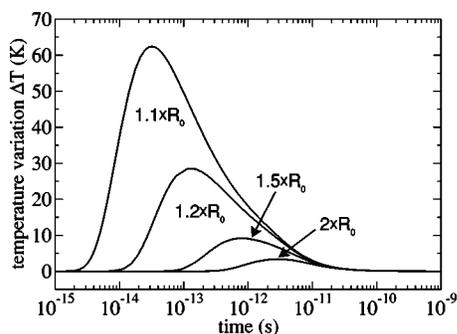


FIG. 4. Temperature variation induced locally by the sudden release of 0.6 eV of heat on the surface of a spherical molecule of radius  $R_0=7.3$  Å, in 5CB host at several distances  $R$  from the center of the molecule, ranging from  $R=1.1R_0$  to  $R=2R_0$ .

that this Arrhenius behavior remains valid also in our non-equilibrium process and at the much higher temperatures reached in proximity of our molecule (actually the rotational diffusion may only become slower than what is predicted by this assumption, owing to the crossover to the inertial regime that may occur at very high temperatures; therefore, our results for the orientational randomization can only be overestimated due to this assumption). In the absence of a clear criterion for this choice, we used different values of the radius  $R$  at which the temperature is actually “sampled,” ranging from  $1.1R_0$  to  $2R_0$ .

Finally, we used these results to compute the total extra angular variance that can be associated with the local heating effect by means of the following equation:

$$\begin{aligned} \overline{\Delta\theta^2} &= 4 \int_0^\infty \Delta D(T(t)) dt \\ &= 4D_0 \int_0^\infty \left( \exp\left\{ \frac{E_a}{k[T_0 + \Delta T(t)]} \right\} - \exp\left\{ \frac{E_a}{kT_0} \right\} \right) dt, \end{aligned} \quad (3)$$

where  $T_0$  is the equilibrium temperature. The square root of this variance—i.e., the rms angular change  $\Delta\theta$  calculated for excess energy  $\Delta E$  values ranging up to 2 eV (as that typically occurring in a radiationless decay to the ground state)—is shown in Fig. 5.

It can be seen from this figure that the predicted local-heat-induced orientational effects are very small for any reasonable choice of the model free parameters. In particular, all model predictions fall well within our experimental upper limit for  $\Delta\theta$ .

## V. CONCLUSIONS

We have shown by a direct experiment that, for a solution of amino-anthraquinone dyes in isotropic 5CB, the orientational randomization induced by the nonradiative dissipation of vibrational energy following each photon absorption is negligible within our uncertainties. This was shown for a maximum dissipated energy of 0.6 eV, corresponding to a local heating of the order of 100 K. The results are in accor-

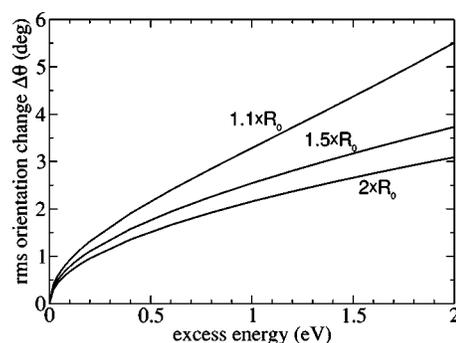


FIG. 5. Root-mean-square random reorientation angle  $\Delta\theta$  predicted by our model as a function of photon excess energy. The distance  $R$  taken for the temperature “sampling” to be used in the evaluation of the rotational diffusion is set equal to  $1.1R_0$ ,  $1.5R_0$ , and  $2R_0$ .

dance with a simple model based on continuum heat diffusion and on the measured temperature dependence of molecular rotational diffusion. An experimental upper limit to the orientational randomization has been estimated. We found instead some evidence that small effects of nonradiative energy relaxation on the molecule “behavior” could be present for a longer time scale, comparable with the state lifetime, but clearly not related with photon-induced local heating.

Based on our experimental result and the associated theoretical understanding, there is no reason to believe that our null result for the orientational effects of photon-induced local heating is specific to our materials: it is probably a rather general result. It is, however, still possible that a measurable effect may be found in systems having characteristic relaxation times very different from ours. In particular, although the random molecular rotation induced at every excitation remains very small, a cumulative effect might become measurable in suitably rigid systems, as, on the other hand, was suggested in the original proposal by Albrecht [11].

A different but related phenomenon of photoinduced molecular randomization is instead still conceivable for systems having cis-trans photoisomerization, such as azodyes systems. Trans-cis or cis-trans photoisomerization involves a nonradiative dissipation of all or most of the photon energy. If this energy is directly dissipated in form of “heat”—i.e., of incoherent random collisions of the molecule with its neighbors—then probably the overall rotational effect will once again be negligible. However, one may form the plausible hypothesis that nonradiative dissipation is associated with some form of *partial or incomplete photoactivated isomerization transition*. This incomplete isomerization is a rapid conformational dynamics starting and ending in the same trans state, but involving enough “coherent” (i.e., directional and synchronous) internal molecular motion to drive a significant random reorientation of the whole molecule [9]. Note that this proposed randomization mechanism does not require a full conformational transition to occur:

therefore, its action could take place *at every absorbed-photon event*, and not only in the small fraction of absorption events that end up in a real conformational transition (typically the latter are 10%–20% of the absorption events, but

this percentage may even vanish in suitable conditions, although PMR may be still present [14,15]). Therefore, that proposed here could be the main mechanism for PMR in azodye systems.

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