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Violation of the Exponential-Decay Law at Long Times

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First-principles quantum mechanical calculations show that the exponential-decay law for any metastable state is only an approximation and predict an asymptotically algebraic contribution to the decay for sufficiently long times. In this Letter, we measure the luminescence decays of many dissolved organic materials after pulsed laser excitation over more than 20 lifetimes and obtain the first experimental proof of the turnover into the nonexponential decay regime. As theoretically expected, the strength of the nonexponential contributions scales with the energetic width of the excited state density distribution whereas the slope indicates the broadening mechanism.

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Within the first-principles treatment of the decay of a metastable state Schrödinger's equation links the probability amplitude, $p(t)$, to the energy distribution density, $\omega(E)$ [1],

$$p(t) = \int e^{-iEt/\hbar} \omega(E) dE. \quad (1)$$

For example, taking $\omega(E)$ as a Lorentzian function for all E yields the well-known exponential decay at all times. However, in real physical systems, $\omega(E)$ must always have a lower limit, which is, for example, associated with the rest mass of scattering particles. Similarly, the energy of the emitted photon in luminescent materials cannot be negative, which implies a lower bound for the energetic distribution spectrum $\omega(E)$ at $E = 0$. Dating back as early as 1958, Khalifin first showed that this "semifiniteness" of $\omega(E)$ implies that the magnitude and the phase of $p(t)$ are connected with each other by integral relations, i.e., both cannot be chosen independently [1]. It turns out that, independent of the exact form of $\omega(E)$, a true exponential function cannot fulfill these integral equations, but that the decay of any metastable state eventually must proceed more slowly. Finally, knowledge of only $|p(t)|^2$, i.e., the real decay kinetics, for all times allows one to analytically calculate $\omega(E)$. The relative intensity of the nonexponential contributions is fully determined by the value of the energy distribution density at the cutoff energy of $\omega(E)$. Consequently, the nonexponential decay contribution is minor for an energy distribution density with small width compared to the difference between the cutoff energy and the center of $\omega(E)$, i.e., for processes with a large energy release and simultaneously narrow spectrum one would only observe the exponential mode. In turn, the value of $\omega(E)$ at the cutoff energy is large for broad density distributions with small energy release leading to early nonexponential contributions. Finally, no exponential decay at all is expected in the extreme case where the width, Γ , of $\omega(E)$ becomes comparable or larger relative to the released energy [2–4].

Experimental searches for such deviations from the exponential law have mainly focused on decays of radioactive isotopes [5]. Unfortunately, in view of the above conditions on E and Γ , such systems are in fact not suitable at all because the released energy is very large ($E \sim \text{MeV}$) compared to the width of the energy distribution ($\Gamma < 10^{-9}$ eV). For the radioactive isotope ^{60}Co , Norman *et al.* observed the decay out to 30 exponential lifetimes, whereas theoretically the deviation from exponential decay is expected at signal intensities of order 10^{-60} of the initial intensity corresponding to 140 lifetimes [5]. More recently, theoretical effort has been directed to a range of atomic states including spontaneous photon emission [6], or auto- and photoionizing states with very small release energies ($E \sim 0.01$ eV) [7]. A common feature for all these atomic systems are the well-defined energy levels, exhibiting only homogeneous broadening, accompanied by (nearly) Lorentzian line shapes and exponential lifetimes that are inversely proportional to the width of the energetic state distribution, $\tau = \hbar/\Gamma$. Though such pure systems may theoretically be accessible using coherent wave functions, when it comes to experimental confirmation, the predicted deviations from exponential decay either occur at immeasurable low signal levels, or for the more exotic atomic states are too difficult to observe.

Instead of small E , one may alternatively look at systems with large Γ . As an example this is achieved if the metastable state exchanges small amounts of energy with a surrounding bath. The width of the decaying state increases with increasing coupling to the bath leading to an earlier turnover into nonexponential decay, which has been nicely shown by Onley and Kumar by means of an exactly soluble system [3]. Another decaying system that couples to a bath is photon emission of dissolved (i.e., isolated) organic molecules, which are studied here. To start with, the excited states in such systems are localized (excitonic), the energy released during the transitions is comparably low ($E \sim 2$ to 3 eV), and, by using short laser pulses the excitation can be achieved in a time much shorter than the exponential lifetime. Likewise for atomic systems, in

the gas phase the excited state energy distribution of small organic molecules is narrow and couples to a whole range of electronic, vibrational, and rotational transitions [8]. Thus, these characteristics of small organic molecules do not constitute any fundamental advantage over atomic systems for the search of nonexponential decay. However, this original narrow width is significantly increased in dissolved systems due to the inhomogeneous broadening induced by the local solvent environment. Furthermore, for large molecules, $\omega(E)$ is further broadened by the particular intermolecular structure, for example, the conjugation length dispersion in conjugated polymers. Importantly, this additional broadening of $\omega(E)$ has neither been paid for by an increase in E nor by reducing the exponential lifetime of the state—unlike for atomic systems, for organics $\tau \neq \hbar/\Gamma$. Using this solvent interaction, one arrives at a significantly reduced ratio E/Γ , which is the essential condition for nonexponential decay [1,3,9].

The decay curves of a range of organic molecules and polymers dissolved in common solvents where thus measured over 20–30 lifetimes, using time-resolved spectroscopy as previously described in detail [10]. Briefly, in our spectrometer the sample is excited by a short laser pulse (170 ps, 7 mJ at 3.5 eV, repetition rate 10 Hz). A very fast gated ICCD camera (4Picos, Stanford Computer Optics, 100 ps gate resolution) then monitors the spectrally dispersed emission between any two user-defined points in time. A time-correlated single photon counting system (excitation at 390 nm, instrument response function 65 ps, detection channel width 5 ps) was employed to verify the measurement of short exponential lifetimes.

For presentation we focus on two systems with prototypical character: the common laser dye Rhodamine 6 G and a blue-emitting polyfluorene-type conjugated polymer with about 100 repeat units, see Fig. 1 for chemical structures. The main part of this figure shows two normalized fluorescence spectra with detection times as indicated. The corresponding decay curves for these emissions are shown in Fig. 2 on a double logarithmical axis. As expected, initially both decays obey exponential laws (yellow and cyan solid lines). However, after a material dependent number of lifetimes (17 for Rhodamine 6 G and 11 for polyfluorene) the fluorescence decays significantly slower, turning into algebraic decay laws.

Before discussing this additional contribution to the exponentially decaying emission in more detail we shall briefly comment on its intra- and monomolecular origin. First, in making use of the full decays, we refer back to the luminescence spectra of Fig. 1. Here, the time settings were chosen such as to obtain characteristic spectra of the two fluorescence contributions. Albeit not exactly identical, certainly the spectra are isoenergetic. Also, the relative intensities of both emission contributions are invariant of excitation energy [10]. In consequence, the algebraic decaying fluorescence contribution cannot be

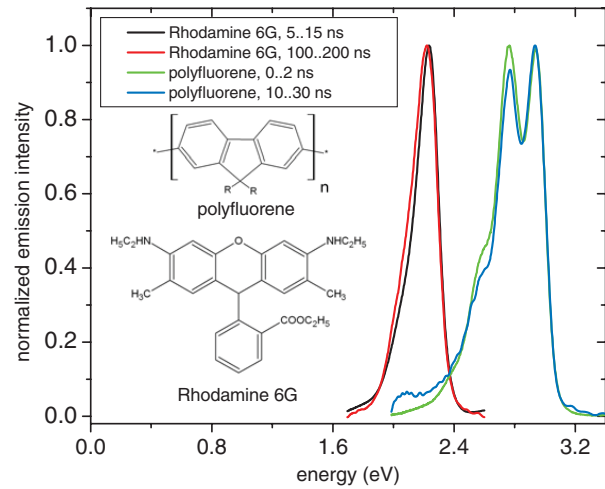


FIG. 1 (color). Normalized prompt and delayed emission spectra as indicated after excitation at 3.5 eV, of polyfluorene and Rhodamine 6 G dissolved at 10^{-5} by weight in toluene and ethanol, respectively. The insets show the chemical structures with $R = 2, 6$ -ethylhexyl.

assigned to spectral diffusion to low-lying energetic states with a potential distribution of long lifetimes or other external impurity or defect sites. As with the exponentially decaying contribution, the long-time fluorescence exhibits a linear dependence on concentration (tested between 10^{-5} and 10^{-3} g/g solvent) and on laser excitation dose (tested between 0.1 and 1000 $\mu\text{J}/\text{cm}^2$) [10]. Both of these observations rule out any potential bimolecular origin of the long-time fluorescence, such as diffusion limited triplet exciton annihilation, which obeys clearly different decay kinetics [10]. Also, intersystem crossing of the (relatively long-lived) triplet excitons back to the singlet manifold (E -type delayed fluorescence) can safely be excluded as for these materials the singlet-to-triplet exciton energy splitting is large compared to the thermal energy (typically $\Delta ST \sim 0.7$ eV). Given that both contributions to the decay can *only* be distinguished by their kinetics, we ascribe the retarded component to the theoretically predicted long-time deviation from the exponential-decay law.

In this case, theory predicts an algebraic decay law for the asymptotic time dependence with exponent, $m \leq -2$ [9], which is consistent with the long-time behaviors shown in Fig. 2. Furthermore, the experimentally observed exponents from all materials tested so far range from -2.1 for some conjugated polymers up to -4.1 in the case of anthracene. In Table I measured data are given for a range of dissolved molecules. Qualitatively the ratio $\tau^{\text{turnover}}/\tau$ provides a measure for the relative intensities of the non-exponential decay contributions, which are larger for smaller values. Theoretically, nonexponential decay is established earlier for an increasing, residual excited state density at the cutoff energy, which in turn is determined by the energetic density of states (DOS) distribution, especially its width, Γ , and its center energy, E . Certainly, the

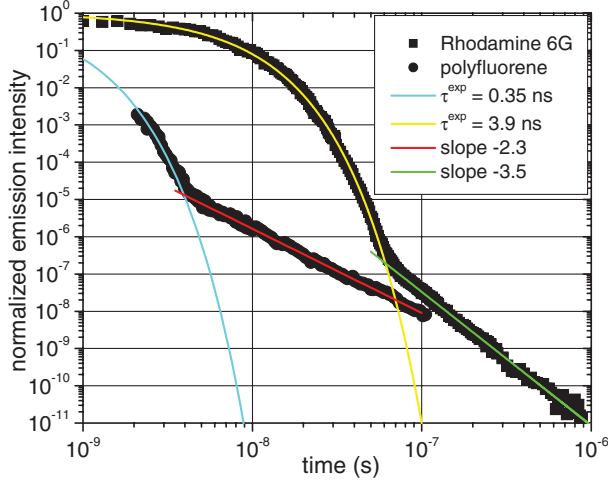


FIG. 2 (color). Corresponding double logarithmic fluorescence decays of the emissions shown in Fig. 1. Exponential and power law regions are indicated by solid lines and the emission intensity at time zero has been normalized.

theoretical description of dissolved organic molecules are extremely complex and no easy expression is yet known that relates the shape and position of the DOS to the turnover time between exponential and algebraic mode and the slope of the algebraic contribution. Nevertheless, for the exactly soluble systems, i.e., particle scattering, etc., that have theoretically been studied it is found that broad transitions (relative to the released energy) result in early relative turnover times: [1–4,11]

$$\frac{\tau^{\text{turnover}}}{\tau} \sim \log \left[\frac{E}{\Gamma} \right]. \quad (2)$$

Given the lack of an exact expression for organic systems, we shall nevertheless qualitatively discuss whether Eq. (2) can justify our observations. However, the situation is further complicated. As a consequence of the numerous overlapping vibrational and rotational transitions, for or-

ganic molecules, Γ is not directly accessible so we cannot test Eq. (2) directly. On the other hand τ , τ^{turnover} , and E can accurately be measured and we may use Eq. (2) to compute relative widths, which are given in the last column of Table I. These values should linearly depend on the real width of the excited state and as such allow for a qualitative comparison of the different materials investigated here.

Relatively low intensities of the nonexponential contributions (i.e., late turnovers, narrow width) are generally observed for small molecules including the laser dyes Coumarin 450 and 500, Rhodamine 6 G, the fluorene oligomer with three repeat units and anthracene. Here, the main contribution to the broadening of $\omega(E)$ is caused by the solvent. Because of its nonrigid structure, ring torsions will additionally add to the value of Γ for the laser dye 2,5-bis(4-biphenyl) oxazole (BBO), which explains its larger width compared to the other dyes. The turnover ratios are significantly reduced from ~ 17 for the rigid small molecules to 11 in case of the long conjugated polymer polyfluorene, which translates into approximately 20 times stronger nonexponential contributions. Essentially this situation is shown in Fig. 2. Besides the matrix effects of the solvent, $\omega(E)$ of these long conjugated polymers is additionally broadened by the variation in effective conjugation length, which is intrinsically limited and much shorter than the length of the molecule. Illuminating in this context is the behavior of the three members of the fluorene family having different numbers of repeat units ($n = 100$, $n = 10$, $n = 3$) otherwise being chemical identical. As the length of the molecule increases, i.e., the confinement of the excited state decreases, the intensity of the nonexponential decay contributions increases. An exception within the long conjugated polymers is polyspirobifluorene [12]. Here the turnover into algebraic decay already occurs after less than nine exponential lifetimes have passed, which translates into roughly 10 times stronger nonexponential emission contributions compared to common conjugated polymers such as poly-

TABLE I. Decay characteristics of a range of dissolved materials. Given are the exponential lifetimes (τ), the crossover times ($\tau^{\text{crossover}}$) relative to τ , the exponent of the nonexponential decay contribution, and a relative width computed using Eq. (2).

Organic material	τ (ns)	E (eV)	$\tau^{\text{turnover}}/\tau$	Algebraic exponent	Relative width Γ (10^{-6} eV)
Polyspirobifluorene	2.1	3.0	8.6	-2.08	552
Polyfluorene, $n = 100$	0.35	3.0	11.1	-2.26	45
Polyfluorene, $n = 10$	0.43	3.0	12.7	-2.46	9.1
Polyfluorene, $n = 3$	0.64	3.1	14.7	-2.68	1.3
Ir(ppy) ₃ , frozen solution	3000	2.4	13.0	-2.1	5.4
Ir(ppy) ₃	933	2.4	13.2	-2.1	4.4
PtOEP, frozen solution	120 000	1.9	15.0	-4.0	0.58
Anthracene	3.6	3.2	14.7	-4.07	1.3
BBO	0.96	3.2	14.7	-2.8	2.4
Coumarin 450	3.6	2.9	16.4	-2.9	0.22
Rhodamine 6G	3.9	2.3	17.5	-3.5	0.058
Coumarin 500	5.0	2.7	17.4	-2.5	0.075

fluorene. In conjunction with one of the highest slopes, -2.08 , the nonexponential effects contribute 0.17% to the overall emission, which is the highest value for all materials measured so far. Unlike polyfluorene, as a consequence of the so-called spiroconjugation for polyspiro-bifluorene the π -conjugation extends into the side groups. Torsional fluctuations of these side groups around the spiro-linkage introduce a third variable, besides the solvent and the normal conjugation length distribution that all contribute to the increase of Γ . The excited state in $\text{Ir}(\text{ppy})_3$ is a metal-to-ligand charge transfer state, which is again strongly affected by the solvent, leading to a lifetime-to-turnover ratio of 13.2 [13]. Because of thermally restricted relaxation, the lifetime of this heavy metal complex significantly increases from 0.9 to $3 \mu\text{s}$ when measured at 77 K compared to room temperature. This, however, only leads to minor spectral changes; especially the apparent width of the spectrum is unaltered [13]. Indeed, at 77 K we observe the turnover into algebraic decay more than 3 times later compared to room temperature, i.e., the ratio of $\tau^{\text{turnover}}/\tau$ remains nearly constant. This in turn translates into a constant spectral width as experimentally observed giving strong evidence for the validity of Eq. (2). Finally, the excited state of the platinum porphyrin complex PtOEP is essentially a metal transition, which is mainly homogeneously broadened by the porphyrin ligand field rather than by the surrounding solvent, which yields a significantly smaller relative width. To summarize the above, the strength of the nonexponential components can, on a qualitative basis, be consistently correlated to a range of effects that cumulatively broaden the density of states distribution.

Also included in Table I are the slopes of the corresponding algebraic decay contributions. Whereas the relative turnover times are linked to the residual excited state density at the threshold, the decay exponents relate to the shape of the DOS [6,9,14]. Here, an exponent of -4 is expected for Lorentzian-type excited state distributions, whereas -2 indicates a Gaussian. This should be seen in view of the general knowledge that Lorentzian and Gaussian are the standard models for homogeneous and inhomogeneous broadening, respectively. Unfortunately, for the materials studied here we cannot evaluate the line shape [and thus $\omega(E)$] directly due to the omnipresent vibronic progression within the emission spectra. Nevertheless, the slopes given in Table I indeed indicate a turnover of the excited state distribution (concomitantly the line shape) with the size of the molecule from a Lorentzian for rigid small molecules such as anthracene towards a Gaussian for long conjugated polymers. For the extremes, the homogeneously broadened metal centered transition of PtOEP and the strongly inhomogeneously

broadened excitonic transition of polyspirobifluorene, we observe the expected slopes close to -4 and -2 consisted with homogeneous and inhomogeneous broadening, respectively. For the latter two, this agrees well with the apparent shape of the corresponding fluorescence spectra.

In conclusion, by using time-resolved spectroscopy and measuring fluorescence decays beyond 20 lifetimes, an additional algebraic contribution to the monoexponential emission decay of many organic materials has been observed. This constitutes the first experimental confirmation of long-time deviations from the exponential-decay law that have theoretically been predicted for many years. However, this was only possible due to the additional broadening of the excited state energy distributions, for example, by the solvent, but has enabled us to verify one of the most general findings of quantum mechanical decay theory. Additionally, in exploiting Khalfin's original work it may be possible to reverse the problem by employing the observed nonexponential decay contributions to analytically gain the density of states distribution of organic materials, which are otherwise hard to measure [1].

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