Singlet-Exciton Fusion in Molecular Solids: A Direct Subpicosecond Determination of Time-Dependent Annihilation Rates

B. I. Greene and R. R. Millard
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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The first kinetic data displaying a time-dependent singlet-exciton–annihilation rate have been observed. Subpicosecond optical excitation of polycrystalline thin-film samples of β-hydrogen phthalocyanine resulted in excitonic saturation of the crystal lattice. The initial exciton decay yields the only unambiguous measurement of a characteristic annihilation interaction rate for molecular excitons on adjacent lattice sites.

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The dynamics associated with singlet-exciton motion in organic crystals, together with the related high-density effect of exciton-exciton annihilation (fusion), has been an active area of both experimental and theoretical research. Numerous nanosecond and picosecond time-resolved fluorescence measurements have unequivocally demonstrated the existence of the singlet-singlet annihilation phenomenon.[1–8] Beyond this, however, no direct measurements of any of the hypothesized microscopic events comprising the effect have been presented. Values for hopping times (τ_H), diffusion constants (D), and characteristic interaction radii (R_0) have nevertheless been proposed on the basis of these measurements. Such values are always contingent on tentative approximations of, or assumptions about, at least one of the aforementioned quantities. In this Letter we present the first experimental data that directly measure a key microscopic event in the annihilation process, the characteristic annihilation rate for singlet excitons on adjacent lattice sites. These novel measurements are facilitated by our ability to saturate a sample (i.e., excite virtually every molecule) and subsequently follow the course of population decay with subpicosecond temporal resolution.

Previous time-resolved annihilation studies have monitored wavelength-integrated fluorescence intensity following pulsed optical excitation to probe excited-state population densities. In the present study we employ the technique of subpicosecond time-resolved absorption spectroscopy, which has the advantages of combining laser-pulsewidth–limited temporal resolution with valuable spectroscopic information obtainable as broad-banded optical absorption spectra.

Samples consisted of polycrystalline thin films of β-hydrogen phthalocyanine (H_2Pc). While not the classic subject of investigation that, for instance, anthracene has been, H_2Pc has several important properties critical to the success of the present measurements. The material is highly absorbing at our laser fundamental (16 000 cm^{-1}) with $\alpha \approx 2\times10^5$ cm^{-1}. High excitation densities (ca. 10^{21} cm^{-3}) are therefore obtainable with available excitation energies and intensities. H_2Pc is readily sublimed to form good optical-quality amorphous films, which can be subsequently annealed to yield polycrystalline samples. These films have been well characterized.[9–12] Spectroscopic and crystallographic evidence supports the notion that the individual microcrystallites (which have a flakelike morphology and in-plane dimensions of 10–100 μm) are isomorphous with the β form of the macroscopic single crystal. The films showed a remarkable resistance to optical damage at all reported excitation intensities. Finally, H_2Pc exhibits an intense excited-state absorption spectrum, with transitions in the visible at least 5 times stronger than those observed in anthracene.

Measurements were performed with amplified laser pulses obtained from a colliding-pulse ring dye laser.[13] These pulses were 0.15 ps FWHM, centered at 625 nm (16 000 cm^{-1}), and occurred at a repetition rate of 10 Hz. Pump and probe measurements were performed with pulses at the fundamental wavelength and white-light continuum pulses, respectively. Details of the experimental technique have been presented previously.[14] The sample was held at ca. 5 K on the cold finger of a continuous-transfer liquid helium cryostat. Films were estimated to be roughly 1000 Å thick.

Transient difference spectra revealed regions of bleaching (due to ground-state depopulation) in addition to regions of excited-state absorption. As the delay time was increased, a dramatic evolution of the entire difference spectrum was observed. Over the first 10 ps subsequent to excitation, there was a rapid decay of the initially induced transient spectrum. This is due to a nonradiative process which efficiently depopulates the initially prepared exciton population. The detailed spectral features of this decay will be the subject of a future report.[15] In the present study, however, we choose to probe kinetics at a spectral position where the observed signal can be unambiguously related to the exciton number density. Such a spectral region occurs in the area of excited-state absorption between 19 000 and 22 000 cm^{-1}, where as a result of a minimal ground-state absorption, there can be little contribution from ground-state recovery processes manifested in the signal. We observed the spectral

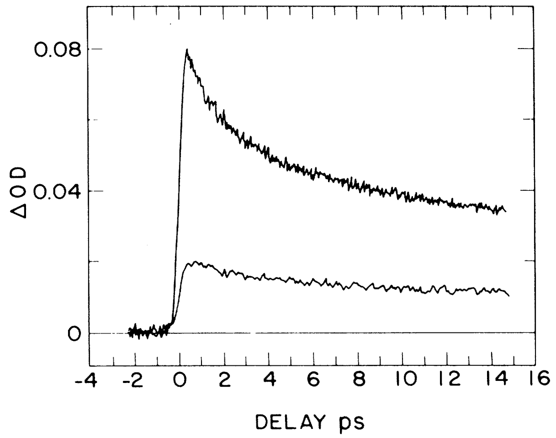

FIG. 1. Optical density at 19 500 cm^{-1} vs delay time for two different excitation intensities. Upper curve, 5×10^{10} $\mathrm{W/cm}^2$; lower curve, 5×10^{9} $\mathrm{W/cm}^2$.

shape of the excited-state absorption in this region to remain constant throughout the decay.

Figure 1 displays single-wavelength pump and probe data obtained with pump pulses at 16 000 cm^{-1} and probe pulses at 19 500 cm^{-1} for two different pump intensities. The decay of these signals was observed to be highly nonexponential. These kinetic traces were observed to be independent of sample temperature over the range 5 to 300 K. Figure 2 shows a plot of peak absorbance signal versus pump intensity. These data display evidence of signal saturation and will be discussed below.

We suggest that the initial rapid decay of the induced-absorbance signal is due to singlet exciton-exciton annihilation. This nonradiative phenomenon has been observed in many kinetic studies of molecular crystals where high densities of excitons are created. This certainly corresponds to our experimental conditions, where with the highest-intensity excitation pulses (55 μJ/pulse, 7×10^{10} $\mathrm{W/cm}^2$), we estimate exciton densities of approximately $(1.0\pm0.5)\times10^{21}$ cm^{-3}. Single-crystal specific-gravity measurements indicate a value for total saturation to be 1.68×10^{21} cm^{-3}.[16]

Exciton annihilation is conceived of as a composite process, separable into two steps: exciton motion and exciton-exciton annihilation (destruction). Previous studies have measured time-independent annihilation rates which are comprised of, and determined by, the individual microscopic rates of these two steps. In principle, however, time-dependent energy-transfer rates are expected in measurements of exciton trapping and annihilation. This arises from the fact that subsequent to the initial creation of a spatially homogeneous exciton population, proximate pairs of excitons, or excitons closest to traps, will interact first. Progressively greater interparticular distances result in decreasing characteristic interaction rates. Both motion-limited diffusion theory and the Förster long-range dipole-dipole interaction picture (in the absence of diffusion) lead to a $t^{-1/2}$ dependence for γ, the bimolecular rate constant.[4,17] For annihilation-dominated kinetics, a simple phenomenological rate equation is written to include this time dependence ex-

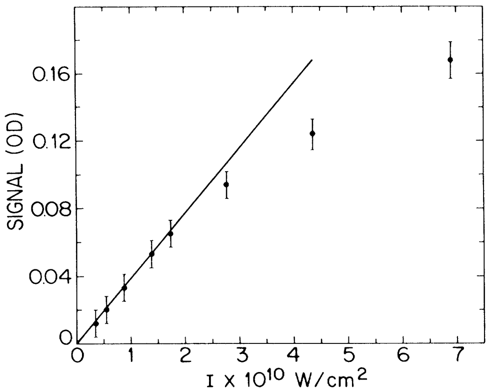

FIG. 2. Peak induced signal at 19 500 cm^{-1} vs excitation intensity.

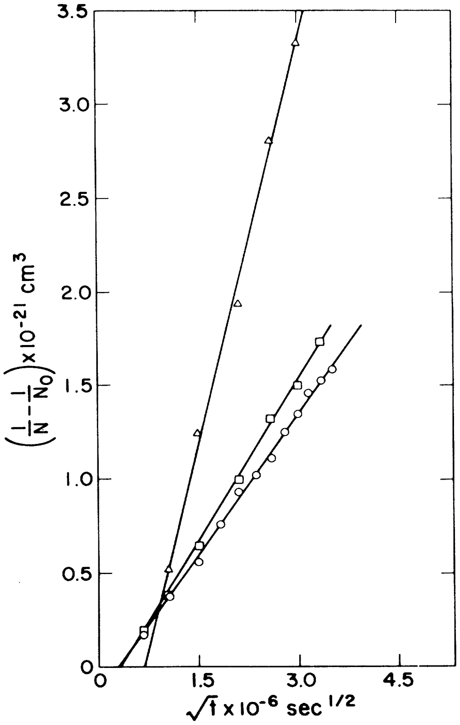

FIG. 3. Plot of decay data showing $t^{-1/2}$ dependence of the bimolecular rate constant γ. Data are plotted for three different pump intensities. Circles, 5×10^{10} $\mathrm{W/cm}^2$; squares, 2.5×10^{12} $\mathrm{W/cm}^2$; and triangles, 5×10^{9} $\mathrm{W/cm}^2$. γ is determined to be $(1.0\pm0.5)\times10^{-16}$ $\mathrm{cm}^3\,\mathrm{sec}^{-1/2}$.

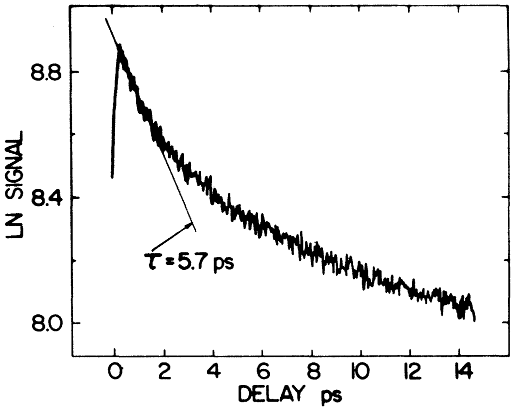

FIG. 4. Semilogarithmic plot of the decay of the 19 500-cm^{-1} absorbance signal vs delay time. A single-exponential fit to the initial decay yields a characteristic lifetime $\tau = 5.7$ psec.

plicitly:

$$dN/dt = -\gamma t^{-1/2} N^2. \qquad (1)$$

Integration of Eq. (1) yields an expression for the exciton-number density as a function of time:

$$N(t) = (2\gamma t^{1/2} + 1/N_0)^{-1}.$$

Figure 3 displays time-resolved absorption data (such as appear in Fig. 1) plotted in the form $1/N - 1/N_0$ vs $\sqrt{t}$. Kinetics obeying the rate law [Eq. (1)] will yield a straight line with slope 2γ.[18] This is observed to be the case, with the additional consideration that in the low-intensity regime, a nonuniform excitation density exists from the front to the back of the sample. We calculate that, when normalized to total exciton population, a ratio of 6.6 in apparent bimolecular rates should exist (for our sample) between a situation of "Beer's Law" absorption (exponential number-density profile) and that of a totally bleached and uniform exciton profile. We measure this ratio for the intensities 1×10^{10} W/cm^2:7×10^{10} W/cm^2 to be 4.4. This provides even further evidence that we are well into the saturation regime at intensities above 5×10^{10} W/cm^2. We extrapolate a value for γ, corrected for nonuniform number-density–excitation profiles, to be $(1.0\pm0.5)\times10^{-16}$ cm^3 sec$^{-1/2}$. It is interesting to note that the line drawn through the data points in Fig. 3 does not go through the origin. We attribute this effect to the discrete nature of the crystal lattice being inadequately described by a model assuming a continuous distribution of exciton-exciton spacings.

Excitonic saturation of the H_2Pc lattice facilitates a clear and simple interpretation of the observed initial rapid signal decay. Since the majority of excitons will have excitons as nearest neighbors, we propose that a single-exponential fit to the data at the earliest delay times corresponds to the lifetime of proximate excitons. Over the first 2 psec, such a fit is quite good yielding a temperature-independent lifetime of 5.7 psec (Fig. 4). This observed rate was independent of pump intensity for intensities above ca. 3×10^{10} W/cm^2. We expect that as the sample becomes saturated, the early-time decay rate will be dominated by the single exponential rate associated with proximate exciton pairs. As such, this study presents the only measurement of an exciton annihilation rate free from the ambiguity or possible influence of exciton motion.

In conclusion, data shown in Fig. 1 are the first to manifest a clear and unmistakable time-dependent singlet annihilation rate. Excitonic saturation has facilitated a novel measurement of the rate associated with purely annihilistic interactions. We note that this rate is quite small compared with approximations frequently made for exciton hopping rates. Previous assumptions of "motion limited" kinetics in molecular crystals should therefore not be taken for granted.[19]

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