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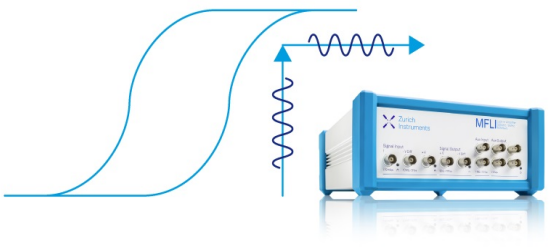

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TWO-PHOTON EXCITATION OF FLUORESCENCE BY PICOSECOND LIGHT PULSES

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Standing wave excitation of two-photon fluorescence in solutions or organic molecules is reported. The observations allow the direct display and measurement of optical pulses as short as $1-2\times10^{-2}$ sec.

This Letter reports the observation of intense blue fluorescence in solutions of 1,2,5,6-dibenzanthracene (DBA) and other organic molecules excited by picosecond duration, 5300 Å optical pulses. Standing wave excitation of this fluorescence has allowed the direct display and photographing of light pulses as short as 1–2 psec. We tentatively attribute the DBA emission to two-photon absorption via virtual states, followed by fluorescence from the ^1L_b level.[1-3]

The experiments made use of 5300 Å light generated in a KDP crystal by a 1.06-μ Nd^{+3} glass laser, mode-locked by the Q-switch dye technique.[4] The crystal output consisted typically of ~20 pulse trains at intervals of 4.6×10^3 psec, twice the optical length of the laser resonator. Photodiode measurements showed the individual trains to have a duration $<6\times10^2$ psec and energy 10^{-3} J. The 5300 Å light had a spectral width of 100–400 cm^{-1}, usually with a prominent 5–20 cm^{-1} central band, in agreement with earlier results.[4,5] After filtering to remove laser fundamental and pump light, and telescoping to a diameter of 1 mm, the beam traversed a 19 mm fluorescence cell. In 0.01 M DBA solution in benzene and in other solutions described below, the beam produced a bright, uniform, blue track with a diameter of 0.7 mm. The emission was primarily in the 4000–4200 Å region with a lifetime $\leq$50 nsec, consistent with previously reported ^1L_b fluorescence.[6] The track produced by a single laser pulse could be readily photographed (f/2.8, Polaroid 3000 film).

A direct display of the structure of the pulse trains was obtained by normal reflection of the beam at a mirror immersed in the solution at the exit end of the cell. Consider the expected two-photon fluorescence due to a train of m identical pulses of peak intensity I, duration between half-intensity points t_1, and separation $t_2 \gg t_1$. The integrated background trace intensity I_B is proportional to $(4m-2p)I^2t_1$. The index $p \leq m-1$ labels the position at which pulses meet thei p^{th} nearest neighbors in the train. At the mirror (R = 100%), $I_p = I_0 = 2I_B$. The length of the bright region at the mirror, between points of half-maximum intensity above background, is $\alpha ct_1/2n$, and of the other bright regions $\alpha ct_1/n$. Here n is the refractive index of the solution, and α is a constant depending on the pulse shape: e.g., $\alpha = 1$ for a Lorentzian pulse, 1/2 for a rectangular pulse. The separation of the bright regions is $ct_2/2n$. In the present work $n = 1.50$.

A typical fluorescence track produced by the standing wave distribution, photographed through a Corning 7-59 filter to eliminate 5300 Å scattering, is shown in Fig. 1. The short bright region of 0.2 mm length at the left occurs at the mirror; three 0.4 mm bright regions occur at 6.1 mm intervals from the mirror. The track is consistent with two-photon (I^2) fluorescence excited by a train of $m \geq 4$ pulses of duration 2–3 psec separated by 60 psec. From the photodiode measurements, $m \leq 10$. It should be noted that 60-psec pulse train generation is expected from our mode-locked laser, in which the beam is coupled out through a plane parallel 0.63 cm quartz flat, the inner surface of which has a 65% reflecting dielectric coating. Since the reflectvitiy spectrum of this element has peaks uniformily spaced by 0.54 cm^{-1}, maximum picosecond pulse reflectivity is available for a train with regular spacing $(0.54\times3\times10^{10})^{-1}$ or 61 psec.[7] It was verified that when the parallel flat was replaced by a wedge, the

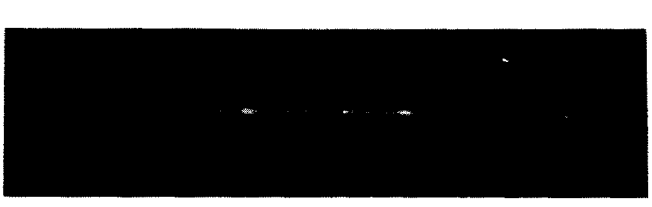

Fig. 1. Two-photon fluorescence track excited by 0.01 M DBA solution by train of 2–3 psec 5300-Å pulses separated by 60 psec. Bright spots indicate pulse intersections. Track length is 19 mm; mirror is located at left end of track. The solution refractive index is 1.5.

pulse train reduced to a single intense pulse.

Densitometer measurements of integrated fluorescence intensity along the track were made from negatives prepared from the Polaroid photographs, whose characteristic curves were individually measured. For the DBA solutions, he ratio I_0/I_B was found to have an average value 1.8 ± 0.2. This result is consistent with a fluorescence intensity proportional to I^2. The monotonic intensity decrement between adjacent peaks was $(0.15 \pm 0.10)I_0$. Pulse trains having $t_2 < 60$ psec, usually 12 psec, were also observed and presumably arise from reflections at elements within the resonator. The shorter spacings were always accompanied by the $\Delta\bar{\nu} = (ct_2)^{-1}$ fringes in the spectrum of the 5300 Å light. The expected 0.54 cm^{-1} fringe spacing characteristic of the dominant 60 psec spacing was visible on some spectra but was not prominent. Figure 2(A) shows a typical densitometer trace of a train of 2-psec pulses, with $t_2 = 60$ psec. Figure 2(B) shows a train with a dominant spacing of $t_2 = 12$ psec, together with the central portion of the spectrum of the exciting 5300 Å light. The expected fringes of $\Delta\bar{\nu} = (ct_2)^{-1} = 2.8$ cm^{-1} are the dominant feature of the spectrum. The spectral width of a 2-psec pulse is ~10 cm^{-1} and is consistent with the width of the intense 5–20 cm^{-1} central spectral bands.[5] A few pulses as short as 1 psec have been recorded. The pulse widths discussed here were calculated assuming $\alpha = 1$, i.e. a Lorentzian pulse.[5]

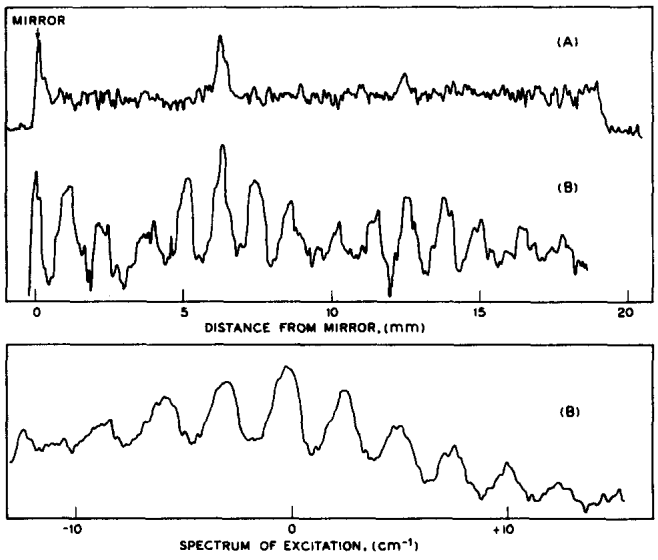

Fig. 2. A: Densitometer trace of two-photon fluorescence track produced by train of 2-psec pulses, pulse separation 60 psec. B *(above):* Track indicating groups of three pulses separated by 12 psec, group separation 60 psec. Each group produces three bright spots at the mirror, five bright spots at the crossing regions centered at 6.3 and 12.5 mm. B *(below):* Central band of 5300-Å pulse spectrum producing the track of B (above). The 2.8 cm^{-1} fringe spacing is in agreement with the 12-psec repetition rate inferred from the track.

We estimate a peak pulse power of 6×10^7 W at 5300 Å in the above experiments, or an intensity I of 2×10^{28} photons cm^{-2} sec^{-1}. The observed fluorescence per 2-psec pulse is 1×10^{12} photons cm^{-3}. These values represent a molecular cross section $\sigma_1 I$ cm^2 for two-photon absorption given by $\sigma_1 = 7 \times 10^{-52}$ cm^4 sec. This result is believed to be accurate to within a factor of about 5.

The agreement between the cross section measured in he present work, and the two-photon (6943 Å) cross sections of 10^{-51} to 10^{-50} cm^4 sec measured by Peticolas et al.[1] and Hall et al.[3] for anthracene, pyrene, and benzpyrene crystals lends support to our interpretation of the above results as primarily two-photon absorption and fluorescence. However, the occurrence[8] in DBA of triplet states at $T_1 = 18{,}300$ cm^{-1} and $T_2 = 37{,}080$ cm^{-1} suggests alternative mechanisms. Two-step absorption via the triplet states and subsequent intersystem crossing appear to be ruled out by the large transition probability ratio $(T_1 \rightarrow T_2)/({}^1A_g \rightarrow T_1)$. The large ratio (>$10^6$) (ref. 8) should lead to a severe ${}^1A_g \rightarrow T_1$ bottleneck and I^1 rather than the observed I^2 fluorescence. Triplet-triplet annihilation is ruled out by the observed picosecond pulse memory. Additional support for the two-photon interpretation is provided by the observation of (slightly weaker) 3000–3600 Å fluorescence and picosecond pulse displays in benzene solutions of highly purified biphenyl and napthalene, which have no triplet states below 21,000 cm^{-1}.

Intense blue fluorescence in 1,2-benzanthracene and anthracene solutions has also been observed with 5300 Å light. The theory of two-photon absorption[2] suggests that the effect should occur widely in molecules having sufficiently low singlet levels.

With lower intensity 6943 Å excitation, strong two-photon fluorescence has also been observed in benzene solutions of 9,10-diphenyl anthracene, 9,10-dimethyl anthracene and other substituted anthracenes. It is believed that triplet mechanisms may play a dominant role under these conditions.[9]

Straightforward extension of the above experiment should facilitate the use of picosecond optical pulses in a variety of experiments of current interest.[10] It is expected that the resolution of the present technique is limited primarily by spatial diffusion of singlet excitation during the fluorescence lifetime, and should be less than 10^{-14} sec.

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PICOSECOND LIGHT PULSE DISPLAY USING TWO DIFFERENT OPTICAL FREQUENCIES

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A new technique for the display and measurement of picosecond light pulses is demonstrated. Two picosecond pulses, of different optical frequencies, are sent on a collision course in a liquid. They produce strong two-photon fluorescence only in the region where they overlap. This results in the direct display of the pulse shapes over a very weak background. In a different arrangement, the two pulses enter the liquid collinearly and simultaneously, and initially generate strong two-photon fluorescence. Subsequently, as the pulses propagate through the liquid, dispersion causes one pulse to overtake the other and the two-photon fluorescence diminishes. This results in a *magnified* display of the pulses.

Recently, Giordmaine, et al.[1] have demonstrated a new technique for displaying picosecond light pulses such as one produced by mode-locked Nd:glass lasers.[2,3] In their experiment, two short pulses at 0.53 μ were made to collide in a liquid exhibiting two-photon fluorescence. Because of the quadratic intensity dependence of two-photon fluorescence,[4] the intensity of fluorescence was greater in the region of the liquid where the pulses overlapped than in the other region where each pulse acted alone, sequentially. The ratio of the fluorescence intensities in the two regions, the contrast ratio, was observed to be approximately 2.0. Clearly, it would be very advantageous if one could eliminate the background fluorescence trace for one would then be able to display weak and complex picosecond signals which could otherwise be obscured in the background fluorescence. In this Letter we wish to report results obtained with a scheme whereby the background fluorescence trace is virtually eliminated. We also present results obtained with a modification of the same scheme whereby spatial picosecond pulse displays are greatly magnified without loss of intensity.

The basic idea behind the experiment is to use light pulses of two different optical frequencies and an appropriate liquid. One pulse has a frequency which is too small to induce two-photon fluorescence in the liquid. The other one, although it has a frequency capable of producing two-photon fluorescence, is of sufficiently weak intensity that it produces little or no fluorescence. The sum frequency of the two pulses is sufficiently high so that simultaneous absorption of two quanta,[5] one from each pulse, leads to fluorescence in the liquid. When the two pulses interact in the liquid they produce strong two-photon fluorescence whose spatial distribution is a direct measure of the pulse shapes. A 5×10^{-2} M solution of diphenylcyclopentadiene (DPCPD) in tetrahydrofuran exhibits strong fluorescence with a maximum at 0.43 μ and satisfies the requirements for two-photon fluorescence stated above when used in conjunction with strong ($\approx$1 GW/cm^2) pulses at 1.06 μ and weaker ($\approx$1 MW/cm^2) pulses at 0.53 μ. We have found that pulses at 1.06 μ alone did not produce any detectable fluorescence, while the 0.53-μ pulses produced a weak flux of blue