DIRECT MEASUREMENT OF THE PICOSECOND DECAY TIME OF THE J AGGREGATE OF PSEUDOISOCYANINE IODIDE USING AN OPTICALLY COMPRESSED FREQUENCY-DOUBLED CONTINUOUS WAVE Nd–YAG LASER AND A SYNCHRONOUSLY OPERATING STREAK CAMERA

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Summary

Using the shorter than 4 ps pulses at 532 nm from a frequency-doubled optically compressed continuous wave Nd–YAG laser, in conjunction with a synchronously operating streak camera, the fluorescence decay of the J aggregates of 1,1′-diethyl-2,2′-cyanine (pseudoisocyanine) iodide has been measured with picosecond resolution to be 24 ps. The power and concentration dependence are also described.

1. Introduction

With the availability of picosecond pulses from mode-locked lasers, the J aggregate bands formed by cyanine dyes in strongly polar solvents [1] have been the subject of recent research [2 - 5]. As well as being important from the physical view of the strong intermolecular interaction, the J aggregates can be used as models for more complex (*e.g.* biological) systems and they are also of great relevance in the field of photography, being used as sensitizers [6]. The majority of the reported experiments have been carried out using the second harmonic of single-shot neodymium glass lasers [2, 4, 5] or an optical parametric oscillator pumped by a 3 Hz repetition rate Nd–YAG laser [3]. Detection techniques employed optical Kerr shutters [2, 3], time-correlated single-photon counting [5] and a single-sweep jitter-free streak camera [5] which permitted an average of 50 shots per fluorescence decay. We report here on the direct measurement of the decay time of the J aggregate band of the dye 1,1′-diethyl-2,2′-cyanine iodide in aqueous solution, using an optically compressed frequency-doubled continuous wave (CW) Nd–YAG laser in conjunction with a synchronously operating streak camera. By using this arrangement averaging over 10^8 pulses s^{-1} was permitted to give a markedly improved sensitivity. Fluorescence decay times of 24 ps for the J aggregate and 11 ps for the monomer

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were recorded at room temperature, which is in fair agreement with previously reported decay times for similar dye systems [2 - 4].

2. Experimental details

The experimental arrangement is shown schematically in Fig. 1. The CW mode-locked Nd–YAG laser (a modified Quantronix model 116) has already been described [7] and it suffices to mention here that it produces about 80 ps pulses at a repetition rate of 100 MHz with an average power of about 7 W. The optical compression technique has proved to be a powerful method in shortening picosecond laser pulses. It is based on the spectral and temporal broadening of the pulses by means of self-phase-modulation-induced chirp and positive group velocity dispersion in propagation through a single-mode optical fibre and the subsequent de-chirp using a suitable negatively dispersive delay line. A review on this subject is given in ref. 8.

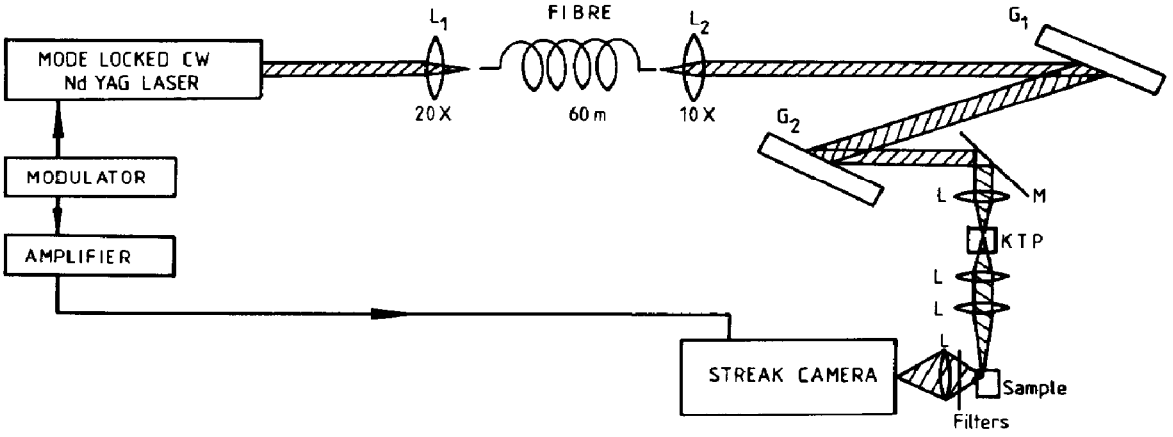

Fig. 1. Schematic diagram of the experimental arrangement.

The optical pulse compressor used in this work has been described elsewhere [9], as well as a detailed experimental study of the parameters involved in optimizing the compression ratio of such a system. However, for the work reported here, in order to obtain a higher average power, only 60 m of single-mode non-polarization preserving fibre was used (rather than 120 m, as in ref. 9). The grating separation was about 1.2 m, to obtain maximum compression. For an input average power of about 5 W, a 50% coupling efficiency through the fibre was obtained and a further 50% reduction occurred after traversing the grating pair, resulting in about 1.2 W 4.2 ps pulses at 1.06 μm. This represents a peak power of approximately 3 kW. The compressed pulse width was measured using the standard non-background free second-order autocorrelation in a potassium dihydrogen phosphate crystal 5 mm thick. Figures 2(a) and 2(b) show the recorded spectra and the auto-

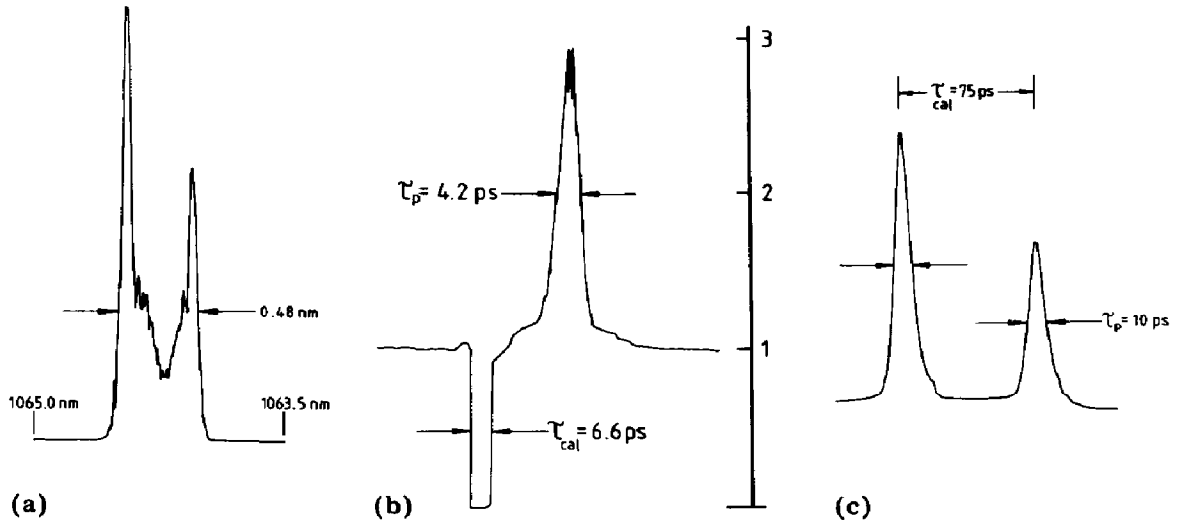

Fig. 2. (a) Spectrum and (b) autocorrelation of an optically compressed pulse from the CW mode-locked Nd–YAG laser; (c) synchroscan recorded trace of the pulse in (a) and (b), showing resolution of about 10 ps.

correlation trace respectively. The measured pulse width of 4.2 ps (assuming a gaussian pulse shape) is greater than should be theoretically obtainable from the transform limit of the corresponding 0.48 nm width ($\Delta t \approx 3.5$ ps).

Frequency doubling of the compressed pulses was carried out using Type II second harmonic generation in a 5 mm long potassium titanyl phosphate crystal with an overall efficiency of about 7%. These 4 ps 80 mW pulses at 532 nm were very stable for several hours, and only slight readjustment in the YAG laser (cavity detuning due to thermal effects) was required.

The synchronously operating streak camera has been utilized before in direct measurement of picosecond decay times of dyes and a review of the principle of operation as well as applications in fluorescence lifetime determination can be found in ref. 10. In order to increase the temporal resolution of the camera system, the sinusoidal sweep velocity was increased by driving at the third harmonic frequency (about 300 MHz) of the input pulse repetition. This was simply achieved by frequency tripling the synchronous signal derived from the laser modulator. Figure 2(c) shows a typical pair of laser pulses separated by 75 ps (for calibration purposes). The measured pulse width of about 10 ps, which was considerably greater than the actual 4 ps pulse width, determined the resolution of the system. This limit is imposed mainly by the jitter inherent in the driving electronics and principally to long-term pulse-to-pulse jitter in the laser due to the pulse formation mechanism in synchronously pumped laser systems. A resolution of about 4 ps has been obtained by driving the streak camera from a fast photodiode [9, 10] monitoring the pulses themselves.

We investigated the decay of the dye 1,1′-diethyl-2,2′-cyanine iodide (Koch-Light Ltd.) in aqueous solution with concentrations ranging from about 5×10^{-3} M (where the J aggregates are present) to about 10^{-4} M

was measured to be 11 ps. This technique can be applied to many measurements of chemical and biological systems while the temporal resolution of the system should be improved to about 5 ps.

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