

Porter G & Windsor M W. The triplet state in fluid media.  
*Proc. Roy. Soc. London Ser. A* 245:238-58, 1958.  
[University of Sheffield, England]

This paper describes the first detection and kinetic investigation of triplet states, in solution, by time-resolved absorption spectroscopy. It made possible the direct study of the primary reactions of triplet states in photochemistry and photobiology. [The SC<sup>1</sup>® indicates that this paper has been cited in over 420 publications since 1958.]

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"The flash photolysis technique that was developed in Cambridge in 1949<sup>1</sup> was at first used exclusively for the detection and study of atoms and free radicals in gases. Up to 1953, no studies in the liquid phase and no detection of excited absorption spectra in gases or liquids had been reported. The catalyst for such work was a visit to my laboratory by John Wilson, director of the British Rayon Research Laboratory. Wilson was concerned about the photochemical tendering of fabrics sensitised by anthraquinone dyes. He offered a research grant for apparatus and a student if we would apply our methods to this problem.

"It was a far cry from diatomic molecules in the gas phase, but I immediately became interested because I had just read a paper by McClure<sup>2</sup> that described the detection of triplet-state absorption spectra in low temperature glasses, and there was every possibility that these long-lived triplets were the states responsible for much of the photochemistry. Maurice Windsor joined me as the research student, and within four months he had put together the apparatus and successfully observed the triplet-state absorption of anthracene in solution at room temperature.<sup>3,4</sup> Many other triplet states were recorded, including that of chlorophyll by Robert Livingston, who was spending half a year in the laboratory in Cambridge at that time.

"Subsequent developments occurred rapidly: the detection of triplet states in the vapour phase, the detection of free radicals in solution, and the first complete time-resolved study of a photochemical reaction in which the excited state was directly observed to form the free radical product. This was the reaction of triplet quinones with organic substrates, the actual phototendering reaction that was the original problem of practical interest. Appropriately it was carried out at the British Rayon Research Association.<sup>5,6</sup>

"After receiving his PhD degree, Windsor went to the US as a postdoctoral fellow but returned to work with me in Sheffield in 1957. This gave us the opportunity to work up and supplement our data on the absorption spectra of triplet states of many organic molecules, their lifetimes and mechanisms of decay, and the effects on them of solvent viscosity and oxygen. This paper, rather than the earlier ones, seems to have attracted most attention, and there are probably two reasons for it. First, it appeared just about the time that the importance of the triplet state across the whole field of photochemistry was beginning to be generally realised, while the earlier papers were too early to find receptive readers. Second, the 1957 paper contained a lot of useful data that was essential to those who were going to work in this field. Although this added little of interest in itself, it was constantly used and, of course, quotation of its source is almost obligatory.

"Just how much, and how little, was known about the photochemistry and photo-physics of the triplet state in solution when this paper was published is illustrated by the Tilden lecture given two years later, which seems antediluvian to a photochemist of today when hundreds of papers and books have been written on the subject. The reactions of a few microseconds duration that seemed incredibly fast at that time are tortoises in these days of nanosecond, picosecond, and femtosecond flash photolysis. But the 'pulse and probe' technique that was used is universally employed today, whatever the time regime."

1. Porter G. Flash photolysis and spectroscopy: a new method for the study of free radical reactions. *Proc. Roy. Soc. London Ser. A* 200:284-300, 1950. (Cited 175 times since 1955.)
2. McClure D S. Excited triplet states of some polyatomic molecules. *I. J. Chem. Phys.* 19:670-5, 1951. (Cited 110 times since 1955.)
3. Porter G & Windsor M W. Triplet states in solution. *J. Chem. Phys.* 21:2008, 1953. (Cited 50 times since 1955.)
4. .... Studies of the triplet state in fluid solvents. *Discuss. Faraday Soc.* 17:178-86, 1954. (Cited 125 times since 1955.)
5. Bridge N K & Porter G. Primary photoprocesses in quinones and dyes. I. Spectroscopic detection of intermediates. *Proc. Roy. Soc. London Ser. A* 244:259-75, 1958. (Cited 225 times since 1958.)
6. .... Primary photoprocesses in quinones and dyes. II. Kinetic studies. *Proc. Roy. Soc. London Ser. A* 244:276-88, 1958. (Cited 155 times since 1958.)