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Photophysical studies on solid C_{60} using diffuse reflectance laser flash photolysis (DRLFP)

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Abstract

The transient absorption of the C_{60} triplet was recorded by diffuse reflectance laser flash photolysis (DRLFP) from a solid sample of commercial C_{60}. The lifetime and shape of the transient spectrum were only slightly dependent on the laser energy. Molecular O_2 deactivates those excited molecules lying on the surface.

Keywords: Solid; C_{60}; Fullerene; Transient

1. Introduction

Since fullerenes were discovered, many efforts have been made to clarify their properties [1]. Their photophysical behaviour has also been extensively studied in solution [2]. Although the excited state behaviour of C_{60} and C_{70} fullerenes in poly(methyl methacrylate) films has been reported [3], surprisingly, there is a lack of information on the transient behaviour of pure and dark fullerenes in the solid state. The eventual application of solid C_{60} derivatives in the field of new materials science requires the clarification of these properties. To shed light in this area, we have carried out an investigation of solid C_{60} fullerene using the diffuse reflectance laser flash photolysis (DRLFP) technique. Since Wilkinson [4] developed DRLFP, the photophysical properties of many solid and opaque substances have been characterized [5].

2. Results and discussion

The C_{60} sample was obtained from Acros Chemical (99.9%). The difference absorption spectrum, recorded using the diffuse reflectance accessory of an LKS.50 instrument (Applied Photophysics Ltd., UK) following 532 nm laser pulse (9 ns width, 5.7 mJ per pulse) excitation of an N_2-purged solid sample, is shown in Fig. 1 (a typical experiment consisted of a series of 4–10 replicate shots per single measurement, carried out at room temperature). We assign this transient absorption, centred at 710 nm, to the solid C_{60} triplet. A large part (80%) of the decay at the maximum follows a double exponential pathway (see inset), and the deduced lifetime is 640±50 μs (cf. 133 μs in benzene [6], 100 μs in poly(methyl methacrylate) films [3] and 40 μs for $^3C_{60}$ when covalently linked to insoluble cross-linked polystyrene [7]). The intrinsic lifetime of $^3C_{60}$ has been calculated to be greater than 280 μs [2b]. The lifetime and shape of the transient absorption spectrum are only slightly dependent on the laser energy: an increase from 5.7 mJ per pulse to 30 mJ per pulse causes only a small increase in the lifetime and a small sharpening in the shape of the spectrum

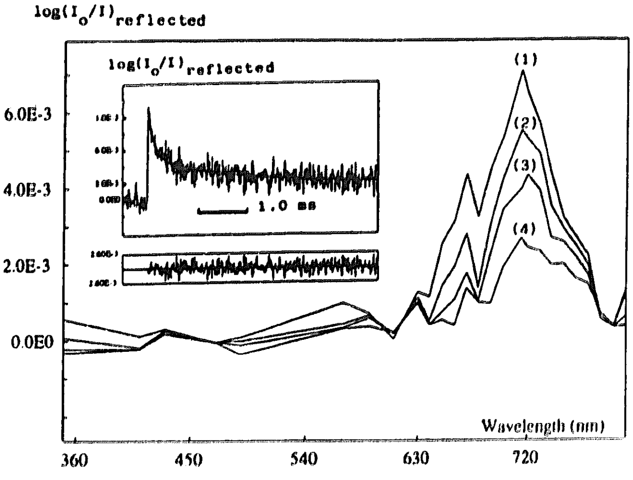

Fig. 1. Transient absorption spectrum of dry, nitrogen-purged, solid C_{60} fullerene (λ_{ex} = 532 nm; intensity, 5.7 mJ per pulse; pulse width, 9 ns): (1) 1.2×10^{-4}, (2) 2.8×10^{-4}, (3) 5.6×10^{-4} and (4) 45×10^{-4} s after laser flash. Inset: decay trace at 710 nm and double exponential fit.

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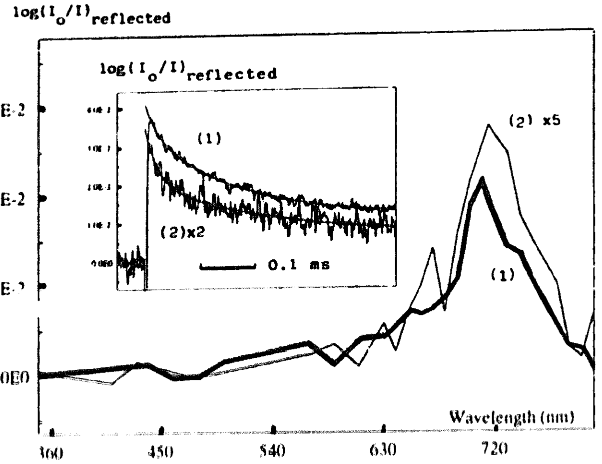

Fig. 2. Transient absorption spectrum of dry, nitrogen-purged, solid C_{60} fullerene, 2.8×10^{-4} s after the laser flash, at $\lambda_{ex}=532$ nm, a laser pulse width of 9 ns and a laser intensity of 30 mJ per pulse (1) and 5.7 mJ per pulse (2). Inset: decay traces at 710 nm at laser intensities of 30 mJ per pulse (1) and 5.7 mJ per pulse (2).

(Fig. 2). Triplet–triplet annihilation and ground state deactivation have been reported to be very efficient processes for the deactivation of excited triplet states of C_{60} in solution [2c]. At larger laser energies, we would expect a larger concentration of triplet states and, eventually, a contribution of triplet–triplet annihilation. Since this is not observed when the energy of the excitation beam is increased, we must conclude that both processes are equally efficient (working in opposite directions) or that they are not operative in the solid state.

Oxygen also deactivates the solid triplets. In an oxygen-saturated sample, the decay at the maximum (710 nm) shows two components (see Fig. 3): we assign the fast component (60% of the decay; deduced lifetime, 250 ± 25 μs) to those C_{60} triplets lying on the surface which are available to the O_2 molecules in the gas phase; we assign the slow component (deduced lifetime, 4.5 ± 1.0 ms) to triplets contained in the interior of the powder which are not available to oxygen. This second lifetime is much larger than the 640 μs deduced above in an N_2 atmosphere from the fast decay. This effect may be explained by the existence of energy migration from $^3C_{60}$ at the surface to C_{60} molecules in the interior to produce new excited triplets whose absorption will be delayed by a few milliseconds.

3. Conclusions

We have found that the transient absorption of $^3C_{60}$ in the solid state is similar to that in solution and only slightly dependent on the laser energy. In addition, we have demonstrated that those excited molecules lying on the surface are deactivated by molecular oxygen.

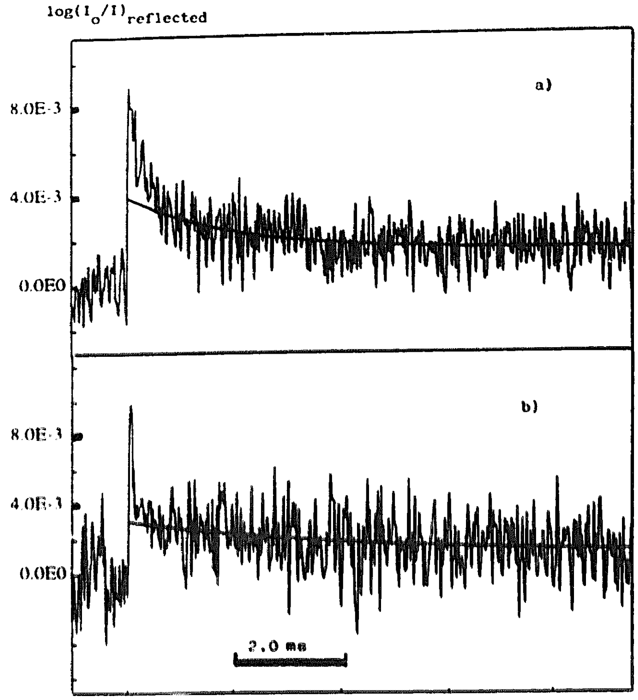

Fig. 3. Decay traces at 710 nm (conditions as in Fig. 1) in: (a) N_2-saturated solid C_{60}; (b) O_2-saturated solid C_{60}.

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