Evidence of delayed light emission of tetraphenyl-butadiene excited by liquid-argon scintillation light

E. Segreto[*,†]

Instituto de Física "Gleb Wataghin" Universidade Estadual de Campinas - Unicamp Rua Sérgio Buarque de Holanda, No 777, CEP 13083-859 Campinas, São Paulo, Brazil

(Received 26 November 2014; revised manuscript received 1 February 2015; published 12 March 2015)

Tetraphenyl-butadiene is the wavelength shifter most widely used in combination with liquid argon. The latter emits scintillation photons with a wavelength of 127 nm that need to be downshifted to be detected by photomultipliers with glass or quartz windows. Tetraphenyl-butadiene has been demonstrated to have an extremely high conversion efficiency, possibly higher than 100% for 127 nm photons, while there is no precise information about the time dependence of its emission. It is usually assumed to be exponentially decaying with a characteristic time of the order of one ns, as an extrapolation from measurements with exciting radiation in the near UV. This work shows that tetraphenyl-butadiene, when excited by 127 nm photons, re-emits photons not only with a very short decay time, but also with slower ones due to triplet states de-excitations. This fact can strongly contribute to clarifying the anomalies in liquid-argon scintillation light reported in the literature since the 1970s, namely, the inconsistency in the measured values of the long decay time constant and the appearance of an intermediate component. Similar effects should be also expected when the TPB is used in combination with helium and neon, which emit scintillation photons with wavelengths shorter than 127 nm.

DOI: 10.1103/PhysRevC.91.035503 PACS number(s): 29.40.Mc, 33.50.Dq, 33.80.Eh, 61.25.Bi

I. INTRODUCTION

Liquid argon (LAr) is a widely used active medium in particle detectors, especially in the fields of neutrino physics and dark matter direct search [1–4]. It is often used in scintillation detectors thanks to its high photon yield (∼40 000 photons/MeV at null electric field for minimum ionizing particles) and to the possibility of discriminating different ionizing particles through pulse shape discrimination techniques (see for instance [5]). The wavelength of the emitted radiation is around 127 nm, which is in the vacuum UV (VUV). The most efficient and viable way of detecting LAr scintillation light is to downshift it to longer wavelengths, where common quartz or glass windowed photodevices are sensitive.

The most popular wavelength shifter used in combination with LAr is tetraphenyl-butadiene (TPB) [6–8], which has been shown to have an extremely high efficiency in converting VUV photons into visible ones (possibly higher than 100% [9]). However, there is no precise knowledge of the TPB emission time spectrum when excited by 127 nm photons. It is usually described by a single decaying exponential with characteristic time in the range of 1 ns, as an extrapolation from measurements performed with exciting radiation in the range of the near UV (around 350 nm) [10,11]. This is perfectly compatible with the photoexcitation of singlet states (S_n) of the Π electrons of the TPB molecules. They decay via internal conversion to the first excited singlet state S_1 in less than one ns. The scintillation photon is produced by the radiative de-excitation of this state to the fundamental state ($S_1 \to S_0$), which typically has a characteristic time of the order of 1 ns [12–14].

The point never considered up to now is that VUV scintillation photon energy (9.7 eV) could very likely exceed the ionization potential of TPB. Actually there are no available data in the literature, but a calculation leads to a value of 5.4 eV [15]. This could appear an extremely low energy, but it is worth noticing that similar compounds like p-terphenyl and anthracene, both used as scintillators or wavelength shifters, have ionization energies between 7 and 8 eV, not so far from that estimated for TPB. Furthermore it is not difficult to find examples of conjugated molecules with responses similar to that of TPB in the UV-visible region with ionization energies in the range of 5–6 eV, such as PTCDA, Alq3, or CuPc [16].

TPB molecules are very likely ionized by LAr scintillation photons and the emitted electron would have enough energy to excite singlet or triplet states of some of the surrounding molecules. Also the recombination of the electron-ion pair can lead to the population of triplet states. Excited singlet states produce the so-called prompt fraction of scintillation within a few ns through the de-excitation of the S_1 states to the ground level. Excited triplet states decay very fast to the lowest lying triplet state T_1 via internal conversion. These long-lived states (the transition $T_1 \to S_0$ is forbidden by selection rules) are the precursors of the delayed fraction of the scintillation in pure aromatic media through the triplet-triplet interaction process: $T_1 + T_1 \to S_1 + S_0$, where the scintillation photon is produced by the de-excitation of the S_1 state [12].

In this paper experimental evidence of the existence of a delayed component of the scintillation light of TPB excited by LAr VUV scintillation photons is presented. A similar effect has already been reported, for example, for sodium salycilate and for p-terphenyl ([17,18] and references therein). This experimental fact can clarify some of the *anomalies* of LAr scintillation reported in the literature. Namely the

[*]ettore.segreto@lngs.infn.it, segreto@ifi.unicamp.br

[†]Formerly at Istituto Nazionale di Fisica Nucleare Sezione di Gran Sasso (INFN) (National Institute of Nuclear Physics Gran Sasso), Assergi, Italy.

inconsistency in the measured values of the long decay time constant and the appearance of an unexpected intermediate component between the fast and the slow ones [19–22]. TPB ionization easily explains the observation of conversion efficiencies for LAr VUV photons higher that 100%, since each absorbed photon could excite more than one TPB molecule at a time.

The same effect must also be present when TPB is used to downshift the scintillation lights of liquid neon and liquid helium, which are more energetic than LAr ones, since they have wavelengths around 80 nm. In particular it could have a role in explaining some of the not fully understood time-dependence features.

II. EXPERIMENTAL EVIDENCE

Measuring the time response of TPB at 127 nm is an extremely difficult task, because a fast pulsed 127 nm light source ($\sim$ few ns FWHM) is required, together with a system that allows one to drive VUV photons on a TPB layer. The experimental approach used in this work is based on the features of the LAr scintillation light itself and in particular profits from the fact that it can be reduced to a very fast pulse if the liquid is heavily contaminated by nitrogen. The effects of nitrogen contaminations on LAr scintillation light have been extensively studied in [19] and the time response of TPB to 127 nm photons can be directly taken from there. In that work, in fact, the scintillation light, quenched by N_2, is wave shifted by a TPB layer and then detected by a photomultiplier and at any level of N_2 contamination studied, the probability density function in time (p.d.f.) of the photons has been measured. The p.d.f. at the highest concentration (3000 ppm) can be confidently interpreted as the time response of TPB to 127 nm photons. At that concentration, LAr scintillation is reduced to a pulse of the duration of few ns and consequently all the features observed in the p.d.f of the detected photons must be attributed to the time dependence of TPB fluorescence. It will be shown in Sec. II A that it has a nontrivial shape and that it contains a delayed component together with the expected prompt/instantaneous one.

To check that the p.d.f. measured with LAr VUV photons effectively represents the response of TPB and is not due to any side effect or uncontrolled systematics, like the unwanted pollution of the liquid by unknown contaminants, a dedicated experimental test has been performed. A TPB film has been directly irradiated with α and β particles and the p.d.f. of its scintillation light has been measured and compared with the one obtained with VUV photons in LAr. The comparison demonstrates that the delayed scintillation in the time response of the TPB to 127 photons is genuine and is a consequence of the triplet-triplet interaction process.

A. TPB response to LAr scintillation photons

The scintillation light of LAr proceeds through the de-excitation of the excited dimer Ar_2^* and shows two decay components: one very fast ($\sim$6 ns) originating from the decay of the lowest-lying singlet state $^1\Sigma$, and one very slow ($\sim$1.3 μs) from the decay of the lowest-lying triplet state $^3\Sigma$ [23,24]. Sometimes an intermediate component with decay time of the order of 100 ns has been observed by experimental groups [19,20,22], which is not expected on the basis of the accepted theory of LAr scintillation mechanism.

It has been clearly shown [19,25] that N_2 contaminations in LAr produce a quenching of the scintillation light, while no other emission phenomenon from N_2 has been observed even at extremely high levels of contamination ($\sim$10%). The quenching process is a collisional one and the net effect is that the decay times of LAr scintillation components are shortened according to

$$\frac{1}{\tau'_{f,s}([N_2])} = \frac{1}{\tau_{f,s}} + k_q \times [N_2], \tag{1}$$

and consequently the relative abundances of the fast and slow components become

$$A'_{f,s}([N_2]) = \frac{A_{f,s}}{1 + \tau_{f,s} \times k_q \times [N_2]}, \tag{2}$$

where $\tau_{f,s}$ and $A_{f,s}$ are the decay times and amplitudes of the fast and slow components for uncontaminated LAr,[1] $[N_2]$ is the nitrogen contamination in ppm, and k_q is the reaction rate that has been measured to be $k_q = 0.11 \pm 0.01\ \mu\text{s}^{-1}\ \text{ppm}^{-1}$ [19].

Taking into account that for γe^- excitations of uncontaminated LAr, $A_f = 0.25$, $A_s = 0.75$, it can be easily found that for $[N_2] = 3000$ ppm one obtains $\tau'_f \simeq 2$ ns, $\tau_s{}' \simeq 3$ ns, $A'_f = 0.1$, and $A'_s = 1.4 \times 10^{-3}$. In general any additional physical scintillation component of LAr would have a decay time below 3 ns. The scintillation light in heavily N_2 doped LAr is a very fast pulse that is ideal for studying the TPB response to 127 nm photons.

In [19] the results of a test of the effects of nitrogen contaminations in LAr are very clearly presented. The detector was constituted by a Polytetrafluoroethylene (PTFE) cell containing about 0.7 l of LAr lined up with a highly reflective foil (VM2000 by 3M) covered by a thin film of TPB (surface density $\sigma \simeq 450\ \ \mu\text{g/cm}^2$) and observed by a single 2-in. photomultiplier. An injection system allowed contamination of the ultrapure LAr with controlled amounts of N_2. The details of the experimental setup can be found in [19]. Contamination levels ranging from 1 ppm to 3000 ppm of N_2 were explored. For each different contamination the LAr cell was exposed to a γ source of ^{60}Co. Scintillation light produced by electrons from γ interactions was wave shifted on the surface of the cylinder and then detected by the photomultiplier. The average of the waveforms collected at 3000 ppm of N_2 contamination is shown in Fig. 1.[2] According to the previous discussion this waveform is obtained with a very fast 127 nm light excitation and it should be regarded as the time response of pure TPB to LAr scintillation photons.

This waveform clearly shows the expected very fast/instantaneous pulse, but also much slower components,

[1]It is assumed here that the probability density function for scintillation photons is $A_f/\tau_f \exp(-t/\tau_f) + A_s/\tau_s \exp(-t/\tau_s)$ and $A_f + A_s = 1$.

[2]This waveform is not shown in [19], but it has been kindly given by the authors.

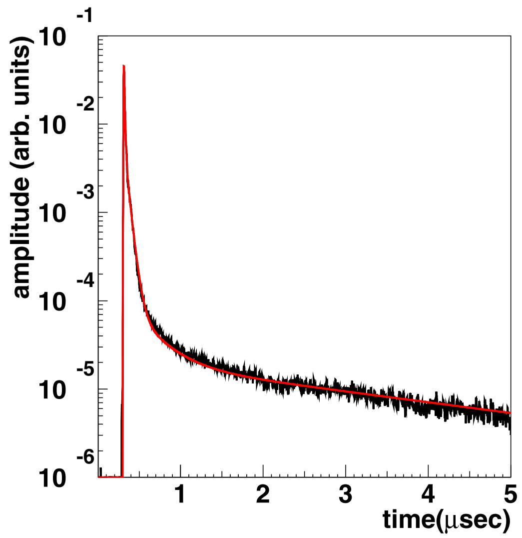

FIG. 1. (Color online) Response function of TPB for 127 nm photons at LAr temperature. It has been fitted with a function made of four decaying exponentials convoluted with a Gaussian (see text). The result of the fit is represented by a red (grey) line.

which are interpreted here as coming from the triplet-triplet interaction process in TPB. It has been clearly demonstrated that the delayed scintillation of unitary organic scintillators is not exponential [12,26–28], but to have a simplified quantitative idea of the time evolution of the emitted light the waveform has been fitted with a function made of four decaying exponentials, convoluted with a Gaussian function that accounts for the photomultiplier response and for the electronic noise. A more adequate treatment of the delayed scintillation will be presented in Sec. II B. The result of the fit is shown in Fig. 1 with a red (grey) line and the abundance and decay time of the components are reported in Table I.

Even if unphysical, the decomposition of the TPB response into exponentials puts into evidence some useful features. The delayed scintillation of TPB accounts for about 40% of the total and it is necessary to integrate the waveform for at least 140 ns to accumulate 90% of the signal. The slow part of the waveform fakes essentially two exponentially decaying components, one with a 50 ns slope, the most abundant, and one with 3.5 μs.

During the N_2 contamination test described in [19], data were taken for many different values of N_2 concentration in

TABLE I. Decay times and relative abundances of the components found in the decomposition into exponentials of the response function of TPB to 127 nm photons. Only statistical errors from the fit are quoted.

	Decay time (ns)	Abundance (%)
Instantaneous component	1–10	60 ± 1
Intermediate component	49 ± 1	30 ± 1
Long component	3550 ± 500	8 ± 1
Spurious component	309 ± 10	2 ± 1

LAr; therefore a very stringent test of the hypothesis that the waveform shown in Fig. 1 represents the response of TPB to LAr scintillation photons has been possible. For each level of [N_2] the average waveform shown in [19] has been fitted with a convolution of a double exponential, assumed to be the p.d.f. of LAr scintillation photons, with the response function of TPB. Some examples of fitted waveforms are shown in Fig. 2. In all cases the fits are almost perfect and the average waveforms are reproduced very precisely along all the time intervals considered (up to 9.7 μs after the onset of the signal). The picture that emerges from this analysis is perfectly consistent and there is no need of invoking exotic mechanisms of LAr scintillation, different from the two excimer-state de-excitation ($^1\Sigma$ and $^3\Sigma$), to explain all the features observed in the LAr scintillation waveforms. This is true in particular for one of the points deeply analyzed in [19] without reaching definite conclusions, which is the existence of an intermediate decaying component between the singlet and triplet de-excitation.

B. Test with β and α interactions

Following the idea that the waveform of Fig. 1 can represent the response of TPB to LAr scintillation photons, a dedicated experimental test has been performed. To check if the observed long tail is effectively related to TPB de-excitation, a sample of pure TPB has been directly irradiated with an ionizing radiation in a vacuum environment. This guarantees the formation of triplet states (through electron-ion recombination, secondary electrons excitations, δ rays, etc.), which are in turn the precursors of the delayed TPB scintillation, with a perfectly δ-shaped excitation function and in a way completely independent from LAr scintillation light.

In general the scintillation of pure organic crystals excited by an ionizing radiation can be well described with the superposition of a prompt component and of a delayed one. The prompt component is found to be exponentially decaying with a time constant identical to the mean lifetime τ_S of the first excited singlet state S_1.

The time evolution of the delayed component depends on the dynamics of the triplet-triplet interaction process. It can be predicted by solving the diffusion-kinetic equation for the triplet density along the ionizing track, assuming a Gaussian shape, with scale parameter r_0, for the initial triplet distribution function [12,26,28]. The asymptotic time dependence of the delayed light ($t \gg \tau_S$) is found to be

$$I(t)_{\text{delayed}} \simeq \eta_S \frac{N}{[1 + Aln(1 + t/t_a)]^2(1 + t/t_a)}, \quad (3)$$

where N and A are constants depending on the nature of the scintillator, η_S is the fluorescence yield, and t_a is a relaxation time that is linked to the diffusion coefficient of triplet states in the scintillator, D_t, through the relation $t_a = r_0^2/4D_t$. The time evolution of the delayed light does not depend on the particle type, but only on the dynamics of the triplet-triplet interaction process. Only the relative abundance of fast and delayed components is expected to depend on the linear energy transfer, and consequently on the particle type.

The experimental setup that has been built consists of a stainless steel vacuum tight chamber that hosts a 2-in.

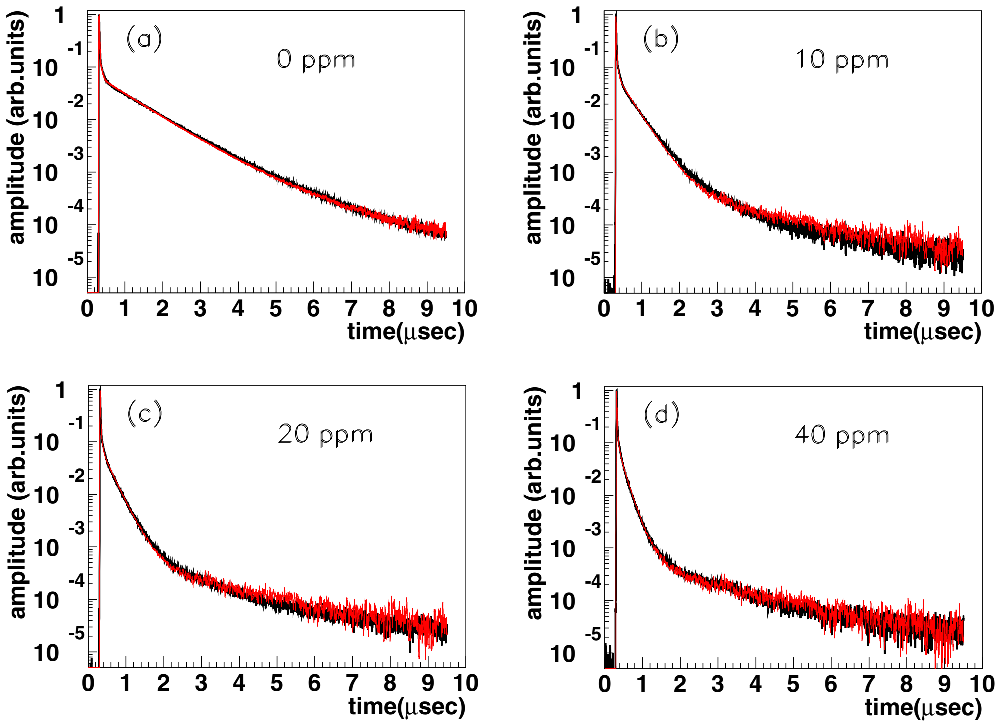

FIG. 2. (Color online) Average waveforms for LAr scintillation light when excited by ^{60}Co γs at different ppm levels of nitrogen contamination. In red (grey) the results of the fits are shown. The fit function is a convolution of the TPB response function (3000 ppm average waveform) with the sum of two decaying exponentials, assumed to be the response of LAr.

photomultiplier (ETL D745UA), a holder for the TPB sample, and one for the radioactive source. A schematic view of the setup is shown in Fig. 3. The TPB sample is a film with a surface thickness $\sim 10^3$ μg/cm^2 evaporated on a highly reflective plastic foil (3M VM2000) circular in shape with a diameter of 8 cm. The choice of having a reflective substrate below the TPB was made to maximize the amount of light that could be collected by the photomultiplier. A drawback of using VM2000 is that it is a weakly emitting light when irradiated by ionizing particles. The film was produced at Gran Sasso National Laboratory (LNGS) with a dedicated evaporation system. More details can be found in [29]. The distance between the sample and the photomultiplier is 5 cm. Two sources have been alternatively used: (i) an α source made of an alloy of uranium and aluminum that emits α particles with a continuous spectrum with an endpoint around 5 MeV, and (ii) a ^{90}Sr β^- source with a Q value of 546 keV.

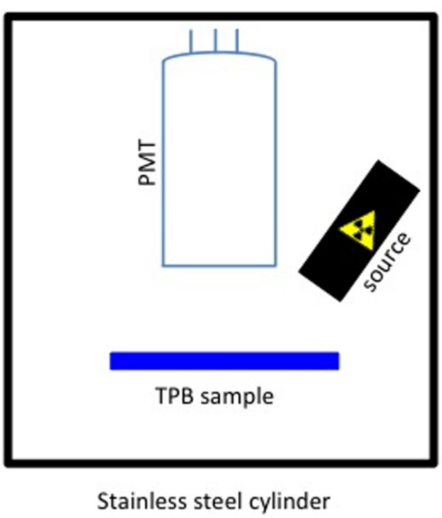

FIG. 3. (Color online) Scheme of the experimental setup used to irradiate TPB films with electrons and α particles.

During each measurement the stainless steel chamber was evacuated down to a pressure of 5×10^{-5} mbar to allow α particles and electrons to hit the TPB film without being captured by air. Scintillation signals detected by the photomultiplier were sent to a fast waveform recorder (Acqiris, DP235 Dual-Channel PCI Digitizer Card). The signal waveforms passing a threshold set at a level corresponding to few photoelectrons were recorded with sampling time of 1 ns over a full record length of 10 μs. All the measurements were performed at room temperature, since it has been shown in [30] that the time dependence of the late components of TPB fluorescence excited by α particles does not change appreciably at LAr temperature.

C. Data analysis and comparison

The average waveforms for the β and α particle tests were calculated applying simple cuts to eliminate waveforms that presented saturations, after pulses, or multiple signals and the result is shown in Fig. 4. The red lower curve refers to β irradiation and the blue upper one to α, while the black curve is the one obtained with LAr scintillation light, already shown in Fig. 1, reported here for visual comparison. β and VUV

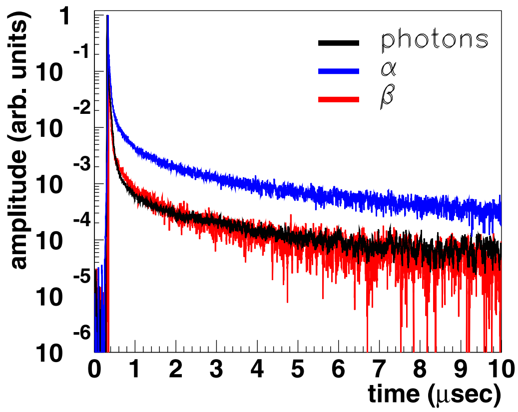

FIG. 4. (Color online) Red (lower grey) line: average waveform obtained by irradiating a TPB film with electrons. Blue (upper grey) line: average waveform obtained by irradiating a TPB film with α particles. Black line: average waveform obtained irradiating TPB with LAr scintillation light quenched by 3000 ppm of nitrogen.

photon curves are nicely overlapped as is observed also for sodium salicylate [17]. The small differences found around 300–400 ns after the onset of the signal could be ascribed to a small effect of fluorescence of the plastic substrate of the TPB film, since the electrons have enough energy to reach and traverse it. α particles, instead, show a much higher abundance of delayed component.

To investigate the details of the tails of the three curves and to check if they are compatible with each other a *single photon counting like procedure* has been adopted. The classical *coincidence single photoelectron counting technique* has been used many times in scintillation lifetime measurements [25,31,32]. The recorded waveforms allow implementation of an offline version of this technique. Starting at 170 ns after the onset of a triggered signal, a single photoelectron finding algorithm is run through the waveform and for each photoelectron pulse (defined by appropriate cuts) the arrival time is stored. To minimize the pile-up of single photoelectrons, which is a time-dependent effect, only waveforms with a total integral below 40 photoelectrons in the case of electron and photon excitations and 20 in the case of αs are considered. In this way the pile-up probability in the first 30 ns is below 5% in all three cases.

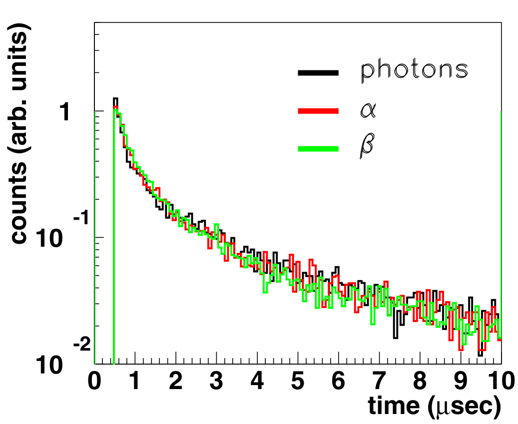

FIG. 5. (Color online) Normalized histograms of the arrival time of single photons. The black curve refers to photon excitation of TPB, the red curve (dark grey) to α excitation, and the green one (light grey) to electron excitation.

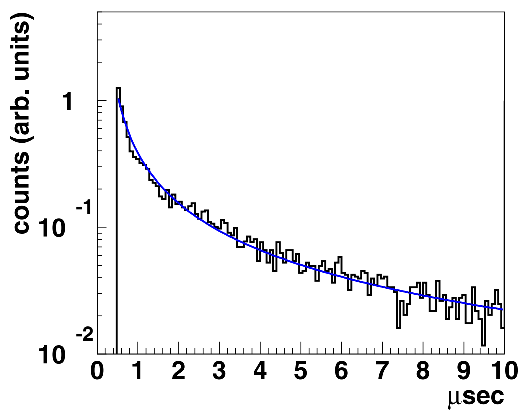

FIG. 6. (Color online) Histogram of arrival times of single photons for TPB excited by VUV photons. The blue (grey) line represents the result of the fit with the function of Eq. (3).

The times of arrival of photoelectrons have been accumulated in three histograms, which are shown in Fig. 5. They are almost perfectly overlapped. The histogram related to VUV photons has also been fitted with the function of Eq. (3) where A, t_a, and the product $\eta_S N$ are left as free parameters. The result of the fit is shown in Fig. 6 with a blue (grey) line. The best fit values for A and t_a are 0.22 and 51 ns respectively, not so different from what is found for anthracene [12], $A = 0.25$ and $t_a = 40$ ns, and for stilbene [12], $A = 0.25$ and $t_a = 80$ ns.

The perfect compatibility of the delayed scintillation of TPB excited by LAr scintillation photons with that induced by ionizing particles clearly demonstrates that it is generated by a triplet-triplet interaction mechanism, started by the ionization of TPB by 127 nm photons. The TPB response function to LAr scintillation light is not a fast decaying exponential, as it is found for near UV excitation, but has a much more complex structure with a delayed component that has a nonexponential shape and accounts for about the 40% of the emitted radiation.

III. DISCUSSION

The waveform shown in Fig. 1 confidently represents the response function in time of TPB to 127 nm. Having demonstrated that convoluting it with the sum of only two exponentially decaying functions allows the reproduction of the average waveforms measured at any level of contamination is a remarkable point. It demonstrates that the time evolution of LAr scintillation light can be described as the sum of only two decaying exponentials, originated from the de-excitation of the lowest lying triplet and singlet states of the Ar_2^* excimer. The observation of an intermediate component with a decay slope in the range of 50–100 ns often reported in the literature [19,20,33] can be totally ascribed to the fluorescence of TPB. It is the slow TPB de-excitation following the fast LAr scintillation pulse. It has been shown in Sec. II A, in fact, that the TPB response function fakes a 50 ns component, if one attempts to decompose it into exponentials. Also the difficulty of determining unambiguously the slope of the slow scintillation component of LAr can be a consequence of the use of TPB or of wavelength shifters in general. The long tail in the TPB response function, resembling a 3.5 μs exponential, distorts the slow component of LAr scintillation photons and consequently any technique to measure its decay constant brings inside a certain amount of uncontrolled systematics if the effect of TPB is not properly deconvolved. It has been shown in [19], for example, that the use of two slightly different fitting procedures leads to two quite different values of the LAr slow decay slope. In this respect the most reliable value appears to be the one of 1300 $\pm$ 60 ns reported in [21], measured without a shifter, and in [19] with sophisticated deconvolution techniques.

LAr is used in several experiments for direct dark matter detection mainly because it allows one to reject efficiently γ and α backgrounds with respect to nuclear recoil events that could be due to a weakly interactive massive particle signal [1,3,34,35]. In fact different ionizing particles produce very different scintillation signals in LAr. In particular the relative abundance of the fast to slow scintillation components are different for electrons, αs, and nuclear recoils, being, respectively, 1/3, 1.3, and 3 [5,20,31]. The most widely used technique to exploit the pulse shape discrimination of LAr is based on the calculation of the prompt fraction of light in the signals. A factor, usually called F_{prompt}, is defined as follows:

$$F_{\text{prompt}} = \frac{\int_0^{t^*} I(t)dt}{\int_0^{\infty} I(t)dt}, \tag{4}$$

where $I(t)$ is the intensity of the detected scintillation signal measured in photoelectrons and t^* is the integration time of the prompt signal that maximizes the separation among different particles. It has been found experimentally by many groups that the optimum value of t^* is around 100 ns [1,3,5,20]. This an indirect but clear confirmation of the existence of the delayed fluorescence of TPB.

According to the picture that emerges from this work, the scintillation of LAr shifted by TPB can be described by the p.d.f.

$$L(t) = AS(t) + (1 - A)T(t), \tag{5}$$

where *S(t)* and *T(t)* are the fast and slow exponential components of LAr both convoluted with the TPB response and A is the fraction of prompt light. It is straightforward to prove that t^* can be found by solving the equation

$$S(t^*) = T(t^*). \tag{6}$$

The graphical solution of Eq. (6) is shown in Fig. 7 and leads to a value of t^* around 120 ns, perfectly compatible with the experimental observations.[3]

If the delayed scintillation of TPB were not present, $S(t)$ and $T(t)$ could be described by two exponentials, with

[3] In this case, for simplicity, the TPB response function is represented in terms of exponentials.

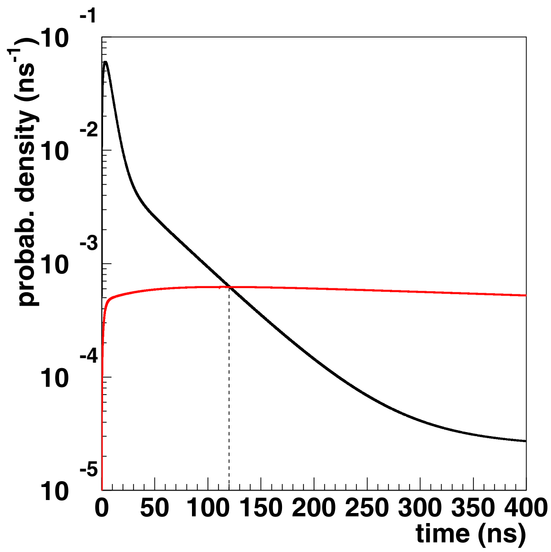

FIG. 7. (Color online) Graphical solution of Eq. (6). In black the function $S(t)$ and in red (grey) $T(t)$. The solution is represented by the crossing point of the two functions, which is found around 120 ns.

characteristic times of $\tau_S \sim 6$ ns and $\tau_T \sim 1300$ ns, that is,

$$L(t) = A\frac{1}{\tau_S}e^{-\frac{t}{\tau_S}} + (1 - A)\frac{1}{\tau_T}e^{-\frac{t}{\tau_T}}. \tag{7}$$

In this case Eq. (6) could be analytically solved and, in the limit of $\tau_T \gg \tau_S$, one obtains

$$t^* = \tau_S \ln\frac{\tau_T}{\tau_S}, \tag{8}$$

which returns a value for t^* around 32 ns, three times lower than its experimental value.

The delayed fluorescence of TPB has also the effect of deteriorating the discrimination capability of LAr that could be obtained in the ideal case of a direct detection of the VUV photons. This is because a fraction of the prompt light is delayed and the two LAr scintillation components are more mixed. A rough calculation can be very explicative. Without the shifter, the average value of F_{prompt} for electrons and neutrons can be easily calculated. Assuming a fraction A for the prompt scintillation of electrons and neutrons of 0.25 and 0.75, respectively, and considering a value of t^* of 32 ns, simple exponential integrations of Eq. (7) lead to F_{prompt} values of 0.27 and 0.75 with a difference $\Delta^{\text{pure}} = 0.48$. In the usual situation, that is, with TPB, a numerical integration of the p.d.f. of Eq. (5) up to $t^* = 110$ ns leads to F_{prompt} values of 0.27 and 0.67 for electrons and neutrons, respectively, with a difference of $\Delta^{\text{TPB}} = 0.4$. The use of the shifter worsens the separation between electrons and neutrons by about 17%.

TPB is widely used also to downshift the scintillation photons of liquid helium (LHe) and neon (LNe) [36,37], that have energies higher than that of LAr ones. This suggests that the same mechanism of TPB delayed fluorescence should be active also in these cases. Despite the fact that it was never explicitly noticed, it could be useful in explaining some of the not fully clarified features of LNe and LHe scintillation. It has been shown in [37] that the scintillation of LHe has a nontrivial time structure. In addition to the expected fast and slow components originated by the de-excitation of the lowest lying triplet and singlet states of the excimer He_2^*, with decay times of ∼10 s and ∼10 ns, respectively, two more components are observed, one exponential with a characteristic time of 1.6 μs and one nonexponential that decays as t^{-1}. The delayed scintillation of TPB could represent a non-negligible contribution to these scintillation components since it is active exactly in the same time range. Even if a direct and quantitative comparison is not reasonable, due to possible effects related to the large difference in temperature, the t^{-1} component resembles the asymptotic behavior of the TPB response function measured in LAr. On the other hand, the experimental evidence that the 1.6 μs exponential decay is different for cold helium gas than for LHe [37] demonstrates that some additional process must be active inside the LHe and the observed features cannot be completely explained by the delayed TPB fluorescence.

A similar situation is found for LNe scintillation, where two approximately exponential intermediate components between the singlet and triplet Ne_2^* de-excitations are found [36], with characteristic times in the range of 100 ns and 1 μs. Their origin is not clear, but it is plausible that TPB delayed scintillation can explain at least a fraction of it.

IV. CONCLUSIONS

This work shows the experimental evidence of the existence of a delayed scintillation component of TPB when excited by the VUV radiation of LAr. The production of the triplet states, which are precursors of the delayed light, is made possible by the high energy of LAr scintillation photons that can ionize the organic molecules of TPB. Its time dependence has been measured with an experimental setup that uses LAr scintillation light quenched by nitrogen contamination to excite TPB. It has been compared to the time behavior of the delayed light of TPB when excited by β and α particles and they have been found to be perfectly compatible with each other. The time shape of the light emission has also been found to be consistent with what is expected from the delayed luminescence of a unitary scintillator as described in literature.

This experiment sheds some light on the most relevant incongruities that have been reported in the past few years concerning the time dependence of LAr scintillation light: namely the presence of an intermediate component with a decay time in the range of 50–100 ns and the ambiguity in the determination of the decay time of the slow component, for which values ranging from 800 to 1600 ns have been reported.

LAr scintillation is often used for particle discrimination since the relative abundance of the fast and slow components strongly depends on the particle type. The use of TPB tends to worsen this feature of LAr since a consistent part of the prompt light is delayed and the two populations are more mixed.

TPB is an exceptionally efficient shifter for the VUV scintillation light of LAr and also a convenient one for its emission wavelength around 430 nm matching the quantum efficiency of many standard photomultipliers, but it has some drawbacks when the time features of the scintillation signals are used since they end up being slightly distorted.

ACKNOWLEDGMENTS

The author acknowledges Prof. F. Cavanna for his contribution to this work with discussions and ideas; Prof. R. Francini for the discussions on molecular processes; Dr. A. A. Machado for her help and patience, Dr. N. Canci for his contribution to the measurements with α and β particles, and the late Antonio Di Filippo for encouraging and inspiring this work.

[1] WArP. Coll., The WArP experiment, J. Phys. Conf. Ser. **203**, 012006 (2010).
[2] ICARUS Coll., Underground operation of the ICARUS T600 LAr-TPC: First results, JINST **6**, P07011 (2011).
[3] DarkSide Collaboration, First Results from the DarkSide-50 Dark Matter Experiment at Laboratori Nazionali del Gran Sasso, arXiv:1410.0653.
[4] MicroBooNE Collaboration, A Proposal for a New Experiment Using the Booster and NuMI Neutrino Beamlines: MicroBooNE, http://www-microboone.fnal.gov/public/MicroBooNE_10152007.pdf.
[5] R. Acciarri, Measurement of the scintillation time spectra and pulse shape discrimination of low-energy electron and nuclear recoils in liquid argon with the WArP 2.3 lt detector, Ph.D. thesis, L'Aquila University, 2010.
[6] R. Francini *et al.*, VUV-Vis optical characterization of tetraphenyl-butadiene films on glass and specular reflector substrates from room to liquid-argon temperature, JINST **8**, P09006 (2013).
[7] C. H. Lally *et al.*, UV quantum efficiencies of organic fluors, Nucl. Instrum. Methods Phys. Res. B **117**, 421 (1996).
[8] D. N. McKinsey *et al.*, Fluorescence efficiencies of thin scintillating films in the extreme ultraviolet spectral region, Nucl. Instrum. Methods Phys. Res. B **132**, 351 (1997).
[9] Gehman V. M. *et al.*, Fluorescence efficiency and visible re-emission spectrum of tetraphenyl butadiene films at extreme ultraviolet wavelengths, Nucl. Instrum. Methods Phys. Res. A **654**, 116 (2011).
[10] J. M. Flournoy *et al.*, Substituted tetraphenylbutadienes as fast scintillator solutes, Nucl. Instrum. Methods Phys. Res. A **351**, 349 (1994).
[11] A. Camposeo *et al.*, Random lasing in an organic light-emitting crystal and its interplay with vertical cavity feedback, Laser Photon. Rev. **8**, 785 (2014).
[12] G. Laustriat, The luminescence decay of organic scintillator, Mol. Cryst. **4**, 127 (1968).
[13] J. B. Birks, *The Theory and Practice of Scintillation Counting* (Pergamon, Oxford, 1964).
[14] J. B. Birks, *Photophysics of Aromatic Molecules* (Wiley-Interscience, New York, 1970).
[15] D. Kafer, Characterization and optimization of growth and electronic structure of organic thin films for applications in organic electronics, Ph.D. thesis, Ruhr-University

Bochum, 2008, available at http://www-brs.ub.ruhr-uni-bochum.de/netahtml/HSS/Diss/KaeferDaniel/diss.pdf.
[16] I. G. Hill *et al.*, Charge-separation energy in films of p-conjugated organic molecules, Chem. Phys. Lett. **327**, 181 (2000).
[17] G. J. Baker *et al.*, Time dependence of sodium salicylate luminescence excited by vuv photons, x-rays and β particles: magnetic field effects, J. Phys. B: At. Mol. Phys. **20**, 305 (1987).
[18] G. Klein and M. J. Carvalho, Highly excited states decay in p-terphenyl crystals, magnetic field effect investigation, Chem. Phys. Lett. **51**, 409 (1977).
[19] R. Acciarri *et al.*, Effects of nitrogen contamination in liquid argon, JINST **5**, P06003 (2010).
[20] W. H. Lippincott *et al.*, Scintillation time dependence and pulse shape discrimination in liquid argon, Phys. Rev. C **78**, 035801 (2008).
[21] T. Heindl *et al.*, The scintillation of liquid argon, Europhys. Lett. **91**, 62002 (2010).
[22] E. Morikawa *et al.*, Argon, krypton and xenon excimer luminescence: From dilute gas to the condensed phase, J. Phys. Chem. **91**, 1469 (1989).
[23] S. Kubota *et al.*, Recombination luminescence in liquid Ar and Xe, Phys. Rev. B **17**, 2762 (1978).
[24] T. Doke, Fundamental properties of liquid argon, krypton and xenon as radiation detector media, Portgal. Phys. **12**, 9 (1981).
[25] S. Himi, *et al.*, Liquid and solid argon, and nitrogen doped liquid and solid argon scintillators, Nucl. Instrum. Methods Phys. Res. **203**, 153 (1982).
[26] R. Voltz and G. Laustriat, Radioluminescence des milieux organiques II. Verification experimentale de l'etude cinetique, J. Phys. France **29**, 297 (1968).
[27] J. B. Birks, in *Proceedings of the International Conference of Organic Scintillators and Liquid Scintillation Counting, Liquid scintillator solvents* (Academic Press, New York, 1971); T. A. King and R. Voltz, The time dependence of scintillation intensity in aromatic materials, Proc. Roy. Soc. A **289**, 424 (1966).
[28] R. Voltz and G. Laustriat, Radioluminescence des milieux organiques I. Etude cinetique, J. Phys. France **29**, 159 (1968).
[29] R. Acciarri *et al.*, Aging studies on thin tetra-phenyl butadiene films, JINST **8**, P10002 (2013).
[30] L. M. Veloce, An Investigation of Backgrounds in the DEAP-3600 Dark Matter Direct Detection Experiment, M.D. thesis, Queens University-Kingston, 2013.
[31] A. Hitachi *et al.*, Effect of ionization density on the time dependence of luminescence from liquid argon and xenon, Phys. Rev. B **27**, 5279 (1983).
[32] M. J. Carvalho *et al.*, Luminescence decay in condensed Argon under high energy excitation, J. Lumin **18–19**, 487 (1979).
[33] C. Amsler *et al.*, Luminescence quenching of the triplet excimer state by air traces in gaseous argon, Journal of Instrumentation **3**, P02001 (2008).
[34] A. Badertscher *et al.*, Status of the ArDM Experiment: First results from gaseous argon operation in deep underground environment, arXiv:1307.0117.
[35] M. G. Boulay, DEAP-3600 Dark Matter Search at SNOLAB, J. Phys. Conf. Ser. **375**, 012027 (2012).
[36] W. H. Lippincott *et al.*, Scintillation yield and time dependence from electronic and nuclear recoils in liquid neon, Phys. Rev. C **86**, 015807 (2012).
[37] D. N. McKinsey *et al.*, Time dependence of liquid-helium fluorescence, Phys. Rev. A **67**, 062716 (2003).