Fluorescence decay-time constants in organic liquid scintillators

T. Marrodán Undagoitia, 1, 2 F. von Feilitzsch, 1 L. Oberauer, 1 W. Potzel, 1 A. Ulrich, 1 J. Winter, 1 and M. Wurm 1

1 Physik-Department, Technische Universität München, James-Franck-Str., 85748 Garching, Germany
2 Physik-Institut, Universität Zürich, Winterthurerstr. 190, 8057 Zürich, Switzerland

The fluorescence decay-time constants have been measured for several scintillator mixtures based on phenyl-o-xylenelethane (PXE) and linear alkylbenzene (LAB) solvents. The resulting values are of relevance for the physics performance of the proposed large-volume liquid scintillator detector LENA (Low Energy Neutrino Astronomy). In particular, the impact of the measured values to the search for proton decay via \( p \to K^+ \bar{\nu} \) is evaluated in this work.

I. INTRODUCTION

Charged particles crossing a liquid-scintillator medium deposit their energy leading partly to fluorescence light. The lifetimes of the molecular excited states in the medium determine the pulse shape of the events in a detector application. For this reason, experiments relying on pulse shape analysis for background discrimination are always dependent on the fluorescence decay-time constants. A common application of pulse shape analysis in neutrino experiments is the separation of \( \alpha \)-events produced by natural radioactivity from neutrino-induced \( \beta \)-events 1. The pulse shape also plays an important role in the search for proton decay via \( p \to K^+ \bar{\nu} \) in the proposed large liquid-scintillator detector LENA as the signature relies on a double-peak structure in time 2.

The LENA (Low Energy Neutrino Astronomy) detector 3 is planned as a large-volume (50 kt) observatory based on the liquid-scintillator technology which will be highly suitable for the investigation of a variety of topics in astrophysics, geophysics and particle physics. In the analysis of the proton decay reaction \( p \to K^+ \bar{\nu} \), the two-peak time structure is used to discriminate proton decay events from the background due to atmospheric neutrino events 2. The detection efficiency depends upon the fluorescence decay-time constants and therefore, the laboratory experiments presented here have been performed to determine these constants for several scintillator mixtures.

Fluorescence decay measurements of liquid scintillators have been performed earlier in feasibility studies for the Borexino experiment with a scintillator mixture based on PC (pseudocumene) as solvent 4, 5. In addition, similar measurements have been carried out for indium-loaded scintillators for the proposed solar neutrino experiment LENS 6. A desirable scintillator for the proposed LENA detector would feature fast decay times, large attenuation lengths and reasonable costs. This paper reports results obtained for the fluorescence decay constants of important current scintillator candidates. Non-metal loaded scintillators based on PXE and LAB have been tested. In addition, the impact of the decay constants on the sensitivity of the LENA detector to proton decay is shown.

II. EXPERIMENTAL METHOD

The main goal of the experiment is the determination of the ‘probability density function’ (PDF) which describes the time-dependence of the photon emission in the fluorescence processes. A sampling of the photon-emission time after excitation of the medium is required. The experiment uses the ‘start-stop’ method 4 which measures the emission times for single photons. In this method, the start signal accounts for the starting point of the pulse: approximately the time of the energy deposition. If a light detector is able to measure a large number of photons of an event, the start time can be extracted from the first detected photon. A second detector monitoring the same event provides the stop signal. This detector should be designed in such a way that the probability of detecting a single photon of an event is in the few % regime. This guarantees that the probability to detect more than one photon in an event is almost zero. The PDF of a certain scintillator mixture results from the time difference between the start and the stop signals.

The main setup consists of two photomultipliers (PMTs) which detect the light emitted from a liquid-scintillator sample. The sample is irradiated by a \( ^{54}\text{Mn} \) \( \gamma \)-source (834 keV). Figure 1 shows a scheme of the experimental setup. A sample of scintillator is filled into a \( \sim 10 \text{ ml} \) cylindrical container made of black PTFE (Polytetrafluoroethylene, high density) material with quartz windows at both faces. The maximum energy for the recoiling Compton electron for this source is 639 keV (backscattering, i.e. Compton-edge energy). Compton electrons deposit their energy in the scintillator leading to the fluorescence light-emission. One of the PMTs is directly coupled to the scintillator container (close PMT). It de-
tects a large number of photons per event and thereby sets the starting point for the event. The second PMT is placed \( \sim 30 \text{ cm} \) away from the sample (far PMT). This distance was chosen to assure single-photon events due to the small solid angle. The probability to detect a photon from a Compton event in the far PMT is \(< 3\%\). This value has been calculated conservatively assuming a light emission of \( 10^4 \text{ photons}/\text{MeV} \) and an energy deposition corresponding to the Compton edge of \(^{54}\text{Mn}\).

One PMT is directly coupled to the container and the second PMT is located at a distance of \( 30 \text{ cm} \). The scintillator is excited by a \(^{54}\text{Mn} \) source. This setup produces two \( 511 \text{ keV} \) gamma rays from \( e^+ e^- \) annihilation. The far PMT is optically decoupled from the fluorescence system by a black blocking filter. A Cherenkov radiator (Plexiglas piece) is placed in front of the far PMT. This provides an instantaneous signal as the Cherenkov photons are produced within picoseconds time after the energy deposition of a \( 511 \text{ keV} \) gamma. Pairs of \( \gamma \) rays from the annihilation are emitted isotropically but always in opposite directions. Sometimes both gammas interact simultaneously in the liquid scintillator and in the Cherenkov radiator and those coincident events have been recorded. Using the time difference between one \( 511 \text{ keV} \) signal in the Cherenkov radiator and a second one in the liquid scintillator sample, the time resolution of the system is determined.

### III. TIME RESOLUTION AND BACKGROUND SOURCES

The time resolution of the fluorescence-measurement system mainly depends upon the single-photoelectron transit time jitter of the PMT. Photoelectrons produced at different positions of the cathode have different propagation distances to the first dynode resulting in a smearing of the transit time through the tube. The specification for the time jitter of the PMTs used is \( 0.98 \text{ ns} \). Smaller contributions to the loss in time-resolution are the error of the determination of the start time of a pulse and the time jitter of the electronic readout chain, the latter, however, usually being a small contribution.

Figure 2 shows the distribution of the time differences between the start signal given by the scintillator and the arrival of the Cherenkov photons measured in the setup with the \(^{22}\text{Na} \) source. Although the main peak is well described by a Gaussian function, there are small contributions at times below and above the main peak. The shoulder on the left side of the Gaussian curve is due to pre-pulses of the single-photon tube. Further to the left, there is a contribution which can be interpreted as photons which cross the cathode producing a photoelectron directly in the dynode-chain. The total contribution of the events to the left side of the Gaussian peak is about \( 5\% \) of all pulses.

The pulses on the right side of the Gaussian peak \((t < 20 \text{ ns})\) can be explained by the reflection of photoelectrons by the first dynode back to the cathode. This effect occurs in about \( 2\% \) of all pulses and has also been reported in [1]. The pulses at still later times \((t > 20 \text{ ns})\) contribute about \( 2\% \) to the total number of pulses. Their origin is unknown but may be interpreted as a weak flu-
FIG. 2: Distribution of the time differences between the start signal in the scintillator and the arrival of Cherenkov photons. The time resolution of the system (the events are plotted on a semi-logarithmic scale) is well described by a Gaussian curve.

orescence of the photomultiplier housing and window as the radioactive source was placed very close to the tube. When removing the Plexiglas piece, it was found that the number of pulses with $t > 20$ ns increase relative to the previous measurement pointing to a background related to direct $\gamma$-hits on the PMT. Altogether, about 91% of the pulses are beneath the Gaussian curve.

In addition to the loss of time resolution due to the effects described above random coincidences due to the dark-count rate of the far PMT contribute to the background of the experiment. This coincidence rate has been estimated by measuring the dark current of the far PMT and taking the trigger rate by the close PMT. About 30 random coincidences are expected for an 8 hours measurement ($\sim 0.06\%$ of all recorded pulses).

IV. MEASURED SAMPLES

The samples investigated consist of a mixture of an organic liquid solvent and one or two wavelength-shifters as solutes. The solvents PXE (phenyl-o-xylylethane) and LAB (linear alkylbenzene) have been studied because of their high light yield and low risk properties.

The wavelength-shifters dissolved were PPO (2,5-diphenyl-oxazole), pTP (para-terphenyl), bisMSB (1,4-bis-(o-methyl-styryl)-benzene) and PMP (1-phenyl-3-mesityl-2-pyrazoline). To characterize these compounds a spectrum of the emitted light has been recorded when the compounds were dissolved in PXE. To this end, the medium was excited with UV-light of a deuterium lamp [10]. The spectra were recorded with a compact spectrometer with 0.53 nm resolution and fiber optic coupling (Ocean Optics HR2000) [11]. They were corrected with the spectrometer’s sensitivity curve and also for possible shifts in the wavelength [12]. Figure 3 shows the emission spectra of the wavelength-shifters PPO, bisMSB and PMP. The data is normalized such that the maximum of the spectrum is at 1. All solutes have been dissolved with a concentration of 2 g/ℓ in PXE.

FIG. 3: Emission spectra of PPO, bisMSB and PMP, all with a concentration of 2 g/ℓ in PXE solvent.
V. ANALYSIS AND RESULTS

The first step in the analysis is the determination of the start time for both recorded pulses (close and far PMTs). The start time is derived in a constant-fraction method by setting the starting point of each pulse to the 40\% height in the leading edge of the pulse. The distribution of the photon emission time results from the difference between the starting point of the close PMT pulse (zero-point) and that of the far PMT. Pulse height cuts are performed to reject dark-current pulses and overflow pulses below and above the single photon peak, respectively. In addition, pulses with more than one peak in the single-photon PMT are also rejected (double pulses or noise pulses).

The probability density function (PDF), \( F(t) \), of the scintillation-light emission can be described by a convolution of a multi-exponential function with the time resolution of the measuring system:

\[
F(t) = \left( \sum_i N_i \frac{\tau_i}{\tau_i} e^{-\frac{(t-t_0)}{\tau_i}} \right) \otimes R(t)
\]

where \( \tau_i \) is the decay-time constant of the exponential decay function \( i \) and \( N_i \) is the contribution of this component such that \( \sum_i N_i = 1 \). \( t_0 \) is the time at which the exponential decay starts and \( R(t) \) is the time-resolution function. In good approximation, the time resolution can be represented by a Gaussian curve:

\[
R(t) = e^{-\frac{t^2}{2\sigma^2}}
\]

where \( \sigma \) is a known parameter. The time resolution of the system is affected by the uncertainty in the determination of the pulse start-time mentioned above. For the close PMT, the start time is more accurate for scintillators with a high light yield due to the better photon statistics. Therefore, the resolution depends on the scintillator sample and has to be determined for every mixture. This has been achieved by fitting a Gaussian curve to the left (sharply rising) part of the measured PDF distribution. This method gives compatible results with the direct time-resolution measurement described in section III.

The ROOT-based RooFit toolkit is used to perform the fit of equation (1) to the measured data. In its default configuration, RooFit performs a maximum likelihood fit and minimizes \(-\log(L)\) where \( L \) is the likelihood function. This minimization is performed by calling the Minuit package from CERN libraries. Figure 4 shows the measured PDFs for four examples of different scintillator mixtures: PXE + 2 g/fPPO + 20 mg/fbisMSB, PXE + 2 g/fPPO, LAB + 2 g/fPPO and PXE + 2 g/fPMP. The data is presented in histograms with a bin size of 1 ns together with the statistical errors. A fit using the convolution of the sum of several exponential functions with a Gaussian curve is also depicted by the red curve.

The abbreviated names of the mixtures for which the fluorescence decay-time constants have been measured are summarized in Table IV. The sub-index \( c \) corresponds to the concentration of the corresponding solute.

Tables II - V summarize the parameters of the fits according to equation (1). Depending on the scintillator mixture and the solute concentration, either three or four decay components perform the best fit. Fit parameters are the time resolution \( \sigma \), the decay constants \( \tau_i \), the amplitudes \( N_i \) of each exponential function and the start time \( t_0 \) of the decay function. The amplitude of the last component \( (N_{i_{\text{cat}}}, \text{third of fourth depending on the fit}) \) has been calculated according to \( \sum_i N_i = 1 \) using the fit values. Its error depends on the other amplitudes. To estimate a maximum error (\( \Delta N_{\text{max}} \)) for this parameter, the uncertainties \( \Delta \tau_i \) and \( \Delta N_i \) consist of a statistical error \( \delta_{\text{stat}} \) which is obtained from the fit and a systematic error, \( \delta_{\text{sys}} \). The latter has been derived from a systematic study where the parameter \( \sigma \) is varied within one standard deviation of its value \( (\sigma + \Delta \sigma, \sigma - \Delta \sigma) \). It was found that the systematic error is of the same order of magnitude as the statistic one. Both systematic and statistic uncertainties are in general asymmetric. To evaluate the quality of a certain fit, both the convergence of the fit and the value of the likelihood function \( (-\log(L)) \) have been considered.

VI. DISCUSSION

For each sample, the shortest decay-time constant obtained, \( \tau_1 \), has a value of few nanoseconds \((2 - 8 \text{ ns})\) and represents the main contribution of the photon emission (its amplitude varies between 60\% and 95\% of the total emission). This contribution is related to the transition between the lowest excited singlet spin-state \( S_1 \) in the solute and its ground state \( S_0 \). The additional two or three components arise from further molecular processes such as the de-excitation of electrons in triplet spin-states. In general, the data shows that mixtures based on LAB solvent show longer decay constants. This observation has been made by other groups as well. Concerning the wavelength-shifters, PPO shows

| Name | Mixture |
|------|---------|
| PC   | PXE + c g/f PPO |
| LC   | LAB + c g/f PPO |
| MC   | PXE + c g/f PMP |
| PB   | PXE+2 g/f PPO+20 mg/fbisMSB |
| PTb  | PXE+2 g/f PTP+20 mg/fbisMSB |

TABLE I: Nomenclature used for the mixtures of which the fluorescence decay constants have been measured. The subindex \( c \) corresponds to the concentration of the corresponding solute.
FIG. 4: Probability density function of the scintillator mixtures (mix) PXE + 2 g/ℓ PPO + 20 mg/ℓ bisMSB, PXE + 2 g/ℓ PPO, LAB + 2 g/ℓ PPO and PXE + 2 g/ℓ PMP. The plots show the time dependence of the light emission fitted (curve in red) according to equation [1].

TABLE II: Results of the fits for the mixtures based on PXE + 2 g/ℓ PPO and 2 g/ℓ PTP, both with 20 mg/ℓ bisMSB as secondary wavelength-shifter. All decay times $\tau_i$, the time $t_0$, as well as the time resolution $\sigma$ are given in ns. The amplitudes $N_i$ are given in % with $N_{i,cal}$ calculated from $\sum_i N_i = 1$. The errors $\Delta \tau_i$ and $\Delta N_i$ include both statistic and systematic uncertainties.

| Mixture (mix) | PPb | PTb |
|---------------|-----|-----|
| $\sigma$ (ns) | $1.61 \pm 0.01$ | $1.50 \pm 0.01$ |

| mix | $\tau_1 \pm \Delta \tau_1$ | $\tau_2 \pm \Delta \tau_2$ | $\tau_3 \pm \Delta \tau_3$ | $\tau_4 \pm \Delta \tau_4$ | $t_0 \pm \Delta t_0$ |
|-----|----------------------------|----------------------------|----------------------------|----------------------------|---------------------|
| PPb | $2.61 \pm 0.02$ | $7.7 \pm 0.2$ | $34 \pm 2$ | $205 \pm 13$ | $6.75 \pm 0.06$ |
| PTb | $2.38 \pm 0.01$ | $7.3 \pm 0.2$ | $35 \pm 2$ | $162 \pm 10$ | $6.66 \pm 0.08$ |

| mix | $N_1 \pm \Delta N_1$ | $N_2 \pm \Delta N_2$ | $N_3 \pm \Delta N_3$ | $N_{i,cal} \pm \Delta N_{max}$ |
|-----|----------------------|----------------------|----------------------|--------------------------|
| PPb | $0.857 \pm 0.007$ | $0.097 \pm 0.006$ | $0.034 \pm 0.002$ | $0.02 \pm 0.01$ |
| PTb | $0.62 \pm 0.01$ | $0.30 \pm 0.01$ | $0.057 \pm 0.002$ | $0.02 \pm 0.01$ |

shorter values for $\tau_1$ than PMP. The addition of the secondary wavelength-shifter bisMSB to a mixture containing PPO has only a small effect on the decay times.

For three scintillator systems (PXE-PPO, LAB-PPO and PXE-PMP), the evolution of the shortest decay time constant $\tau_1$ with the solute concentration $c$ has been studied. From the variation of this decay-time constant, information on the energy transfer in the different systems can be obtained. The energy transfer mechanism can be described in the following way [18][6]. After the energy
**TABLE III:** Results of the fits for mixtures of the solvent PXE with different concentrations of PPO. Further details as in table II

| mix | PP1   | PP2   | PP6   | PP10  |
|-----|-------|-------|-------|-------|
| $\sigma$ (ns) | 1.45 ± 0.01 | 1.229 ± 0.007 | 1.066 ± 0.006 | 1.171 ± 0.007 |

| mix | $r_1 \pm \Delta r_1$ | $r_2 \pm \Delta r_2$ | $r_3 \pm \Delta r_3$ | $r_4 \pm \Delta r_4$ | $t_0 \pm \Delta t_0$ |
|-----|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| PP1 | 3.16 ± 0.03 ± 0.08 | 7.7 ± 0.7 ± 0.6 | 34 ± 4 ± 0 | 218 ± 26 ± 19 | 6.631 ± 0.006 ± 0.01 |
| PP2 | 2.63 ± 0.02 ± 0.01 | 8.8 ± 0.3 ± 0.2 | 43 ± 3 ± 0.0 | 242 ± 27 ± 2 | 6.661 ± 0.005 ± 0.004 |
| PP6 | 2.03 ± 0.01 ± 0.01 | 9.0 ± 0.1 ± 0.1 | 47 ± 3 ± 1 | 203 ± 16 ± 10 | 6.733 ± 0.004 ± 0.007 |
| PP10| 2.04 ± 0.01 ± 0.01 | 8.6 ± 0.4 ± 0.4 | 40 ± 2 ± 3 | 207 ± 14 ± 1 | 6.627 ± 0.005 ± 0.006 |

| mix | $N_1 \pm \Delta N_1$ | $N_2 \pm \Delta N_2$ | $N_3 \pm \Delta N_3$ | $N_{l\text{cal}} \pm \Delta N_{max}$ |
|-----|-------------------------|-------------------------|-------------------------|-------------------------|
| PP1 | 0.84 ± 0.02 ± 0.03 | 0.12 ± 0.02 ± 0.02 | 0.029 ± 0.003 ± 0.001 | 0.011 ± 0.002 ± 0.008 |
| PP2 | 0.852 ± 0.005 ± 0.003 | 0.103 ± 0.004 ± 0.003 | 0.031 ± 0.002 ± 0.001 | 0.014 ± 0.007 ± 0.003 |
| PP6 | 0.822 ± 0.003 ± 0.002 | 0.105 ± 0.002 ± 0.001 | 0.046 ± 0.002 ± 0.001 | 0.027 ± 0.004 ± 0.002 |
| PP10| 0.802 ± 0.003 ± 0.002 | 0.105 ± 0.002 ± 0.001 | 0.061 ± 0.002 ± 0.001 | 0.032 ± 0.005 ± 0.002 |

**TABLE IV:** Results of the fits for mixtures of the solvent LAB with different concentrations of PPO. Further details as in table III

| mix | LP1   | LP2   | LP6   | LP10  |
|-----|-------|-------|-------|-------|
| $\sigma$ (ns) | 1.92 ± 0.01 | 1.58 ± 0.01 | 1.236 ± 0.009 | 1.133 ± 0.008 |

| mix | $r_1 \pm \Delta r_1$ | $r_2 \pm \Delta r_2$ | $r_3 \pm \Delta r_3$ | $r_4 \pm \Delta r_4$ | $t_0 \pm \Delta t_0$ |
|-----|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| LP1 | 7.46 ± 0.07 ± 0.06 | 22.3 ± 0.9 ± 0.4 | 115 ± 3 ± 1 | - | 4.01 ± 0.01 ± 0.01 |
| LP2 | 5.21 ± 0.05 ± 0.05 | 18.4 ± 0.8 ± 0.2 | 118 ± 3 ± 1 | - | 4.161 ± 0.009 ± 0.006 |
| LP6 | 2.71 ± 0.08 ± 0.08 | 6.7 ± 0.6 ± 0.3 | 30 ± 2 ± 1 | 136 ± 5 ± 2 | 4.577 ± 0.007 ± 0.001 |
| LP10| 1.94 ± 0.05 ± 0.05 | 5.9 ± 0.3 ± 0.2 | 26.9 ± 1 ± 0.9 | 137 ± 4 ± 1 | 4.550 ± 0.007 ± 0.001 |

| mix | $N_1 \pm \Delta N_1$ | $N_2 \pm \Delta N_2$ | $N_3 \pm \Delta N_3$ | $N_{l\text{cal}} \pm \Delta N_{max}$ |
|-----|-------------------------|-------------------------|-------------------------|-------------------------|
| LP1 | 0.759 ± 0.009 ± 0.006 | 0.21 ± 0.008 ± 0.005 | - | 0.31 ± 0.001 ± 0.002 |
| LP2 | 0.777 ± 0.009 ± 0.006 | 0.170 ± 0.008 ± 0.005 | - | 0.353 ± 0.001 ± 0.002 |
| LP6 | 0.65 ± 0.04 ± 0.03 | 0.21 ± 0.02 ± 0.01 | 0.100 ± 0.004 ± 0.003 | 0.040 ± 0.003 ± 0.002 |
| LP10| 0.56 ± 0.02 ± 0.01 | 0.27 ± 0.01 ± 0.01 | 0.133 ± 0.004 ± 0.002 | 0.037 ± 0.003 ± 0.002 |

**TABLE V:** Results of the fits for mixtures of the solvent PXE with different concentrations of PMP. Further details as in table III

| mix | PM1   | PM2   | PM6   | PM10  |
|-----|-------|-------|-------|-------|
| $\sigma$ (ns) | 2.12 ± 0.01 | 1.77 ± 0.01 | 1.362 ± 0.009 | 1.258 ± 0.009 |

| mix | $r_1 \pm \Delta r_1$ | $r_2 \pm \Delta r_2$ | $r_3 \pm \Delta r_3$ | $t_0 \pm \Delta t_0$ |
|-----|-------------------------|-------------------------|-------------------------|-------------------------|
| PM1 | 4.30 ± 0.01 ± 0.01 | 21.4 ± 0.6 ± 0.6 | 212 ± 7 ± 3 | 4.466 ± 0.007 ± 0.009 |
| PM2 | 4.15 ± 0.01 ± 0.01 | 23.7 ± 0.8 ± 0.2 | 255 ± 2 ± 2 | 4.567 ± 0.007 ± 0.008 |
| PM6 | 3.62 ± 0.01 ± 0.01 | 18.5 ± 0.7 ± 0.3 | 137 ± 3 ± 1 | 4.375 ± 0.006 ± 0.008 |
| PM9 | 3.44 ± 0.01 ± 0.01 | 17.6 ± 0.7 ± 0.3 | 135 ± 3 ± 1 | 4.381 ± 0.006 ± 0.008 |

| mix | $N_1 \pm \Delta N_1$ | $N_2 \pm \Delta N_2$ | $N_{l\text{cal}} \pm \Delta N_{max}$ |
|-----|-------------------------|-------------------------|-------------------------|
| PM1 | 0.956 ± 0.001 ± 0.001 | 0.632 ± 0.001 ± 0.001 | 0.012 ± 0.001 ± 0.001 |
| PM2 | 0.955 ± 0.001 ± 0.001 | 0.635 ± 0.001 ± 0.001 | 0.006 ± 0.001 ± 0.001 |
| PM6 | 0.935 ± 0.002 ± 0.002 | 0.648 ± 0.002 ± 0.002 | 0.017 ± 0.003 ± 0.003 |
| PM9 | 0.919 ± 0.006 ± 0.006 | 0.647 ± 0.002 ± 0.001 | 0.024 ± 0.006 ± 0.006 |
deposition by a charged particle, the solvent molecule (PXE or LAB) rapidly reaches the first excited state. Via collisions with neighboring solvent molecules, the excitation energy can propagate between solvent molecules with a rate $k_h \text{[s}^{-1}\text{].}$ This process is also known as energy hopping \cite{14}. The excitation energy moves spatially until a solute molecule is encountered to which the energy is transferred by dipole-dipole interaction \cite{20}. The measured decay constant $\tau_1$ is mainly the sum of the energy-hopping time $\tau_1(c) = \frac{n(c)}{k_h}$ and the intrinsic lifetime of the solute $\tau_s$, $\tau_1 = \tau_s + \tau_1(c)$. The number of solvent-solvent collision processes $n$ depends on the solute concentration $c$, the higher the concentration the lower the value for $n$, the faster the energy transfer from a solvent to a solute molecule.

Assuming a linear dependence of the transfer rate on the solute concentration \cite{21,22} and defining an effective hopping rate $k_h$, it follows that: $k_l/n(c) = k_h \cdot c/c_0$ and the measured decay constant $\tau_1$ can be written as:

$$\tau_1(c) = \tau_s + \frac{c_0}{k_h \cdot c} \tag{3}$$

where $c_0 = 1 \text{g/}\ell$. By fitting this formula to the experimental data, the intrinsic lifetime of the solute $\tau_s$ can be extracted. Moreover, the value of $k_h$ represents the efficiency of the energy transfer via collisions (hopping) between solvent molecules until the energy reaches a solute molecule.

Figure\ref{fig:5} shows the evolution of $\tau_1$ with the PPO concentration for PPO being dissolved in the solvents PXE (upper panel) and LAB (middle panel). The lowest panel shows the concentration dependence for the solute PMP dissolved in PXE. The errors assigned to the data points are the linear sum of the statistic and systematic uncertainties. The fit applied to the data points corresponds to equation\ref{eq:3}. For each plot, the right upper-box shows the fit results where the parameter $\tau_s$ is labeled with the name of the solute and $k_h$ with the name of the solvent. The fit takes both the uncertainties in the solute concentrations and the errors in the decay-time constants into account, with the latter errors being asymmetric.

From the fits, the intrinsic lifetime of the PPO singlet-state $S_1$ can be extracted. For the PXE-PPO mixtures $\tau_{s,PPO} = 1.85 \pm 0.03 \text{ns}$ is obtained and $\tau_{s,PPO} = 1.19 \pm 0.15 \text{ns}$ for the mixtures of LAB-PPO. Thus, the obtained value for $\tau_s$ is lower when the LAB solvent is used. The solute lifetime changes with the solvent type because the interaction between both molecules changes. In the literature, the value for the intrinsic lifetime of the $S_1$ state of PPO varies slightly. In \cite{23} the values $1.44$ and $1.8 \text{ns}$ are reported. They result from different theoretical calculations of the $S_1 \rightarrow S_0$ transition and include a factor which takes the index of refraction of the solvent medium into account (cyclohexane in the published cases). Finally, in \cite{24} the value $1.6 \text{ns}$ has been used. The measured values for the PPO lifetime do not agree within the given error. We attribute this difference to solvent effects. The theoretical values given in the literature are in fair agreement with the results for $\tau_s$ presented here.

The parameter $k_h$ quantifies, as explained above, the transfer of energy between solvent molecules via collisions. This transfer rate is faster for PXE than for LAB

![FIG. 5: Evolution of the fluorescence decay time $\tau_1$ for different concentrations of PPO in the solvents PXE (upper part) and LAB (middle). Bottom: evolution of $\tau_1$ for different concentrations of PMP in PXE.](image-url)
which explains why for low PPO concentrations the measured \( \tau_1 \) values are much shorter than those for PPO dissolved in LAB. As an example, for a concentration of 2 g/l PPO, \( \tau_{s,PXE} = 2.63 \text{ ns} \) and \( \tau_{s,LAB} = 4.03 \text{ ns} \) (see equation \( 3 \)).

The obtained value for the intrinsic lifetime of PMP, \( \tau_{s,PMP} = 3.30 \pm 0.05 \text{ ns} \) is close to the measured value of 3.01 ns given in reference \( 22 \). \( \tau_{s,PMP} \) is significantly larger than the intrinsic lifetime of PPO. This might be due to the fact that the overlap between absorption and emission spectra in PMP is significantly lower than in PPO. The value of \( K_{h,PXE} \) of PMP is compatible to the one measured in the PXE-PPO system (\( K_{h,PXE} = 0.57 \pm 0.09 \) when PMP is used and \( K_{h,PXE} = 0.72 \pm 0.08 \) for the mixture with PPO). The measured \( \tau_1 \) constants increase with concentration and can well be fitted by equation \( 3 \). However, for large detectors solute self-absorption increases with concentration as well leading to longer \( \tau_1 \). This is due to the additional time which the light reemission takes \( 10 \).

VII. IMPACT ON SCINTILLATION-DETECTOR PERFORMANCE

The measurements of the fluorescence decay-time constants show that the main component of the light emission \( (\tau_1, N_1) \) is significantly dependent on the scintillator mixture. The impact of this variation on the potential of the proposed LENA detector to search for proton decay \( (p \rightarrow K^+ \nu) \) has been investigated in the present paper. The signature of these decay events consists of two pulses close in time \( 2 \). The first arises from the energy deposited by the kaon, the second from the energy of its decay particles \( (K^+ \rightarrow \mu^+ + \nu_\mu \text{ and } K^+ \rightarrow \pi^+ + \pi^0, \) with 63.4 and 20.9% branching ratios, respectively). Due to the short lifetime of the kaon (12.4 ns) these signals overlap significantly. However, the double-peak structure in the time can be used to discriminate those events from atmospheric neutrino background. The sensitivity of LENA to search for proton decay has been studied with a Geant4 \( 20 \)-based Monte Carlo simulation presented in reference \( 2 \). In those simulations, a main decay time constant \( \tau_1 \) of 3.5 ns was used. A sensitivity to the proton lifetime of \( 4 \cdot 10^{34} \text{ y} \) has been derived from the analysis.

Using the results of the present work, new simulations have been performed for two possible values of \( \tau_1 \) (3 and 6 ns) which are reasonable according to the presented measurements. For some samples, the decay time constant \( \tau_1 \) measured was even shorter than the chosen values. However, light propagation also has an influence on the pulse shape as scattering and solute self-absorption smear slightly the time information. The values of the absorption and scattering lengths are set to 20 m each as laboratory measurements have shown that those are realistic values. The resulting attenuation length is 10 m. All other scintillation constants were kept at their previous values. The time jitter of the photomultipliers is also included in the simulation. Further details are discussed in \( 2 \). The resulting efficiencies for proton decay detection in LENA via \( p \rightarrow K^+ \nu \) are 65% and 56% for the decay values \( \tau_1 = 3 \text{ ns} \) and \( \tau_1 = 6 \text{ ns} \), respectively. This means that the choice of the scintillator mixture can have an effect of about 20% on the achievable proton lifetime limit.

VIII. CONCLUSIONS

Fluorescence decay-time constants have been studied for several scintillator mixtures which could be relevant for the LENA detector. The effects of variation of the solvent type, solute type and concentration have been investigated systematically. In the measured samples, there is a short decay-time constant \( (\tau_1) \) which accounts for the main part of the emitted light (60 to 95%). For this decay constant, large differences from 2 to 8 ns have been obtained for various scintillator mixtures. Concerning the fluorescence decay-time constants, attenuation lengths and the solute self-absorption, a mixture containing PXE, about 2 g/l PPO and \( \sim 20 \text{ mg/l} \) bisMSB shows the best performance for LENA. The emission spectrum of bisMSB is shifted to longer wavelength values (see figure \( 4 \)) in comparison with spectra of usual primary wavelength-shifters like PPO. Since absorption and scattering lengths increase with the wavelength, the addition of bisMSB is favored. In principle, mixtures of PXE with PPO show a shorter \( \tau_1 \) but the self absorption of the wavelength-shifter plays also a role in the light propagation over large distances smearing the time information. The addition of a mineral oil like dodecane is currently under discussion. It has the advantage of being very transparent (long attenuation length) and has a large number of free protons. The latter is important for the detection of \( \nu \) via their capture on free protons \( 27 \). However, the addition of dodecane would result in slower decay-time constants \( 28 \).

The performance of the liquid scintillator in LENA has direct implications on the physics potential. This has been studied within a Monte Carlo simulation. If the shortest fluorescence decay-time constant is increased from 3 to 6 ns, the detection efficiency and therefore the sensitivity is reduced by 20%.

Acknowledgments

We want to thank C. Buck and F. X. Hartmann for valuable discussions. This work has been supported by funds of the Maier-Leibnitz-Laboratorium (Munich), the Deutsche Forschungsgemeinschaft (DFG) transregio TR27 (Neutrinos and beyond) and the Munich Cluster of Excellence (Origin and structure of the Universe).
[1] C. Arpesella et al. (Borexino Collaboration), Phys. Rev. Lett. 101, 091302 (2008), arXiv:0805.3843v2 [astro-ph].
[2] T. Marrodán Undagoitia et al., Phys. Rev. D 72, 075014 (2005), arXiv:hep-ph/0511230.
[3] T. Marrodán Undagoitia et al., Prog. Part. Nucl. Phys. 57, 283 (2006), arXiv:hep-ph/0605229.
[4] G. Rannucci et al., Nucl. Instrum. Meth. 350, 338 (1994).
[5] F. Elisei et al., Nucl. Instrum. Meth. A400, 53 (1997).
[6] C. Buck, F. X. Hartmann, D. Motta, and S. Schoenert, Chem. Phys. Lett. 435, 252 (2007).
[7] G. Alimonti (Borexino Collaboration) (2008), arXiv:0806.2400v1 [physics.ins-det].
[8] Agilent Technologies. Acqiris, www.acqiris.com/.
[9] Electron Tubes, www.electrontubes.com/.
[10] T. Marrodán Undagoitia, Ph.D. thesis, Technische Universität München, Garching, Germany (2008), http://mediatum2.ub.tum.de/doc/667813/667813.pdf.
[11] Ocean Optics (2007), http://www.oceanoptics.com/.
[12] T. Marrodán Undagoitia et al., to be published (2009).
[13] W. Verkerke and D. Kirkby, The roofit toolkit for data modeling. http://roofit.sourceforge.net/.
[14] F. James and M. Roos, Comput. Phys. Commun. 10, 343 (1975).
[15] J. B. Birks, The Theory and Practice of Scintillation Counting (Pergamon Press, London, 1964).
[16] C. Buck, private communication (2007).
[17] C. Kraus and M. Chen, private communication (2007).
[18] C. Buck, Ph.D. thesis, Ruperto-Carola Universität, Heidelberg, Germany (2004).
[19] F. X. Hartmann, private communication (2008).
[20] T. Forster, Discuss. Faraday Soc. 27, 7 (1959).
[21] I. B. Berlman, J. Chem. Phys. 33, 1124 (1960).
[22] I. B. Berlman, J. Chem. Phys. 34, 598 (1961).
[23] I. B. Berlman, Handbook of fluorescence spectra of aromatic molecules (Academic press, New York and London, 1971).
[24] G. Alimonti et al. (Borexino Collaboration), Nucl. Instrum. Meth. A440, 360 (2000).
[25] H. Guesten, P. Schuster, and W. Seitz, AIP Conf. Proc. 82, 459 (1978).
[26] S. Agostinelli et al. (Geant4 Collaboration), Nucl. Instr. Meth. A 506, 250 (2003).
[27] M. Wurm et al., Phys. Rev. D75, 023007 (2007), arXiv:astro-ph/0701305.
[28] M. Wurm, diploma thesis, Technische Universität München, Garching, Germany (2005).