A Kinetic Model for Xenon-Doped Liquid Argon Scintillation Light

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Abstract

Scintillation from noble gases is an important technique in particle physics including neutrino beam experiments, neutrino-less double beta-decay and dark matter searches. In liquid argon, the possibility of enhancing the light yield by the addition of a small quantity of xenon (doping at $\sim 10 - 1000$ ppm) has been of particular interest. While the pathway for energy transfer between argon and xenon excimers is well known, the time-dependence of the process has not been fully studied in the context of a physics-based model. In this paper we present a model of the energy transfer process together with a fit to xenon-doped argon data. We have measured the diffusion limited rate constant as a function of xenon dopant. We find that the time dependence of the energy transfer is consistent with diffusion-limited reactions. Additionally, we find that commercially obtained argon can have a small xenon component ($\sim$4 ppm). Our result will facilitate the use of xenon-doped liquid argon in future experiments.

Keywords: liquid argon, scintillation, xenon doping

1. Introduction

The use of Liquid Noble Gases (LNG) as detectors and active vetoes in physics experiments has become a mainstay, especially for low rate, large volume/mass applications for direct dark matter detection [1], neutrino beam experiments [2], and the neutrino-less double beta decay experiment LEGEND [3]. In particular, liquid argon (LAr) has become widely used because
of its low cost. Due to the short wavelength of the argon scintillation light (128 nm), LAr experiments require the use of a wavelength shifter (typically Tetraphenyl Butadiene, TPB) for the detection of the light. The possibility of shifting the light to the xenon dimer emission wavelength (175 nm) is therefore tantalizing [4]. Previous work has demonstrated that a small dopant concentration of ∼ 10 ppm is sufficient to transfer a large portion of the scintillation to the xenon emission wavelength and to increase the total light yield [5],[6].

2. Model

LAr emission results from two argon excimer states, a singlet and a triplet. The singlet lifetime is short (∼ 7 ns) while the triplet state is quoted as having a much longer lifetime (∼ 1100 – 1600 ns) [7]. The spread in these values is often attributed to experimental methods, and has yet to be fully understood.

The scintillation energy transfer in xenon-doped liquid argon is well understood [8]. First, the argon excimer forms in one of two ways:

\[2\text{Ar} \rightarrow \text{Ar} + \text{Ar}^* \rightarrow \text{Ar}_2^*\]
\[2\text{Ar} \rightarrow \text{Ar} + \text{Ar}^+ \rightarrow \text{Ar}_2^+ \rightarrow \text{Ar}_2^*\] (1)

The argon excimer diffuses through the liquid and can, if there are impurities (like oxygen, nitrogen, xenon, etc.) transfer its excitation energy to any of the impurities. If it is a nitrogen or oxygen atom, the excited impurity can de-excite through heat without giving off light. If the argon excimer interacts with a xenon atom, it can form a mixed state (Ar-Xe) excimer. If this mixed state excimer interacts with another xenon atom, it can create a xenon excimer:

\[\text{Ar}_2^* + 2\text{Xe} \rightarrow \text{Ar} + \text{ArXe}^* + \text{Xe} \rightarrow 2\text{Ar} + \text{Xe}_2^*\] (2)

The time evolution of these states can be described by coupled, time dependant differential equations. We label the number of molecules of a certain kind at a given time as: argon excimer singlet \(S(t)\), argon excimer triplet \(T(t)\) , mixed excimer \(M(t)\) , and xenon excimer \(X(t)\). The change in the number of states depends the exponential lifetimes: argon singlet \(\tau_s\), argon triplet \(\tau_t\) and xenon \(\tau_x\) (the xenon triplet and singlet times are taken
together as an average, since both are relatively short compared to the argon triplet lifetime and the diffusion time) and the collision energy transfer time characterized by a diffusion rate \(k_1\):

\[
\dot{S} = -S/\tau_s - k_1 S
\]

\[
\dot{T} = -T/\tau_t - k_1 T
\]

\[
\dot{M} = k_1(S + T) - k_1 M
\]

\[
\dot{X} = k_1 M - X/\tau_x
\]

Because LAr vessels are often not completely full, we must also take into account emission from cold argon gas in the ullage,

\[
\dot{G} = -G/\tau_g
\]

where \(\tau_g\) is the argon triplet in the cold gas. From Henry’s law we deduce that a negligible amount of xenon is mixed into the argon gas at our xenon doping levels in the liquid (see Section 4.2). Additionally, we ignore the singlet from the gas as in this work we do not fit the singlet light.

We could, in principle, also take into account energy transfer to non-scintillating states, as occurs with contaminants such as oxygen and nitrogen. This would simply add another diffusion rate dependent transfer out of the excimers. In this work, our argon was purified to ppb levels of these contaminants, so we neglect those terms here.

As noted above, in our solution to these differential equations, we ignore the singlet component as we did not have sufficient time resolution to resolve it. Furthermore, the simple exponential would have to be convoluted with the detector time resolution as well as the spatial dependence of the ionization deposition in the detector. Thus, ignoring the singlet, these equations are easily integrated analytically. Defining the time constants: \(1/\tau_{t'} = 1/(\tau_t + k_1)\), \(1/t_1 = (1/\tau_x - k_1)\) and \(1/t_2 = (1/\tau_x - 1/\tau_{t'})\), then the solutions are:

\[
T(t) = T_0 e^{-t/\tau_{t'}}
\]

\[
M(t) = T_0 \tau_t k_1 \left( e^{-k_1 t} - e^{-t/\tau_{t'}} \right)
\]

\[
X(t) = T_0 \tau_t (k_1)^2 \left[ t_1 e^{-k_1 t} - t_2 e^{-t/\tau_{t'}} + (t_2 - t_1) e^{-t/\tau_x} \right].
\]
For the gas component,

\[ G(t) = G_0 e^{-t/\tau_G} \]

and finally, the corresponding light emission \( L(t) \) is given by,

\[ L(t) = T(t)/\tau_t + X(t)/\tau_x + G(t)/\tau_g \]

We have not, as yet, included important experimental effects, which could be determined via simulation, including geometric effects, light transmission and reflection, trigger effects, etc. We simply use this as an empirical model and fit the data. Despite the lack of any attempt to model the detected light, the model fits the main features of our data. Moreover, we can extract a value for the transfer constant \( k_1 \) that is in good agreement with what we expect theoretically.

3. Fit to Data

The data used in this paper has been previously described \[6\]. Our apparatus is a 100L liquid argon cryostat viewed by one 3\( '' \) Hamamatsu R11065 PMT with a TPB coated acrylic disk fixed to the front of the tube. We inserted xenon corresponding to added concentrations of 0, 1, 2, 5, and 10 ppm with an uncertainty of 6\%. The data was taken under two trigger conditions: a PMT trigger (referred to in \[6\] as a random trigger, RAN) and a cosmic ray muon trigger (MU) derived from coincidence between scintillator panels placed above and below the cryostat. All the data was taken with the RAN trigger except for the 10 ppm (amount of added xenon) data which was taken with both MU and RAN triggers. The light curves \( L(T) \) were derived from pulses with integrated charge normalized to the single photon response (SPE). The six data sets were normalized to the number of triggers in each set (see Figure 1). It can be seen that our PMT produced considerable after-pulsing, presumed to be from helium leaked into the PMT. No attempt was made here to correct for the after-pulsing, which limits our determination of the shape of the time spectra at short times. However, the observation of the trend towards increasing light yield and decreased emission time with increasing xenon concentration remains clear.

For the samples with a visible gaseous tail (sets 4,5,6), we fit the tail in the range \((7 - 10) \mu s\) (where the spectra is simply exponential) to determine the gaseous triplet lifetime. For the sets 1,2,3 the large argon triplet component prevents us from properly fitting the tail lifetime. The average triplet lifetime
Figure 1: The six data sets normalized to number of events: Set1: 0 ppm MU (dark orange), Set2: 1 ppm RAN (blue), Set3: 2 ppm RAN (red), Set4: 5 ppm RAN (green), Set5: 10 ppm RAN (cyan), Set6: 10 ppm MU (magenta).
in the gas in these sets is $3.2 \pm 1.4 \, \mu s$, consistent with previously measured value $3.48 \pm 0.01 \, \mu s$ \cite{9}. The average gaseous component in sets 4-6 is $G_0/T_0 = 0.06$, which is a factor of $\sim 60$ higher than GEANT simulations (see Section 4.2 for a discussion).

We then fit all sets to our model. In sets 1-3 we set the argon gas triplet lifetime to the average from sets 4-6 and allow the parameter $G_0$ to float. Because of the relatively strong correlation between several of the fit parameters and the after-pulsing at short times, we fix the liquid argon triplet lifetime to the measured value in gas $3.48 \, \mu s$ and the xenon lifetime to $20 \, ns$. We chose the value of $3.48 \, \mu s$ rather than the standard value in liquid of $1.4 \, \mu s$ for two reasons: 1) as we find xenon in our pure argon, the fundamental lifetime of the argon excimer must be larger than the apparent lifetime from the scintillation time distribution, and 2) we performed fits to all six data sets with the same $\tau_t$ using several values from $1.2 \, \mu s$ to $4.0 \, \mu s$ and found that the best fit to the data corresponded to approximately $3.0 \, \mu s$.

The remaining parameters allowed to vary in the fit to the data were $T_0$ and $k_1$ (and the component of light in the gas $G_0$ in sets 1-3). The fit results are shown in Figure 2.

| X [ppm] | $T_0$ [µs] | SPE [µs] | $k_1$ [µs$^{-1}$] | $L_{Xe}$ | $G_0/T_0$ |
|--------|---------|--------|-------------------|--------|---------|
| 0      | 1656 ± 45 | 2044 ± 45 | 1.26 ± 0.04 | 0.81 ± 0.05 | 0.250 ± 0.012 |
| 1      | 3190 ± 178 | 3611 ± 60 | 0.83 ± 0.03 | 0.74 ± 0.04 | 0.165 ± 0.104 |
| 2      | 3622 ± 85  | 3907 ± 63  | 1.22 ± 0.03 | 0.81 ± 0.03 | 0.088 ± 0.017 |
| 5      | 3780 ± 63  | 4022 ± 63  | 2.06 ± 0.03 | 0.88 ± 0.03 | 0.068 ± 0.001 |
| 10     | 3732 ± 62  | 3983 ± 63  | 3.05 ± 0.05 | 0.91 ± 0.02 | 0.063 ± 0.001 |
| 10     | 4387 ± 67  | 4605 ± 68  | 3.15 ± 0.04 | 0.92 ± 0.02 | 0.047 ± 0.001 |

Table 1: Fitted values $T_0$ in SPE per event and $k_1$ in $(\mu s)^{-1}$ by dopant concentration $X$ [ppm] and trigger condition, together with the integral light yield in SPE and gaseous component. The argon triplet lifetime was set to $3.48 \, \mu s$ (see text). The column $L_{Xe}$ is the fraction of triplet light from Xe (175 nm). Note that the last 10 ppm set was taken with the MU trigger. All other sets were taken with the RAN trigger.

4. Analysis

4.1. Diffusion Constant

The self diffusion rate, $k_{diff}$ is given by

$$k_{diff} = 4\pi \times D \times R \times C$$
Figure 2: Fits of the data to our model (black line) with $\tau_t$ fixed to 3.48 $\mu$s as described in the text. The components are: triplet argon (red line), xenon (green line), gas (yellow line).
where \( D = 2.07 \times 10^{-5} \text{cm}^2/\text{s} \) is the argon self-diffusion constant, \( R = 4.0 \times 10^{-8} \text{cm} \) is the xenon-argon dimer Van der Waals separation, and \( C \) is the concentration of xenon in atoms per \( \text{cm}^3 \). Using the value for liquid argon density (1.4g/cm\(^3\)), Avagadro’s number, and the molar atomic weight of argon, we arrive at the diffusion-limited reaction rate \( k_{\text{diff}} = 0.219 \ [\mu \text{s}^{-1}] \times X \) where \( X \) here is the true Xe concentration in parts-per-million (ppm).

The extracted values of \( k_1 \) from our model versus dopant concentration is shown in Figure 3. The fitted line is \( k_1 = aX + b \ [\mu \text{s}^{-1}] \) where \( X \) is the added Xe dopant concentration in ppm, \( a = 0.226 \pm 0.004 \) (stat) \( \pm 0.03 \) (sys) and \( b = 0.844 \pm 0.021 \). The measured slope is in good agreement with our theoretical value given above for \( k_{\text{diff}} \). The intercept corresponds to xenon in our “pure” argon with a concentration of 3.74 \pm 0.03 (stat) \pm 0.4 (sys) [ppm].

The systematic error is due to the \( \sim 60\% \) correlation between \( k_1 \) and \( \tau_l \) in the fit. This level of xenon in commercial argon is consistent with previous studies of impurities in LAr [10], and may be expected since the atmospheric concentration of argon is 0.934\% by volume compared to xenon which is 87\% by volume [11].

4.2. Ullage Light

The light from the gaseous argon above our liquid is a complicating factor in this study. We first estimate the mole fraction of Xe in the ullage using ideal solution theory. The vapor pressure equation for Xe is

\[
P = P_{\text{atm}} \exp \left[-\frac{L}{R} \left(\frac{1}{T} - \frac{1}{T_b}\right)\right], \tag{6}
\]

where \( L \) is the latent heat of vaporization and \( T_b \) is the boiling temperature of pure Xe. The latent heat is 12.6 kJ/mol and the boiling temperature at atmospheric pressure is 165 K [12]. Thus, the Xe vapor pressure at the boiling point of Ar is \( 2.8 \times 10^{-4} \) atm. (The boiling point elevation of Ar by a few ppm Xe is negligible compared with their difference in boiling temperatures.) Raoult’s law states that the partial pressure is the vapor pressure of the pure substance multiplied by the mole fraction in the liquid. Thus, at ppm Xe doping, the ullage contains a negligible concentration of Xe, i.e., \(< 1 \) ppb.

A simulation of the experimental setup has determined that this light should be less that the light from the liquid argon by a factor of \( \sim 1000 \). The ratios of the initial triplet states in the gas to the liquid, \( G_0/T_0 \) is listed in the last column of Table 1. Where the values of \( G_0 \) are well determined by the
Figure 3: Fitted rate constant $k_1$ for each of the run sets versus set doping concentration. The fitted line is $k_1 = aX + b \,[\mu s^{-1}]$ where X is the added Xe dopant in parts per million (ppm), $a = 0.226 \pm 0.004\,(stat)$ and $b = 0.845 \pm 0.021$. The intercept corresponds to a xenon concentration in our “pure” liquid argon $3.74 \pm 0.03\,(stat) \pm 0.4\,(sys) \,[ppm]$. 
long-time tail, the extracted ratios are a factor of 60 higher than determined in the simulation.

There are several possible explanations for this discrepancy. The most mundane explanation is that the factor of the energy loss ratio between the ullage and the liquid was underestimated, since some scintillation in the liquid occurs below the PMT, and will have a much lower likelihood of being detected. This is, at most, a factor of two. Another more intriguing possibility is that the xenon is not fully mixed in the liquid argon, with more at the bottom of the cryostat (since it more massive). While this is something that has worried those that have proposed xenon-doped liquid argon, we find this extremely unlikely in this case, since the behavior of the time spectra with added xenon is well characterized by the model, and a gravity-based gradation of the xenon concentration would lead to very different shapes (sums of light from different concentrations) than what is seen in the data. In a follow-on experiment, we plan to minimize the ullage as much as possible (by filling to a higher level) to better understand this component.

4.3. LAr Triplet Lifetime

An empirical fit of our 0 ppm data to a single exponential gives a lifetime of $\sim 1.4 \, \mu s$, a number consistent with the typically reported value for the triplet lifetime of liquid argon. We have shown that this un-doped sample actually has a xenon content of about $3.74 \pm 0.03(\text{stat}) \pm 0.4(\text{sys}) \, \text{ppm}$. We believe this short empirical lifetime is an artifact of the residual xenon in typically available argon. The current data, which is hampered at short times by the after-pulsing, does not allow for a better determination of the “true” triplet lifetime, since, as can be seen in Figure 4, only the early times ($< 3 \, \mu s$) show a significantly different shape.

Additionally, fits to the data where the liquid triplet lifetime is allowed to float, suggests that the argon triplet lifetime decreases with xenon dopant concentration. While the quality of the data does not allow for this to be unambiguously determined, one could speculate that the presence of xenon might reduce the real triplet lifetime as well as transferring the energy to the xenon dimer.

4.4. Increase in Light Yield

One of the most important motivations for doping LAr with xenon is the reported increase in total light yield, as mentioned in the introduction. Our results are summarized in Figure 5 and Table 1. In Table 1 two measures of
Figure 4: Model results with 3 ppm (left) and 13 ppm (right) of total xenon in LAr. These two values roughly correspond to set 1 and sets 5 and 6 of the data. Each plot shows two curves corresponding to triplet lifetimes of 1.4 (black) and 3.5 (blue) \( \mu s \). One can see that only the shapes of the light curves at early times (\(< 3.0 \mu s\)) can easily differentiate these two (quite different) triplet lifetimes.

the total light from the scintillation are included. First, the value of \( T_0 \) can be used as a surrogate for the total light emission since this is the number of triplet states initially created, the ratio of the initial triplet to the initial singlet should be a fixed number, and we assume all the triplet plus singlet states eventually lead to scintillation. For the second measure of light yield, we integrate the actual light curves from just before the singlet light (\( \sim 1 \mu s \)) to 10 \( \mu s \) in SPE. For the lowest doped sets, this will underestimate the light because of the long time scale of light emission. Also, we note that the SPE values include the contribution from the ullage (\( \sim 10\% \)), whereas the values of \( T_0 \) exclude this light.

The ratio of the \( T_0 \) at 10 ppm to 0 ppm (both with the PMT (RAN) triggers, one finds a factor of more than two increase in the light yield. From simulation (as has been previously reported for this data \[6\]), a factor of approximately two is found. The reason given for this increase in reference \[6\] is the increase in the transparency of LAr to the 175 nm scintillation of xenon compared to the 128 nm scintillation of argon. This increase in transparency itself has been attributed to the xenon presence in commercial argon \[13\]. However, by examining the fraction of the total light from xenon scintillation, \( (L_{Xe}) \), as a function of xenon added, the model fit finds that there is only a \( \sim 15\% \) increase in light from xenon scintillation (Figure \[6\]). The model (red line in Figure \[6\]) predicts that the xenon fraction of the total light increases non-linearly with dopant in agreement with the data. It should be
Figure 5: Fitted $T_0$ and integrated light curves as a function of added xenon concentration. PMT (RAN) triggers are red and cosmic muon triggers are blue, while solid markers are the fit values, $T_0$, and open markers are the light curve integral values.
noted that both the fitted data and the model curve are dependant on the argon triplet lifetime, with the curve rising less steeply for a shorter triplet lifetime. With a lifetime of $\tau_t = 1.40$ ns, the xenon fraction starts at about $\sim 50\%$ and increases to $\sim 80\%$ at the maximum absolute xenon concentration. Therefore, it seems unlikely that better transparency is the only reason for the increase in total light if the model parameterization of this data given here is correct.

Figure 6: Ratio of xenon light (SPE) to total (SPE) versus absolute xenon concentration using our fitted extrapolation with $\tau_t = 3.48$ ns, where 0 ppm doped corresponds to 3.74 ppm absolute xenon concentration. The red line is the model prediction, with the line thickness showing the model uncertainty due to the extrapolated value of $k_1$. With variation of $\tau_t$ the fitted values and curve remain consistent, but the shape varies considerably. See discussion in text.

5. Conclusion
We have shown that a simple model for the kinetics of excimer diffusion and light yield of liquid argon doped with small amounts of xenon is in good agreement with our experimental data. Our result supports the conclusion
that xenon doping at the small amount of the order of 10 ppm can significantly enhance the light yield of liquid argon.

This model can be used to predict the light yields at both xenon and argon wavelengths in xenon-doped liquid argon for future LAr detector experiments. This may become important when determining the best detector design for a particular experimental application. In subsequent work we will separately measure the 128 nm and 175 nm light. We hope to be able to achieve a better understanding the origin of the increased light yield seen with xenon doping.
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