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Development of a liquid scintillator containing a zirconium β-keto ester complex for the ZICOS experiment

Yoshiyuki Fukuda

Department of Physics, Miyagi University of Education, Sendai, Miyagi 980-0845, Japan

Takahiro Gunji

Faculty of Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan

Shigetaka Moriyama

Kamioka Observatory, Institute for Cosmic Ray Research, The University of Tokyo, Hida, Gifu 506-1205, Japan

Izumi Ogawa

Faculty of Engineering, Fukui University, Fukui, Fukui 910-8507, Japan

Abstract

A liquid scintillator containing a zirconium β-keto ester complex has been developed for the ZIrconium Complex in Organic Scintillator (ZICOS) neutrinoless double beta decay experiment. We are aiming to develop a detector which has a good energy resolution (4% at 2.5 MeV), a large light yield (60% that of BC505) and a low background rate (0.1 counts/tonne·year) with several tonnes of ^{96}Zr isotope, so we have investigated the zirconium β-keto ester complexes tetrakis(isopropyl acetoacetato)zirconium and tetrakis(ethyl acetoacetato)zirconium, which have high solubility (over 10 wt.%) in anisole. We measured the performance of liquid scintillators containing these zirconium β-keto ester complexes and obtained 40% of the light yield of BC505 and energy resolution of 4.1% at 2.5 MeV assuming 40% photo coverage of the photomultiplier in the ZICOS detector. Thus we almost achieved our initial goal. Preliminary investigations indicate that tetrakis(diethyl malonato)zirconium will give us no quenching of the light yield and an energy resolution of 2.9% at 2.5 MeV. This will be a suitable complex for the ZICOS experiment, if it has a large solubility.

Keywords:
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1. Synthesis of zirconium β-keto ester complex and its properties

We have synthesized tetrakis(isopropyl acetoacetato)zirconium ($Zr(ipcac)_4$) and tetrakis(ethyl acetoacetato)zirconium ($Zr(etac)_4$) β-keto ester complexes [2]. Their chemical formulas and the molecular weight are $Zr(CH_3CCOCHCOOCH(CH_3)_2)_4$ (MW = 711.92) and $Zr(CH_3CCOCHCOOCH_2CH_3)_4$ (MW = 665.81), respectively.

We measured the solubility of these complexes in anisole and they were over 10 wt.%. We also measured the absorbance spectra, and the absorption peaks of $Zr(iprac)_4$ and $Zr(etac)_4$ were shifted to a shorter wavelength ($\sim$ 240 nm) than the emission wavelength of anisole. In other words, there is almost no overlap between the absorption spectrum of the β-keto ester com-

plex and the emission spectrum of anisole in hexane, which was reported by Ref. [1] in case of $Zr(acac)_4$. Optical properties of a complex, such as absorbance, are generally determined by the ligand and are not affected by the nucleus. The absorption peak was almost determined by the energy band of the peripheral electrons of the ligand, and the electron was provided by the nucleus.

As we reported in Ref. [2], we have observed small bump appearing around 290 nm in the absorbance spectra. We expected that this bump was caused by some impurities in the complex, which could be separated by precipitation in a solvent, such as hexane or diethyl ether, because the absorbance spectra showed no bump just a few weeks after the bump was observed. However, the impurities could not be precipitated in anisole, because the light yield did not recover even after a few weeks. Although we could not directly see the absorbance spectra below 300 nm in anisole due to the huge absorption, we considered those impurities to be dissolved in anisole. Recently, we have started to keep the complex under nitrogen, with the storage vial filled with nitrogen instead of air. We found that the newly delivered complex did not exhibit such a bump in the absorbance spectra. On one occasion air was accidentally introduced into the storage vial. Then, the newly delivered complex showed the bump again. This indicates that the impurities might be produced by air, particularly oxygen.

2. Performance of liquid scintillators containing zirconium β-keto ester complexes

The performance of a liquid scintillator form the point of view of neutrinoless double beta decay should be evaluated by its energy resolution. To distinguish between $2\nu\beta\beta$ and $0\nu\beta\beta$, and avoid γ rays from ^{208}Tl in U/Th (total energy $\sim$ 2.7 MeV), our initial goal was that (a) the light yield should be larger than 60% that of BC505, and (b) the energy resolution should be 4% at 2.5 MeV for a 10 wt.% concentration of zirconium β-keto ester complex.

To measure the light yield and energy resolution, we must use not only the Compton edge but also the single energy peak obtained by using the backscattering method. To select the scattering angle of 150 degrees, we collimated the γ rays using lead blocks, and the scattered γ rays was measured by NaI scintillator. We could see the single peak in both detectors. The calculated energy of NaI obtained from the scattering angle was 224 keV and the fitted value was 221 keV; therefore the experimental measurements should be correct.

To perform measurements at 10 wt.% concentration, it was necessary to have about 2 g of $Zr(iprac)_4$ and $Zr(etac)_4$; however, we had only about 1 g of each complex. Therefore, we could not measure the light yield and energy resolution for 10 wt.% concentration. However, the absorbance spectra of the complex and the ligand should be basically the same because the optical properties of the complex should be determined by the energy band of the orbital electrons in the ligand. The absorbance spectra of $Zr(iprac)_4$ and isopropyl acetoacetate are actually quite similar. Therefore, at this time, we measured the performance using isopropyl acetoacetate instead of $Zr(iprac)_4$ for large concentrations.

The light yield fraction for the standard cocktail as a function of the concentration of $Zr(iprac)_4$, isopropyl acetoacetate, and $Zr(acac)_4$ were measured. At high concentrations we used isopropyl acetoacetate to measure the light yield, because of a lack of $Zr(iprac)_4$ complex, as described above. To evaluate at same concentration of ligand, we used a fourfold larger molar number for isopropyl acetoacetate. For comparison, the light yield fraction for $Zr(acac)_4$ is also shown in same figure. The light yield of $Zr(iprac)_4$ obtained by fitting the data is almost 30% to 40% of that of the standard cocktail at a 10 wt.% concentration. It appears that there is a difference between isopropyl acetoacetate and $Zr(iprac)_4$; namely, the light yield of the complex may be about half that of the ligand. We thought that this might be due to the difference in absorbance shape, as the complex has a small bump appearing around 290 nm. If we can use the controlled complex that should have the same absorbance shape as the ligand, then we will get the same light yield of about 30% that of BC505. This number is quite a bit smaller than our initial goal which was 60% of the light yield of BC505. However, this does not restrict the performance of the liquid scintillator, because the most important property is the energy resolution.

The right panel of Fig. 1 shows the measured energy resolution as a function of the concentration of $Zr(iprac)_4$ equivalent. Again these data were obtained using isopropyl acetoacetate, not $Zr(iprac)_4$. It appears that the energy repulsion obeys the usual expectation $\sigma = \frac{\sigma_0}{\sqrt{E/E_0}}$, where E, E_0, and σ_0 correspond to the electron energy, the reference energy, and the energy resolution for the reference energy, respectively. The energy should be proportional to the light yield. The obtained energy resolution around 10 wt.% concentration was 14% at 1 MeV, which was estimated by measuring the energy of NaI. In this case, the observed energy in the liquid scintillator was 1 MeV, because we used ^{60}Co as the γ source (1.33 MeV and 1.17 MeV) and the expected

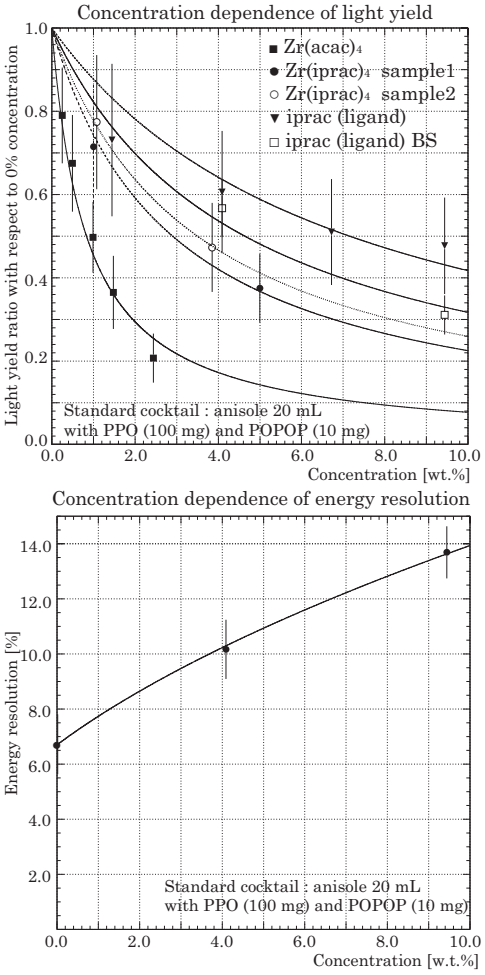

Figure 1: Light yield fraction as a function of the concentration of $Zr(iprac)_4$ and isopropyl acetoacetate (left panel). Measured energy resolution as a function of the concentration of $Zr(iprac)_4$ and isopropyl acetoacetate (right panel).

energy deposited in the liquid scintillator would be calculated as 1.025 MeV (the 0.225 MeV value observed in the NaI scintillator should be subtracted). In this setup, the scintillation photons were collected by two photomultipliers. The photo coverage of this setup was estimated to be about 8.5% using Monte Carlo simulation. On the other hand, the ZICOS detector will have 40% coverage of photomultipliers, so that the energy resolution for the ZICOS detector should be 6.5% at 1.0 MeV. Therefore, the actual energy resolution at 2.5 MeV was estimated to be 4.1%. This value is quite similar to our initial goal. In conclusion, our liquid scintillator system with 10 wt. % concentration of $Zr(iprac)_4$ in anisole has almost achieved our initial goals.

3. Tetrakis(diethyl malonato)zirconium

As described in previous section, it is possible, using $Zr(iprac)_4$, to obtain a liquid scintillator system for the ZICOS detector, which should have the necessary energy resolution for the neutrinoless double beta decay search. However, the light yield is still lower than our goal, so the energy resolution of 4.1% at 2.5 MeV may not be enough, because this is almost the same performance as achieved by the present KamLAND experiment. KamLAND needs better energy resolution to distinguish the background and ^{136}Xe signals. In our case, in order to achieve a better energy resolution, we need to have a much better complex than $Zr(iprac)_4$.

The β-keto ester complex shortened the absorption wavelength by introducing an ester group in the place of a methyl group. Therefore, if we exchange another methyl group with an ester group, the absorption peak should be moved to an even shorter wavelength than 240 nm. Tetrakis(diethyl malonato)zirconium ($Zr(deml)_4$) is one possible complex which has double ester ligand instead of a β-keto ester ligand.

The absorption peak has shifted to around 210 nm, a much shorter wavelength than that of ethyl acetylacetone. This indicates that the light yield and energy resolution of tetrakis(diethyl malonato)zirconium could be improved by the non-overlapping of the absorption spectrum of the complex and the emission spectrum of anisole. The Compton edge distributions of γ rays from the ^{60}Co radioactive source for each ligand (isopropyl acetoacetate, methyl acetoacetate, and diethyl malonate) at almost same concentration (6 –7 wt.%) were measured and they show that the Compton edge of a liquid scintillator containing diethyl malonate is same as that of the standard cocktail. This means that there is no quenching for a liquid scintillator containing diethyl malonate. According to these results, we expect that tetrakis(diethyl malonato)zirconium ($Zr(deml)_4$) will give us the same light yield as BC505, and the energy resolution will be about 2.9% at 2.5 MeV for the ZICOS detector. This value is better than our initial goal, and might be enough to distinguish background and signals. In other words, it is crucial for discrimination in a non-tracking detector such as a liquid scintillator.

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