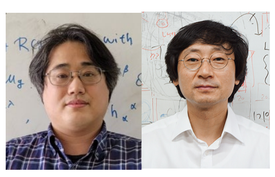
Impurity Detection in Organometallic Complex-Based LAB Liquid Scintillators via Infrared Spectroscopy for Enhanced Neutrino Detection



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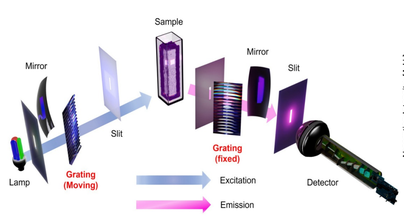
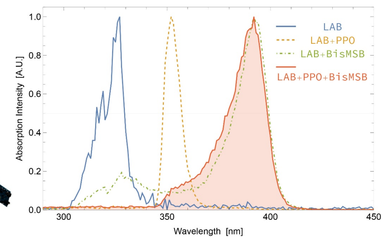
Abstract: Infrared (IR) spectroscopy offers a powerful approach to analyzing the purity of linear alkyl benzene (LAB)-based liquid scintillators. While previous studies have largely focused on electronic transitions using ultraviolet-visible spectroscopy, this work explores the vibrational transitions captured by IR spectroscopy. By examining the unique IR spectral characteristics of these solutions, we provide a comprehensive analysis of impurity detection and identification. This research demonstrates the effectiveness of IR spectroscopy as a quality assurance tool for liquid scintillation solutions, ultimately contributing to the enhancement of neutrino detection experiments.

Motivation

- **Linear Alkyl Benzene (LAB, $C_6H_5 - C_nH_{2n+1}, n = 10 - 12$):** A primary solvent in liquid scintillators (LSs) for neutrino experiments
- **Impact of Impurities**: Impurities (approx. 0.5% to 3%) from raw chemical processes significantly influence the optical properties of LAB-based scintillation solutions, particularly the attenuation length. This is crucial for light collection by Photomultiplier Tubes (PMTs).
- **Previous Research**: Primarily utilized UV-Visible spectroscopy to investigate electronic structures and transitions.

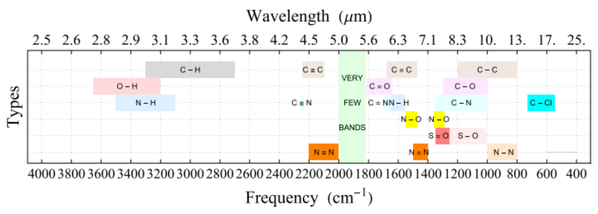




Explaining spectral differences between LAB+bis-MSB and LAB+PPO+bis-MSB samples via PPO-mediated FRET, considering the Stokes shift.
Obtaining excitation spectra using the detector's zero-order diffraction grating, passing all wavelengths by reflection rather than selecting specific diffracted wavelengths from fluorescence.

Introduction

- **Focus of This Study :** Employs Infrared (IR) spectroscopy to analyze vibrational transitions in molecules for impurity detection and identification. The IR region (4000 ~ 400 cm^{-1}) provides a "fingerprint" for each substance via its unique vibrational modes.
- **Objective**: To confirm the presence or absence of common impurities (acetone, water) and three specific impurity compounds (IMP1, IMP2, IMP3) identified by the JUNO Collaboration, thereby ensuring the quality of scintillation solutions and enhancing the performance of neutrino detectors.

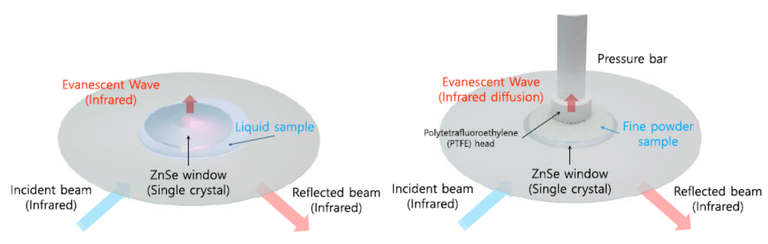


Vibrational Frequencies Overview:

1. Presenting comprehensive data for various chemical bonds, with colored bands highlighting key modes.
2. Noting fewer bands in the 1800-2000 cm^{-1} region due to typical organic structures (absence of relevant triple/double bonds).
3. Acknowledging that presented band ranges can vary with actual conditions.

Methods

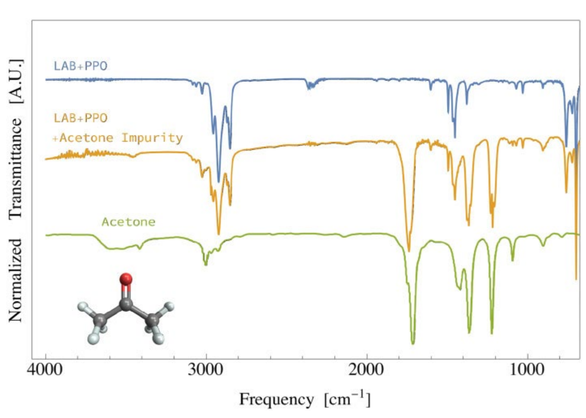
- **Sample Preparation :**
  - Solvent: LAB (provided by Isu Chemical, S. KOREA)
  - Solutes: PPO (2,5-Diphenyloxazole, 3 g/l) and bis-MSB (1,4-Bis(2-methylstyryl)benzene, 30 mg/l) (purchased from Sigma-Aldrich).
  - LAB was used as received without further purification
  - Acetone impurity sample: 5 ml of acetone added to 100 ml of diluted LAB + PPO solution
  - Water impurity sample: Water added to LAB + PPO + bis-MSB samples
- **IR Measurements**:
  - FT-IR spectrometer in single Attenuated Total Reflectance (ATR) mode
  - Liquid samples: A droplet placed on a Zinc Selenide (ZnSe) single-crystal window
  - Resolution: Default 2 cm^{-1}
- **Theoretical Spectrum Calculations (IMP1, IMP2, IMP3)**
  - Liquid samples: A droplet placed on a Zinc Selenide (ZnSe) single-crystal window
  - Method: PBE0 hybrid Density Functional Theory (DFT)
  - Basis Set: $6 - 311 + G\ (2df, p)$
  - This approach is consistent with that used by the JUNO Collaboration for UV/VIS studies of impurities



FTIR-ATR Sample Measurement Overview:

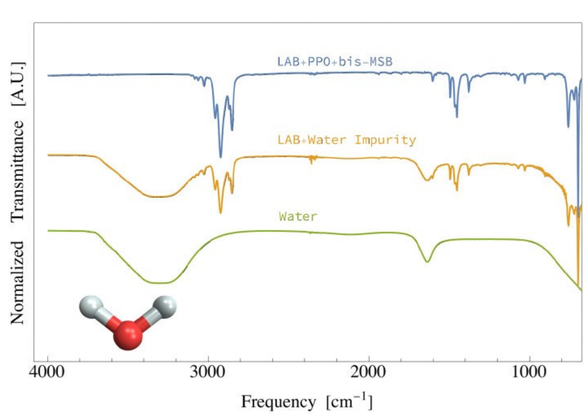
- Measuring liquid/powder samples via FTIR-ATR
- Acquiring baseline data in an equilibrium atmosphere, with real-time readjustments post-each measurement.
- Configuring settings per manufacturer recommendations (default resolution: 2 cm^{-1}, adjusted to 0.5/1 cm^{-1} if necessary).

Results and Discussion



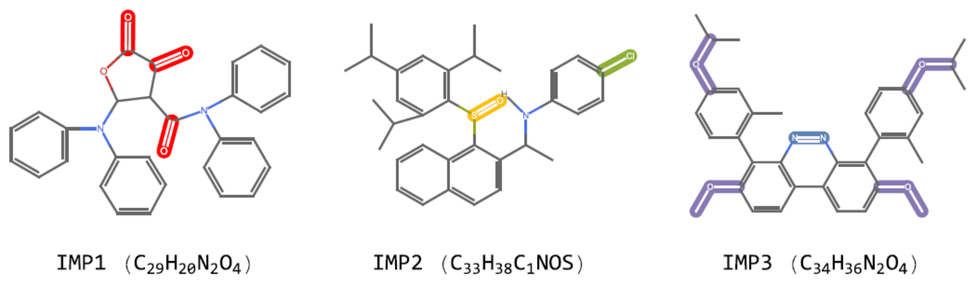
IR Spectra: Acetone Impurity Effects in the samples

- Revealing acetone's presence via dips (1200, 1400, 1700 cm^{-1}) in the orange spectrum.
- Confirming these characteristic dips against the acetone-only (green) spectrum.



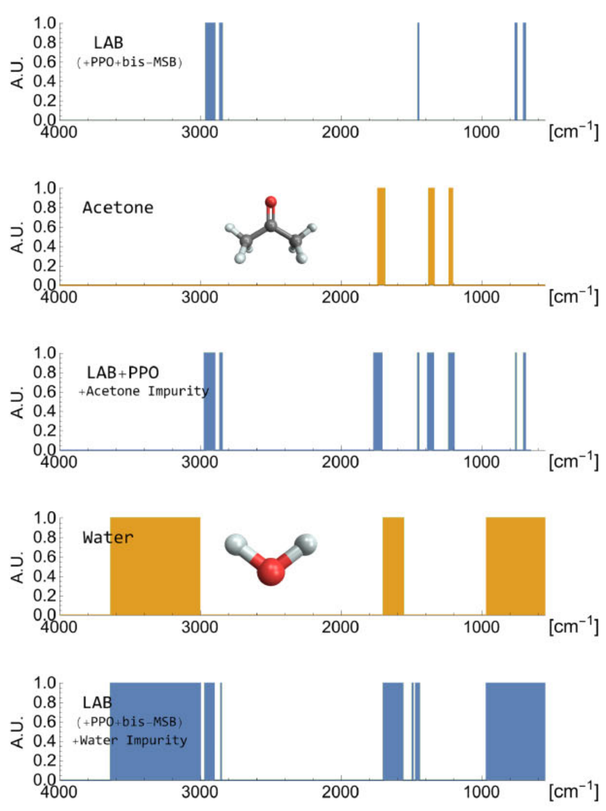
IR Spectra: Water Impurities in the samples

- Revealing water's presence via dips (approx. 3300 & 1600 cm^{-1}) in the contaminated LAB spectrum.
- Confirming these dips against the water-only spectrum.



Key Structural Features and IR Absorptions of IMP1, IMP2, and IMP3

- Illustrating molecular structures of IMP1, IMP2, and IMP3 with key functional groups typically highlighted (e.g., in different colors)
- **IMP1 (Benzene, Carbonyl, Amide):** Characterized by benzene rings, carbonyl groups, and amide groups. Notably exhibiting C=O absorptions around 1730, 1800, and 1940 cm^{-1}, and C-N absorptions near 1610 cm^{-1}.
- **IMP2 (Benzene, Sulfoxide, Thioether, Aryl Chloride):** Distinguished by benzene rings, a sulfoxide group, a thioether group, and an aryl chloride. Showing significant absorptions for S=O (1030–1090 cm^{-1}), C-S-C (700–1000 cm^{-1}), and Ar-Cl (1140 cm^{-1}).
- **IMP3 (Benzene, Azo, Ether):** Notable for including benzene rings, an azo group, and ether linkages. Displaying prominent absorptions around 1650 cm^{-1} (N=N) and at 1180 & 1330 cm^{-1} (C-O-C).
- **Computational Note**: All presented functional group frequencies were calculated using Gaussian16, employing the PEB0 DFT method with the 6-311+G(2df,p) basis set



Comparative IR Spectra for Impurity Identification in LAB-based Scintillators

- This panel presents a comprehensive set of Infrared (IR) spectra, crucial for identifying potential impurities within the Linear Alkyl Benzene (LAB)-based liquid scintillator.
- It is important to note that the width of each spectral band shown does not represent the absolute intensity of the absorption line;
- Rather, it indicates the peak's location and the relative absorption intensity at that specific wavenumber.

- **Reference Spectrum (Top, Blue):** The IR spectrum of the LAB (+PPO + bis-MSB) solution prepared for this study, demonstrating the baseline characteristics of the purified scintillator without the targeted impurities.

- **Common Process Impurities**
- **Acetone**: The spectrum of pure acetone (second from top) is provided for comparison. When acetone is introduced as an impurity into the LAB (+PPO) solution (third spectrum), its presence is clearly marked by distinct absorption peaks at 1200, 1360, and 1700 cm^{-1}, corresponding to C-H/C-C bending and C=O stretching modes, respectively
- **Water**: The spectrum of pure water (fourth from top) highlights its strong IR absorption features. If present in the LAB (+ PPO + bis-MSB) scintillator (fifth spectrum), water contamination is identifiable by characteristic O-H stretching vibrations (a broad band around 3300 cm^{-1}) and H-O-H bending vibrations (around 1600 cm^{-1}).

- **JUNO-Identified Potential Impurities (IMP1, IMP2, IMP3) – Theoretical Spectra:** The IR spectra for three impurity compounds, previously identified by the JUNO Collaboration as detrimental to scintillator performance, were theoretically calculated using DFT.
- **IMP1 ($C_{29}H_{20}N_2O_4$):** Theoretical calculations show strong absorption bands around 1730, 1800, and 1940 cm^{-1} attributed to carbonyl (C=O) groups (highlighted in red), and a significant band near 1570 cm^{-1} for amide (C-N) groups.
- **IMP2 ($C_{33}H_{38}ClNOS$):** This compound is predicted to feature sulfoxide (S=O) absorption around 1090 cm^{-1} (yellow) and aryl chloride (Ar-Cl) absorption near 1140 cm^{-1} (green)
- **IMP3 ($C_{34}H_{36}N_2O_4$):** The calculated spectrum for IMP3 displays characteristic N=N stretching vibrations around 1550 cm^{-1} (blue) and C-O-C (ether) stretching vibrations at approximately 1180 and 1330 cm^{-1} (purple).

Key Finding & Implication:

- A thorough comparison of the reference LAB (+ PPO + bis-MSB) spectrum with the characteristic IR signatures of these common and theoretically predicted impurities confirms the absence of these contaminants in our manufactured scintillator sample within the detection limits of the FTIR technique. This result critically underscores the efficacy of IR spectroscopy as a robust quality assurance methodology, ensuring the high optical purity essential for the optimal performance and accuracy of advanced neutrino detection experiments.