

FEATURES OF NUCLEAR MAGNETIC RESONANCE



SOPHISTICATED ANALYTICAL INSTRUMENT FACILITY
Indian Institute of Technology Madras
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INTERNSHIP REPORT

Submitted in partial fulfilment for the award of the degree of

MASTER OF SCIENCE

in

CHEMISTRY

by

GOWTHAM S

Reg.No. 42910006

(2022-2024)

DEPARTMENT OF CHEMISTRY



SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
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ACKNOWLEDGEMENT

First and foremost, I would like to acknowledge and give my warmest thanks to **Dr. S.S. Bhattacharya**, Prof & Head SAIF, who made this training program possible.

I place on record my sincere thanks to **Dr. Rama K.V**, Senior Technical Officer, SAIF for her helpful suggestions throughout the training program

I would like to express my special thanks to **Ms. Stella Mary**, Junior Technician, SAIF for her constant support during my training program.

THANK YOU ALL

INTERNAL EXAMINER

EXTERNAL EXAMINER

PREFACE

Nuclear Magnetic Resonance (NMR) is an analytical method used to examine the dynamics and structure of molecules. It depends on the magnetic characteristics of some atomic nuclei, such as carbon-13 and hydrogen. These nuclei generate signals that may be examined to provide details about the chemical environment, structure, and interactions inside a sample when they are subjected to radiofrequency pulses and put in a high magnetic field. NMR is frequently used to analyse molecular interactions, look into biomolecular structures, and determine the chemical composition of organic molecules.



WORKING PRINCIPLE

The basic working principle of NMR spectroscopy involves the interaction of nuclear spins with an external magnetic field and the absorption of radiofrequency energy.

Here are the key steps in the working principle of NMR spectroscopy:

➤ **Nuclear Spin:**

Certain nuclei possess a property called nuclear spin. Nuclei with a non-zero spin, such as hydrogen nuclei and carbon-13 nuclei, are commonly studied in NMR spectroscopy.

➤ **External Magnetic Field (B_0):**

When a sample containing nuclei with a non-zero spin is placed in an external magnetic field, the nuclear spins align either parallel or antiparallel to the magnetic field. The energy associated with these alignments is influenced by the external magnetic field.

➤ **Resonance Condition:**

The energy difference between the two spin states (parallel and antiparallel) can be matched by applying radiofrequency energy. The RF energy is applied perpendicular to the external magnetic field, and when it matches the energy gap, it induces a transition between the two spin states. This is known as the resonance condition.

➤ **Absorption of RF Energy:**

When the RF energy matches the energy gap, nuclei absorb the energy and temporarily move to a higher energy state. The absorption of RF energy is detected and measured.

➤ **Relaxation:**

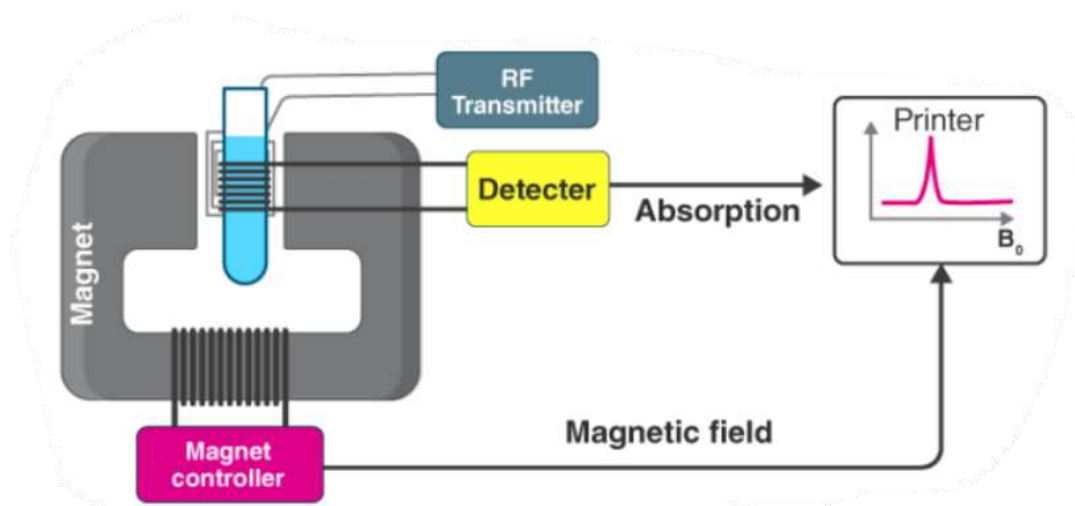
After absorbing RF energy, the nuclei return to their original spin states, releasing the absorbed energy. These processes influence the NMR signals and provide additional information about the sample.

➤ **NMR Signal Detection:**

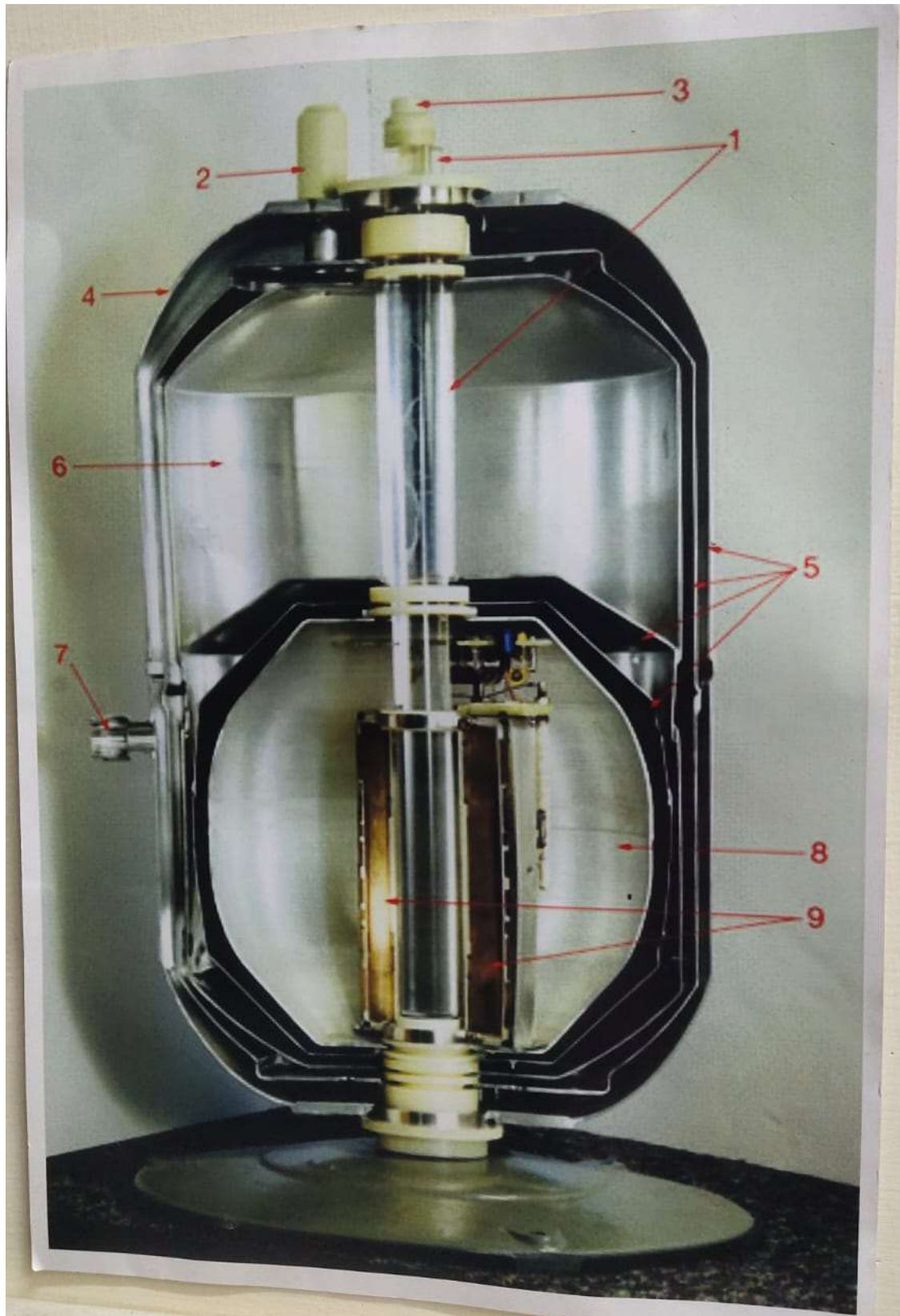
The emitted RF signals during relaxation are detected by a coil or antenna. The resulting NMR signal is then processed to generate a spectrum, which represents the distribution of nuclear spins in the sample.

➤ **Chemical Shift and Coupling:**

The NMR spectrum provides information about the chemical environment of the nuclei, known as chemical shift. Additionally, coupling between neighbouring nuclei provides information about their spatial proximity and connectivity within a molecule.



INSTRUMENTATION



1. Bore Tube of the magnet

The bore tube in an NMR instrument is the cylindrical space within the magnet where the sample is placed, crucial for the proper functioning of the experiment. In high-field NMR instruments, it is a narrow, elongated space where the sample is inserted, requiring precise placement within the homogeneous magnetic field region for accurate measurements.

2. Liquid Nitrogen Vent Port

Liquid nitrogen is commonly used in high-field NMR spectrometers for cryogenic purposes, ensuring the proper functioning of components like the cryogenic probe and superconducting magnet. The liquid nitrogen filling port allows users to refill the system when needed, ensuring low temperatures. The superconducting magnet is typically cooled to low temperatures, close to the boiling point of liquid helium, but due to its high cost and limitations, liquid nitrogen is often used to maintain a stable cryogenic environment.

3. Liquid Helium Vent Port

Liquid helium is commonly used in high-field NMR instruments, particularly those with superconducting magnets. It cools the magnet to extremely low temperatures, close to absolute zero, allowing it to operate in a superconducting state. A designated liquid helium filling port is connected to a reservoir, allowing users to replenish the supply when needed. This low temperature is crucial for maintaining a strong and stable magnetic field. Regular maintenance, including monitoring and refilling the liquid helium, is essential for the proper functioning of these instruments.

4. Aluminium Outer shell

The outer shell of an NMR machine is often made of aluminium for its non-magnetic properties, lightweight and durable nature, excellent thermal conductivity, corrosion resistance, and effectiveness as a radiofrequency shield. Additionally, aluminium provides an aesthetically pleasing finish

5. Vacuum Chamber

A vacuum chamber in NMR spectroscopy is used to eliminate air and gases around the sample. This helps reduce interference, prevents signal broadening caused by paramagnetic molecules, enhances sensitivity by minimizing signal loss, and can contribute to maintaining sample purity in certain experiments.

6. Liquid Nitrogen cryostat

Liquid nitrogen cryostat is utilized to cool the sample or magnets to very low temperatures. This enhances spectral resolution and stability in high-field NMR experiments. The cryostat includes a Dewar flask for liquid nitrogen, temperature control mechanisms, and may be used with cryogenic probes to improve sensitivity.

7. Vacuum outlet

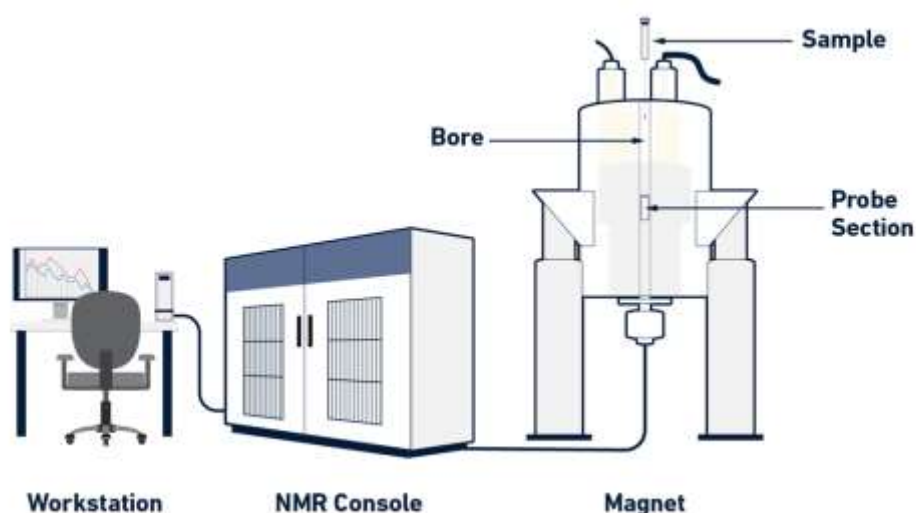
A vacuum outlet is a feature in NMR instruments, particularly those used for solid-state NMR or experiments involving volatile samples. It serves several purposes, including sample preparation, sample transfer, reducing air interference, and preserving sample sensitivity. The outlet allows for the attachment of a vacuum pump to remove residual solvents or volatile components, ensuring a dry and stable sample before analysis. It also helps maintain a low-pressure environment, which is crucial for accurate data acquisition.

8. Liquid Helium cryostat

In NMR spectroscopy, a liquid helium cryostat is used to cool the superconducting magnets, which are crucial for generating strong and stable magnetic fields in high-field NMR spectrometers. The cryostat maintains the low temperatures necessary for superconductivity, ensuring the accuracy and stability of NMR measurements.

9. Super conducting magnet

Superconducting magnets are essential in high-field NMR instruments for generating strong and stable magnetic fields. They generate higher magnetic fields than resistive magnets, enabling high-resolution NMR spectra. Superconducting magnets exhibit zero electrical resistance when cooled to cryogenic temperatures, ensuring constant magnetic field without energy losses. They require cryogenic cooling, typically liquid helium, to maintain the superconducting state. They provide homogeneity across the sample region, ensuring reliable results. These magnets are valuable for experiments requiring stronger magnetic fields, such as large biological molecules or materials science applications. They also reduce operating costs compared to resistive magnets.



SAMPLE PREPARATION

10 mg of the solid sample
is taken NMR tube



Then the needed solvent is added in
drops using micro pipette and
shaken well till the solute particles
completely dissolves.



Next the NMR tube is placed in a
spinner.



Then the sample is loaded in NMR
machine



After which required experiment is
selected in Top Spin software

SOLVENT USED IN SAMPLE PREPARATION

When it comes to solvent selection, we need to consider two parameters in account

- The selected solvent should not react with the sample particles.
- We need to know the exact peak range for the chosen sample.

On basis of this parameters some solvents have been given below:

Solvent used in NMR	Peak Range
D2O	4.7
CDCl ₃	7.26
DMSO	2.5
ACETONE	2.05
BENZENE	7.16

TMS – Tetramethylsilane (CH_3)₄Si is used as a reference.

The peak of TMS will be at 0 due to its most shielded nuclei's.



TOP SPIN SOFTWARE

The Top spin software is used for Bruker's NMR machine to carry out the experimental part. Once the sample is loaded in the machine, we can customize our experiment in this software. On selecting the experiment, it will check whether other parameters are ready to proceed the experiment.

The parameters are:

➤ **Auto tuning and matching (ATM)**

Auto tuning and matching is an automated process in NMR spectroscopy, which optimizes the performance of an NMR spectrometer. It ensures efficient transmission and reception of radiofrequency pulses, resulting in high-quality NMR spectra. The tuning process optimizes the resonance frequency of the RF coil with the applied RF pulses, while the matching process ensures the impedance of the RF coil is matched to the RF electronics, minimizing signal losses.

➤ **Locking**

The NMR experiment uses RF pulses to manipulate nuclear spins, maintaining resonance by matching the Larmor frequency. A locking system monitors and adjusts the RF pulse frequency, typically with a feedback loop, to detect deviations between the Larmor frequency and the RF pulse frequency.

➤ **Shimming**

Shimming in NMR spectroscopy is a process used to optimize the homogeneity of the magnetic field within the NMR sample. A homogeneous magnetic field is crucial for obtaining high-quality NMR spectra with well-defined and sharp peaks. Shimming involves adjusting the magnetic field to minimize variations in strength across the sample, ensuring that different nuclei experience the same magnetic environment.

DIFFERENT TYPES OF 1D EXPERIMENTS IN NMR

➤ Proton NMR

This experiment analyses the structure and environment of hydrogen atoms in a sample molecule. Chemical shifts indicate electron density, identifying functional groups. Proton NMR shows splitting patterns, revealing molecule connectivity. Different chemical environments lead to different shifts, confirming structure. Coupling patterns determine hydrogen atom connectivity.

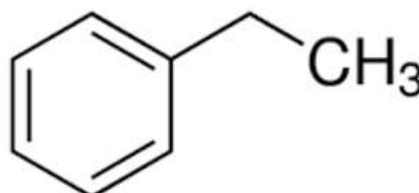
➤ Carbon 13 NMR

This experiment is used to provide information about the structure and environment of Carbon atom within the sample molecule. Carbon 13 being a stable isotope of carbon allows to study the isotopic labelling to trace the fate of isotope labelling in carbon atom.

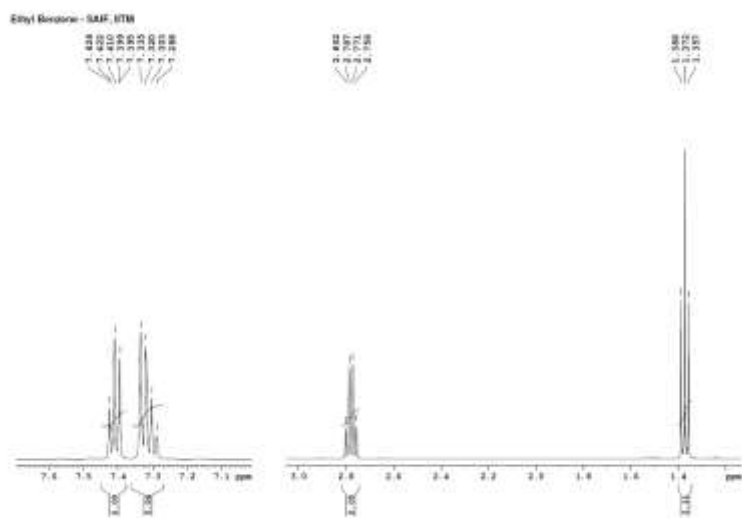
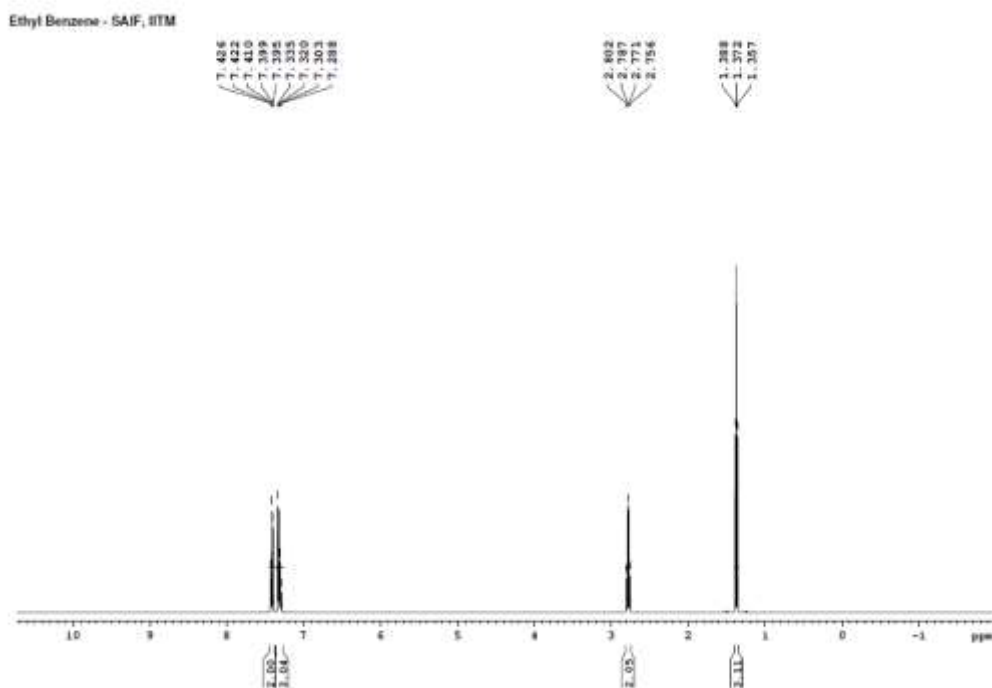
➤ DEPT – Distortion less Enhancement By Polarization Transfer

This experiment is used to determine the multiplicity of carbon atom like they are C, CH, CH₂ or CH₃. Used to enhance the signals of specific types of carbon or proton atoms in a molecule

For further understanding of the 1D experiments, the compound **ETHYL BENZENE** – (C₆H₅-CH₂-CH₃) has been done with ¹H Proton NMR, C¹³ NMR and DEPT. The results have been given in upcoming pages



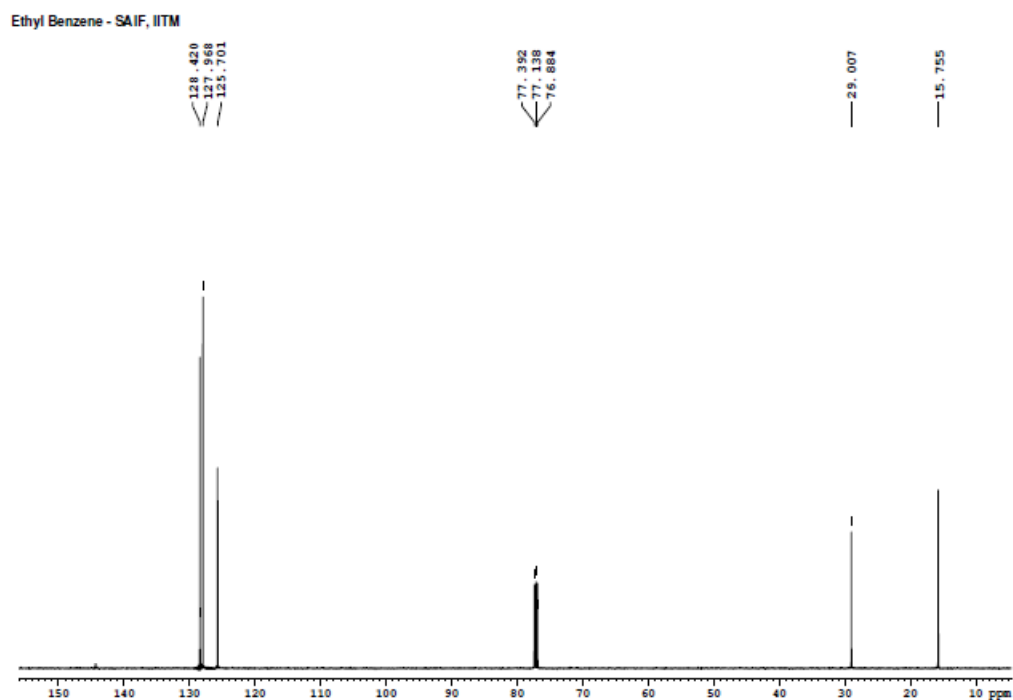
PROTON NMR FOR ETHYL BENZENE



Key Inference

- Triplet peaks at the at 1.3 ppm region denotes CH_3 .
- Quartet peaks at 2.8 ppm region denotes CH_2 .
- The group of peaks at 7.4 ppm denotes the C_6H_5

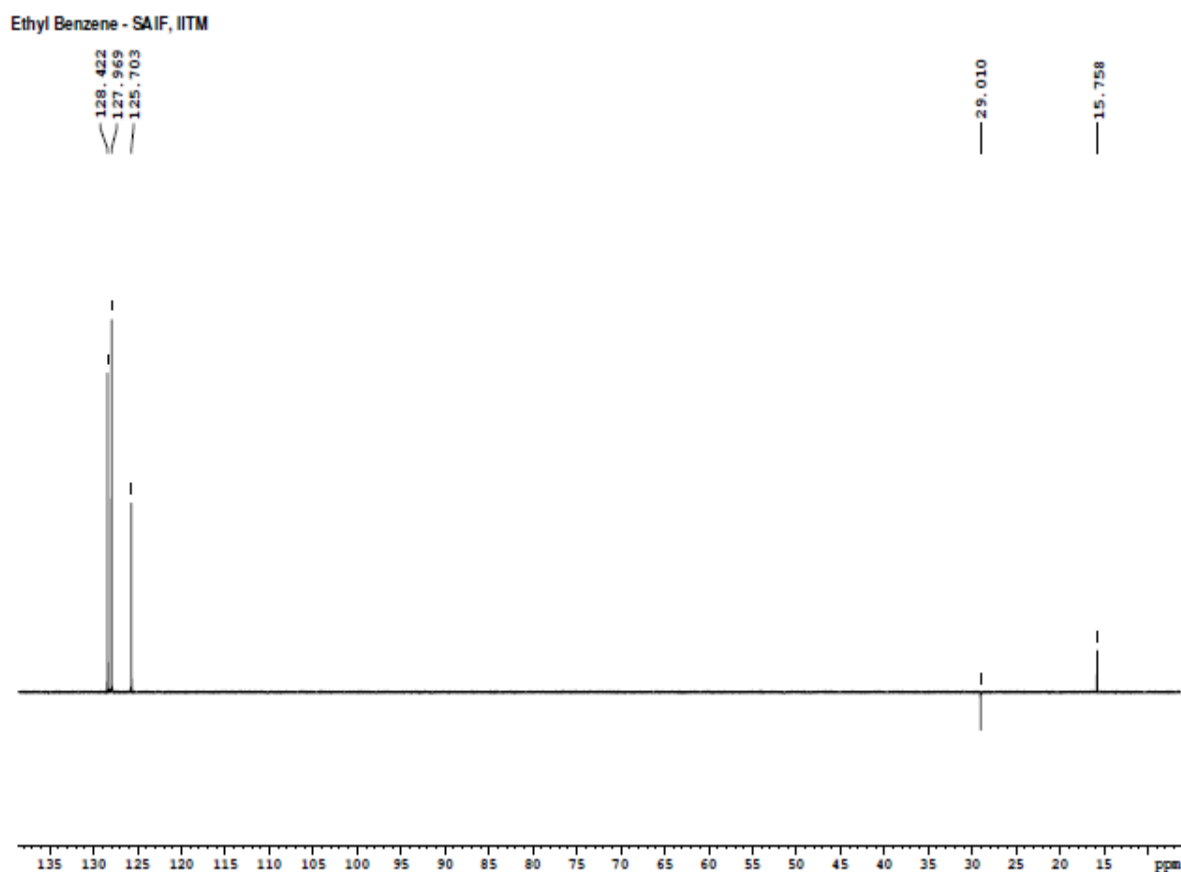
C13 NMR FOR ETHYL BENZENE



Key Inference

- The peak at 15.75 ppm denotes the Carbon atom in CH₃.
- The peak at 29 ppm denotes the Carbon atom in CH₂.
- Three peaks at 128 ppm region denotes the Carbon atom in C₆H₅.
- The peak at 77 ppm denotes the Carbon atom in solvent CDCl₃.

DEPT FOR ETHYL BENZENE



Here CH and CH₃ peak will be formed on upside of the graph. Whereas CH₂ peak will be formed downside. This phenomenon is to differentiate the Carbon present Ethyl benzene

Key Inference

- The upside peak at 15.75 ppm denotes the Carbon atom in CH₃.
- The downside peak at 29 ppm denotes the Carbon atom in CH₂.
- Three upside peaks at 128 ppm region denotes the Carbon atom in C₆H₅.

CLOSURE

In this Internship report, I have conveyed everything that has been taught to me in SAIF, IITM during this training period. I have learnt the basics of Nuclear Magnetic Resonance. I have seen and understood all the methodologies starting from sample preparation to sample loading till getting the final spectrum of the experiment. On successful completion of this training program, I was awarded with a certificate from that organization which I would like to attach in this report with a NPTEL course merit certificate on Analytical Chemistry.

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HEAD

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Friday, October 6th, 2023

This is to certify that Mr. S. Gowtham, a MSc (Chemistry) II year student of Sathyabama University underwent a training program at SAIF IITM for two weeks (14-9-2023 to 6-10-2023). During this period he has learnt the following features of NMR:

1. Basics of NMR (Magnetic field, spin quantum number, ppm, chemical shift, coupling constant, Zeeman effect, shielding and de-shielding, levitation)
2. Sample preparation using deuterated solvents
3. Principle and fundamentals of NMR instrumentation
4. 1D NMR (^1H , ^{13}C , DEPT)
5. 2D NMR (COSY, HSQC, HMBC, TOCSY, NOESY)
6. Ethylbenzene – (^1H , ^{13}C , DEPT, COSY & HSQC)
7. Cryogen filling (liquid helium and liquid nitrogen)
8. Topspin software (Auto tuning and matching, rotation, locking, shimming and calibration)

The training program was completed successfully.


S.S. BHATTACHARYA

अधीक्षक / Head
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IIT Madras, Chennai - 600 036

SAIF, IITM



Elite

NPTEL Online Certification

(Funded by the MoE, Govt. of India)



This certificate is awarded to

GOWTHAM S

for successfully completing the course

Analytical Chemistry

with a consolidated score of **66** %

Online Assignments	22.81/25	Proctored Exam	43.5/75
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Total number of candidates certified in this course: 626

Jul-Oct 2023

(12 week course)

Prof. Haimanti Banerji
Coordinator, NPTEL
IIT Kharagpur



Indian Institute of Technology Kharagpur



Roll No: NPTEL23CY59S733500349

To verify the certificate



No. of credits recommended: 3 or 4