I. The IR spectrum below is for isopropanol; identify any useful IR absorptions $>1500 \text{ cm}^{-1}$. Based upon the spectrum, comment on whether you expect that it was a pure sample or diluted in a different solvent.

Since the $\text{O-H}$ stretch is broad and at lower freq. ($\text{cm}^{-1}$) the sample has sufficient concentration to be H-bonded. No evidence of a free $\text{O-H}$ stretch is present as would be expected in the gas-phase or dilute solution. See Section 12.4D in London.
II. Using the mass spectrum of 1-propanol shown below, answer the questions that follow about its fragmentation. Remember that you are not expected to interpret all signals in a mass spectrum.

A. Why does the peak at \( m/z = 15 \) have such a low relative intensity?

Methyl cation (\( \text{CH}_3^+ \)) is not a stable fragment relative to its parent ion(s). The central carbon is very electron deficient.

B. Draw a valid resonance structure of the molecular ion (\( m/z = 60 \)). Draw a molecular ion responsible for the small peak at \( m/z = 61 \).

The small peak at \( m/z = 61 \) is due to heavy isotope substitution, mostly \(^{13}\text{C}\) substitution at natural abundance (~1.1%).
C. In fragmentations of cations and radical cations, a single molecular (parent) ion can give rise to several fragments. Provide fragmentation mechanisms from the molecular ion \((m/z = 60)\) that will rationalize the formation of ions with values of \(m/z = 59, 42,\) and \(31\). For clarity, it may help to show each fragmentation in a different color.

![Fragmentation Mechanisms](image)

D. What can you conclude about the formation and decomposition of the ion responsible for the signal at \(m/z = 31\)?

The signal at \(m/z = 31\) is the base peak and its intensity is automatically set to 100%. The ion(s) responsible for the base peak must form easily/rapidly and decompose relatively slowly for a large population of \(m/z = 31\) particles to arrive at the detector.
III. Using the mass spectrum of 2,2,4-trimethylpentane (isoctane, C₈H₁₈) shown below, answer the questions that follow about its fragmentation.

A. In this case, the molecular ion is of such a low intensity it is not detected. Draw the molecular ion of 2,2,4-trimethylpentane and determine its m/z value. What does the low intensity indicate about its stability?

B. Draw a fragmentation mechanism that explains how the molecular ion can produce ions with values of m/z = 57 and 56.

See Loudon Study Problem 12.4.

**A.** The molecular ion decomposes so rapidly that very little of it arrives at the detector. All σ bonds are weakened!!!

**B.** Radical cation

---

**½ σ bond is made of one C− only.**
C. The ion responsible for the signal at \( m/z = 56 \) can be represented by a set of resonance structures. Depict the most important resonance structures and a resonance hybrid.

\[
\begin{align*}
\text{C-H} & \quad \text{C-H} \\
\text{[C-H]} & \quad \text{[C-H]} \\
\text{radical} & \quad \text{radical}
\end{align*}
\]

D. An alternate fragmentation mechanism from the molecular ion can be used to rationalize the production of ions with values of \( m/z = 43, 42, \) and 41. Provide an electron pushing mechanism for this fragmentation pathway.

- C-H
- C-H
- C-H

\[
\begin{align*}
m/z = 43 & \quad \text{isopropyl cation} \\
m/z = 42 & \\
m/z = 41 & \quad \text{allyl cation}
\end{align*}
\]

E. Two separate fragmentations of the molecular ion can lead to ions with \( m/z \) values of 99; provide them below.

- C-H
- C-H
- C-H

\[
\begin{align*}
m/z = 99 & \\
m/z = 99 & \\
m/z = 99 &
\end{align*}
\]

The tertiary cation is much more stable than the secondary cation, which makes the tertiary cation much more abundant. Also, there is a \( \frac{3}{2} \) statistical preference for the \( 3^\circ \) cation due to the greater number of available methyl groups.
IV. Using the mass spectrum of 2-pentanone (C$_5$H$_{10}$O) shown below, answer the questions that follow about its fragmentation.

A. Draw a valid resonance structure of the molecular ion ($m/z = 86$). Explain the source of the small peak at $m/z = 87$.

The peak at $m/z = 87$ is mostly due to the naturally-occurring $^{13}$C-atom substitution. Carbonyl-containing radical cations have weakened $\sigma$-bonds between the carbonyl (-atom and their $\alpha$-substituents (see London Section 19.5E).
B. Important decomposition pathways for the molecular ion of carbonyl-containing compounds such as 2-pentanone involve α-cleavage. Beginning with both viable α-cleavage decomposition pathways, draw fragmentation mechanisms that lead to ions with m/z values of 71, 43, 15. Make sure your mechanisms account for two different ions with m/z values of 43.

C. The other major decomposition pathway arises from a McLafferty rearrangement of the molecular ion followed by the loss of an ethylene gas molecule. Show an electron-pushing mechanism for this decomposition which will rationalize the peak with a value of m/z = 58.
V. A mixture of regioisomers \( \text{o-vanillin} \) and \( \text{vanillin} \) (\( \text{C}_8\text{H}_6\text{O}_3 \)) were analyzed by IR and GC-MS. Analyze the spectra below and answer the accompanying questions.

A. Identify any useful IR absorptions that can help identify this sample as a mixture of \( \text{o-vanillin} \) and \( \text{vanillin} \). Is it possible to use the IR of the mixture to identify each component?

The molecules are too similar to be easily distinguished by IR spectroscopy without a detailed study of the fingerprint region.
B. Use the GC-Mass spectrum of the mixture provided below to determine the ratio of vanillin to o-vanillin. The most intense signals of vanillin are $m/z$ values of 152 and 106, while the most intense signals of o-vanillin are $m/z$ values of 152 and 151.

![Vanillin and o-vanillin spectra](image)

C. Provide an electron-pushing mechanism for the fragmentation of o-vanillin that can rationalize the presence of ions with $m/z$ values of 152, 151, and 123. There are many other fragmentations possible, you only need to analyze the pathway that produces the indicated signals above.

![Fragmentation mechanism](image)
VI. Use the GC-Mass spectrum of the student product obtained from the Friedel-Crafts acylation of bromobenzene (shown on page 12) to answer the following questions. Only signals with intensity greater than 15% relative intensity to the base peak are shown for clarity.

\[ \text{Benzene} + \text{Acetyl Chloride} \to \text{Benzyl Chloride} + \text{Water} \]

A. Which of the peaks (1 – 3) detected in the GC are the reactant(s)? Which of the peak(s) in the GC are the product(s)?

\[ \text{Peaks } 2 + 3 = \text{products} \]

B. In any of the mass spectra provided for GC peaks 1 – 3, how can you tell which ions contain bromine?

\[ m/z \geq 79, 81 \text{ with approximately } 1:1 \text{ intensity separated by } 2 \text{ m/z units. This pattern occurs due to the natural abundance of } Br. \]

C. Provide a fragmentation mechanism that will account for the signals listed below for each molecule detected in the GC trace. Identify the species most likely responsible for the following m/z signals:

\[ \text{Peak } #1 = 158, 156, 77, 51, 50 \]

**Diagram: Fragmentation mechanisms and m/z signals**
D. What is the conversion percentage from reactant to the total products by GC?

A total of \( \approx 85.27\% \) of the sample is due to the major and minor product. Approximately, \( 14.73\% \) is the starting material.

E. What is the ratio of the major to minor product by GC?

\[
\frac{82.77\%}{2.50\%} = \frac{33.1 \text{ major}}{1 \text{ minor}} \quad \text{or} \quad \frac{33.1}{1} \text{ major:minor}
\]
Friedel-Crafts Acylation of Bromobenzene

Peak Report TIC

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<th>Peak#</th>
<th>R.Time</th>
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Starting material

- Likely another regioisomer, meta

Acylum cation

Aromatic ring

Contains H, Br + Br

Spectrum