Section 22.20
Spectroscopic Analysis of Amines
the N—H stretching band appears in the range 3000-3500 cm\(^{-1}\)

primary amines give two peaks in this region, one for a symmetrical stretching vibration, the other for an antisymmetrical stretch
Infrared Spectroscopy

primary amines give two N—H stretching peaks,
secondary amines give one
compare chemical shifts in:

\[ H_NMR \]

H\(_3\)C-\(\text{CH}_2\text{NH}_2\) \(\delta\ 3.9\ ppm\)

H\(_3\)C-\(\text{CH}_2\text{OH}\) \(\delta\ 4.7\ ppm\)

N-\(\text{C}\)-\(\text{H}\) is more shielded than O-\(\text{C}\)-\(\text{H}\)
Carbons bonded to N are more shielded than those bonded to O.

\[ {^{13}C \text{ NMR}} \]

\[ \text{CH}_3\text{NH}_2 \quad \delta \ 26.9 \text{ ppm} \quad \text{CH}_3\text{OH} \quad \delta \ 48.0 \text{ ppm} \]
An amino group on a benzene ring shifts $\lambda_{\text{max}}$ to longer wavelength. Protonation of N causes UV spectrum to resemble that of benzene.
Compounds that contain only C, H, and O have even molecular weights. If an odd number of N atoms is present, the molecular weight is odd.

A molecular-ion peak with an odd $m/z$ value suggests that the sample being analyzed contains N.
Nitrogen stabilizes carbocations, which drives the fragmentation pathways.

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 & \rightarrow e^- \\
\text{(CH}_3\text{)}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 & \rightarrow \text{(CH}_3\text{)}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{(CH}_3\text{)}_2\text{N} & \rightarrow \text{CH}_2 + \text{CH}_2\text{CH}_2\text{CH}_3
\end{align*}
\]
Nitrogen stabilizes carbocations, which drives the fragmentation pathways.

\[
\text{CH}_3\text{ÑHCH}_2\text{CH}_2\text{CH(CH}_3)_2 \xrightarrow{e^-} \text{CH}_3\text{ÑHCH}_2\text{CH}_2\text{CH(CH}_3)_2
\]

\[
\text{CH}_3\text{ÑHCH}_2\text{CH}_2\text{CH(CH}_3)_2 \xrightarrow{\dot{+}} \text{CH}_3\text{ÑH} \equiv \text{CH}_2 + \cdot\text{CH}_2\text{CH(CH}_3)_2
\]