

CHAPTER OVERVIEW

3: IONIZATION TECHNIQUES

A variety of ionization techniques are used for mass spectrometry. Most ionization techniques excite the neutral analyte molecule which then ejects an electron to form a radical cation $M^{+\bullet}$. This radical cation is the molecular ion and is produced by removing a single electron from a neutral molecule. Other ionization techniques involve ion molecule reactions between an ion and a neutral molecule that produce an adduct ion like $[M+H]^+$. Many of these reactions cause the addition of a proton H^+ to the analyte molecule but other ions can also be formed. The most important considerations for selecting an ionization technique are the physical state of the analyte and the ionization energy needed. Electron ionization and chemical ionization are only suitable for gas phase ionization. Fast atom bombardment, secondary ion mass spectrometry, electrospray, and matrix assisted laser desorption are used to ionize condensed phase samples. The ionization energy is significant because it controls the amount of fragmentation observed in the mass spectrum. Although this fragmentation complicates the mass spectrum it provides structural information for the identification of unknown compounds. Some ionization techniques are very soft and only produce molecular ions, the intact ionized analyte molecule, while other techniques are very energetic and cause ions to undergo extensive fragmentation.

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