Guideline

1. The relative intensity of the molecular ion peak is greatest fro the straight chain compound and decreases as the degree of branching increase.
2. The relative intensity of the molecular ion peak usually decreases with increasing molecular weight in a homologous series. Fatty esters appear to be an exception.
3. Cleavage is favored at alkyl-substituted carbon atoms; the more substituted, the more likely is cleavage. This is a consequence of the increased stability of a tertiary carbocation over a secondary, which in turn is more stable than a primary. Generally, the largest substituent at a branch is eliminated most readily as a radical, presumably because a long-chain radical can achieve some stability by delocalization of the lone electron.
4. Double bonds, cyclic structures, and especially aromatic (or heteroaromatic) rings stabilize the molecular ion and thus increase the probability of its appearance.
5. Double bonds favor allylic cleavage and give the resonance-stabilized allylic carbocation. This rule does not hold for simple alkenes because of the ready migration of the double bond, but it does hold for cycloalkanes.
6. Saturated rings tend to lose alkyl side chains at the alpha bond. This is merely a special case of branching. The positive charge tends to stay with the ring fragment. Unsaturated rings can undergo a retro-Diels-Alder reaction.
7. In alkyl-substituted aromatic compounds, cleavage is very probable at the bond beta to the ring, giving the resonance-stabilized benzyl ion, or more likely, the tropylium ion.
8. The C-C bonds next to a heteroatom are frequently cleaved, leaving the charge on the fragment containing the heteroatom whose nonbonding electrons provide resonance stabilization.
9. Cleavage is often associated with elimination of small, stable, neutral molecules, such as carbon monoxide, alkenes, water, ammonia, hydrogen sulfide, hydrogen cyanide, mercaptans, ketones, or alcohols, often with rearrangement.