MASS SPECTROMETRY

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LECTURE -5

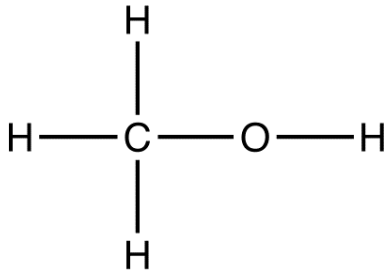
NITROGEN RULE and INTERPRETATION OF SPECTRA IN MASS SPECTROMETRY

The **Nitrogen Rule** is not a rule, as much as a general principle which may prove useful when attempting to solve organic mass spectrometry structures. This rule is derived from the fact that, perhaps coincidentally, for the most common chemical elements in neutral organic compounds (hydrogen, carbon, nitrogen, oxygen, silicon, phosphorus, sulfur, and the halogens), elements with even numbered nominal masses form even numbers of covalent bonds, while elements with odd numbered nominal masses form odd numbers of covalent bonds, with the exception of nitrogen, which has a nominal (or integer) mass of 14 (even), but has a valency of 3(odd).

The nitrogen rule is only true for neutral structures in which all of the atoms in the molecule have a number of covalent bonds equal to their standard valency (counting each sigma bond and pi bond as a separate covalent bond for the purposes of the calculation). Therefore, the rule is typically only applied to the molecular ion signal in the mass spectrum. Inorganic molecules do not necessarily follow the rule. For example the nitrogen oxides NO and NO2 have an odd number of nitrogens but even masses of 30 and 46, respectively

The nitrogen rule states that a molecule that has no or even number of nitrogen atoms has an even nominal mass, whereas a molecule that has an odd number of nitrogen atoms has an odd nominal mass.

Eg.1



molecular formula = CH_4O

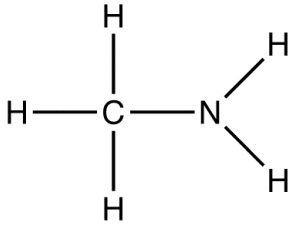
nominal mass = (1x12) + (4x1) + (1x16)

= 32

N atoms = 0

nominal mass = 32 (even #)

Eg.2



molecular formula = CH_5N

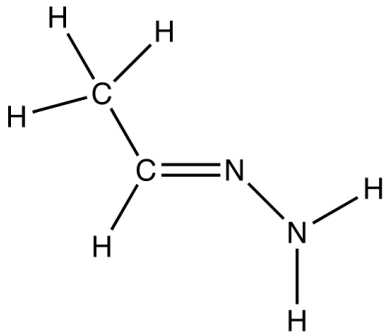
nominal mass = (1x12) + (5x1) + (1x14)

= 31

N atoms = 1 (odd #)

nominal mass = 31 (odd #)

Eg.3



molecular formula = $C_2H_6N_2$

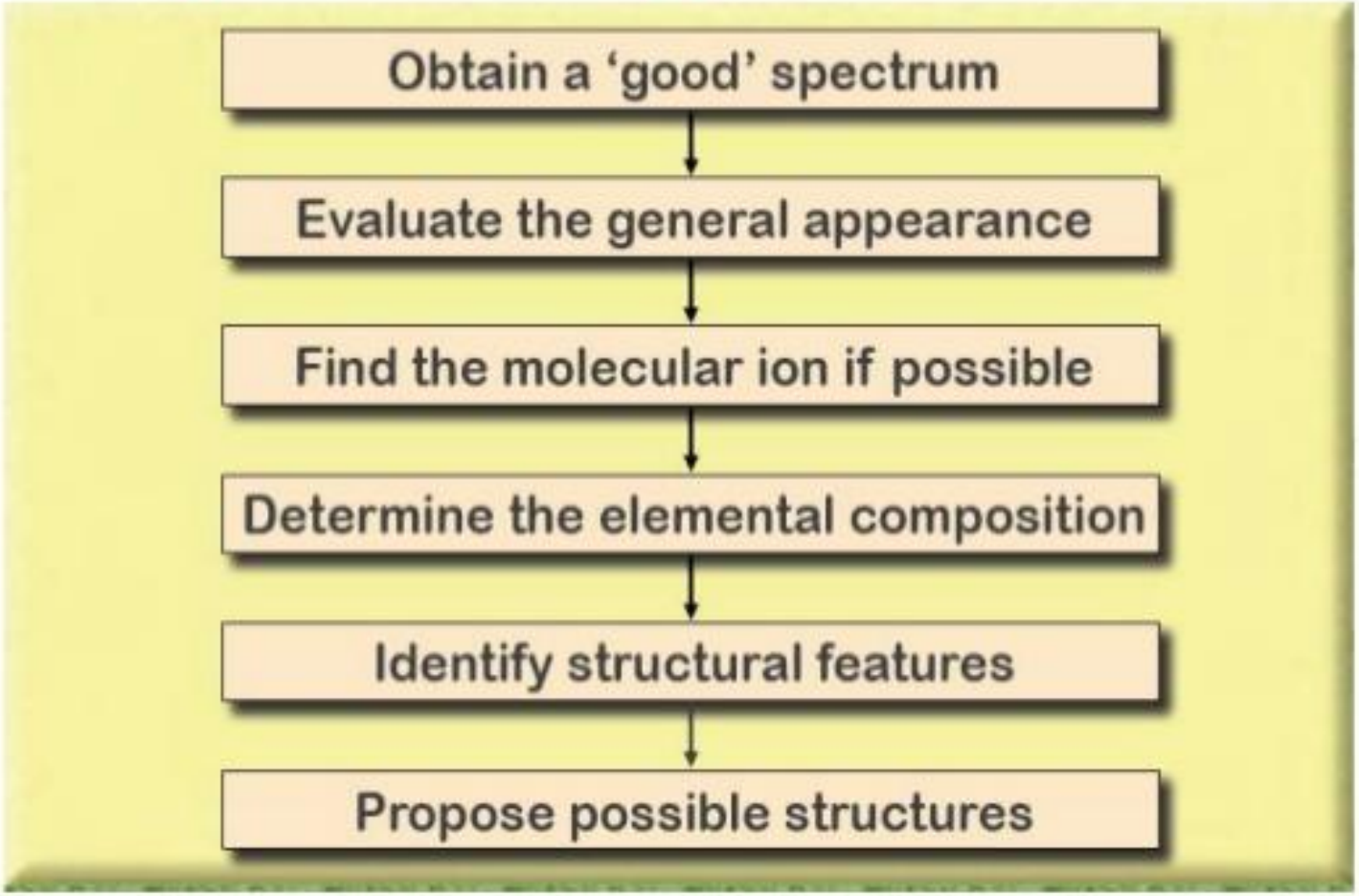
nominal mass = (2x12) + (6x1) + (2x14)

= 58

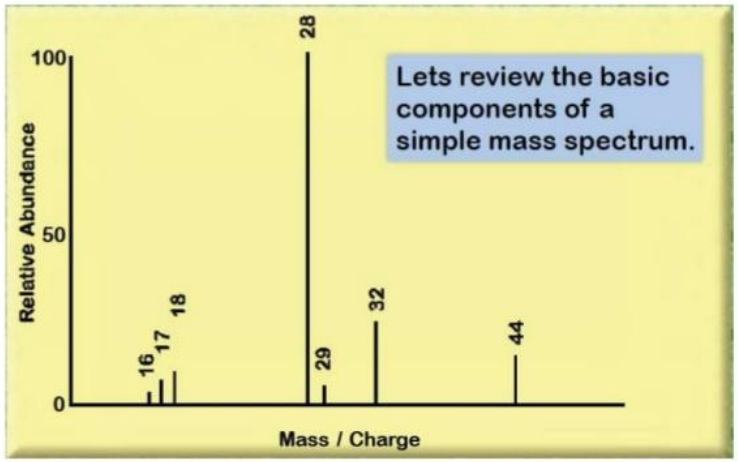
N atoms = 2 (even #)

nominal mass = 58 (even #)

General steps in mass spectral interpretation



What is a mass spectrum



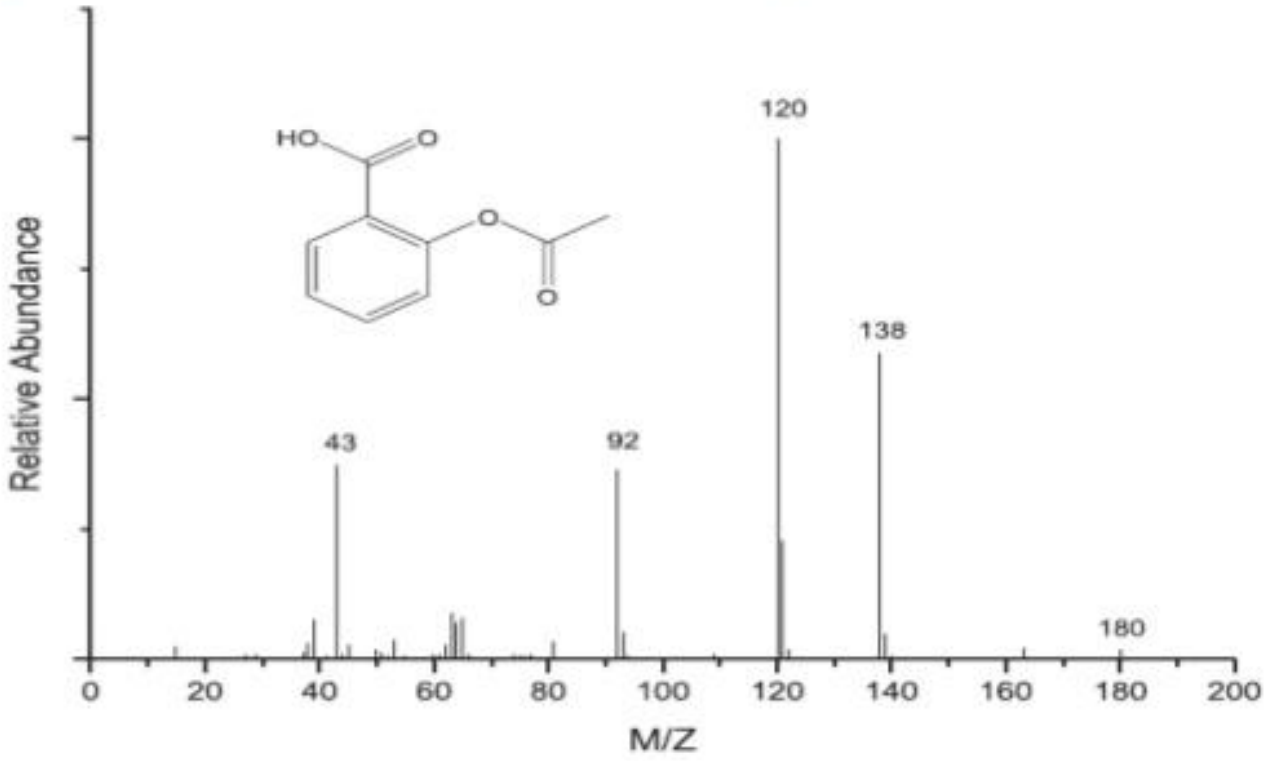
All proteins are sorted based on a mass to charge ratio (m/z)

m/z ratio:

Molecular weight divided by the
Charge on this protein

ASPIRIN (or) SALICYLICACID(m.wt-180)

Mass Spectrum **Empirical Formula C9H8O4**



THANKS

LECTURE -6

Application of Mass Spectrometry

Application of Mass Spectrometry

1. Mass Spectrometry in Proteomics

MS has become a powerful tool in proteomics research to precisely determine the molecular mass of peptides and proteins and the sequences. In tandem mass spectrometry, fragmentation of peptides and proteins gives sequence information for protein identification as well as identification and localization of post-translational or other covalent modifications.

2. Protein identification by mass spectrometry

Mass spectrometry has become the major method for protein identification. There are two main MS-based protein identification methods, including de novo sequencing and peptide mass fingerprinting (PMF) database searching. Proteins are finally identified from the peaks of the captured mass spectra using computational methods, where each peak theoretically represents a peptide fragment ion.

3. Mass Spectrometry in Glycomics

Glycosylation is one of the most important PTMs and there are more than 50% of all proteins in mammals can be glycosylated. Glycomics, a subset of glycobiology, aims to identify the structure and function of the glycome. MS-base glycomics is widely used to analyze free oligosaccharides, glycosaminoglycans, as well as the glycan portions of glycoproteins, proteoglycans, and glycolipids.

4. Mass Spectrometry in Metabolomics

Metabolite refers to the small molecules that participate in general metabolic reactions and that are required for the maintenance, growth and normal function of a cell, and the metabolomics is the identification and quantification of all metabolites in a biological system.

MS and nuclear magnetic resonance (NMR) are commonly used analytical tools for small-molecule analysis in metabolomics. MS-based metabolomics studies the effect of drugs, toxins, and various diseases on metabolite levels, to trace metabolic pathways and measure fluxes

THANKS