**Interpretative Spectroscopy**

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**Lecture 44**

**Types of Mass Spectrometry**

Once again it is my pleasure to welcome you all to MSB lecture series on Interpretative Spectroscopy. Let me continue discussion on Mass Spectrometry. In my last lecture, I was discussing about the mass spectrum of crown ether, which I showed you, also I showed you how to arrive at the name of a crown ether. This is 18 crown 6 ether, this one. We have 6 oxygen atoms here, it is ideally suited to accommodate a metal ion with octahedral geometry. In this one, the molecular ion peak is 264. From this one, it loses 43 mass corresponds to $C_2H_3O$ to give this peak with a molecular value of 221 and then again it incrementally loses 44 that is due to $C_2H_4O$ moiety and then on regularly until it arrives at the last one with a m/z value of 45 that is $C_2H_4OH$ plus. That means, wherever we have this $CH_2O$ moiety, one can see the fragmentation following this sequence. Now, let us look into metal carbonyls, we come across a large number of metal carbonyls the simple mono nuclear to poly nuclear clusters and cages.

For example, here how to look into the spectrum? How to get information extracted from mass spectra of metal carbonyls and of course, we all know the fact that metal carbonyls are relatively more volatile and provide spectra which may be easily interpreted. The fragmentation process involves the loss of carbonyl ligands in the form of carbon monoxide gas. That means you can clearly distinguish between the parents from the parent peak to the bunches of peaks. We will see here with gradation of a CO means about 28 mass loss.

So, this is an electron impact mass spectrum of dihydridetriosmiumdecacarbonyl complex, $H_2Os_3(CO)_{10}$ and it is originated from $OS_3(CO)_{12}$. So, from this one two carbon monoxide have been eliminated and $H_2$ has come. So, if $H_2$ is written like this you should assume neutral $H_2$ binding is there, in this fashion and in case, if they have written something like this, it is hydride and osmium will be in plus 2 state. Let us assume it is in 0 valence state. This was taken from this article appeared in JACS in 1988 and the fragmentation pattern you can see here. Initially after bombardment, it generates a parent peak, a cation radical and then the gradation is there. For example, M minus one CO (M-CO) goes until we get the metal ion with all the carbon monoxide being stripped off.

This EI provides accurate mass information for polynuclear metalcarbonyls and pyrolysis of $OS_3(CO)_{12}$ produces a range of higher nuclearity clusters and $OS_5C(CO)_{15}$, $OS_6(CO)_{18}$ and $OS_7(CO)_{21}$ and $OS_8(CO)_{23}$ this is how higher analogs are made starting from the simplest one such as $OS(CO)_5$ or $OS_3(CO)_{12}$ and similarly in case of iron we use $Fe(CO)_5$ and from that one can make $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ and so on. They are known for undergoing disproportionation reaction to form high nuclearity clusters, and from the clusters apart from the parent peak molecular ion, we can also see the loss of CO and until it hits the naked metal ion. So EI mass spectrometry provides correct molecular formula for these compounds and also it can give information about the presence of interstitial atoms carbides in this case as I mentioned on heating thermally, pyrolysis means heating at high temperature, carbon monoxide comes out and in that process what happens one or two carbon atoms can also go to the interstitial and form carbides in that case the presence of carbon can also be identified using mass spectrum. Here that is the advantage of mass spectrum here. Other techniques such as elemental analysis, IR NMR spectroscopy are unable to provide this information. For example, if carbon monoxide degrades to give a carbide unit that is in the cluster so in that it is very difficult to extract that information from other techniques apart from x-ray crystallography. It is difficult for IR NMR as they cannot really tell about this vital information. From that point of view, mass spectrometry is very important in case of organometallic compounds. So, here I have shown for ferrocene, ferrocenium cation is there. Here, due to the of loss of one $C_5H_5$, we get this one and eventually other Cp group is also lost to get Fe plus is pretty simple and EI mass spectrum of ferrocene showing high abundance of molecular ion, the base peak is 121 here. This is the one accounts for CpFe plus. Now this is for cobalt rich acetate again, base peak is there, and then with loss of methyl group, it comes here. Again, loss of methyl group, you can see here 100 percent peak and the corresponding ones are shown here.

Now let us look into some other spectrometers we use in case of mass. One such instrument for high molecular weight measurement is MALDI-TOF mass spectrometry that means matrix assisted laser desorption ionization time of flight mass spectrometry, quite lengthy, but it is abbreviated as MALDI-TOF MS and this is commonly used MS mass technique. MALDI is a soft ionization technique unlike EI to create ions with minimal fragmentation by using a laser energy. In TOF, the protonated ions are accelerated by an electric field to make an ion to attain the kinetic energy as any other ions having the same charge. The velocity of the ion depends on the m/z ratio and the time that taken for the ion to reach the detector, where it is measured. So MALDI-TOF mass spectrometry can analyze a wide variety of biomolecules including peptides and carbohydrates. That means, the advantage with this one is you can go for higher molecular weight complex molecules such as peptides and carbohydrates. The another one is triple quadrupole mass spectrometry and this is abbreviated as TQMS or QAQ. It is a tandem mass spectrometry, in which the first and third quadrupole act as mass filters and the second acts as collision

cell to fragment the selected precursor or parent ions and to generate fragment or daughter ions.

TQMS is widely used tandem MS and is relatively simple and easy to use with good reproducibility to offer various applications at a very low cost and the TQMS can be used for structural elucidation that can provide information about fragmentation patterns also. Very useful quantitative studies also one can take up with this instrument. Due to increased sensitivity and specificity yielding lower detection and quantification limits TQMS is a vital option for many areas such as pharmaceutical development, clinical research and environmental studies and so on where quantification is the prime objective when they are characterized. Next one is quadrupole trap mass spectrometry, it is a hybrid triple mass spectrometer. Different from classical triple quadrupole mass spectrometry, the Q3 is also can work as either a standard quadrupole mass filter or a linear ion trap LIT with higher sensitivity than traditional 3D ion trap. This instrument retains the classical triple quadrupole scan functions and also it can be used for sensitive ion trap experiments.

There is one more hybrid linear ion trap orbitrap mass spectrometry: This one combines a linear ion trap and high resolution orbitrap and one of the tandem mass spectrometers in use today. LIT uses a set of quadrupole rods to confine ions radially and a static electrical potential on the end electrodes to confine the ions axially.

Orbitrap consists of an axially symmetrical mass analyzer that makes ions move in an orbital motion around the spindle. Then the image current is detected and converted into a mass spectrum by the Fourier transform. This hybrid mass spectrometer is widely used in proteomics and metabolomics analysis. This is where its role comes into picture and the other one is quadrupole orbitrap mass spectrometry, combines high performance quadrupole precursor selection with high resolution accurate mass orbitrap detection. The first mass analyzer is a quadrupole and the second is a high resolution orbitrap. It can be widely used in various fields like proteomics, metabolomics, food safety, toxicology and so on. Very specially designed for very special purposes. These ones may not be needed for routine examination of molecules that are generated in chemistry laboratories. How to choose an ionization technique as several ionization techniques are there. That usually depends on what information is required from mass spectrometry analysis and based on that one can choose an appropriate ionization technique.

For example, a hard ionization method such as electron impact may be used for a complex molecule in order to determine the component parts by fragmentation. If the molecule itself is complex and if you are not getting molecular ion peak then we have to use hard

ionization like electron impact, in that case what happens fragmentation is very high in that case by looking into different fragmentations, we can get back into the constituent molecules from which it is formed. On the other hand, a high molecular weight sample of polymer or protein may require an ionization method such as MALDI because electron impact we know that we cannot go beyond 1000 molecular weight, but if the compounds or samples have high molecular weight then MALDI is an ideal. Often samples may be easily analyzed using multiple ionization methods and the choice is simplified to choosing the most convenient method. For example, electro spray ionization may be easily coupled to liquid chromatography systems as no additional sample preparation is required.

That means, they have some flexibility of combining with one or more other devices for further studies and analysis and separation. Here I have given a table of information, we are looking for and also the ionization technique one should use based on what we are looking for. Simple elemental analysis; if you want to know the composition, inductive coupled plasma is used in typical elemental analysis instrument, micro analysis. In depth profilling, fast atom bombardment (FAB) secondary and ion mass spectroscopy. Chemical speciation/component analysis, we should go for electron impact. In case of molecular species identification of compound soluble in common solvents, ideal one is electro spray ionization. For molecular species identification of hydrocarbon compounds, field ionization. Molecular species identification of high molecular weight compounds, matrix assisted laser desorption ionization MALDI and then molecular species identification of halogen containing compounds, the best one ideally suited is chemical ionization, the negative mode. I think this much will be good enough. Whatever the information desired is listed on left side and then appropriate ionization technique that has to be used or employed is also given here. It will give some information about the device we should look for and an electron ionization. Mass spectrum does not show neutral species and radicals and their mass may be obtained from the mass difference between analyte and product ion.

For example, what we do not get the molecular ion peak? In that case what happens we should look for the fragments and also the mass difference from that one, we should be able to identify the sample molecular weight.

Ion sources in gas phase methods: I mentioned, we can use electron ionization, chemical ionization, direct analysis in real time, inductively coupled plasma, matrix assisted laser desorption ionization MALDI, fast atom bombardment FAB, thermal ionization sources, plasma ionization.

These are used in case of analysis. These are the ion sources used in gas phase methods. Now, let us try to be familiar with some of the terms. So, I have given the glossary of terms here that is used in mass spectrometry.

**CI:** Chemical Ionisation. Reagent ions, generated *in situ*, are used to ionise molecules through transfer of a proton, electron or other charged species from one species to another.

**EI:** Electron Ionisation (same as **electron impact**). An energetic beam of electrons interacts with sample and ionises gas-phase molecules.

**ESI:** Electrospray Ionisation. Ions are transported into the gas phase by spraying a solution through a capillary at high potential. Solvent is evaporated by heating or by a warm bath gas.

**FAB:** Fast Atom Bombardment. A fast-moving beam of inert gas atoms desorbs ions dissolved in a liquid *matrix*. Also see *LSIMS*.

**GC/MS:** Gas Chromatography/Mass Spectrometry. A mass spectrometer with an *EI* or *CI* source is used as a detector for a gas chromatography column. A very powerful technique for the analysis of complex, volatile mixtures.

**ICP-MS:** Inductively coupled plasma mass spectrometry. A sample is entrained in a flow of gas and carried into a high temperature plasma, where it is converted into monatomic ions.

**LC/MS** Liquid chromatography/mass spectrometry. A mass spectrometer with an *ESI* or *APCI* source is used as a detector for a high performance liquid chromatography (HPLC) column. Avery powerful technique for the analysis of complex mixtures of soluble polar compounds

**LSIMS:** Liquid Secondary Ion Mass Spectrometry. An energetic beam of ions (typically Csþ) strikes a liquid *matrix* in which the analyte is dissolved, ejecting secondary (analyte) ions into the gas phase. Closely related to *FAB*.

MALDI: Matrix Assisted Laser Desorption/Ionization. A solid *matrix co*crystallized with a small amount of analyte is ablated by a laser. The matrix absorbs most of the energy and is vapourised to form an energetic plume in which the analyte is ionized.

**m/z:** The mass-to-charge ratio. A dimensionless quantity obtained by dividing the mass of an ion by the number of charges it carries. Alternatively, *Th* (Thomson).

**SIMS:** Secondary Ion Mass Spectrometry. A fast-moving ion beam is used to abrade a surface, removing and ionizing material. Conditions may be set in such a way as to obtain a depth profile.

I think let me stop here. While continuing in my next lecture, I will start discussion on EPR or ESR electron paramagnetic resonance or electron spin resonance and once that is completed in 3 or 4 lectures, I will come back again to look into problems. Initially related with NMR and then probably IR and mass and then tackling problems with combination of all these entities, until then have an excellent time. Thank you.