Mass Spectrometry of Inorganic, Coordination and Organometallic Compounds
Tools – Techniques – Tips

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Mass Spectrometry of
Inorganic, Coordination and
Organometallic Compounds
Inorganic Chemistry

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Mass Spectrometry of Inorganic, Coordination and Organometallic Compounds
Tools – Techniques – Tips

William Henderson
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and
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University of Victoria, Canada

John Wiley & Sons, Ltd
This book is dedicated to our families:

Angela, Laura and Liam (WH)

Angela, Seth and Grace (JSM)
Bill Henderson was born in Darlington, County Durham, and grew up in Stockton-on-Tees, both in the North-East of England. He studied chemistry and geochemistry at the University of Leicester, and stayed at Leicester for his PhD in organometallic chemistry under the supervision of Dr. Ray Kemmitt, studying metallacyclic complexes of platinum, palladium and nickel. An NSF-supported postdoctoral fellowship at Northwestern University, Evanston, Illinois, USA with Professor Du Shriver followed. This included a period of collaborative research involving metal clusters as catalyst precursors at Hokkaido University in Sapporo, Japan with Professor Masaru Ichikawa. Bill then returned to England, with a period spent in industry with Albright & Wilson Ltd in the West Midlands, where he carried out research and development work in organophosphorus chemistry and surfactants. In 1992, a lectureship in New Zealand beckoned, at the University of Waikato in Hamilton, where he has been ever since. Since 2000 he has been an Associate Professor, and has been Head of Department since 2002.

Research interests cover a range of areas, with the characterisation of inorganic compounds using mass spectrometry being one of the central themes. Other research areas include the chemistry of the platinum group metals and gold, and applications of organophosphorus chemistry to the synthesis of novel ligands and the immobilisation of enzymes. He has published over 150 articles in refereed journals, together with three textbooks.

Bill is married to Angela, a high school teacher, and they have two children, Laura and Liam. In his spare time, other interests include music, gardening and English mediaeval history.

Born in Rotorua, New Zealand, Scott McIndoe completed all his degrees at the University of Waikato in Hamilton. His DPhil in organometallic chemistry was supervised by Professor Brian Nicholson. The New Zealand Foundation for Research, Science & Technology (FRST) awarded him a postdoctoral fellowship in 1998 to work in the
group of Professor Brian Johnson FRS at the University of Cambridge, England. In 2000
he took up the post of college lecturer at Trinity and Newnham Colleges, also at
Cambridge. After three years in this position, he moved to an assistant professorship at
the University of Victoria in British Columbia, Canada. Scott’s research interests focus
around using mass spectrometry as a first-resort discovery tool in organometallic
chemistry and catalysis.

In curious symmetry with Bill, Scott is also married to an Angela who is a high school
teacher, and they have two children, Seth and Grace. His other interests include cricket,
windsurfing and finding excuses to add to his power tool collection.
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Mass spectrometry (MS) is just one of many powerful instrumental techniques that is available to the inorganic, coordination or organometallic chemist. When we set out to write this book, our principal aim was to make it understandable by a typical inorganic or organometallic chemist who might use mass spectrometry, but who is by no means an expert in the field. Our own scientific backgrounds – as synthetic chemists who have discovered the power of mass spectrometry techniques for studying inorganic systems– are in accord with this philosophy.

Mass spectrometry applied to the analysis of inorganic substances has a long and fruitful history. However, relatively recent developments in ionisation techniques have placed two of these – MALDI (Matrix Assisted Laser Desorption Ionisation) and especially ESI (Electrospray Ionisation) – at the forefront of the pack. These are extremely powerful, soft ionisation methods that provide valuable mass spectrometric information to the chemist. Furthermore, the gentle nature of these ionisation techniques often results in spectra that can be easily analysed by chemists, as opposed to experts in mass spectrometry, as was often the case with harsher ionisation methods. Coupled with major advances in instrument robustness, automation, computer hardware, operating software and ease of operation and maintenance, such instrumentation is becoming widely used by inorganic chemists worldwide. We therefore felt that a textbook describing the mass spectrometric characterisation of inorganic and organometallic compounds was timely.

Many excellent textbooks and review articles cover the principles behind the various ionisation techniques and their applications, which are dominated by organic and biochemical systems. Readers wanting more detailed expositions on the finer points of mass spectrometry are encouraged to consult these texts.

This book is roughly divided into two main sections. In the first half of the book (Chapters 1 to 3), the basic principles of operation of various types of mass spectrometry systems are included, with an emphasis on mass analysers and ionisation techniques. Again, this has been written with the chemist in mind, so the treatment is primarily descriptive rather than mathematical. Also included are fundamental aspects such as resolution, data presentation methods and the use of isotope information. We have tried, where possible, to provide helpful suggestions for practical use, in the form of end-of-section summaries.

The second half of the book (Chapters 4 to 7) describes the applications of just one ionisation technique – electrospray – that without doubt is the most versatile and widely used mass spectrometry technique for the characterisation of inorganic and organometallic compounds today. The material is divided into chapters according to the type of compound, for example, coordination compounds (Chapter 5) and transition metal organometallic compounds (Chapter 7). In these chapters we have endeavoured to discuss the behaviour patterns of the various classes of compounds, such that the reader will be able to successfully apply modern mass spectrometry techniques to their own area.
of chemistry. Finally, Chapter 8 discusses some ‘Special Topics’ involving the application of modern mass spectrometry techniques in imaginative ways to particular inorganic and organometallic systems.

William Henderson
and
J. Scott McIndoe
Acknowldegements

We are grateful to our publishers, John Wiley & Sons, for the opportunity to write this book, and to the other publishers who have generously allowed reproduction of some of the figures.

JSM

Many thanks to David McGillivrav for running the LSIMS and El mass spectra, and to Orissa Forest for assisting in collating, tabulating and graphing the data in the Appendices. I greatly appreciate the discussions I’ve had with many chemists and mass spectrometrists who have shown me and described in detail their laboratories and instrumentation. Also those I’ve met at conferences, many of whom made extremely useful comments and suggestions on a wide variety of topics. Brian Fowler of Waters Canada went well beyond the call of duty in installing my mass spectrometer by answering an incessant stream of questions about componentry. The Canada Foundation for Innovation, the British Columbia Knowledge Development Fund and the University of Victoria are thanked for their support for purchasing and maintaining this instrument. Also thanks to Brian Nicholson (Waikato) and Brian Johnson (Cambridge), inspiring mentors and educators, and to Paul Dyson (EPFL), for posing thoughtful problems that led to many of our collaborative ventures. Pat Langridge-Smith (Edinburgh) gave me a unique introduction to some of the more esoteric aspects of mass spectrometry. Members of my research group – notably Nicky Farrer, Sarah Luethtgen and Colin Butcher – and numerous undergraduates have asked good questions requiring clear answers that have helped clarify my own thinking.

WH

I am indebted to Pat Gread and Wendy Jackson, for their dedication in maintaining the Waikato mass spectrometry instrumentation, and to the University of Waikato for their generous investment in mass spectrometry. I would also like to thank Brian Nicholson for numerous fruitful discussions concerning all aspects of chemistry, including mass spectrometry, and my students, past and present, who have each made distinctive contributions. Through mass spectrometry I have been able to develop a number of productive and enjoyable collaborations with other chemists around the world, and especially acknowledge Professor Andy Hor and his coworkers at the National University of Singapore.
# List of commonly-used abbreviations

## Mass spectrometric

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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>API</td>
<td>Atmospheric Pressure Ionisation</td>
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<tr>
<td>APCI</td>
<td>Atmospheric Pressure Chemical Ionisation</td>
</tr>
<tr>
<td>CE</td>
<td>Capillary Electrophoresis</td>
</tr>
<tr>
<td>CI</td>
<td>Chemical Ionisation</td>
</tr>
<tr>
<td>CIS</td>
<td>Coordination Ionspray</td>
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<tr>
<td>CID</td>
<td>Collision Induced Dissociation</td>
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<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<tr>
<td>EDESIE</td>
<td>Energy-Dependent Electrospray Ionisation</td>
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<tr>
<td>EI</td>
<td>Electron Impact (ionisation)</td>
</tr>
<tr>
<td>ESI</td>
<td>Electrospray Ionisation</td>
</tr>
<tr>
<td>ES, ESMS</td>
<td>See ESI</td>
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<td>FAB</td>
<td>Fast Atom Bombardment</td>
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<tr>
<td>FD/FI</td>
<td>Field Desorption/Field Ionisation</td>
</tr>
<tr>
<td>FTICR</td>
<td>Fourier Transform Ion Cyclotron Resonance</td>
</tr>
<tr>
<td>FTMS</td>
<td>Fourier Transform Mass Spectrometry</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>GCMS</td>
<td>Gas Chromatography Mass Spectrometry</td>
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<tr>
<td>HPLC</td>
<td>High Pressure Liquid Chromatography</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma Mass Spectrometry</td>
</tr>
<tr>
<td>LCMS</td>
<td>Liquid Chromatography Mass Spectrometry</td>
</tr>
<tr>
<td>LDI</td>
<td>Laser Desorption Ionisation</td>
</tr>
<tr>
<td>LSIMS</td>
<td>Liquid Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>MALDI</td>
<td>Matrix Assisted Laser Desorption Ionisation</td>
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<tr>
<td>MCA</td>
<td>Multi Channel Analysis</td>
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<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
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<tr>
<td>MS/MS</td>
<td>Mass Spectrometry/Mass Spectrometry</td>
</tr>
<tr>
<td>$\text{MS}^n$</td>
<td>$n^{th}$ generation Mass Spectrometry</td>
</tr>
<tr>
<td>$m/z$</td>
<td>Mass-to-charge ratio</td>
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<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
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<tr>
<td>PDMS</td>
<td>Plasma Desorption Mass Spectrometry</td>
</tr>
<tr>
<td>PSD</td>
<td>Post Source Decay</td>
</tr>
<tr>
<td>Q</td>
<td>Quadrupole</td>
</tr>
<tr>
<td>rf</td>
<td>Radiofrequency</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>TIC</td>
<td>Total Ion Current</td>
</tr>
<tr>
<td>TOF</td>
<td>Time-of-Flight</td>
</tr>
<tr>
<td>oa-TOF</td>
<td>orthogonal Time-of-Flight</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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Non-SI units often encountered in mass spectrometry

Atm  Atmospheric pressure, defined as 101 325 Pa.
Bar  \(10^5\) Pa. Unit of pressure approximating to one atmosphere.
Low pressures often listed in millibar, 1 mbar = 100 Pa.
Da  Dalton, the unified atomic mass unit = \(1.660 540 \times 10^{-27}\) kg.
\(^{12}\text{C}\) = 12 Da exactly.
eV  electron volt, the kinetic energy acquired by an electron upon acceleration through a potential difference of 1 V = \(1.602 177 \times 10^{-19}\) J.
mm Hg one atmosphere of pressure will force a column of mercury to a height of 760 mm, so 1 mm Hg = 1/760 atm = 133.32 Pa. Equivalent to Torr.
Torr see mm Hg.
Th  Thomson, unit for mass-to-charge ratio i.e. 1 Th = 1 m/z.

Chemical

acac  Acetylacetonate anion (2,4-pentanedionate)
An  Actinide metal
bipy  2,2’-bipyridyl (also 2,2’-bipyridine)
Cp  \(\eta^5\)-cyclopentadienyl (\(\text{C}_5\text{H}_5\))
Cp* \(\eta^5\)-pentamethycyclopentadienyl (\(\text{C}_5\text{Me}_5\))
Cy  Cyclohexyl
DMSO  Dimethylsulfoxide, S(O)Me₂
EDTA  Ethylenediamine tetra-acetic acid or anion thereof
en  Ethylene-1,2-diamine (1,2-diaminoethane), \(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2\)
Fc  Ferrocenyl, \((\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\)
GSH  Glutathione (Glu-Cys-Gly)
HMPA  Hexamethylphosphoric triamide OP(NMe₂)₃
L  Ligand coordinated to a metal centre
Ln  Lanthanide metal
M  Metal centre
MeCN  Acetonitrile
py  Pyridine, \(\text{C}_5\text{H}_5\text{N}\)
PPh₃  Triphenylphosphine
PPN  Bis(triphenylphosphine)iminium, \([\text{Ph}_3\text{P}=\text{N}=\text{PPh}_3]^+\)
pta  Phosphatriaza-adamantane
R  Alkyl or aryl group
THF  Tetrahydrofuran
TM  Transition Metal
X  Halogen
1 Fundamentals

1.1 Introduction

A mass spectrometer is an instrument for generating gas-phase ions, separating them according to their mass-to-charge ratio using electric fields (sometimes magnetic fields as well) in an evacuated volume, and counting the number of ions. A computer system controls the operation and stores, manipulates and presents the data. The features of the mass spectra so produced relate to the properties of the original sample in a well understood way. This chapter deals with some of the fundamental aspects of mass spectrometry: how samples are introduced to the instrument (inlets); how the ions are fragmented; how ions are counted (detectors) and the type of output and how it is manipulated (data systems and data processing) and interpreted (isotope patterns). How the ions are separated (mass analysers) is dealt with in Chapter 2 and the how the ions are formed (ionisation techniques) in Chapter 3.

Figure 1.1 is a schematic drawing of a mass spectrometer. The sample is introduced through an inlet to the ionisation source. The source generates gas-phase ions, which are transferred to the mass analyser for separation according to their mass-to-charge ratio. A detector registers and counts the arriving ions. The data system controls the various components of the mass spectrometer electronically, and stores and manipulates the data. All mass spectrometers have a vacuum system to maintain the low pressure (high vacuum) required for operation. High vacuum minimises ion-molecule reactions as well as scattering and neutralisation of the ions.

Modern instruments often have the facility to perform more than one mass analysis on a single sample, i.e. MS/MS or even MS\textsuperscript{n} (where \(n\) = number of stages of mass spectrometry). Such machines require more than one mass analyser, or alternatively, have the facility to trap ions in a small volume of space and carry out repeated experiments on them. Both types of mass spectrometer require the ability to fragment ions, and this is usually achieved by collision-induced dissociation, another topic covered in this chapter.

1.2 Inlets

The way in which a sample is introduced to the mass spectrometer is very dependent on its phase (gas, liquid, solid or solution) and the means by which ionisation is induced. Gaseous samples are easily transferred to a mass spectrometer, as the gas may simply be allowed to leak into the low pressure source region. The effluent from the capillary
column of a gas chromatograph (GC) may be conveniently plumbed directly into the source of a mass spectrometer. Condensed phase analytes (liquid or solid) are placed on a sample holder and passed through a door into the instrument. The door is closed, sealed and the inlet/source region is evacuated, after which time whatever ionisation technique being used is applied. Analytes dissolved in a solvent are usually introduced to the mass spectrometer via a combined inlet/ionisation source, in which sample introduction, desolvation and ionisation are intimately related. The solution is commonly the effluent from a liquid chromatograph (LC), or it may be injected directly into the instrument by means of a syringe pump.

1.3 Collision-Induced Dissociation

Collision-induced dissociation (CID, sometimes known as collision-activated decomposition, or CAD) of ions occurs when some of the translational energy of an accelerated ion is converted into internal energy upon collision with a residual gas (typically nitrogen or one of the noble gases helium, argon, xenon). The increase in internal energy can induce decomposition (fragmentation) of the ion. CID was of limited importance in mass spectrometry – indeed, some instruments were fitted with ‘metastable suppressors’ designed to eliminate this troublesome effect – until the advent of soft ionisation techniques. The ability of these techniques to obtain practically intact molecular ions for many classes of compound was enormously useful in itself, but obtaining structural information through characteristic fragmentation patterns is also highly desirable and CID proved to be the ideal answer to this problem.

The first step in the CID process is the actual collision between a fast-moving ion and an immobile neutral target, resulting in an increase in the internal energy of the ion. The ion then rapidly redistributes this extra energy amongst its vibrational modes, which number $3N - 6$ for an ion with $N$ non-linear atoms. The much slower second step is the unimolecular decomposition of the excited ion to generate product ions and neutral fragments. Because the timescale of the first step is very much shorter than the second, large ions are more difficult to fragment using CID as they have more vibrational modes in which to deposit the extra energy, making decomposition of the ion less likely. Two collision regimes for CID may be defined, low energy (tens of electron volts (eV)) and high energy (thousands of eV).

In practice, low-energy CID is carried out by allowing an accelerated beam of ions to traverse a volume occupied by gas molecules or atoms as the target. In MS/MS
Instruments in which the mass analysers are separated in space, such as the triple quadrupole (QqQ) or hybrid quadrupole-Time-of-flight (QqTOF), an rf-only quadrupole (the ‘q’ in QqQ) encloses this volume, called a collision cell. The directional focusing abilities of the rf-only quadrupole are used to good effect here, redirecting ions back on to the right axis after collisions drive them off-course. However, the potential well created by a rf-only quadrupole field is not particularly steep-sided and ion losses do occur. Better ion guides are rf-only hexapoles or octapoles and the recently introduced ion tunnels. The latter are a series of ring shaped, alternately charged electrodes, 60 or more of which describe a hollow cylinder inside of which the ions are tightly confined. Whatever its configuration, the collision cell is separated from the mass analysers either side by narrow apertures and is filled with an inert gas. Ions emerging from the first mass analyser are fragmented (and often scattered) upon collision with the gas, strongly refocused back on to the ion optical axis by the rf-only field, transmitted to the second mass analyser and then detected. A large number of collisions is allowed to occur in the collision cell, so collision yields (the percentage of fragmented ions that reach the detector) are frequently very high for this form of CID. In MS/MS instruments that rely on each stage of MS being carried out sequentially (in time) in the same space, such as ion traps or Fourier Transform Ion Cyclotron Resonance (FTICR) analysers, the collision gas is simply introduced to the chamber. The ions are energised and fragmented by CID. The process is especially simple for ion traps, which typically contain a background pressure of helium gas at about $10^{-3}$ mbar during operation, so the trap does not even need to be filled and emptied between stages of MS/MS.

The nature of the target gas is important in low-energy CID. A large proportion of the translational energy of the ion is transformed into internal energy upon collision with an effectively stationary target, the mass of which has a significant effect on the spectra (so the extent of dissociation increases He < Ar < Xe). Atomic gases are more efficient than polyatomic gases in causing CID, because the latter can be vibrationally excited themselves upon collision and hence reduce the amount of energy transferred to the ion. The chemical effects of the target are also important due to the possibility of ion/molecule reactions, so if dissociation of the precursor ion only is sought, an inert target gas is desirable (making the noble gases doubly appropriate). However, there are some circumstances in which ion/molecule reactions are of great interest.

Low-energy CID spectra are very sensitive to small absolute changes in the collision energy, to collision gas pressure and to the mass of the neutral target. These factors conspire to make the reproducibility of low-energy CID spectra between instruments poor compared to electron ionisation mass spectra, for which searchable libraries of spectra are very well established.

Instruments with an atmospheric pressure source have another region in which low-energy CID can occur, located just before the ions enter the high-vacuum region of the mass spectrometer. Here, the pressure is low enough that the mean free path length of the accelerating ions is sufficiently long that they can attain a high enough velocity for collisions with residual solvent molecules and/or desolvation gas to cause fragmentation. This process is called in-source CID, and is an especially important facility for instruments with a single mass analyser. The ions are accelerated by application of a variable voltage between the sampling cone and the skimmer cone (which separate differentially pumped regions of the instrument; Chapter 3, Section 8 on electrospray ionisation gives more details), and this ‘cone voltage’ generally has the most profound effect on the mass spectrum of any of the parameters used to tune the instrument.
High-energy CID is the preserve of sector instruments (Chapter 2, Section 2), which accelerate and analyse ions with energies of thousands of eV. rf-only multipoles are useless as collision cells under these circumstances, as they are unable to refocus such energetic ions after a collision. A simple reaction region containing the collision gas is quite sufficient; ions deflected more than a few tenths of a degree upon collision are lost. The lack of means by which to refocus errant ions and a peak-broadening effect due to kinetic energy release upon collision conspire to make high-energy CID markedly less efficient in terms of conversion of precursor ion to detected product ion than its low-energy cousin. The distribution of energies transferred at collision energies of thousands of eV is broad, and high-energy processes result in some product ions that do not appear at all in low-energy CID spectra.

1.3.1 Bond Dissociation Energies from CID Studies

Bond dissociation energies may be obtained from low-energy (‘threshold’) CID studies, by analysing the kinetic energy dependence of the reactions of metal complexes with an inert collision gas, and ion thermochemistry remains an active research field. Threshold CID experiments are carried out using guided ion beam mass spectrometers, custom-made instruments that allow the sequential generation, thermalisation (cooling), mass selection, fragmentation and mass analysis of ions. To obtain precise data, multiple ion-neutral collisions are eliminated, careful consideration is taken of internal energies of the complexes and their dissociation lifetimes, and the experiments are backed up by Density Functional Theory (DFT) calculations. Fundamental information such as the stepwise energies for dissociation of $[\text{Pt(NH}_3\text{)}_x]^+$ ($x = 1 - 4$) or $[\text{Cr(CO)}_x]^+$ ($x = 1 - 6$) complexes can be obtained using this approach. The main limitation for wider applicability of this technique is that experiments cannot yet be implemented on commercially available instruments. Metal-ligand bond dissociation energies have also been established using FTICR experiments under single-collision conditions.

1.3.2 Presentation of CID Data

Detailed CID investigation of a compound can generate huge quantities of data – in a typical low-energy CID experiment, the collision energy can be varied from $0 - 200$ eV, and the analyst must decide which spectra are most representative and informative. This is traditionally carried out by means of a stacked plot, selecting values for the collision energy so that all product ions show up in at least one of the spectra chosen. Numerous examples of this approach can be seen in Chapters 4 to 7 (e.g. Figures 4.3, 4.6, 5.6, 5.8 etc.).

If the appearance/disappearance potentials of a particular ion are of special interest, the breakdown graph is an effective way of presenting this data. A breakdown graph plots the intensity of a given ion against the fragmentation energy, represented by the cone voltage (for in-source CID) or collision voltage (for CID in a collision cell). Multiple ions may be presented on a single breakdown graph (Figure 1.2).

In more complicated cases, where there are many fragment ions, and/or a mixture of ions, it may be beneficial to collect spectra across the entire energy range and present all the information simultaneously. This approach is encapsulated in energy-dependent electrospray ionisation mass spectrometry (EDESI MS), which uses a presentation style reminiscent of two-dimensional NMR spectra. The precursor and all product ions appear as cross-peaks in a contour map, where the contours represent ion intensity. The approach is best illustrated with an example (Figure 1.3).
Figure 1.2
Breakdown graphs obtained by CID of protonated H-Gly-Gly-Leu-OH. From Harrison. Reproduced by permission of Wiley Interscience.

Figure 1.3
EDES[, mass spectrum of a mixture of four anionic metal carbonyl clusters, [Ru₅Co(CO)₁₆]⁻, [HRu₄Co₂C(CO)₁₅]⁻, [Ru₃Co(CO)₁₃]⁻ and [RuCo₃(CO)₁₂]⁻.¹⁰ Note how each component of the mixture is clearly discriminated in the map, but the summed spectrum at the top is uninformative.
1.4 Detectors

The abundance of ions at each mass-to-charge ratio \((m/z)\) value must be measured, and this is the role of the **detector**. The ideal detector will have a wide dynamic range (able to detect a few ions arriving just as well as tens of thousands) and a response as linear as possible (provide a peak \(100 \times\) larger for 1000 ions than that produced for 10). In the earliest days of mass spectrometry detectors were simply photographic paper but this method was essentially made obsolete by the introduction of electron multipliers. These devices convert the kinetic energy of the arriving particles into electrical signals. The incoming ions strike a surface called a dynode, which is capable of releasing one or more electrons when struck by a particle having an energy above a certain level. Usually, there are a series of dynodes and the released electron is accelerated towards the second dynode, which releases further electrons (Figure 1.4). By repeating this input and release process many times, the number of electrons increases in a geometrical progression \((10^6 \text{ to } 10^8 \times)\).

![Diagram of an electron multiplier](image)

**Figure 1.4**
An electron multiplier. An ion travelling at high speed causes secondary electrons to be ejected from a metal surface (a dynode) upon impact. These electrons are accelerated through an electric potential towards a second dynode, releasing more electrons, and so on until a blizzard of electrons strikes the final dynode, producing a detectable current which may be amplified further.

A scintillator or ‘Daly detector’ accelerates the secondary electrons (generated when the incoming ions strike the first dynode) towards a dynode made of a substance that emits photons (a phosphor). A photomultiplier tube enhances the signal which is ultimately converted into an electric current. This arrangement has some advantages over the electron multiplier as the photomultiplier may be sealed from the vacuum of the mass spectrometer and does not suffer ill effects from the presence of residual gas or discharged ions, significantly increasing the lifetime of the detector.

In some applications it is advantageous to collect ions over an area using an **array detector**, rather than a point detector which relies on ions arriving sequentially at a single location. Array detectors can detect ions arriving simultaneously at different points in space. This property is particularly useful in sector instruments, which disperse ions in space, so a number of detectors arranged in a line are capable of measuring a section of the mass spectrum in the same amount of time that a single detector can measure a single \(m/z\) value. For example, an array detector containing ten collectors could simultaneously...
measure ten times the mass range that a single collector could in the same time. The efficiency of detection is thus greatly improved, important in applications requiring high sensitivity.

TOF instruments generate a pulse of ions of a wide range of \( m/z \) values, all of which arrive at the detector within a few microseconds, and ions of adjacent \( m/z \) value are separated in time by less than a nanosecond. A detector is required that has a very fast recovery time. Furthermore, orthogonal-TOF mass analysers pulse a whole section of an ion beam at once, and this spatial dispersion in the original direction of travel is preserved as the ions progress down the flight tube. The ions arrive at the detector across a broad front, demanding a detector able to accept ions over an equally wide area. Both of these obstacles are solved by the use of a microchannel plate (MCP), which consists of a large number (thousands) of tightly packed individual detection elements all connected to the same backing plate. Each of these ‘microchannels’ is a tiny electron multiplier tube, and an ion arriving in any of them sets off a cascade of electrons to provide a detectable signal. A time-to-digital converter (TDC) sets up timing increments separated by intervals of less than a nanosecond, and a signal detected in any of these intervals is recorded as an arrival time. It does not, however, record the intensity of the signal, so two ions arriving with the same time interval on different parts of the MCP are still recorded as a single arrival time. Generally, this does not pose a problem; a TOF analyser is typically recording 30 000 spectra per second so the number of ions arriving in any one individual spectrum is low. However, it becomes an issue when recording particularly high ion currents, and is exacerbated by the fact that the TDC itself has a ‘dead time’, in which it takes some time to recover before it can record a new event. These effects conspire to affect the quantitative response of TOF detectors, and high ion currents tend to distort peak shape and underestimate intense signals, though computer processing does mitigate the detrimental effects to a large degree.

1.5 Mass Resolution

The resolution of a mass spectrometer represents its ability to separate ions of different \( m/z \). It is manifested in the sharpness of the peaks seen in the mass spectrum. An instrument with high resolving power will be able to distinguish two peaks very close in mass. Calculating the resolution is done in one of two ways. Magnetic instruments tend to give peaks which are essentially Gaussian in shape, and the usual definition is \( R = m/\Delta m \), where \( m \) is the mass of an ion peak and \( \Delta m \) is the distance to another peak overlapping such that there is a 10 % valley between the two peaks (Figure 1.5).

In the figure, \( m = 1000 \) and \( \Delta m = 0.208 \), so the 10 % valley definition gives a resolution of \( 1000/0.208 = 4800 \). It is generally more convenient to conduct the calculation on a single ion, in which case \( \Delta m \) is the full width of the peak at 5 % of its maximum intensity. Another common resolution calculation uses the full width of the peak at half maximum intensity (FWHM). This definition is commonly used for TOF and ion trap instruments, which typically have relatively broad-based peak profiles and as such the 5 % definition exaggerates the peak width and hence gives an unreasonably low value for the resolution. In the figure shown, \( \text{FWHM} = 1000/0.1 = 10 000 \). Clearly, when comparing resolution performance between instruments it is important to apply the same definition in each case. Generally in this text, ‘resolution’ will correspond to the FWHM definition unless otherwise stated.
The ability of instruments with different resolution to differentiate between low-mass ions of the same nominal mass is illustrated in Figure 1.6. At low resolution (1000, e.g. quadrupole/ion trap in low resolution mode or linear TOF), the three ions are not discriminated at all and just a single peak is observed. At slightly higher resolution (2500, e.g. quadrupole/ion trap in maximum resolution mode) the higher \( m/z \) ion is differen-
tiated, but the remaining two ions appear as just a single peak at an \( m/z \) value intermediate between the two real values. Three peaks can be clearly observed at a resolution of 5000 (e.g. reflectron TOF), and the signals are baseline resolved at 10,000 resolution (e.g. magnetic sector, high performance reflectron TOF, FTICR).

However, the major criterion for an inorganic/organometallic chemist should be the ability to provide good baseline-resolved isotope patterns in the \( m/z \) range of most interest. The need for high resolution becomes less stringent when it is isotope pattern information that is required. Baseline resolution of the individual members of the isotopomer envelope is the most important criterion for satisfactory data. The majority of coordination complexes and organometallic compounds are below 1000 Da, at which a resolution of 2500 is generally sufficient for good data (Figure 1.7).

However, a resolution much below 2500 will drastically reduce confidence in assignment, as can be clearly seen in the lumpy, indistinct and unsatisfactory profile observed for the spectrum collected at a resolution of 1000. Higher resolution than 2500 is always desirable, especially when collecting data on ions of mass > 1000 Da and for multiply charged ions, and the higher quality the data the correspondingly higher confidence can be had in assignment. A resolution of 2500 can be achieved for practically all modern research level instruments, regardless of type – even relatively inexpensive ion trap and quadrupole machines can be scanned slowly over the isotope envelope region (usually not