

HIGH DEFINITION MASS SPECTROMETRY AS A TOOL FOR STRUCTURAL INVESTIGATION OF HIGH M/Z ION SPECIES

Iain Campuzano and Kevin Giles
Waters Corporation, Manchester, UK

INTRODUCTION

Over the past 10 years, interest in high mass non-covalent analysis has increased due to the ability of the current mass spectrometers and electrospray sources to preserve the non-covalent interactions, allowing one to analyze compounds in their native conformation and stoichiometry.¹ The transfer of non-covalently associated complexes from solution to the gas phase using electrospray ionization generally results in the formation of ions possessing relatively few charges. As a result, these species appear high on the m/z scale, making Time-of-Flight mass spectrometry ideal for their mass analysis. The utility of ion mobility spectrometry (IMS) in probing the structures of relatively large complexes has been highlighted previously.¹

Here we present the use of high-efficiency IMS (Triwave™ technology) on a SYNAPT™ High Definition Mass Spectrometry™ (HDMS™) System for analysis of high m/z caesium iodide clusters over the m/z range 1,000–20,000. This demonstrates the utility of the SYNAPT HDMS System for the mass measurement of high m/z species, such as in the analysis of non-covalent protein complexes.

EXPERIMENTAL

The instrument used in this study was a SYNAPT HDMS System, which combines high-efficiency ion mobility based measurements and separations with a hybrid quadrupole orthogonal acceleration

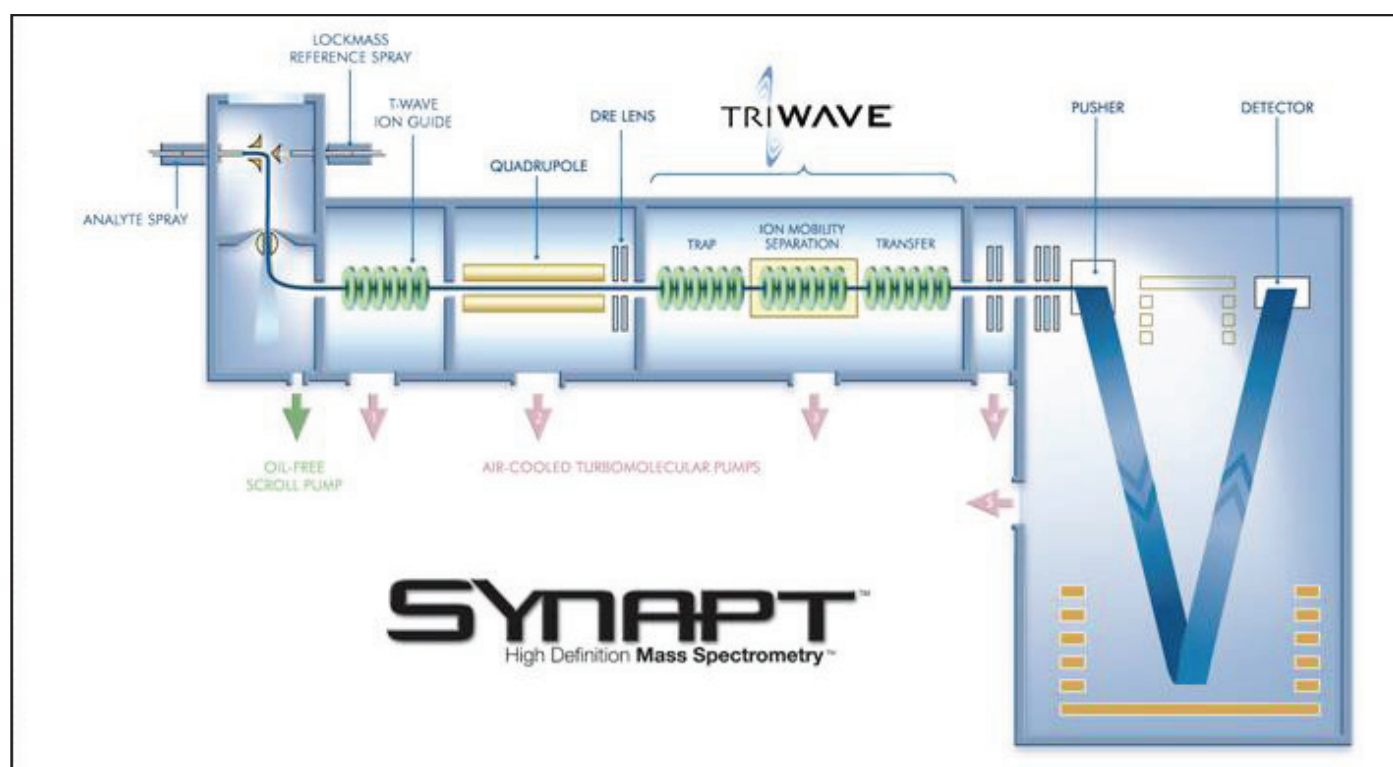


Figure 1. Schematic of the SYNAPT HDMS System.

Time-of-Flight (oa-ToF) mass spectrometer, Figure 1². Samples were introduced with a borosilcate-glass nano electrospray-spray tip and sampled into the vacuum system. The ions pass through a quadrupole mass filter to the enabling Triwave device. Triwave consists of three travelling wave (T-Wave™) ion guides. The TRAP T-Wave accumulates ions (with high efficiency), after which these ions are released as discrete packets into the IMS T-Wave, where the ion mobility separation of ions is performed. The TRANSFER T-Wave is used to deliver the ion mobility-separated ions into the oa-ToF analyzer. Each IMS separation was 51 ms long and the ions were released from the TRAP T-wave in 500 μ s wide packets. The gas pressure in the TRAP and TRANSFER T-Wave regions was 0.07 mbar (Argon) and the pressure in the IMS T-Wave was 0.5 mbar (Nitrogen). The traveling wave used in the IMS T-Wave for ion mobility separation was operated at a velocity of 250 m/sec. The wave amplitude was ramped from 0 to 30 V over the period of the mobility separation for optimum performance over the large m/z range used (m/z 1,000 to 32,000).

RESULTS

Upon MS acquisition of a concentrated caesium iodide solution, intense ion clusters can be observed as high as m/z 20,000, with each cluster's composition based on the formula $Cs(n+1)I_n$. From the mass spectrum generated it is evident that a number of overlapping series, differing in charge state and intensity profile, are present over the m/z scale (Figure 2). However, the HDMS (IMS/MS) analysis clearly illustrates discrete distributions, which are related by their m/z and drift-time, as shown in Figure 3.

MS conditions

MS system:	SYNAPT HDMS System
Ionization mode:	nanoESI positive
Capillary voltage:	1000 V
Cone voltage:	150 V
Source temp:	40 °C
Acquisition range:	1,000 to 32,000 m/z
IMS T-wave ramp:	0 to 30V over IMS experiment
IMS T-wave speed:	250 m/sec
IMS pressure:	0.5 mbar (nitrogen)

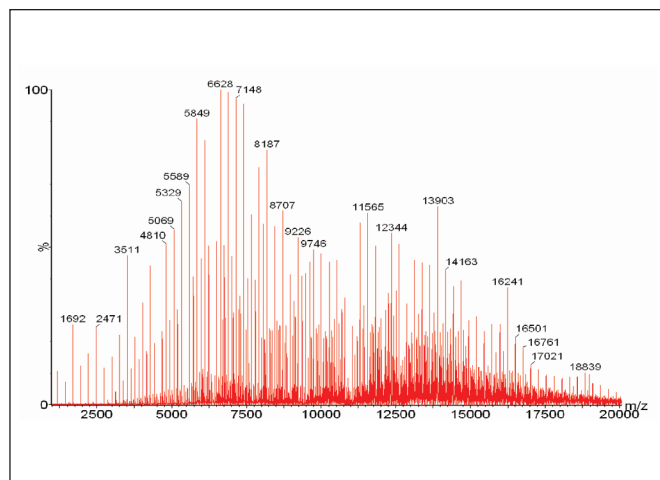


Figure 2. Mass spectrum of CsI (m/z 1,000 to 20,000).

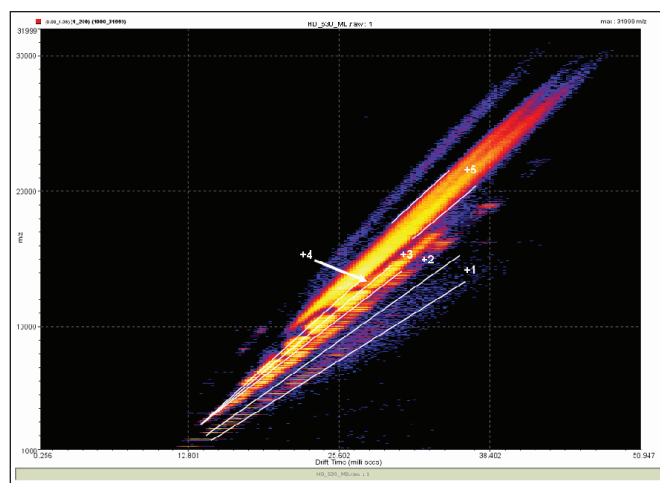


Figure 3. HDMS analysis: Drift-time vs m/z plot of CsI (m/z 1,000 to 32,000).

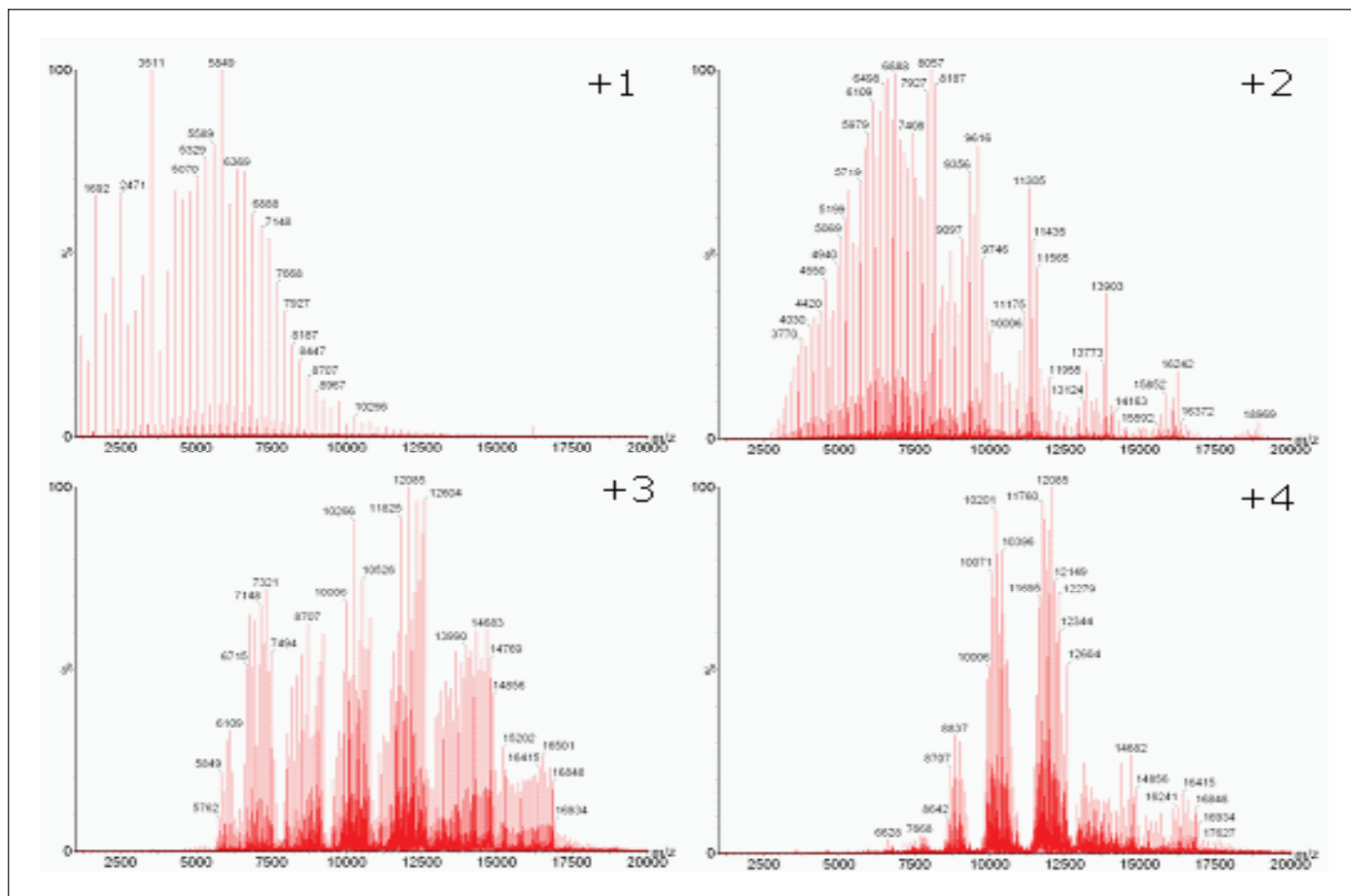


Figure 4. Charge state distributions of Csl.

The drift-times of the cluster ions seem to increase monotonically with increasing m/z values for the different charge state species, although with increasing charge state series up to +4, distinct m/z stability regions become clear, as shown in Figure 4.

CONCLUSION

- HDMS provides greater definition of even relatively simple samples, such as inorganic Csl clusters.
- High mass analysis of Csl clusters up to m/z 20,000 has been shown.
- Csl clusters have been successfully separated into five charge states series, demonstrating the ability of HDMS (high-efficiency IMS combined with oa-ToF mass spectrometry) for differentiating high mw species based on their mobility.
- Csl can be used to tune, optimize, and calibrate the SYNAPT HDMS System over a wide m/z range prior to high mass acquisitions being carried out.

References:

1. Ruotolo, Giles, Campuzano, Sandercock, Bateman & Robinson, *Science*, 310 (2005) 1658-1661.
2. Pringle, Giles, Wildgoose, Williams, Slade, Thalassinou, Bateman, Bowers, Scrivens, *Int. J. Mass Spectrom.*, 261 (2007) 1-12.

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Waters Corporation
34 Maple Street
Milford, MA 01757 U.S.A.
T: 1 508 478 2000
F: 1 508 872 1990
www.waters.com

