

Surface acoustic wave nebulization (SAWN) for homemade explosives synthesis product characterization

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Introduction:

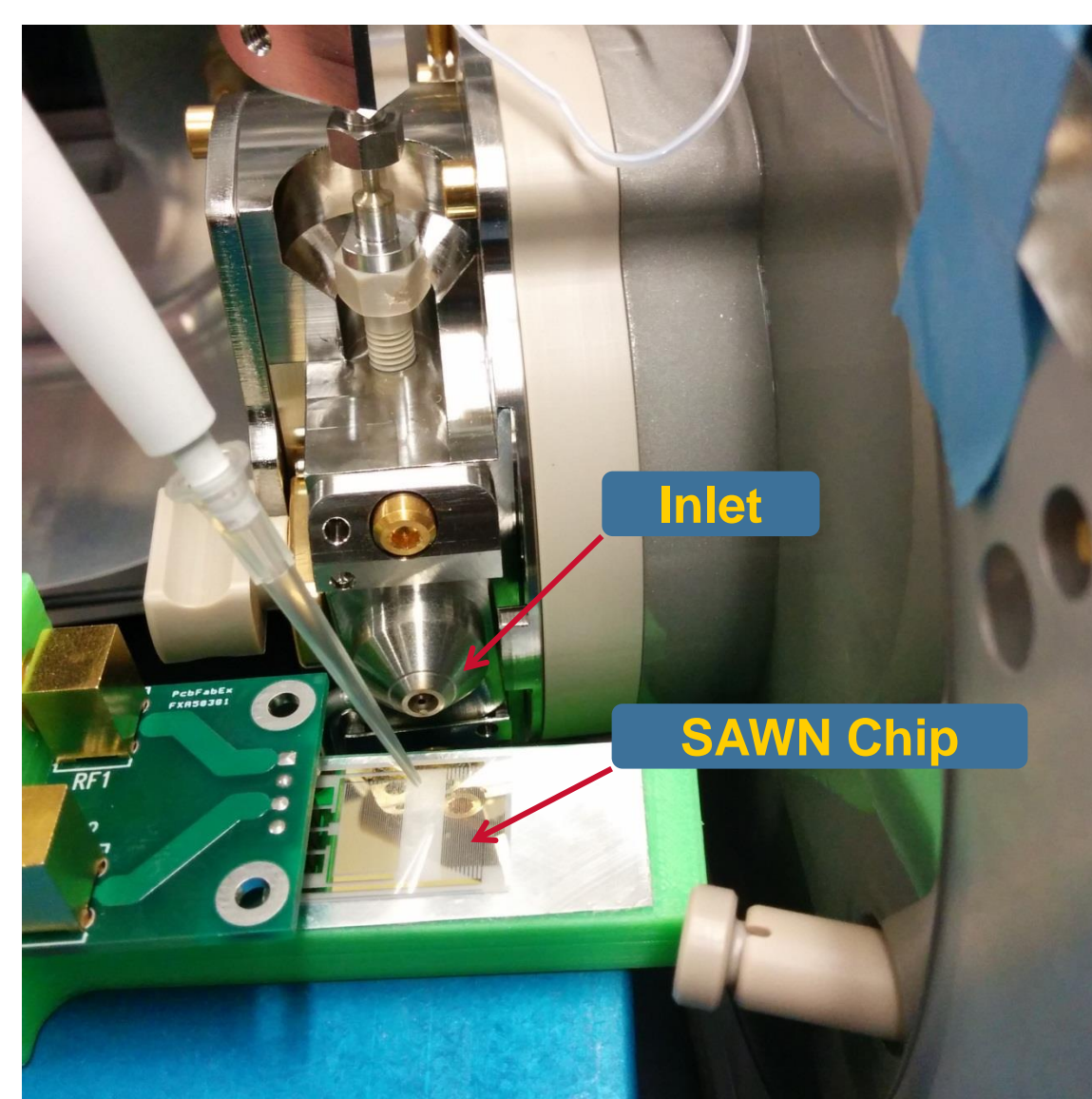
Conventional and homemade explosive (HME) materials are a ubiquitous threat to both military and civilian populations throughout the world. HMEs are particularly problematic because they are usually easy to synthesize and are not easily attributable. To our knowledge, explosives have never before been analyzed by surface acoustic wave nebulization (SAWN) ionization coupled to any mass spectrometer. Herein we describe analysis of several of these compounds by coupling SAWN to a commercial ion mobility spectrometry-mass spectrometry (IMS-MS) instrument. Our aim in developing this SAWN ionization method is to produce a simple mass spectrometric interface which can be incorporated into robotic liquid synthesis systems used to test and assess the viability of "internet"-type recipes for HMEs.

The SAWN apparatus replaces the nanospray needle in a conventional atmospheric pressure ionization inlet source. It comprises a small 1" x 1" LiNbO₃ piezoelectric chip, patterned with two opposing sets of interdigitated electrodes which are used to generate a standing surface acoustic wave (SAW) on the surface of the chip. ~1 μL aliquots of solution, pipetted onto the surface of the chip, absorb the SAW energy and are nebulized, whereupon a pressure gradient draws this atomized plume into the mass spectrometer for analysis. This technique has been characterized and published elsewhere for analysis of biological molecules [1-3]. A pictorial representation of the SAWN process is presented in Figure 1.



Methods:

Example solutions of trinitrotoluene (TNT), hexamethylene triperoxide diamine (HMTD) and triacetone triperoxide (TATP) in acetonitrile were analyzed by SAWN ionization mass spectrometry (MS). Additional samples have been spiked into beer (Heineken, Netherlands) as an example complex matrix, before analysis (spectrum not shown).



1 μL pipetted onto chip

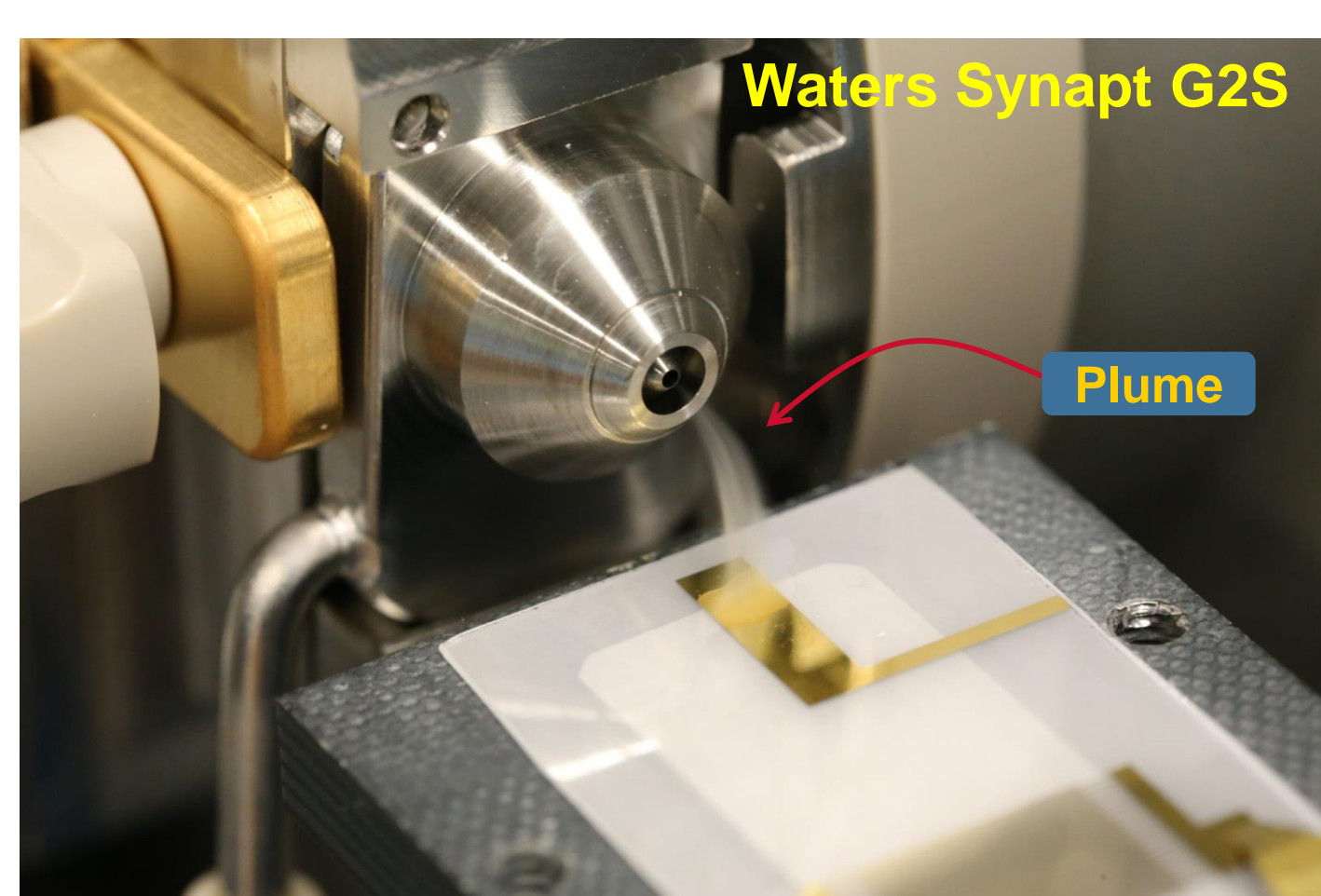
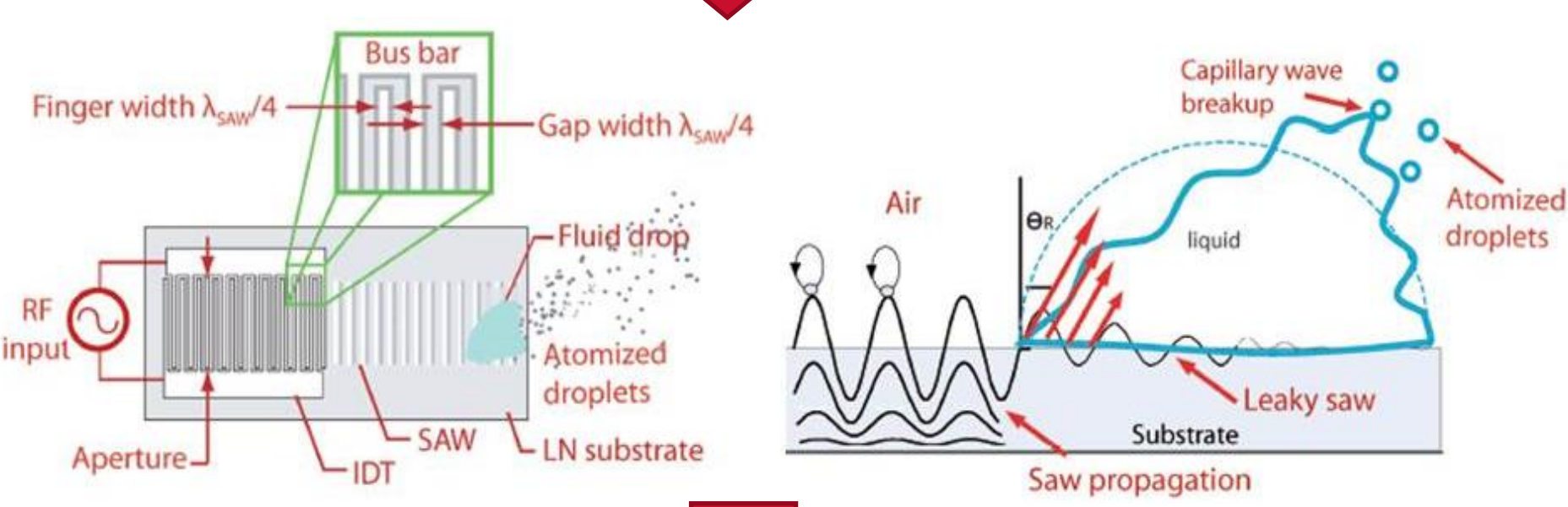
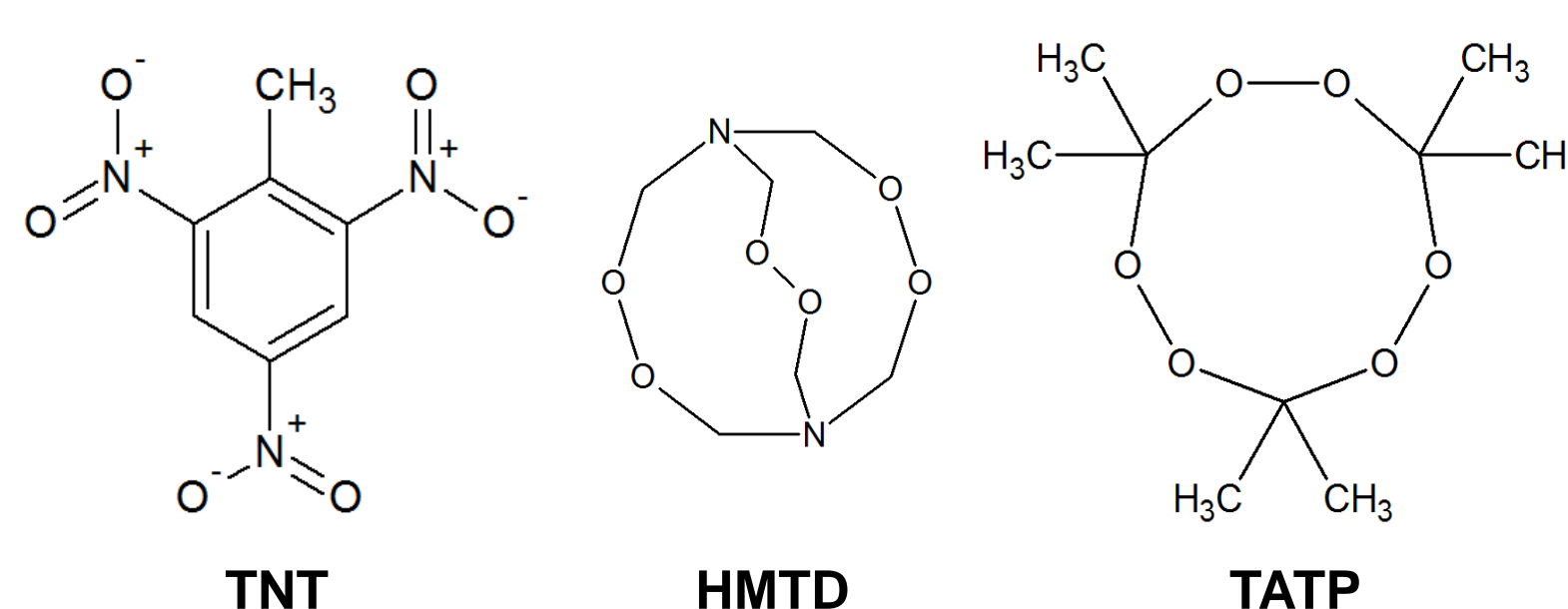


Figure 1. SAWN MS setup on the Waters Synapt G2S

Methods cont'd:

HMTD and TATP were also analyzed in several metal chloride salt solutions in order to investigate their metal ion chelation properties in the gas phase. A subsequent, preliminary molecular modeling experiment was performed to develop a hierarchical model of alkali and alkaline earth metal ion chelation by a doubly oxidized form of HMTD (known as TMD³) observed in the mass spectrum.

Results:



As shown in Figure 2 below, HMTD produced metal ion adducted, doubly oxidized dialdehyde forms (TMD³) exclusively when analyzed by SAWN-MS under ambient conditions. Many peaks in the spectrum correspond to clusters of TMD³ adducted to one or more metal ions.

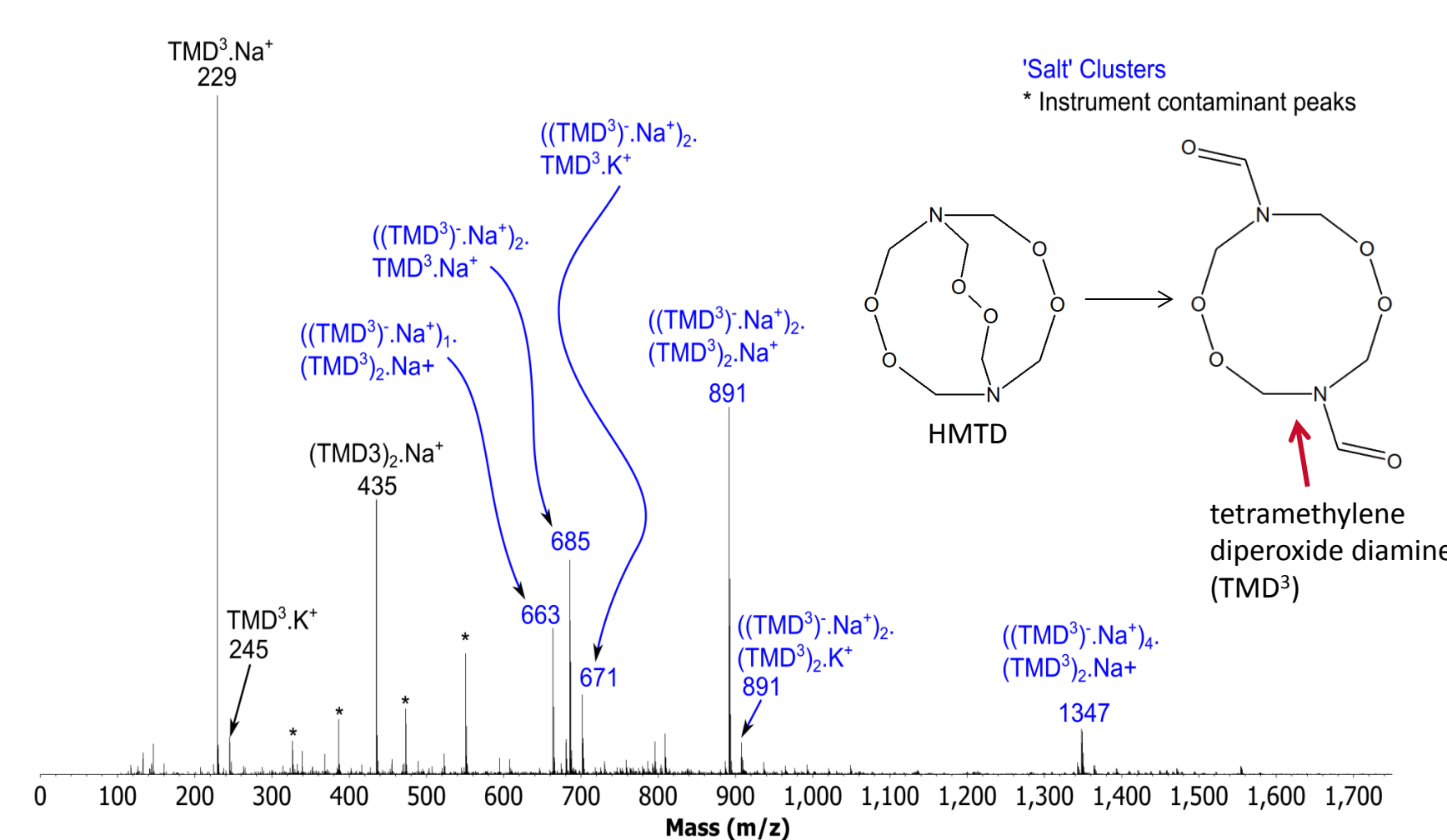


Figure 2. SAWN-TOF mass spectrum of HMTD (TMD³)

To confirm the quality of the HMTD reference standard, both proton (data not shown) and ¹³C (Figure 3 below) NMR experiments were conducted on a Varian INOVA 500MHz spectrometer. Only one analyte peak was observed at δ=91.41ppm in the ¹³C experiment, suggesting all equivalent carbons. This spectrum corresponds to HMTD.

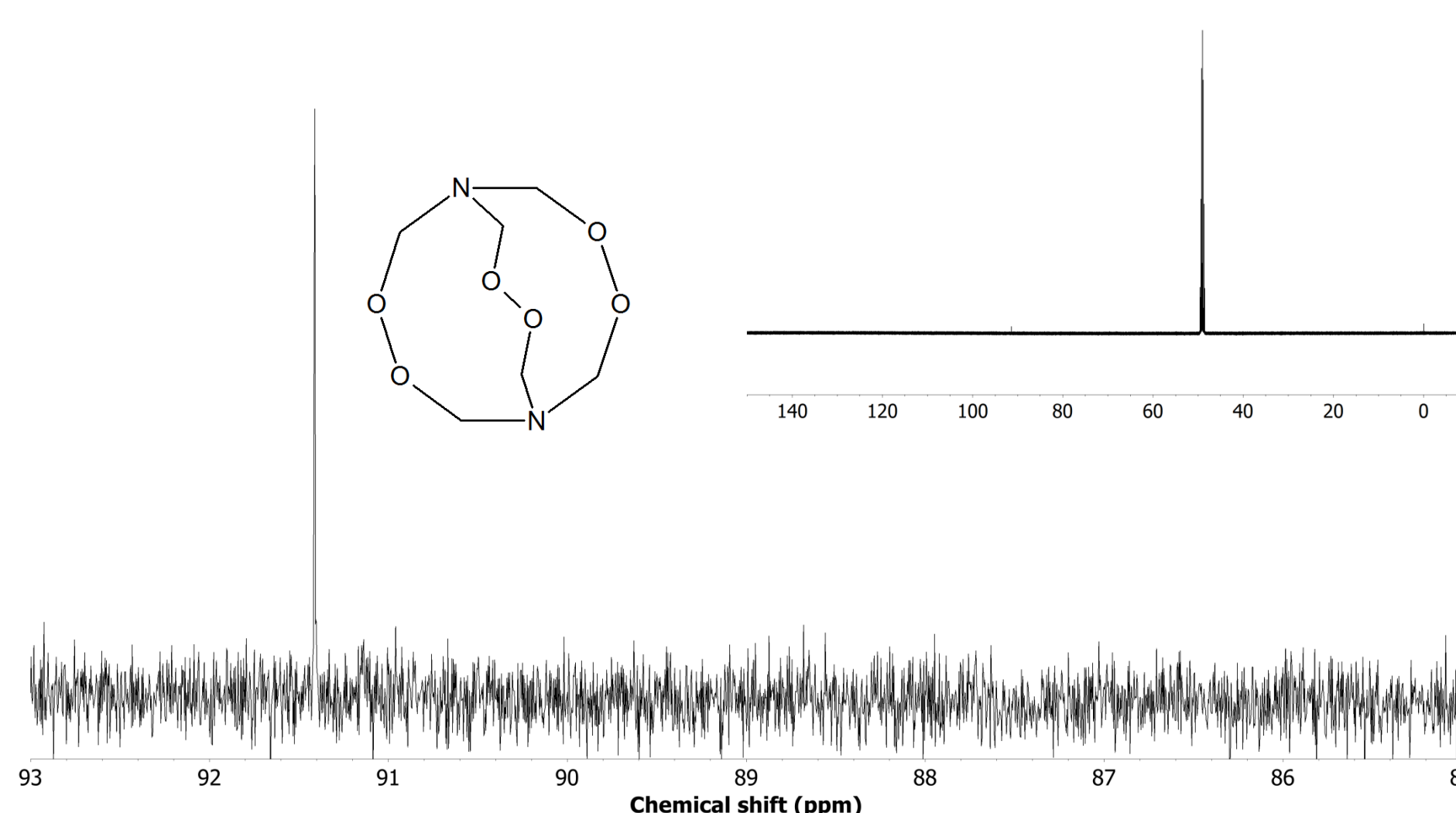


Figure 3. ¹³C 1D NMR spectrum of HMTD in CD₃OD

A preliminary CHARMM molecular force field model was constructed for TMD³ chelation of alkali and alkaline earth metal ions. Ball and stick representations for sodiated and potassiated molecules are shown in Figure 4 below.

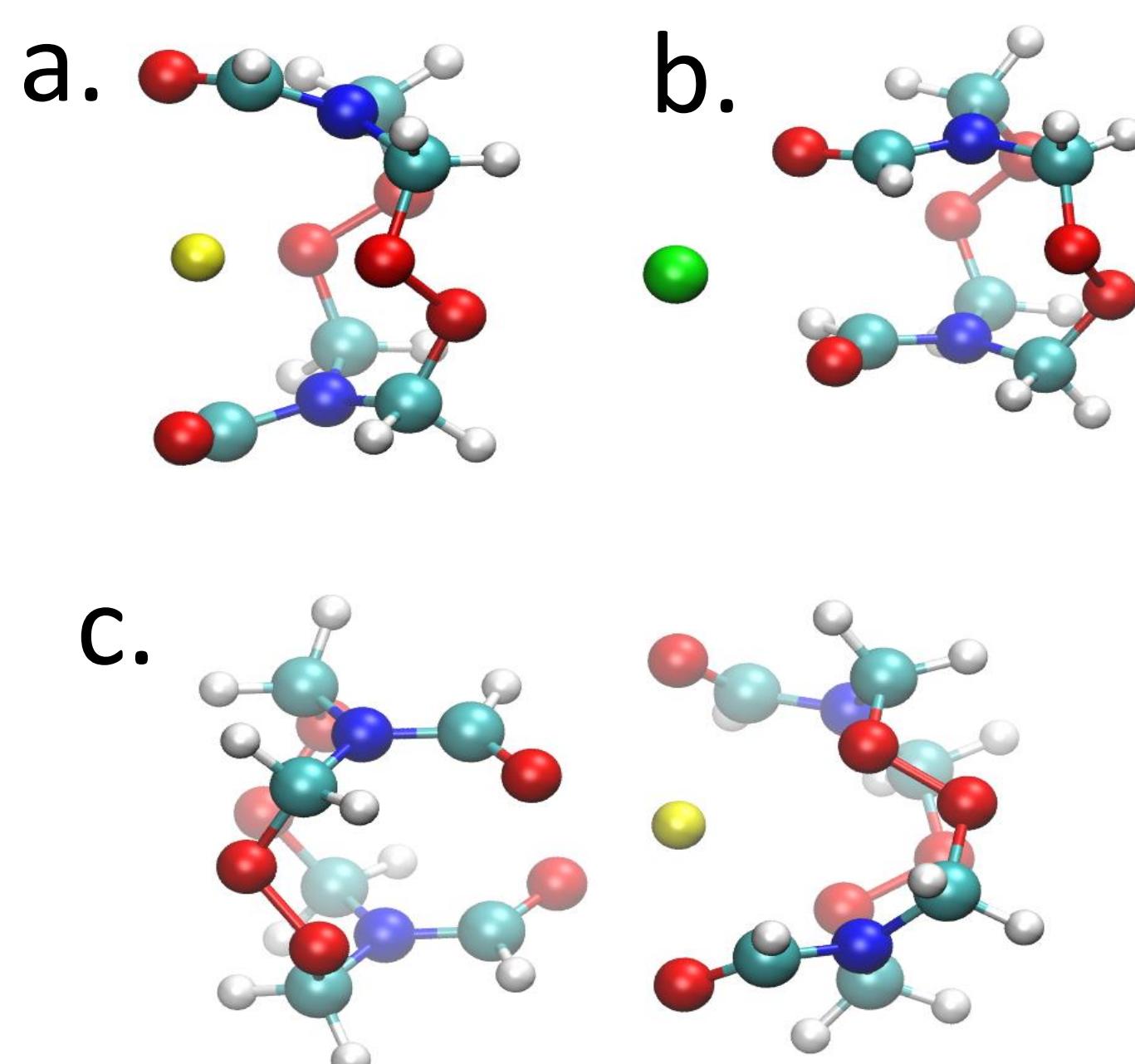


Figure 4. Molecular modeling results for chelation of metal ions by TMD³: a. Na⁺ chelation by TMD³ monomer. b. K⁺ chelation by TMD³ monomer. c. Na⁺ chelation by TMD³ dimer.

Results cont'd:

When analyzing TATP by SAWN-MS, no molecular ion was observed. As shown in Figure 5 below, sodiated forms of two distinct polymer series separated by 74 m/z dominate the spectrum. These series have been previously reported as reaction intermediates [4] although this appears to not be the case here.

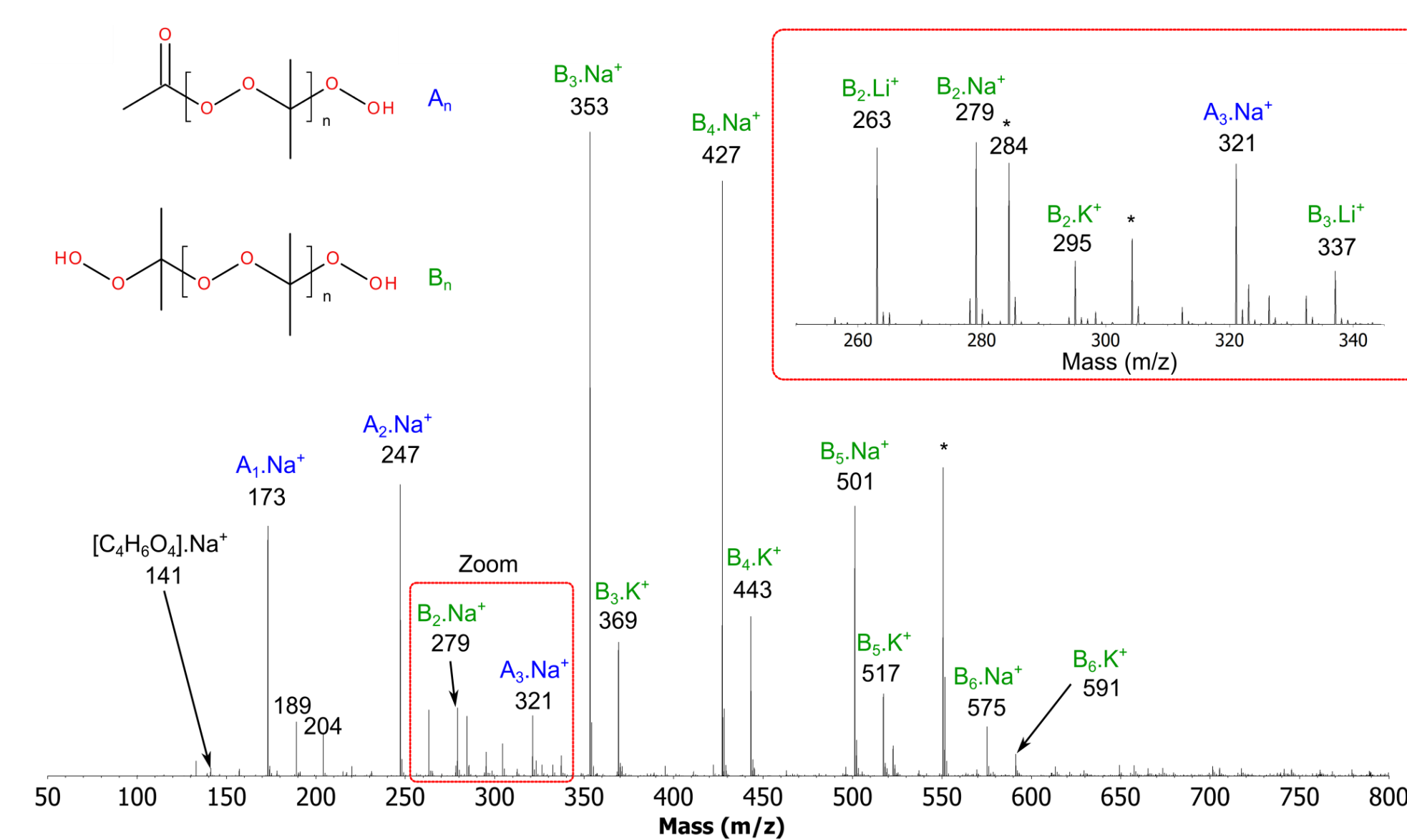


Figure 5. SAWN-TOF mass spectrum of TATP

As demonstrated in Figure 6 below, metal ion adduction to these "intermediates" can be manipulated by changing the concentration of a particular cation in solution.

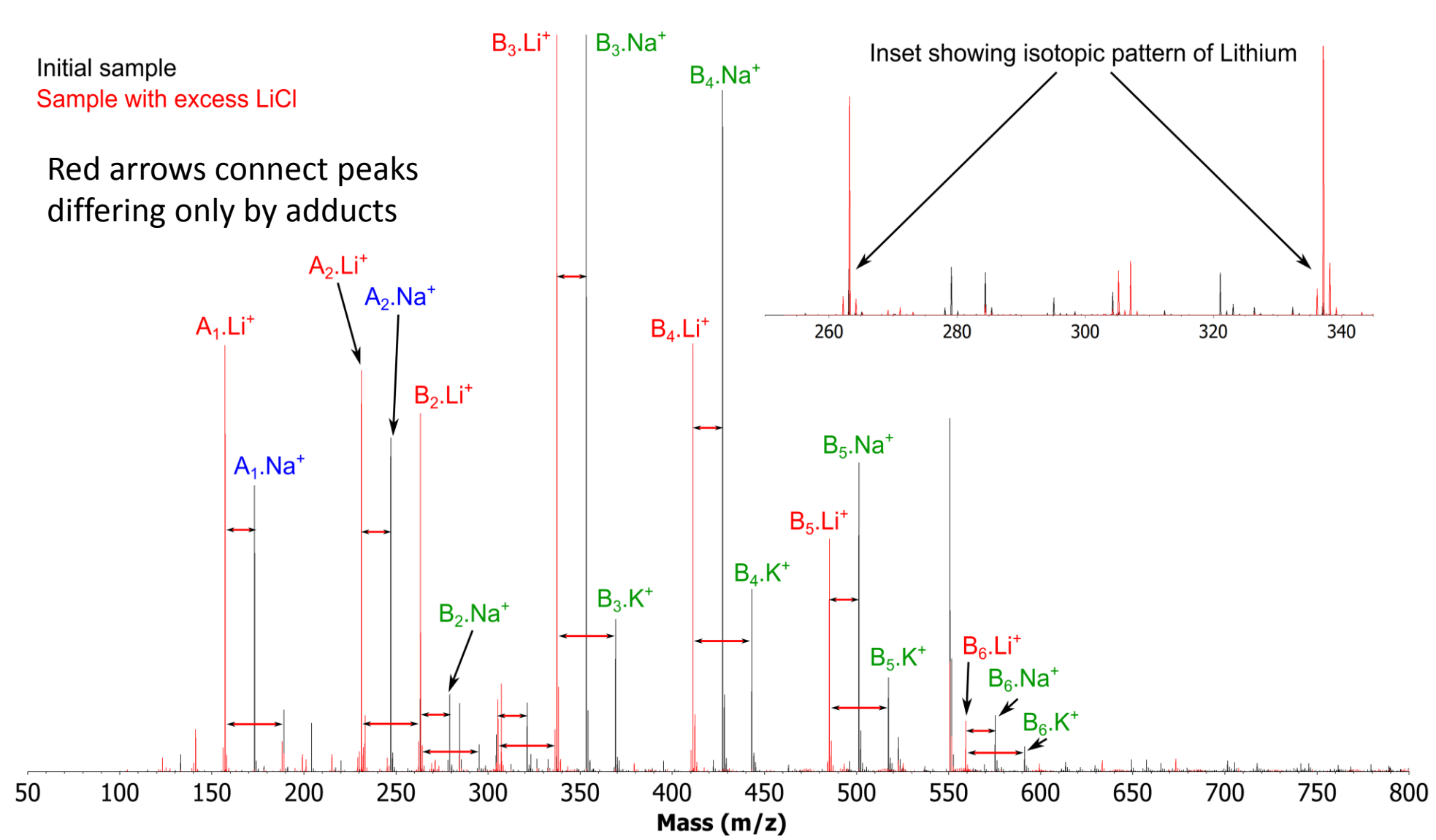


Figure 6. SAWN-TOF mass spectrum of TATP (black) overlaid with mass spectrum of TATP solution with excess LiCl added (red)

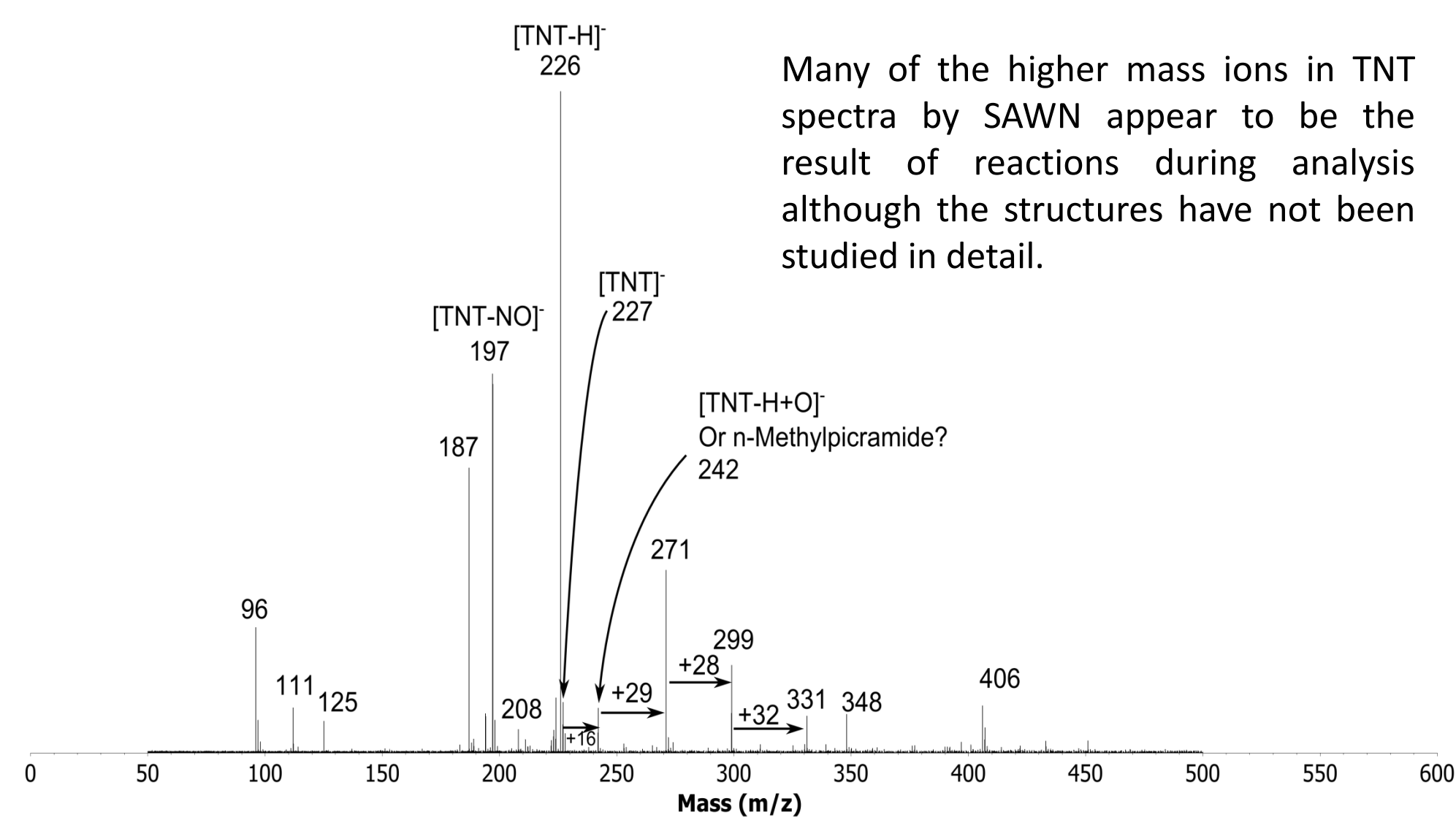


Figure 7. SAWN-TOF mass spectrum of TNT (Peak assignments from [5])

Discussion and Conclusions:

Comparing the results for SAWN and ESI indicates that SAWN is a softer ionization source – for example, both the molecular ion and dimer of HMTD are prominent peaks in the analysis of an HMTD solution by SAWN, whereas they are absent in the same solution analyzed by ESI. In the presence of Heineken (data not shown), the potassiated molecular ion dominates the spectrum. One feature of note in the SAWN MS spectrum of HMTD is that the molecular ion is apparently oxidized to its dialdehyde form during ionization. Proton and carbon NMR experiments confirm that the only measurable component in the HMTD solution is HMTD, not the oxidized form. Future experiments will include SAWN-MS in an oxygen depleted environment. Interestingly, spectra of peroxide explosives can be easily manipulated by changing metal ion composition of the matrix. It is unlikely that prevalent ions in the mass spectra for HMTD and TATP are reaction intermediates as previously reported for ESI. They are most likely oxidation products formed during ionization.

References:

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