



# University of Wuppertal

## Comparative study of fatty alcohol alkoxyate copolymers fragmentation patterns by MALDI-MS/MS using low energy and high energy CID

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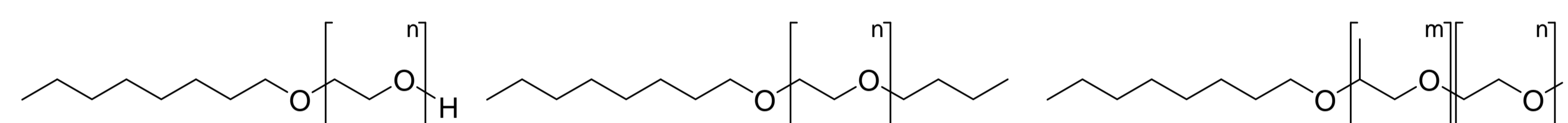
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### Introduction

The class of fatty alcohol alkoxyates describes surfactants that are synthesised by reaction of fatty alcohols with alkoxydes like ethylene oxide, propylene oxide and others. Fatty alcohol alkoxyates are used as nonionic surfactants in home and industrial cleaning and washing agents. They have important properties like foam suppression, foam control and wetting effects in these products. Furthermore alkoxyates are also relevant in a broad range of chemical industry applications (e.g. in coating and polymerisation additives or agrochemicals), where these serve as dispersal agents and emulsifiers.



Structures of different fatty alcohol alkoxyate copolymers analysed

Here we present a comparative analysis of fatty alcohol alkoxyate copolymers using MALDI-MS/MS with low energy trap and high energy collision cell technique.

### Results

#### ethoxylated fatty alcohol, not endcapped

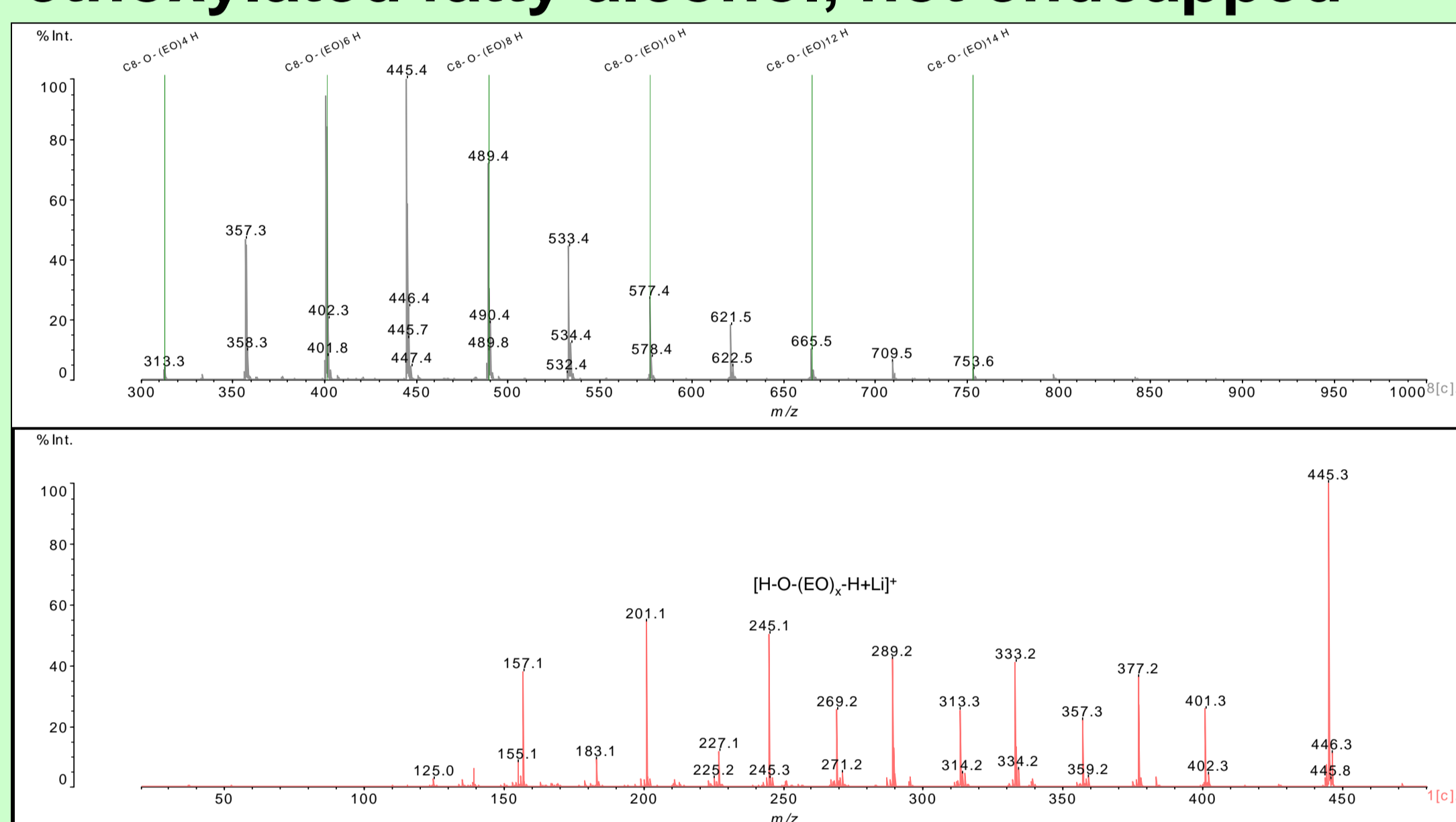


Figure 1: MALDI-Trap-TOF spectrum  $[M+Li]^+$  and MALDI low energy CID MS/MS spectrum of precursor ion  $[M+Li]^+$   $m/z$  489

#### ethoxylated fatty alcohol, n-butyl endcapped

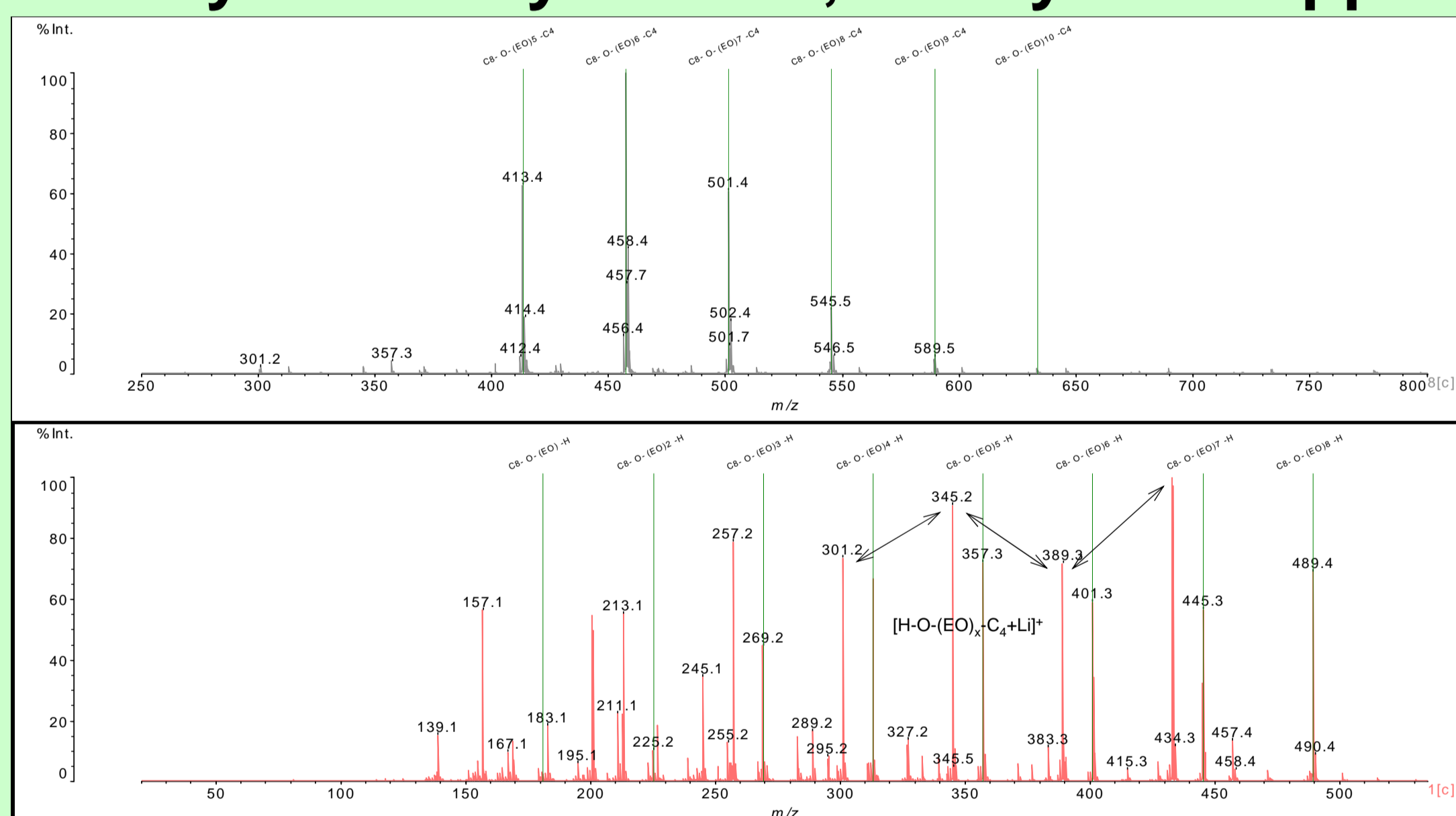


Figure 3: MALDI-Trap-TOF spectrum  $[M+Li]^+$  and MALDI low energy CID MS/MS spectrum of precursor ion  $[M+Li]^+$   $m/z$  545

#### fatty alcohol - PO/EO - block copolymer

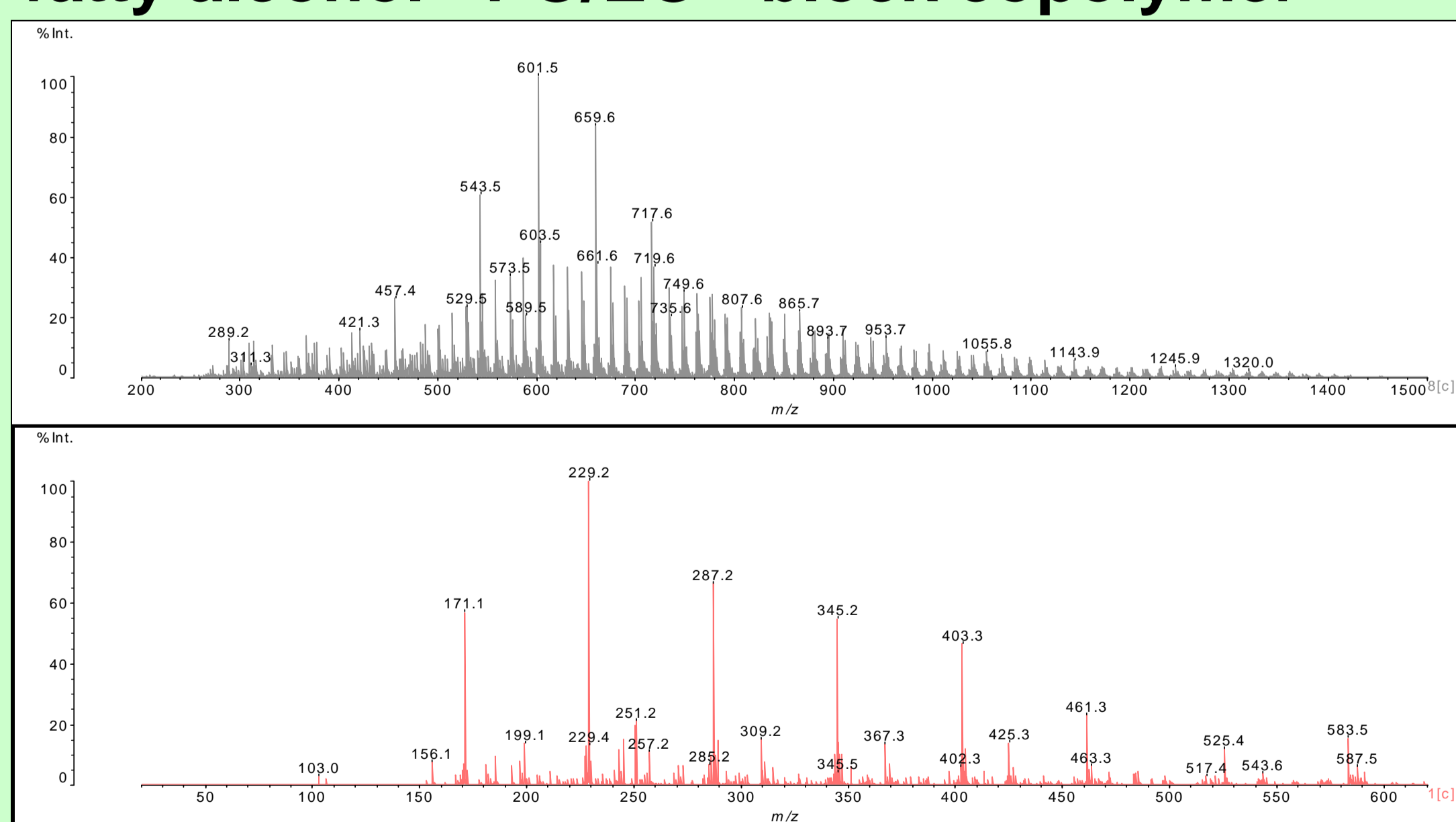


Figure 5: MALDI-Trap-TOF spectrum  $[M+Li]^+$  and MALDI low energy CID MS/MS spectrum of precursor ion  $[M+Li]^+$   $m/z$  631.5

Samples were diluted in THF to a concentration of 4 mg/ml. Cationizing salts were used at concentrations of 0.1 mol/l in MeOH/water (volume ratio 1:1). MALDI measurements were performed with Dithranol, 10 mg/ml in THF. The target spot was pre-coated with 1.3 µl of the salt solution. Sample and matrix solutions were premixed in a volume ratio of 1:1 and applied onto the MALDI target.

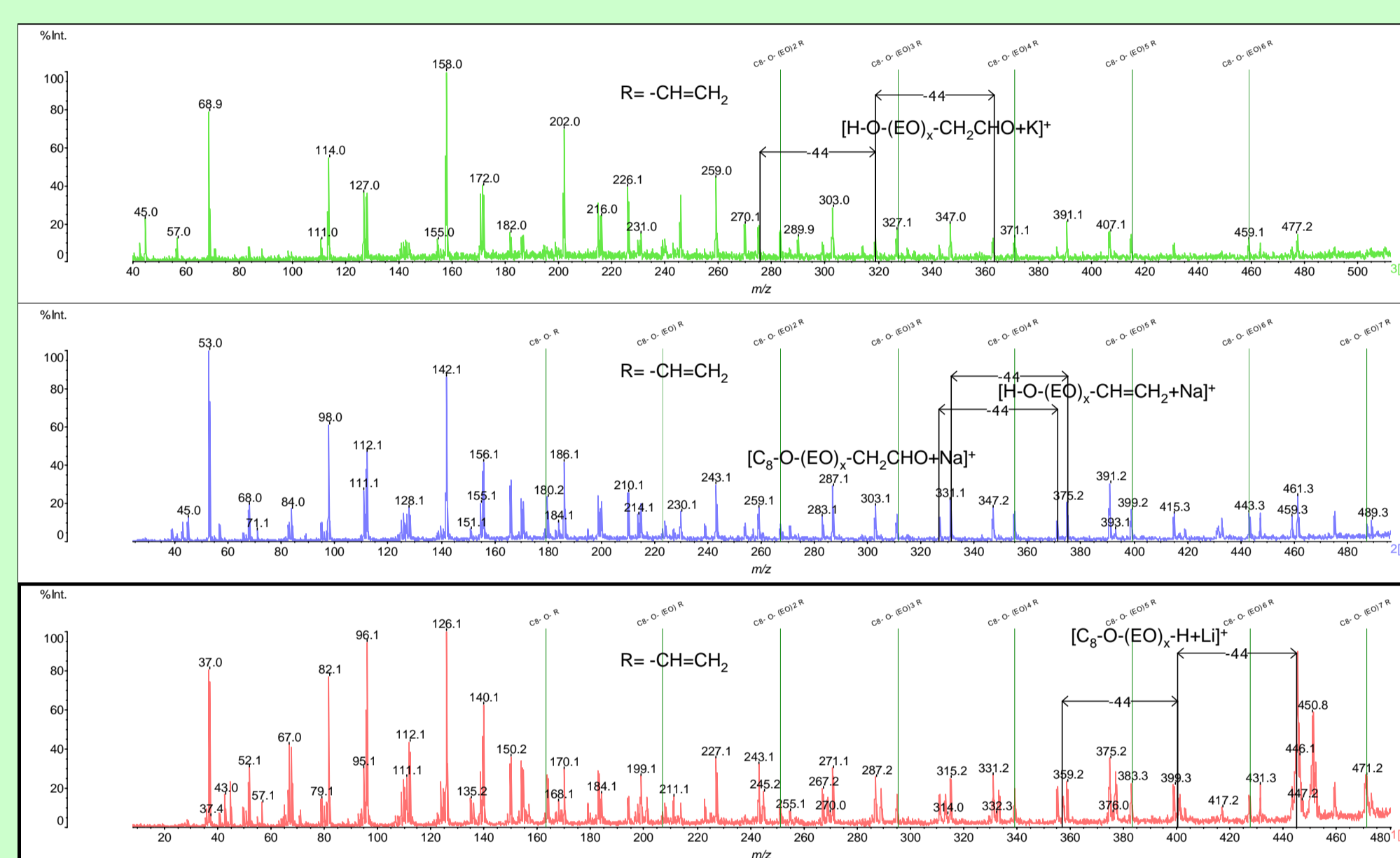


Figure 2: MALDI high energy CID MS/MS spectra of precursor ions  $[M+Li]^+$   $m/z$  489,  $[M+Na]^+$   $m/z$  505 and  $[M+K]^+$   $m/z$  521

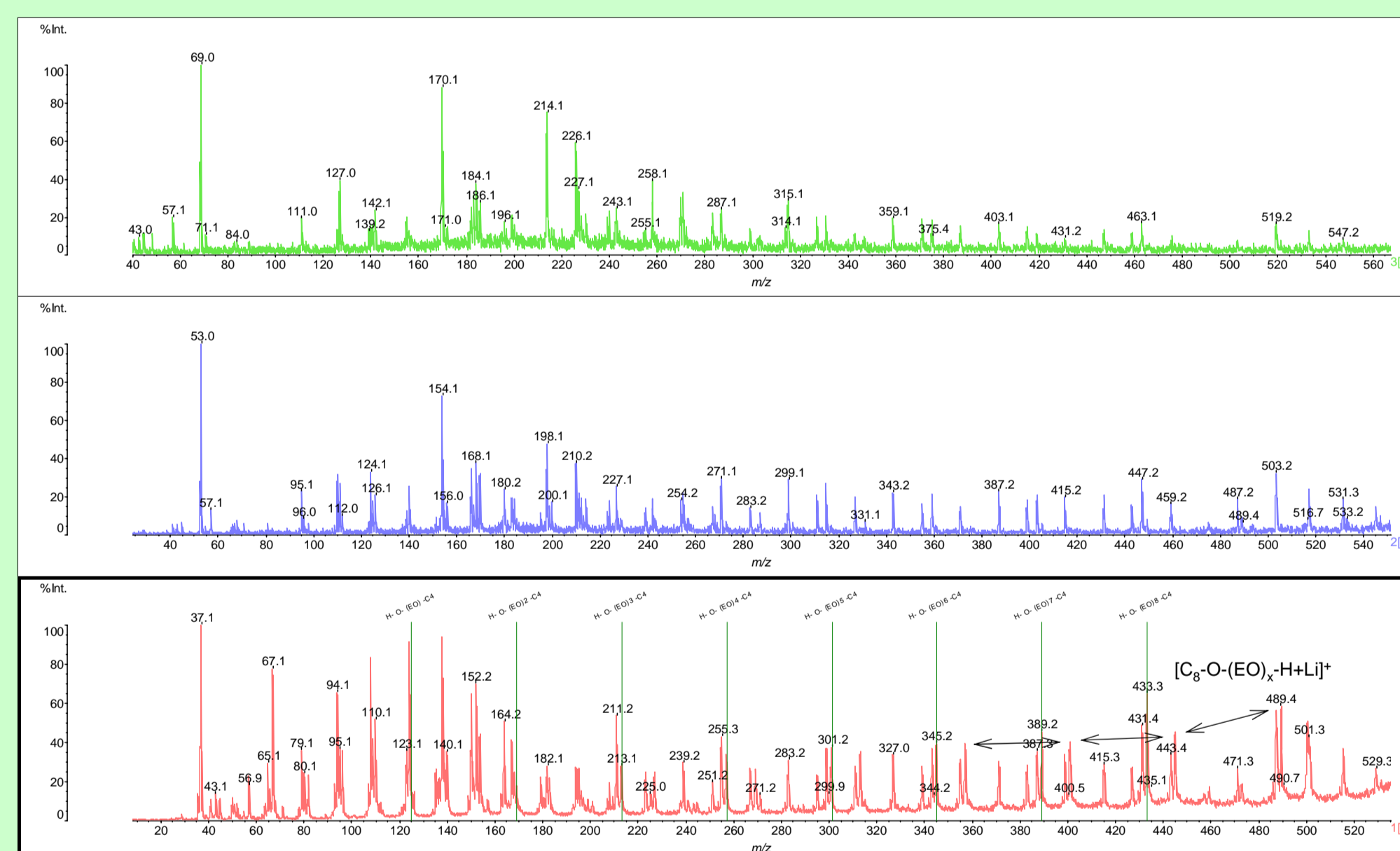


Figure 4: MALDI high energy CID MS/MS spectra of precursor ions  $[M+Li]^+$   $m/z$  545,  $[M+Na]^+$   $m/z$  561 and  $[M+K]^+$   $m/z$  577

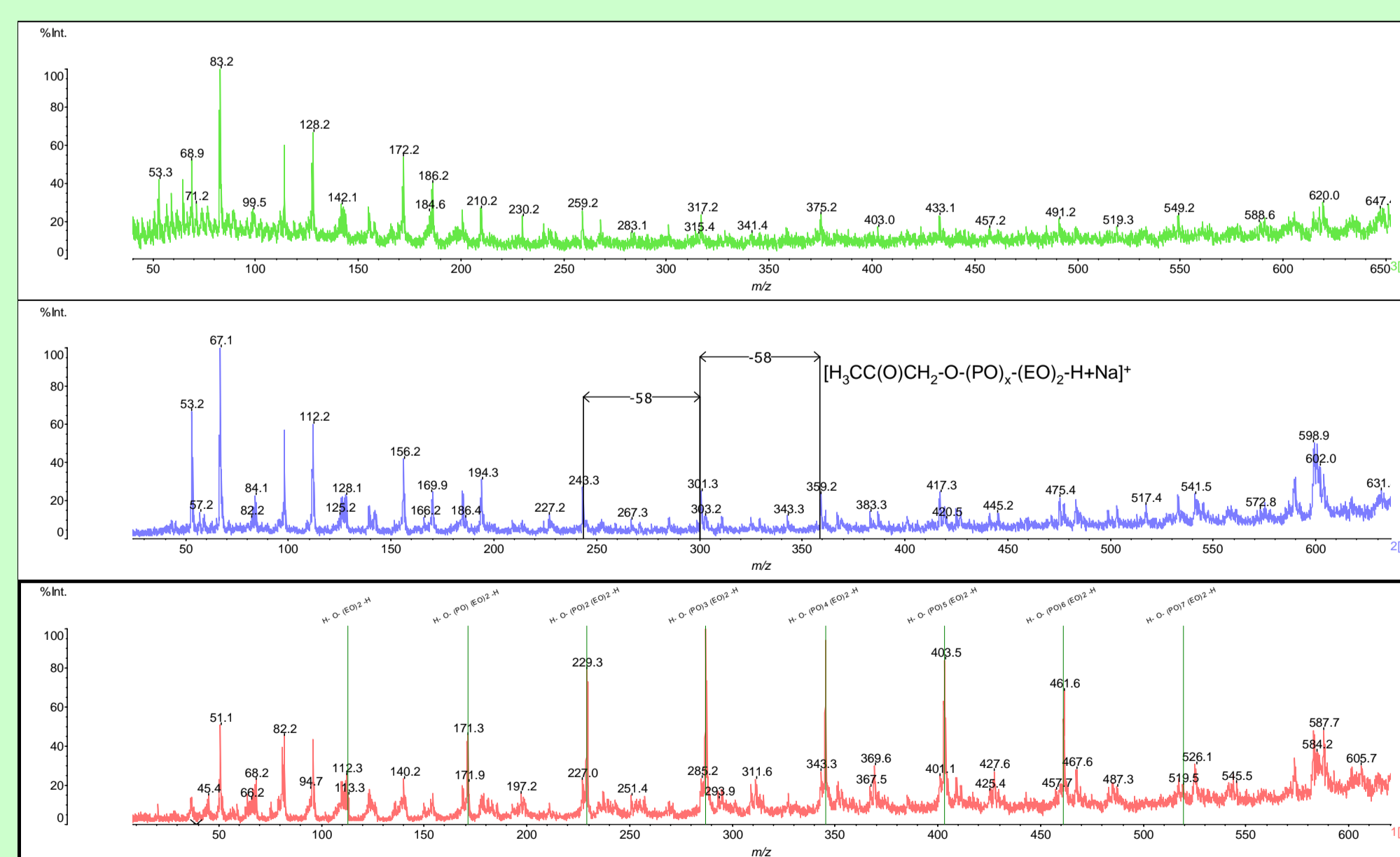


Figure 6: MALDI high energy CID MS/MS spectra of precursor ions  $[M+Li]^+$   $m/z$  631.5,  $[M+Na]^+$   $m/z$  647.5 and  $[M+K]^+$   $m/z$  663.5

High energy CID MS/MS experiments were performed using a MALDI-reflectron-TOF mass spectrometer (AXIMA Performance™, Shimadzu Biotech, Manchester, UK). The accelerating voltage used was 20 kV. Helium was used as collision gas.

Low energy CID MS/MS experiments were performed using a MALDI-Trap-TOF hybrid mass spectrometer (AXIMA Resonance™, Shimadzu Biotech, Manchester, UK). Argon was used as collision gas.

High energy CID MALDI MS/MS spectra of fatty alcohol alkoxyate copolymers show different fragmentation patterns for alkali adduct ions. The spectra show additional fragmentation information for the Li adduct ion compared to the fragment spectra of the sodium and potassium adduct ions (Fig. 2, 4, 6). While the fragmentation of sodium and potassium adducts results in vinyl- or carbonyl- endgroups lithium adducts additionally show ethoxy- or propoxy- group reduced hydroxyl group fragments (red CID spectra in Fig. 2, 4).

Low energy CID MALDI MS/MS spectra show less fragmentation patterns (hydroxyl group fragments) for the Li adduct (Fig. 1, 3, 5) in comparison to the high energy CID MALDI MS/MS spectra shown. The additional fragmentation information can only be obtained from high energy CID experiments exclusively. The low energy CID MALDI MS/MS spectrum of the n-butyl endcapped polymer shows fragmentation by starting with an octyl- and also with a butyl-group cleavage (Fig. 3).

As a general rule, the energy transferred in a low energy CID event of a lithium adduct should be sufficient enough to break one bond by cleavage of one monomer unit without subsequent rearrangement to a vinyl- or carbonyl-endgroup. High energy CID MALDI MS/MS events result in less selective fragmentations (Fig. 2, 4).

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### Discussion and Conclusion

MALDI-MS/MS was successfully used for the endgroup identification of alkoxyated fatty alcohols. In connection with these results alkali adduct ions of such copolymers show differences in fragmentation patterns related to high energy and low energy CID. Low energy CID MALDI MS/MS experiments and the use of lithium salts as cationisation reagents can be meaningful for a simplified characterisation of these copolymer products.

### References

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