

# Molecular characterisation of biogenic secondary organic aerosols using ion mobility spectrometry - quadrupole time-of-flight mass spectrometry

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## Introduction

Molecular characterisation of unknown organic compounds is challenging, in particular the molecular identification of secondary organic aerosol constituents is extremely demanding due to their low quantities and high complexity of the sample matrix. The presence of multiple structural isomers and their complex structures often make the synthesis of reference compounds very difficult, hindering a positive identification of these compounds.

Traditionally, chromatographic separation is coupled to mass spectrometry for the structural elucidation of unknown compounds in atmospheric aerosol samples. Chromatographic separation provides information on the volatility or polarity of the unknowns and mass spectrometry provides their structural and/or molecular mass information. In particular, the applications of derivatisation GC/MS and HPLC/ESI-MS techniques in recent years brought significant advances in our understanding of SOA constituent structures, leading to the identification of methyltetrols from isoprene oxidation (Claeys et al., 2004), tricarboxylic acid from  $\alpha$ -pinene oxidation (Szmigielski et al., 2007), and structural proposals for various organosulfates (Gómez-González et al., 2008; Iinuma et al., 2007ab, 2009; Surratt et al., 2007, 2008)

Ion mobility spectrometry coupled to mass spectrometry (IMS-MS) is an analytical tool which offers a rapid separation of molecules by their mobilities in the gas phase, hence their collision cross-sections (CCS). The CCSs of the ions can be calculated through the measurement of ion mobilities, and structural information of the ions can be obtained by comparison with computer model estimated CCSs. Here we provide the results from the first application of IMS-TOFMS on molecular characterisation of monoterpene originating organosulfates and nitroxy-organosulfates.

## Methods

### Instrumentation

Samples were analysed using an ultra performance liquid chromatography coupled to electrospray ionisation ion mobility spectrometry and quadrupole time-of-flight mass spectrometry (UPLC/(-)ESI-IMS-QTOFMS, Waters Synapt HDMS). Figures 1 and 2 show schematic diagrams of the IMS-QTOFMS used in this study.

The drift times of ions in the IMS are linearly related to their mobilities. The mobility ( $K$ ) of a gas phase ion is defined as  $K = v_D/E$  where  $v_D$  and  $E$  are the drift velocity and the electric field, respectively. The mobility is related to CCS as follows:

$$K = \frac{\sqrt{18\pi}}{16} \sqrt{\frac{1}{m} + \frac{1}{m_B}} \frac{q}{\sqrt{kT}} \frac{1}{N\Omega}$$

where  
 $q$ : ion charge  
 $m$ : mass of ion,  $m_B$ : mass of buffer gas  
 $k$ : Boltzmann constant  
 $T$ : temperature  
 $N$ : buffer gas number density  
 $\Omega$ : collision cross section

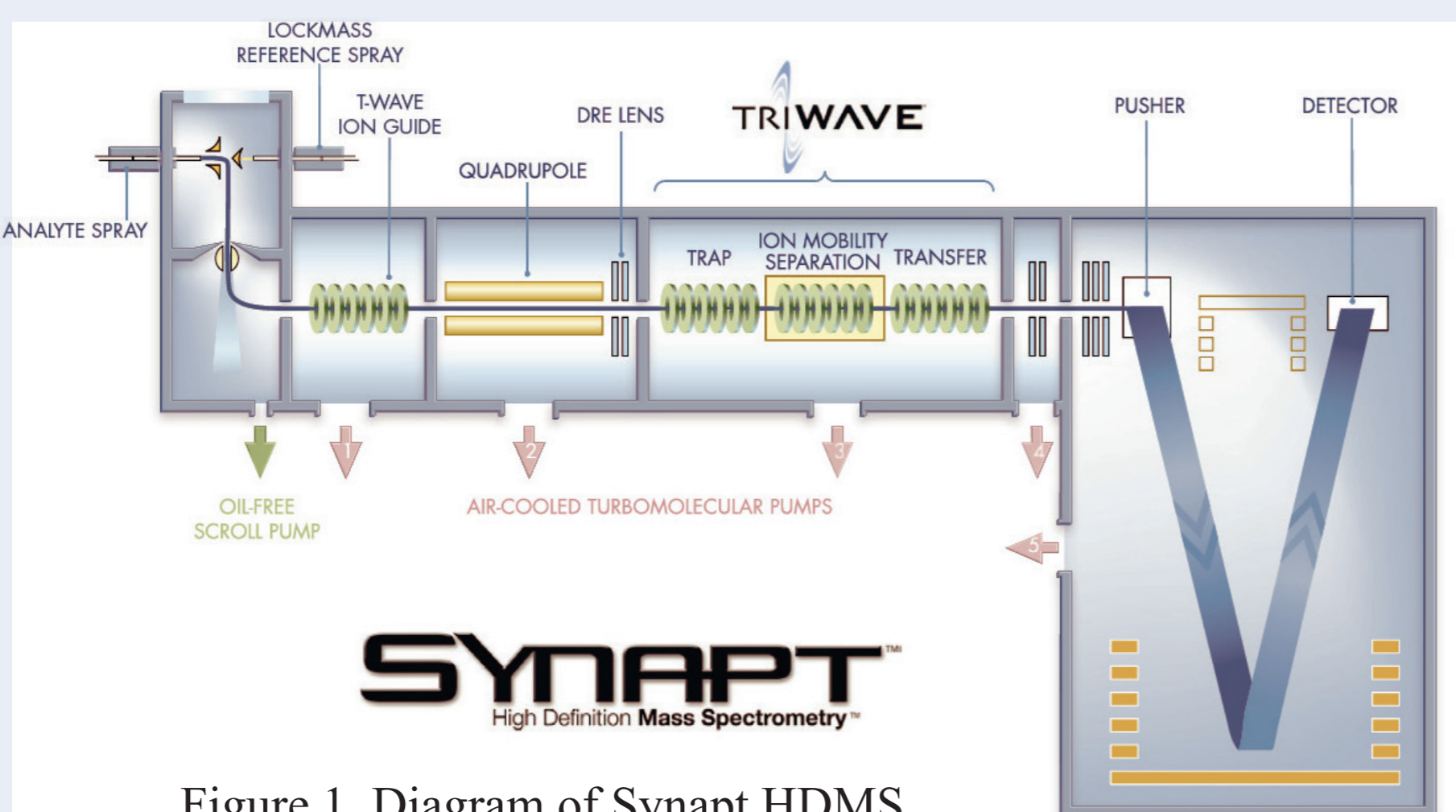


Figure 1. Diagram of Synapt HDMS

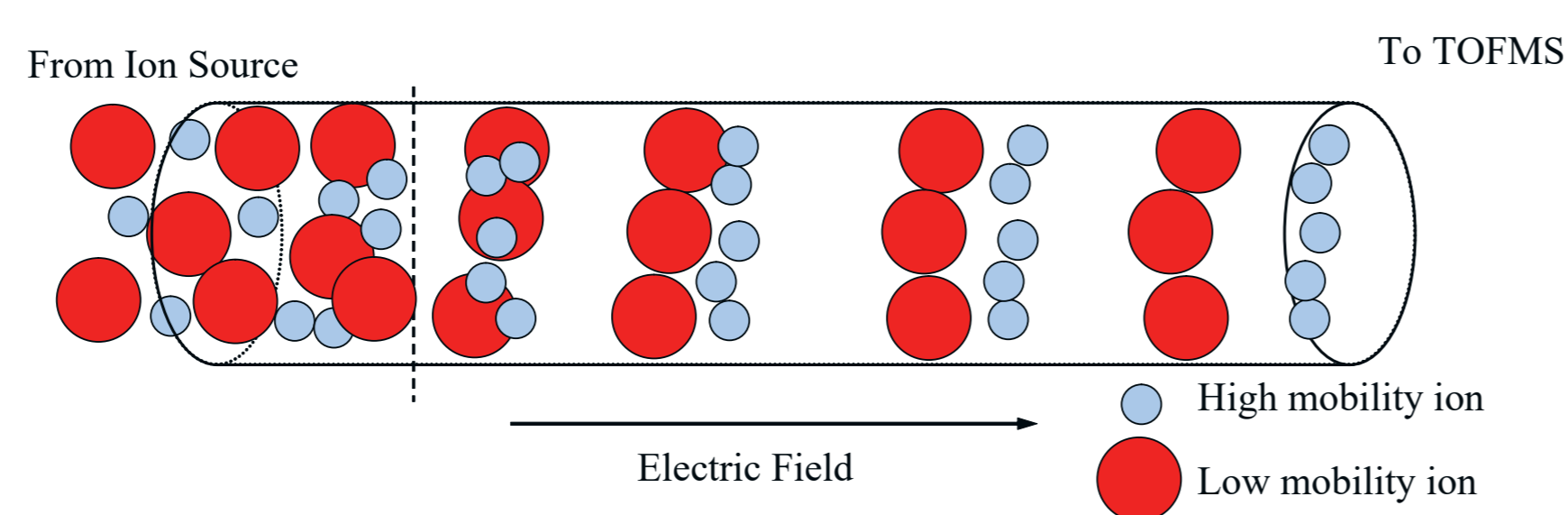


Figure 2. Separation of gas phase ions in a drift tube

When the accurate  $T$  and  $N$  cannot be measured, ions of known CCSs can be used to calibrate the drift time measurements (Ruotolo et al., 2008). In the present study, CCS values available for polyamino acids (Wytenbach et al., 1998; Henderson et al., 1999) are used for the calibration of the instrument. Figure 3 shows a calibration curve used in this study. The correlation coefficient,  $R^2 > 0.99$ , is sufficiently higher than the recommended value of 0.98 in Ruotolo et al. (2008).

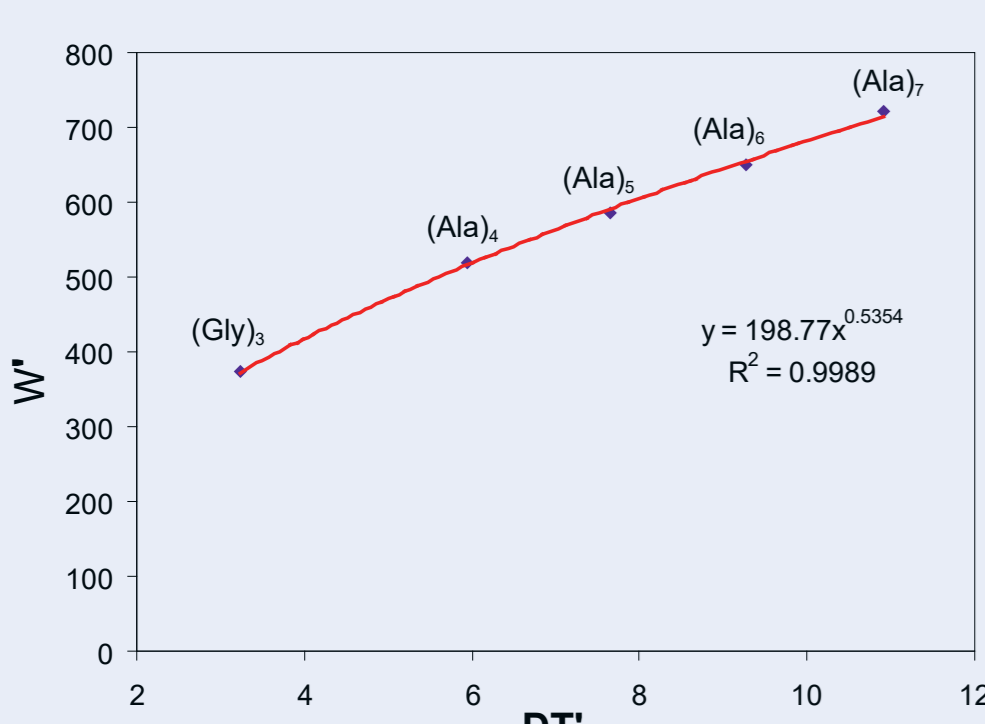


Figure 3.  $W'$  as a function of  $DT'$ . Gly = glycine. Ala = Alanine.

### Molecular modelling

Detailed protocol for CCS estimation reported by Ruotolo et al. (2008) is used in the present study. Briefly, CCSs are estimated using open source software MOBCAL (Mesleh et al., 1996). A molecular coordinate file that contains a structure of target compound is created using Maestro software (Schrödinger, <http://www.schrodinger.com/>). A trajectory method is used to estimate CCSs.

## References

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## Results and discussion

### $\alpha$ -Pinene originating organosulfates

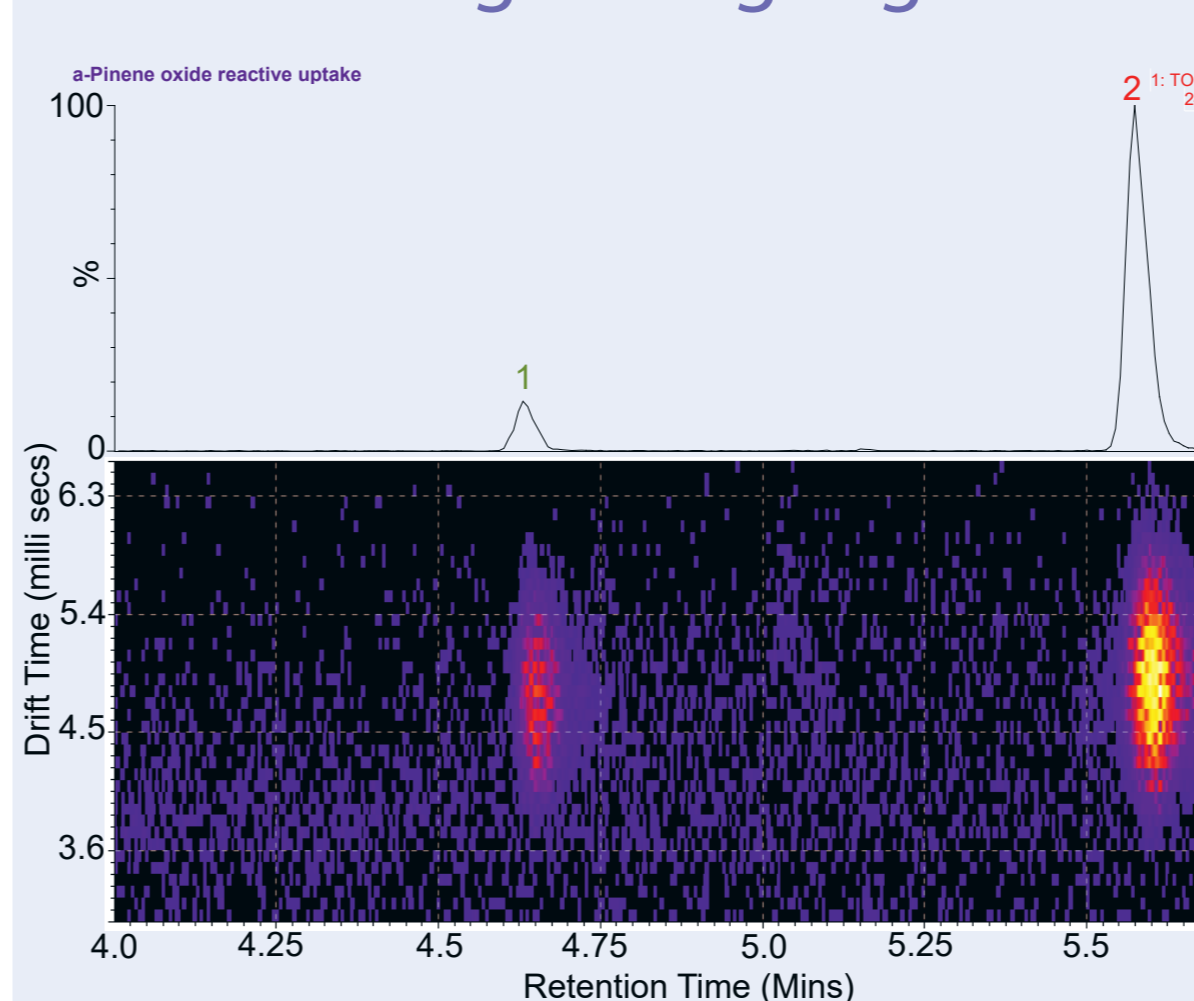


Figure 4 shows an extracted ion chromatogram (EIC), drift times and fragmentation patterns for  $\alpha$ -pinene originating organosulfates ( $C_{10}H_{17}O_5S$ ,  $m/z$  249.0802) reported in Surratt et al. (2008) and Iinuma et al. (2009). Peak 1 produces a  $SO_4$  radical ( $m/z$  95.9), a characteristic fragment for a tertiary carbon substituted organosulfates. Peak 2 produces only  $HSO_4$  ion ( $m/z$  96.9), indicating that this peak corresponds to a secondary carbon substituted isomer.

Based on the modelled and measured CCS values, the peak 1 is likely a 2S, 3S structure. No stereoisomer information can be obtained for the peak 2 as estimated CCSs agreed well for both isomers.

Peak	Measured CCS ( $\text{Å}^2$ )	MOBCAL estimated CCS ( $\text{Å}^2$ )	Error %
Peak 1	89.3	88.2 / 85.0	1.2 / 4.8
Peak 2	91.2	90.9 / 91.0	0.3 / 0.2

\*It is noted that only trans isomers are expected from acid catalysed nucleophilic addition of sulfate to  $\alpha$ -pinene oxide which was used as a precursor compound.

Figure 4. EIC (top), drift times (middle) and fragmentation data (bottom) for  $m/z$  249.

### $\beta$ -Pinene originating organosulfates

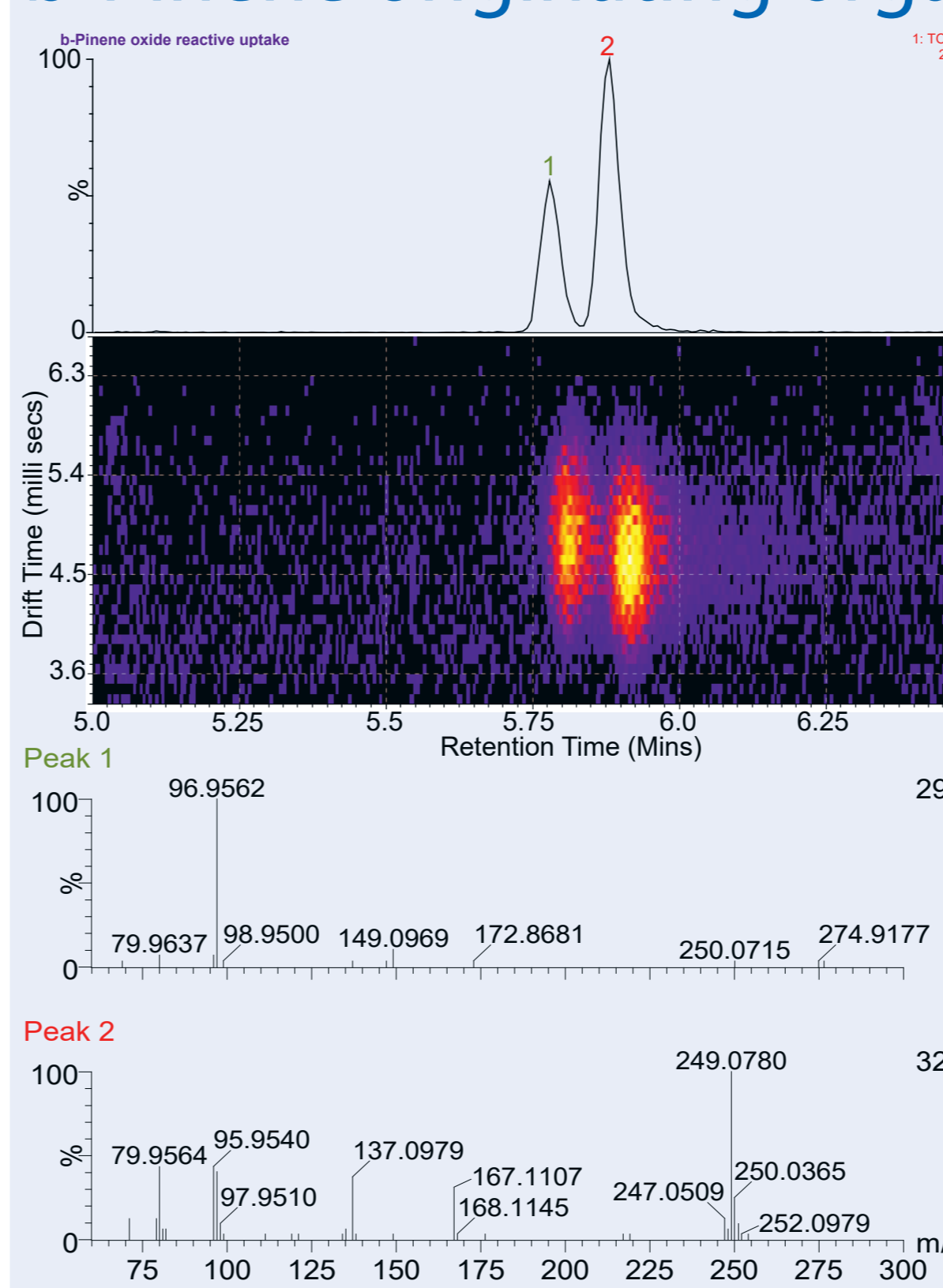


Figure 5 shows an EIC, drift times and fragmentation patterns for  $\beta$ -pinene originating organosulfates ( $C_{10}H_{17}O_5S$ ,  $m/z$  249.0802) reported in Surratt et al. (2008) and Iinuma et al. (2007a, 2009). The peak 1 is assigned to a primary carbon substituted organosulfate and the peak 2 is assigned to a tertiary carbon substituted isomer based on the fragmentation data. Measured CCSs are somewhat smaller than the estimated CCSs for the peak 1. This likely originates from an H-bond between a sulfate and a hydroxyl group as the inclusion of H-bond in the model structure makes the estimated CCS values closer to the measured CCS.

Peak	Measured CCS ( $\text{Å}^2$ )	MOBCAL estimated CCS ( $\text{Å}^2$ )	Error %	MOBCAL estimated CCS with H-bond ( $\text{Å}^2$ )	Error %
Peak 1	94.2	89.3	-4.4%	88.4	-1.7%
Peak 2	90.2	88.6	-1.8%	88.9	-0.6%

Figure 5. EIC (top), drift times (middle) and fragmentation data (bottom) for  $m/z$  249.

### Nitroxy-organosulfates (NOS) originating from monoterpenes

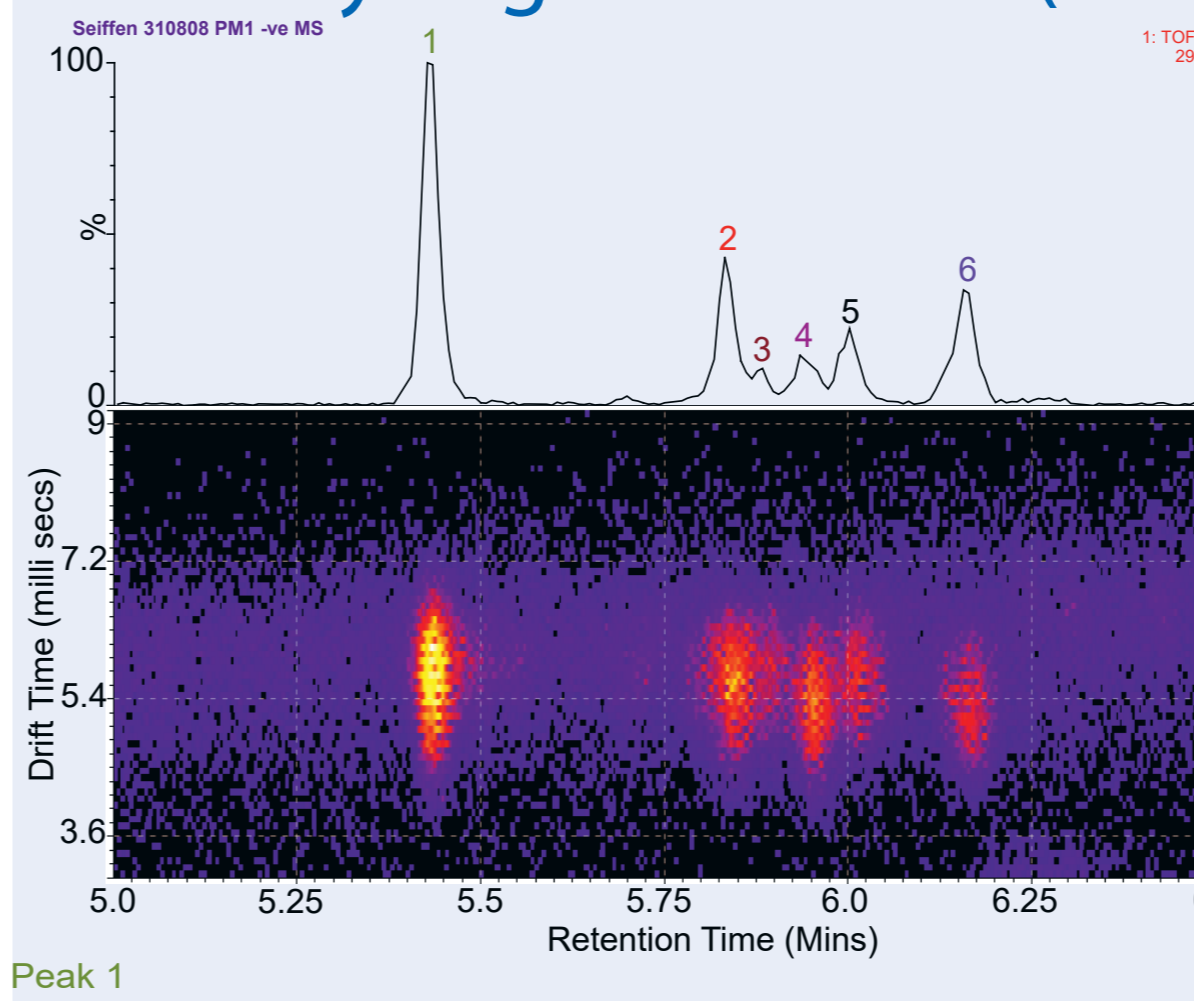


Figure 6 shows an EIC, drift times and fragmentation patterns for NOSs originating from monoterpenes ( $C_{10}H_{16}NO_7S$ ,  $m/z$  294.0653) reported in Iinuma et al. (2007a) and Surratt et al. (2008). Only  $\alpha$ -pinene originating NOSs are compared in this study as no other monoterpenes are reported to produce atmospherically relevant NOSs so far (Surratt et al., 2008). Six peaks are observed in the EIC. Peaks 1-5 produce  $SO_4$  radical, suggesting a sulfate group at a tertiary carbon atom for these peaks (tNOS). Estimated CCSs for tNOS agree well with measured CCSs for the peaks 1-5. The measured CCS for the peak 4 is somewhat smaller than the others, inferring a Z isomer structure for this peak. Measured and estimated CCSs for NOS with a sulfate group at a secondary carbon atom (sNOS) did not agree well (peak 6). Further study is needed to elucidate the structure of this peak.

Peak	Measured CCS ( $\text{Å}^2$ )	MOBCAL estimated CCS ( $\text{Å}^2$ )	Error %
Peak 1	99.3	98.4	-0.9%
Peak 2	99.5	96.7	-2.8%
Peak 3	98.4	96.7	-1.7%
Peak 4	98.4	96.7	-1.7%
Peak 5	96.7	96.7	0%
Peak 6	96.7	96.7	0%

tNOS: NOS with sulfate group at tertiary carbon atom; sNOS: NOS with sulfate group at secondary carbon atom.

Peak	Measured CCS ( $\text{Å}^2$ )	MOBCAL estimated CCS ( $\text{Å}^2$ )	Error %
Peak 1	99.3	98.4	-0.9%
Peak 2	99.5	96.7	-2.8%
Peak 3	98.4	96.7	-1.7%
Peak 4	98.4	96.7	-1.7%
Peak 5	96.7	96.7	0%
Peak 6	96.7	96.7	0%

Figure 6. EIC (top), drift times (middle) and fragmentation data (bottom) for  $m/z$  294.

### Summary

- Structural isomers with less than a few  $\text{Å}^2$  CCS difference can be separated using IMS-TOFMS.
- A combination of measured and estimated CCS allows us to infer structural information of stereoisomers.