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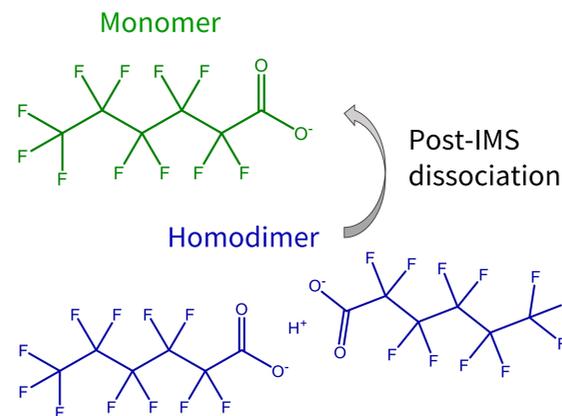
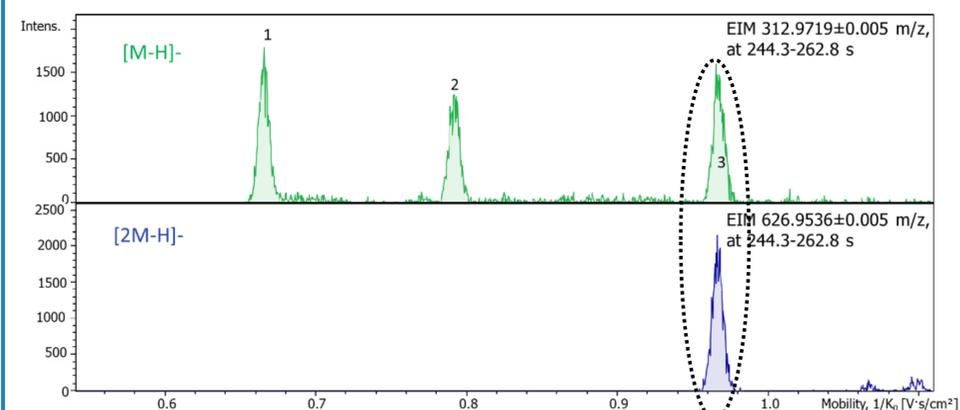
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## Ion mobility for PFAS

Per- and polyfluoroalkyl substances (PFASs) are emerging pollutants of great concern, with over 5,000 compounds currently reported. Hyphenated techniques such as ion mobility spectrometry (IMS) coupled with LC-HMRS is a promising approach for the non-targeted screening of these substances due to improved peak capacity of the LC-IMS-MS coupling. In addition, the extracted collision cross-section (CCS) can be seen as a descriptor related to the bulk apparent density of gas-phase ions, providing an additional point of identification. In the case of PFASs, CCS-m/z trends are observed and help the evaluation of the shape evolution when increasing the -(CF<sub>2</sub>)- repeating units (as #FC) of the ions in the gas phase.

## Preliminary data : dimeric ions of PFCAs detected during LC-TIMS-TOF experiments

Perfluorohexanoic acid (PFHxA) example (5 μL of a 100 ng/mL solution)



## Methods for CCS trendlines determination

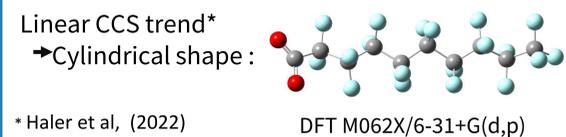
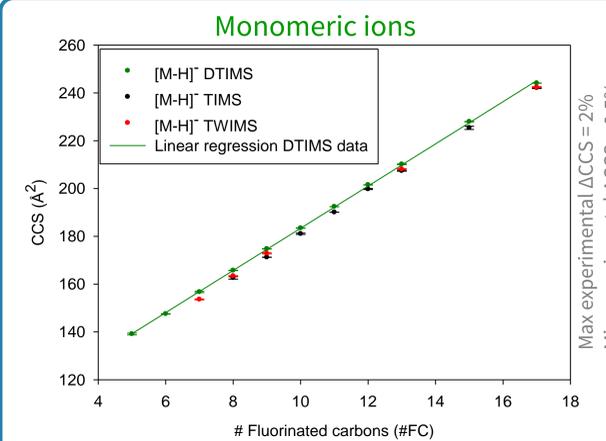
### IMS Experiments

- Direct injection of 300 ng/mL PFCA standards solutions in methanol spiked with 0.1% formic acid, in the negative electrospray ionization mode.
- The solutions were mixtures of two asymmetric PFCA homologues capable of forming isobaric dimers, e.g., C<sub>4</sub>+C<sub>14</sub> and C<sub>8</sub>+C<sub>10</sub>.
- 3 IMS set-ups (all calibrated using the Agilent Tuning Mix):
  1. Agilent 6560 DTIM-QTOF
  2. Bruker timsTOF Pro2
  3. Synapt G2 HDMS (TWIMS)

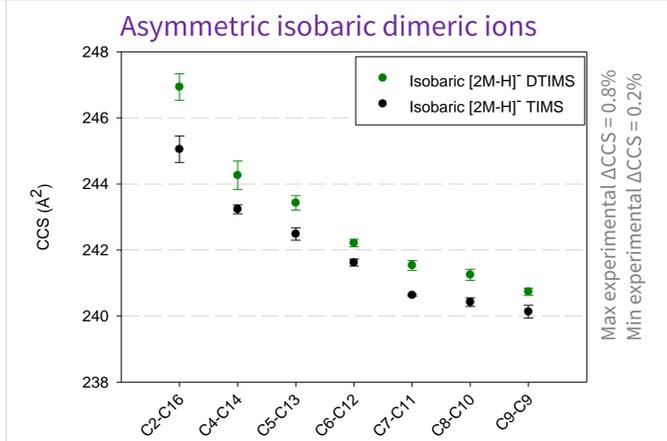
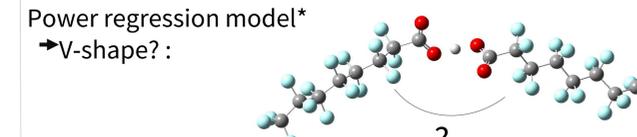
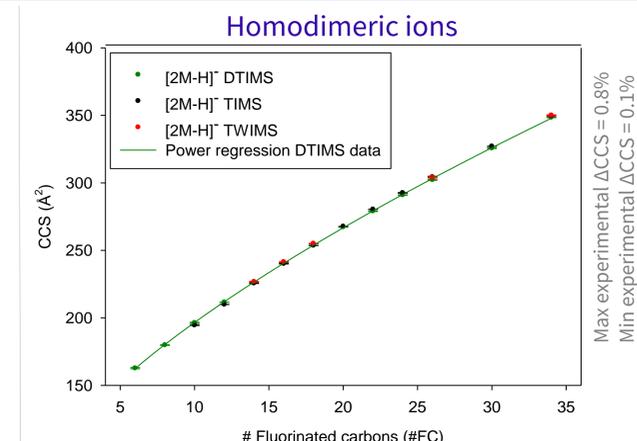
### Computational chemistry and predictions of CCS values

- 1) Geometry optimization (Gaussian 16)
  - Start with 15 initial geometries (different orientations of the two fluorinated chains with respect to the proton)
  - First pre-optimization using a semi-empirical method (PM6)
  - DFT optimization with M062X functionals and 6,31+G(d,p) orbital set
- 2) CCS predictions (IMoS software)
  - Use of the trajectory method to predict the CCS values for each optimized geometry (partial charge description = NBO)
  - Calculation of a Boltzmann-weighted (BW) CCS value for each dimer

## CCS-Fluorinated Carbon number (#FC) trendlines



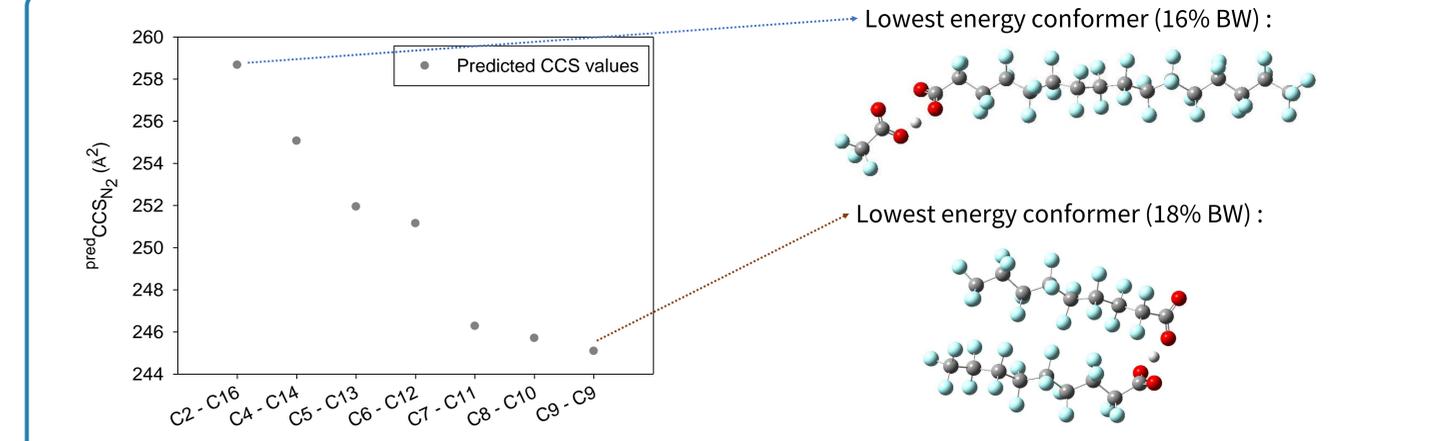
\* Haler et al, (2022)  
10.1021/jasms.1c00266



Decreasing chain length asymmetry

- The CCS values decrease with increasing symmetry
- CCS of heterodimers ruled by the longest chain

## Computational chemistry results for asymmetric isobaric dimers



Preliminary theoretical calculations suggest that as symmetry increases in the dimers, a parallel organization of the two fluorinated chains might be favored, in good agreement with the experimental CCS-m/z trends. However, the difference in theoretical CCS values between two asymmetric dimers is higher than those obtained experimentally. It could be explained by wrong assumption of the temperature (298K) during the CCS computing with IMoS. L-J parameters and NBO values might not be suitable for polyfluorinated ions, or not inadequately suited parameters in IMoS.

## Conclusions and perspectives

- The workflow used for the theoretical predictions of CCS values leads to encouraging results for the asymmetric but isobaric PFCA dimers.
  - The same workflow will be used with other functionals that account for long-range interactions (e.g. WB97XD, CAM-B3LYP, LC-wHPBE).
- Similar theoretical calculations are performed on the homodimeric ions to determine whether the trend observed experimentally can be predicted.
- The influence of monocharged cations other than the proton (H<sup>+</sup>) on the experimental and theoretical CCS trend curves of the PFCA homo- and heterodimers will also be investigated.

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## Acknowledgements

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