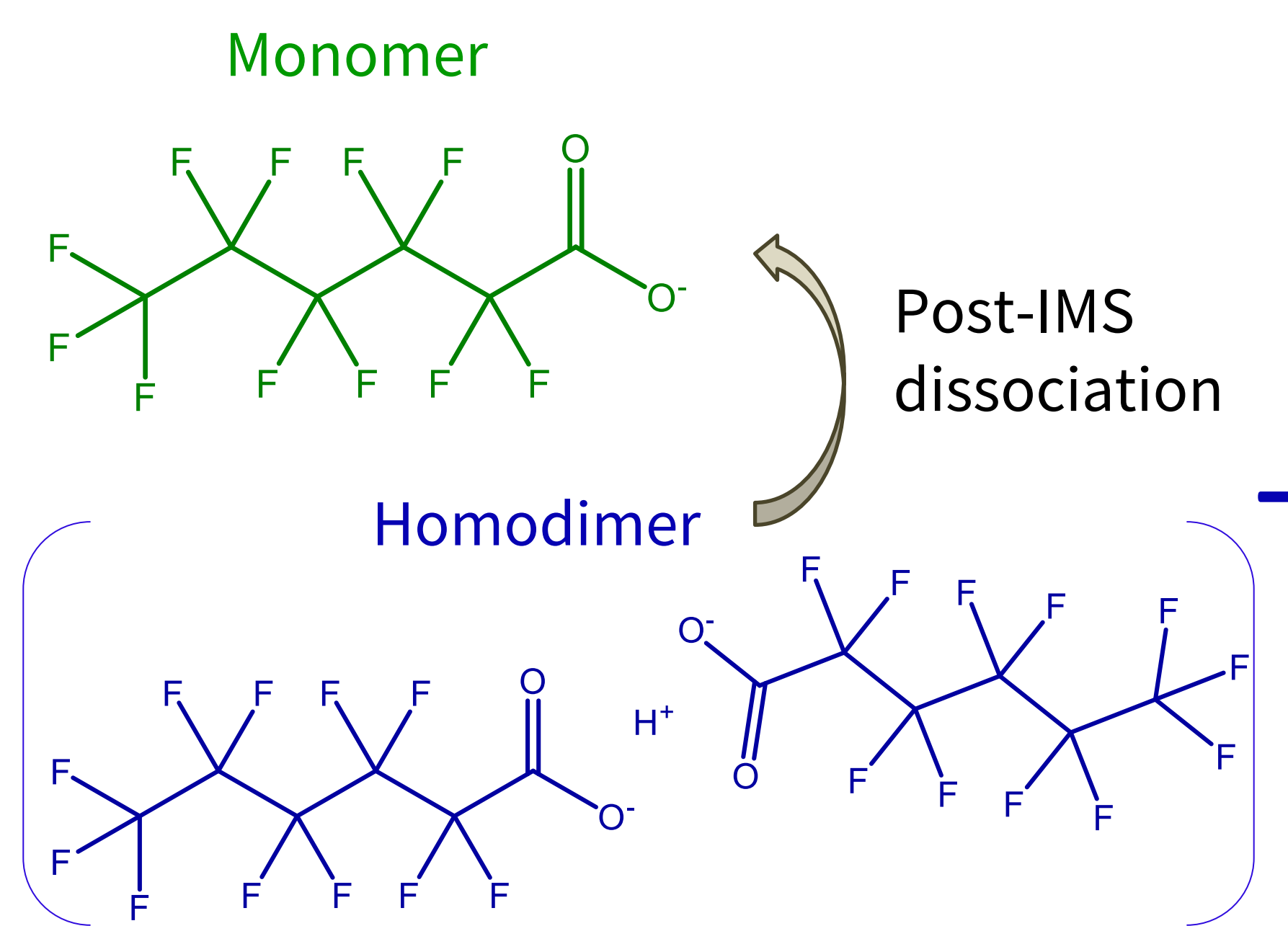
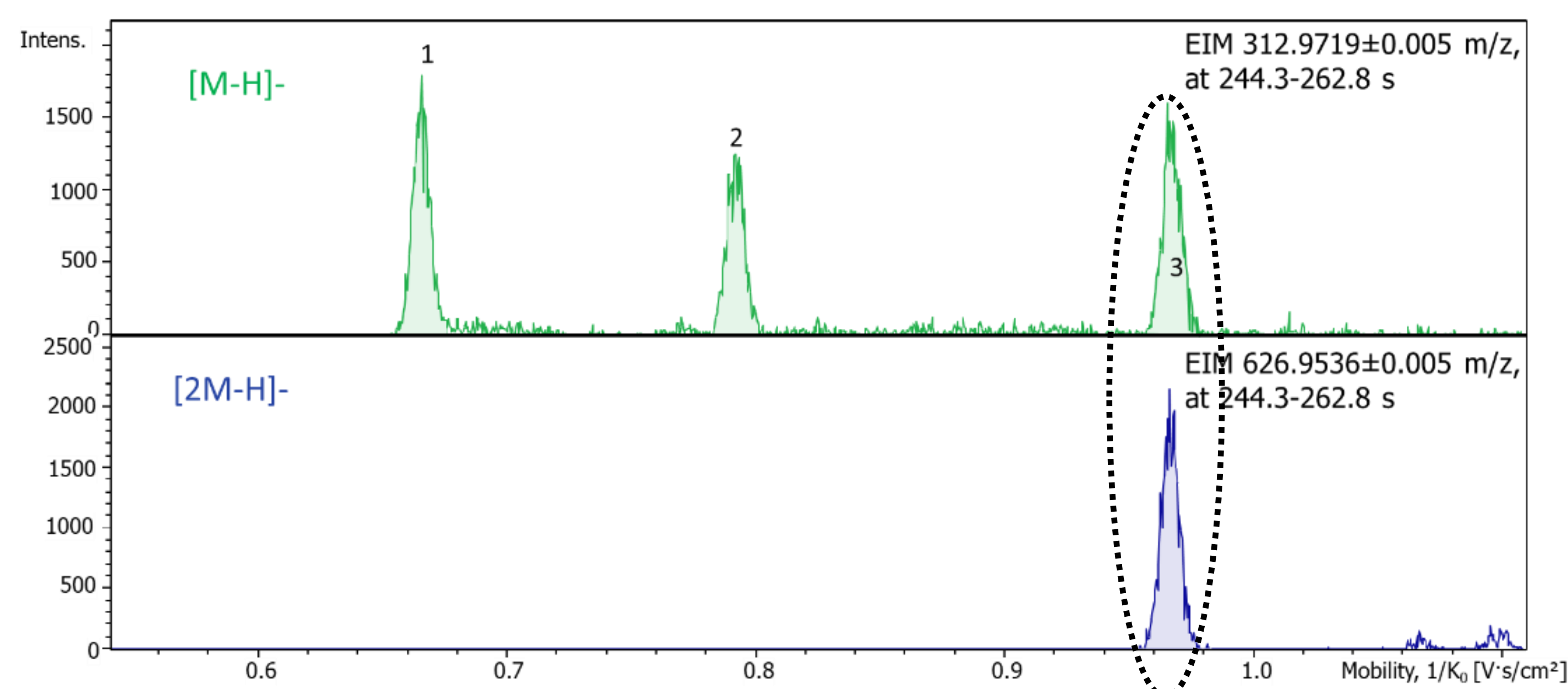


Ion mobility for PFAS analysis

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 hold promise for the non-targeted screening of these substances. This is because, in addition to the additional separation dimension, IMS also provides a descriptor related to molecular shape via the collision cross-section (CCS), supplying an additional identification point. Furthermore, in the case of compounds with repeating units such as PFASs, CCS- m/z trends are observed and can increase confidence in homolog identification.

Preliminary data : dimeric ions of PFCAs observed in TIMS

Perfluorohexanoic acid (PFHxA) example



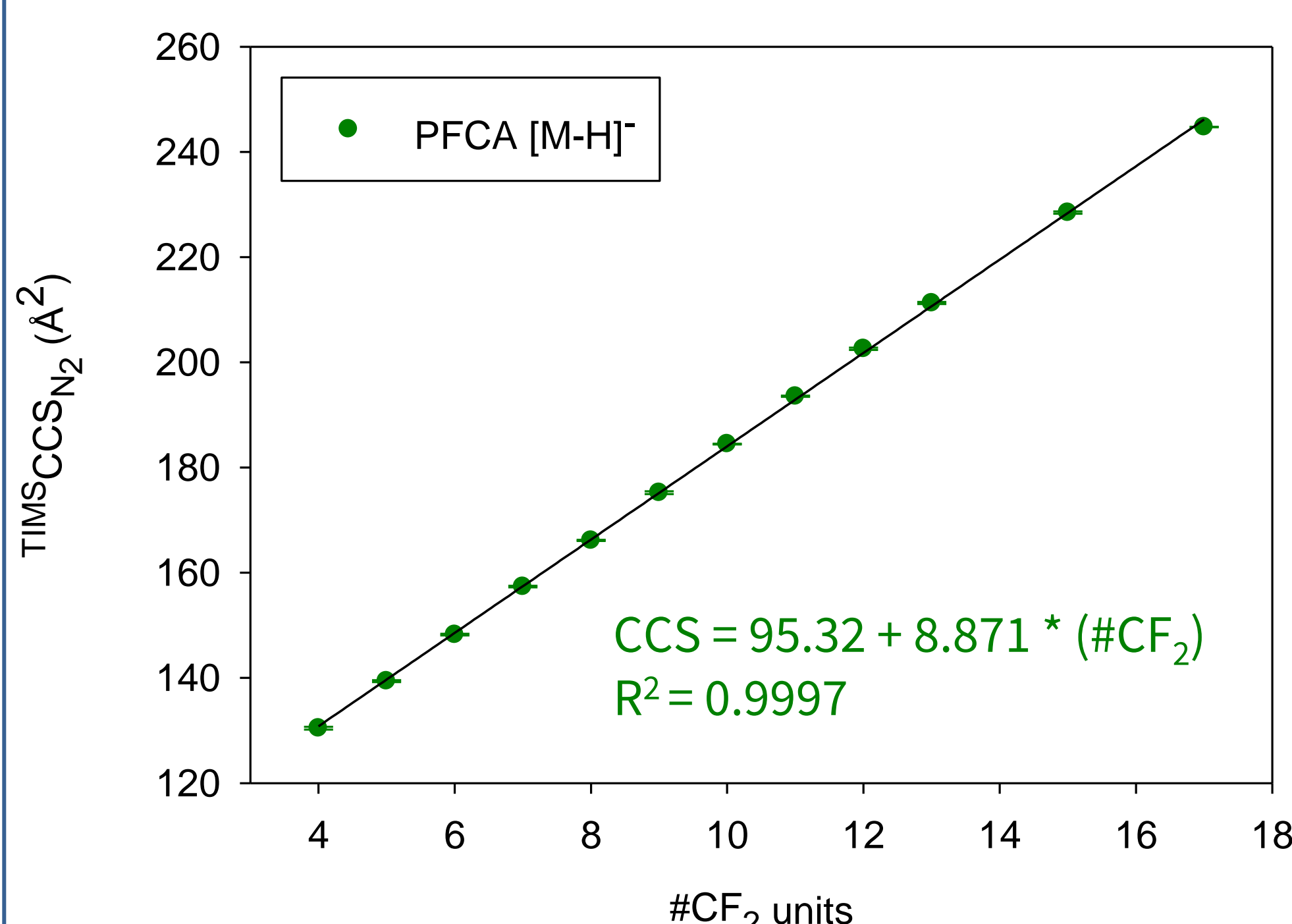
Aim of the study

Gain insight into a plausible conformation for dimeric PFCA ions, based on:

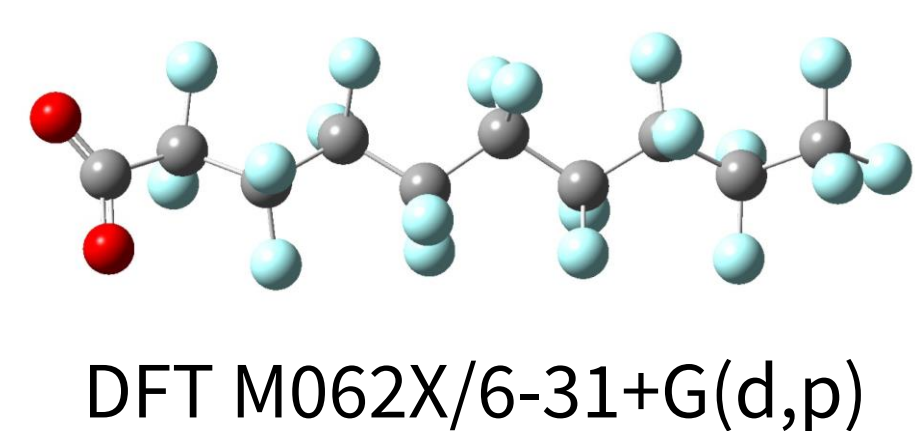
- The CCS- m/z trend of proton-bound homodimeric ions of several PFCA homologs
- The evolution of the CCS values of asymmetric but isobaric PFCA dimeric ions
- Preliminary theoretical predictions of CCS values based on DFT-optimized conformations of dimeric ions

CCS- $\#CF_2$ trendlines

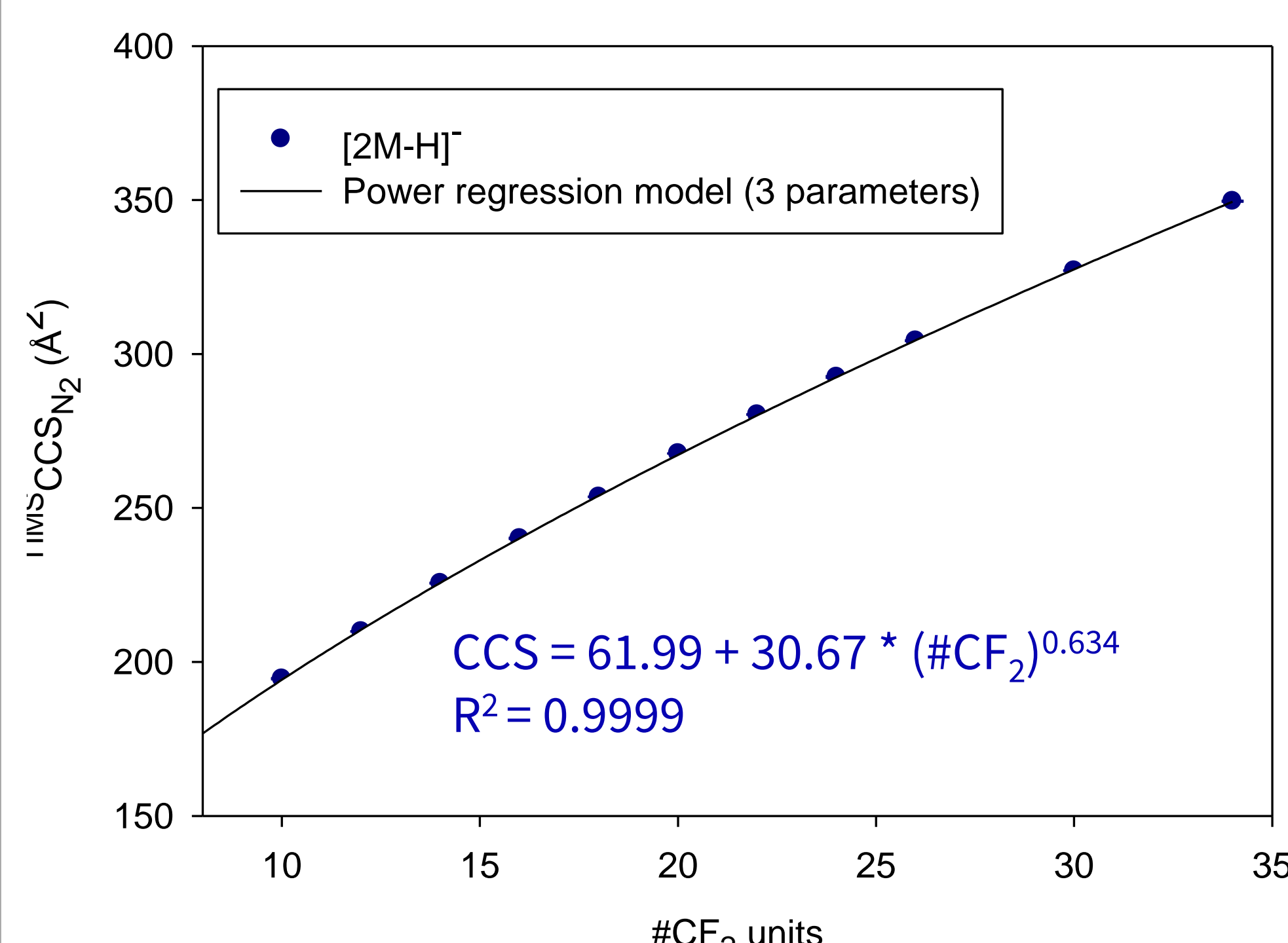
Monomeric ions



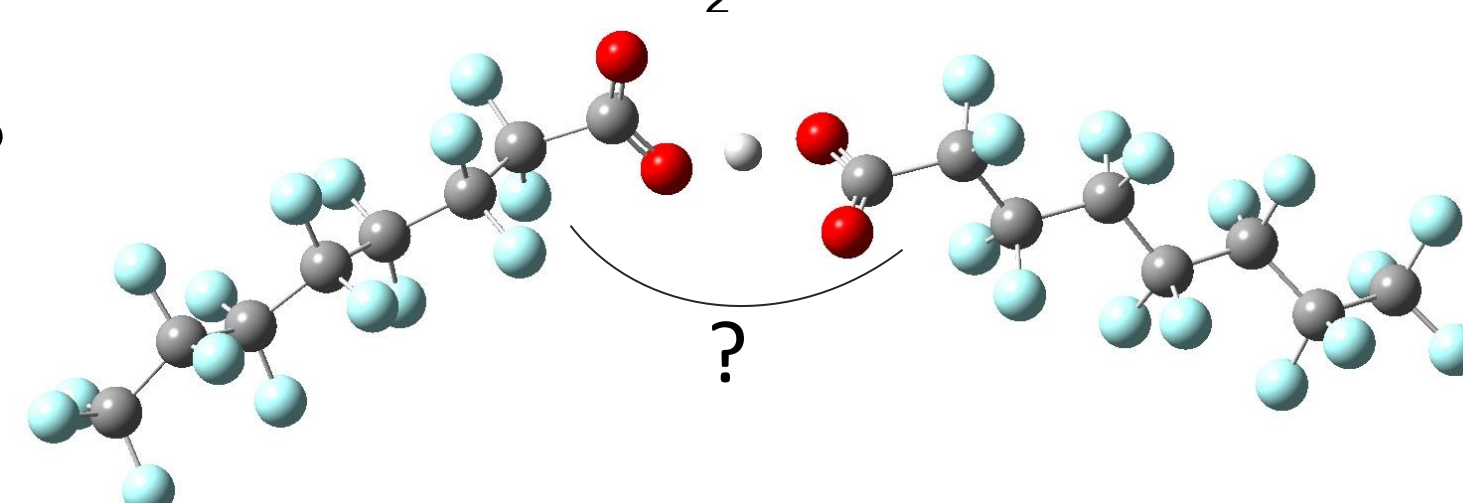
Cylindric shape:



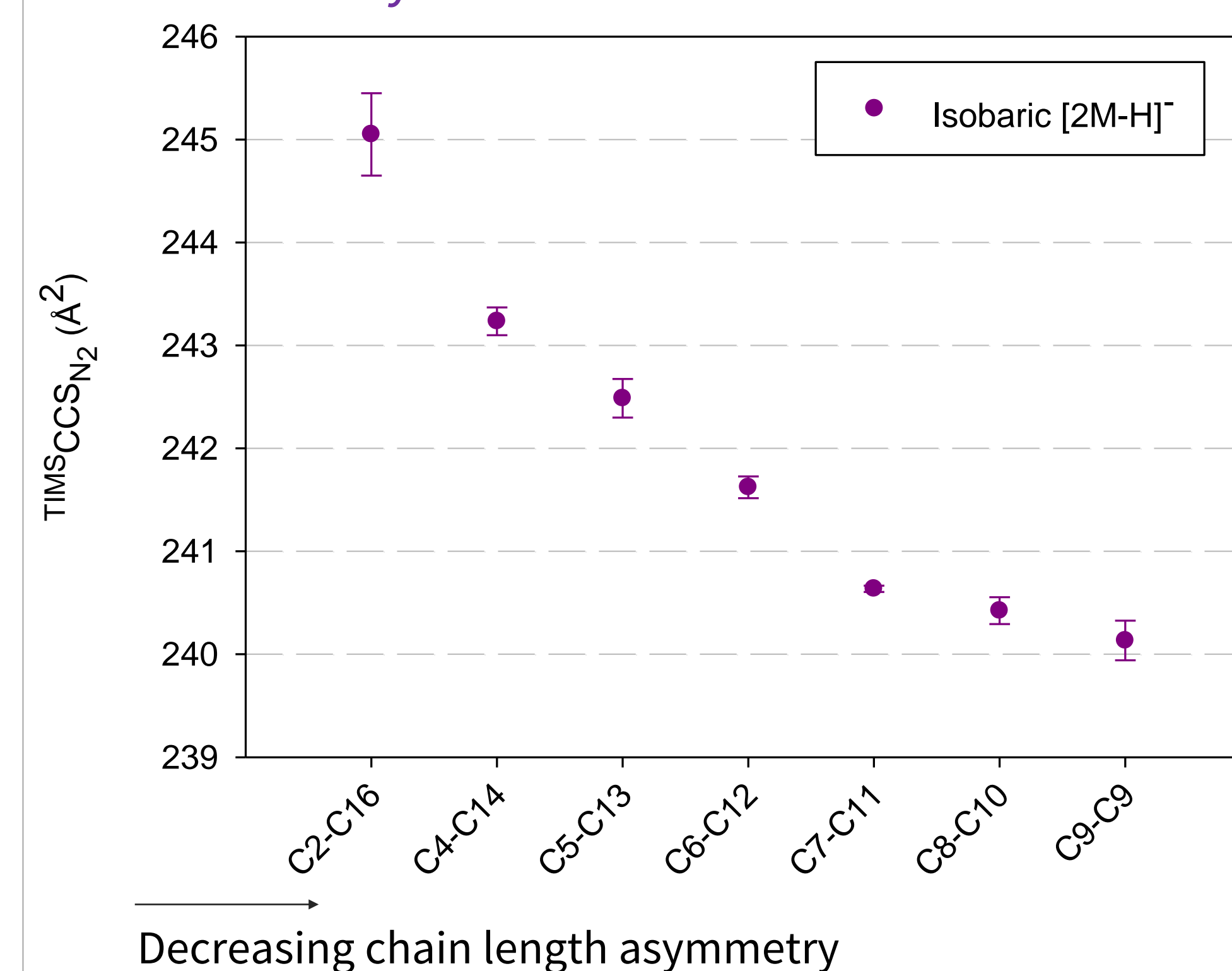
Homodimeric ions



V-shape?



Asymmetric isobaric dimeric ions



- The CCS values decrease with increasing symmetry
- The two fluorinated chains are not intertwined

Theoretical calculations for asymmetric isobaric dimers

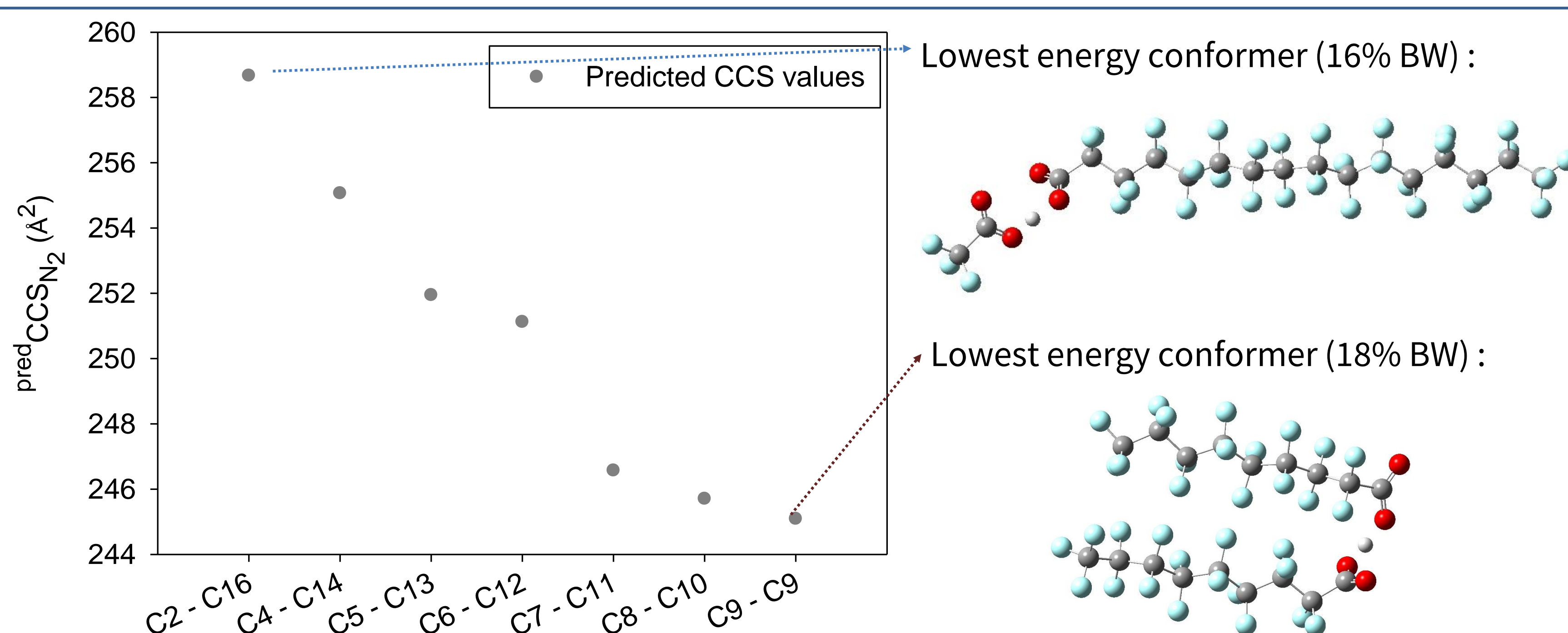
Workflow

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



Conclusions and perspectives

- The linear CCS trends of monomeric PFCA ions suggest an overall cylindrical shape. However, the power regression model for the CCS trendlines of the homodimeric ions might suggest an overall V-shape.
- For asymmetric but isobaric PFCA dimers, the more asymmetric the dimer is, the higher is its CCS value, suggesting that the two fluorinated chains are not intertwined in the dimer. In addition, preliminary theoretical calculations suggest that as symmetry increases in the dimers, a parallel configuration of the two fluorinated chains might be favored, which could explain the trend observed experimentally. However, the difference in CCS values between two asymmetric dimers is higher in the prediction than experimentally. This could be due to the fact that the predictions are performed at 298 K, which may not be the effective temperature of the ions in IMS. In addition, the L-J parameters used for the calculations might also not be suitable for polyfluorinated ions.
- 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⁺) on the experimental and theoretical CCS trend curves of the PFCA homo- and heterodimers will also be investigated.

Acknowledgements