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Oral Communication Yes
Poster (A0 portrait) Presentation No
Poster + flash Presentation No

Title: **Structural Characterization of Dimeric Perfluoroalkyl Carboxylic Acid Using Experimental and Theoretical Ion Mobility Spectrometry Analyses**

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Abstracts (max 400 words): Per- and polyfluoroalkyl substances (PFAS) are contaminants of increasing concern, with over seven million compounds inventoried in the PubChem PFAS Tree, according to the OECD definition. Ion mobility spectrometry (IMS) combined with liquid chromatography (LC) and high-resolution mass spectrometry (HRMS) has recently advanced PFAS analysis. Interestingly, under negative electrospray ionization, perfluoroalkyl carboxylic acids (PFCAs) form dimeric ions ($[2M-H]^-$). These dimers were detected using traveling wave, drift-tube, and trapped ion mobility. It is still unclear how the formation of dimers affects the analytical performance of analytical methods aiming to qualitatively and/or quantitatively analyze this compounds class. Additionally, as PFCA dimer conformations are unknown, this study aimed at proposing potential gas-phase structures for these ions. Preliminary data revealed that the CCS versus mass-to-charge ratio (*m/z*) for PFCA dimers suggested that proton-bound PFCA homodimer ($[2M-H]^-$) likely adopt a V-shaped structure, as the dimer trend deviated from the linearity observed for cylindrical shapes (Haler *et al.*, JASMS, 2022) and was best described by a power regression model. This hypothesis was supported by using DFT modeling and CCS calculations tools. The workflow used was the following: generating of large set of conformers, selecting a subset for CCS calculations, and the lowest-energy conformer with CCS values within 2% of experimental measurements was considered plausible. Two general structural trends were identified for PFCA dimers: either both fluorinated chains align closely, or one chain bends near its carboxyl group toward the other. These findings raise questions about whether such conformations are maintained when dimers are complexed with larger cations like Na^+ or K^+. Preliminary CCS data for such cation-bound dimers have been acquired, and further

modeling is ongoing. Additionally, perfluoroether carboxylic acids (PFECAs) were observed predominantly as dimers, suggesting a role for oxygen atoms in influencing dimer geometry. Finally, MS/MS breakdown curve experiments are currently being conducted for these different dimers to obtain additional structural information and insights into their relative stability.

To be sent (pdf file):

Oral : before **June 30, 2025** to pascal.gerbaux@umons.ac.be

Poster (+ flash) : before **July 15, 2025**