

Environmental stability of new PFAS through MS-fragmentation and quantum chemistry methods – on the way to degradable PFAS

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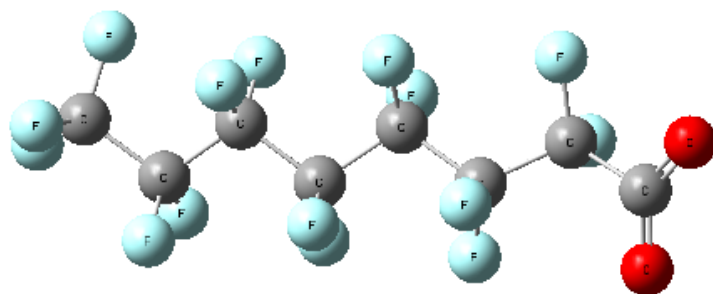
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WARNING: The study is purely theoretical,
if not speculative

To be discussed:

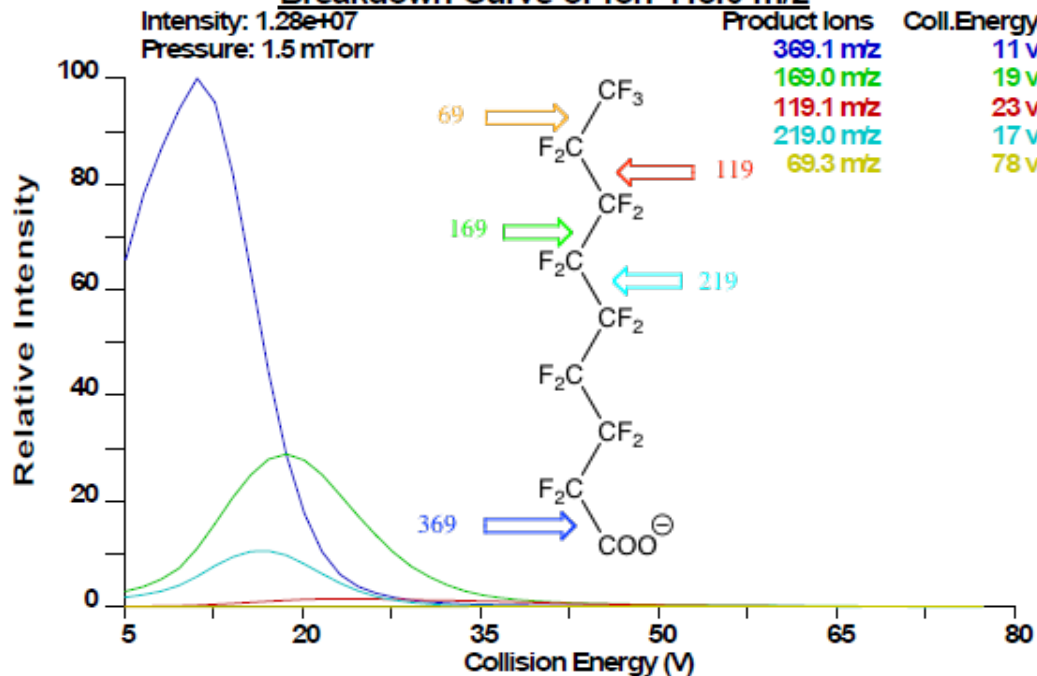
- (ESI) MS-MS fragmentation as semi-quantitative measure of stability
- Correlation of fragmentation, quantum chemistry ΔG and apparent chemical stability
- Transformation vs degradation
- Stability of new PFAS
- Design of a degradable PFAS structure

PFOA: MS-MS fragment intensity vs collision energy



Structure optimized
Gaussian-09
RB3LYP/6-31+G(d,p)

Breakdown Curve of Ion 413.0 m/z

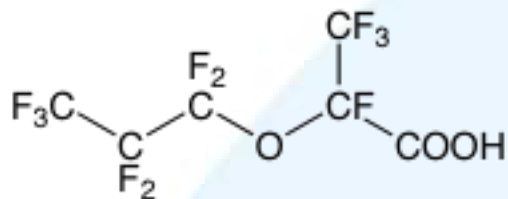


PFOA by LC-MS-MS :
Good fragmentation in MS
= UNSTABLE in MS

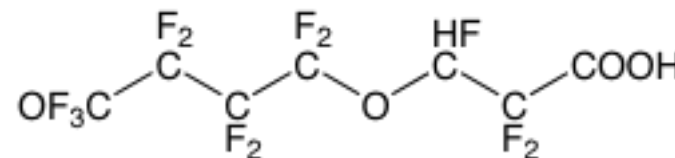
Lower energy, higher intensity
= easier transformation

C₇F₁₅COO anion in (ESI) MS –
same as in the environment

PFOA-alternatives: How stable/unstable are they (relative to PFOA) ?



Gen-X



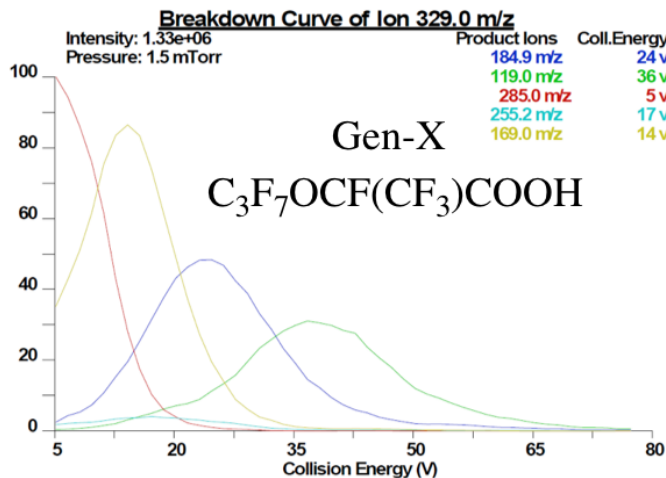
ADONA

There is something we can follow along with analysis:

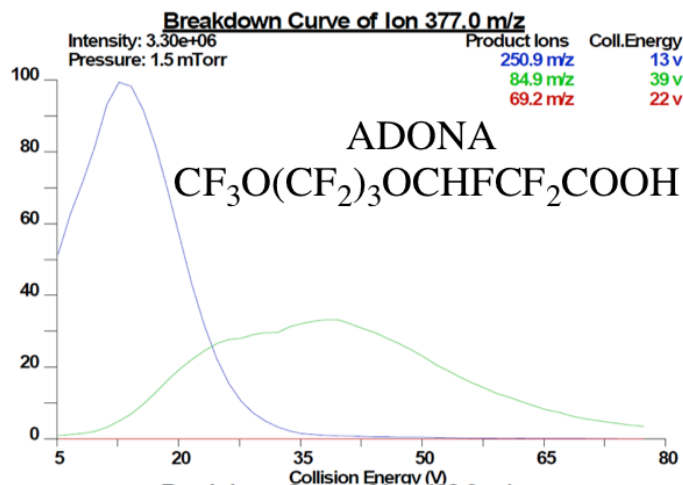
- decomposition in the ESI-source
- MS-MS fragmentation

Decarboxylation/Fragmentation of PFAS

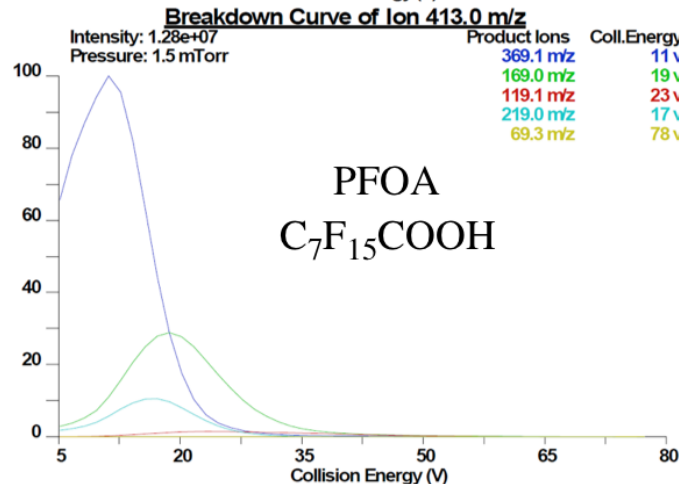
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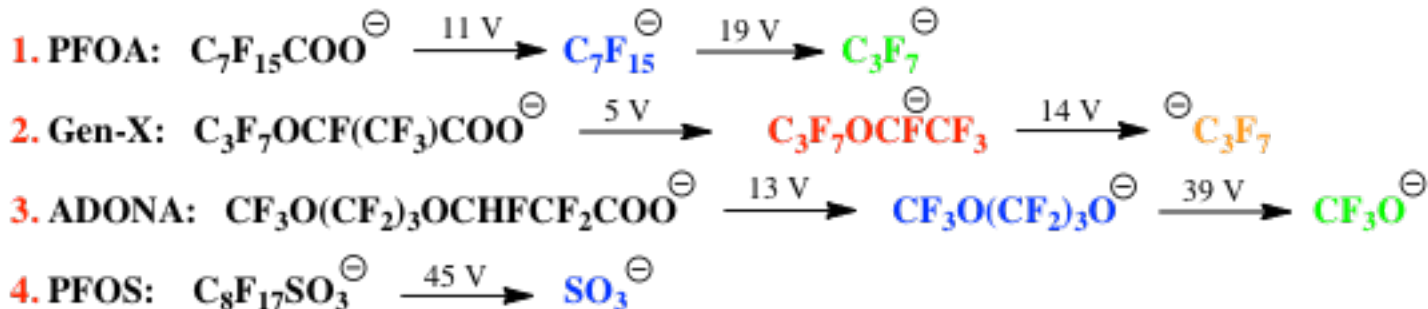
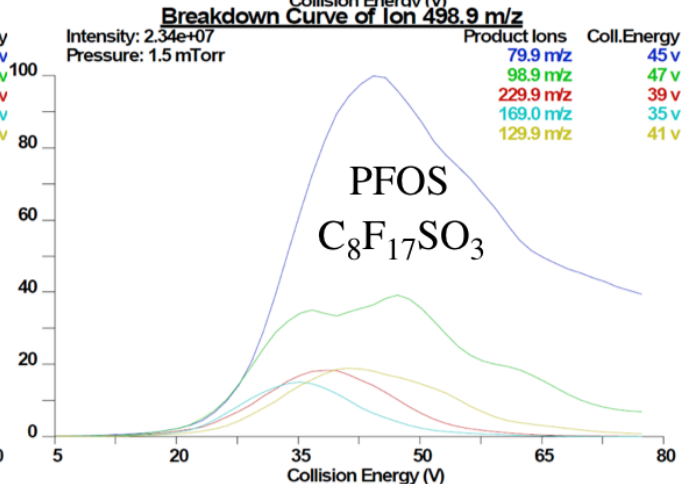
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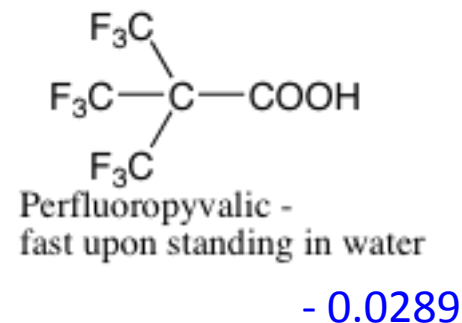
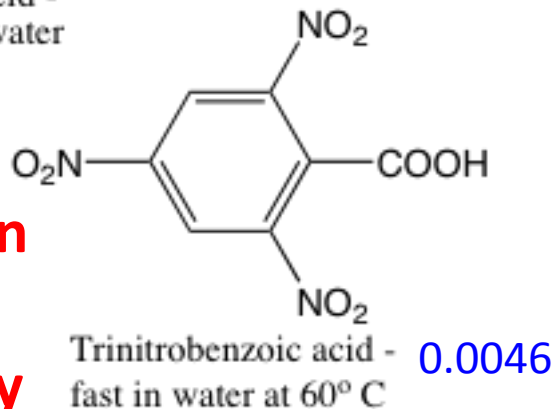
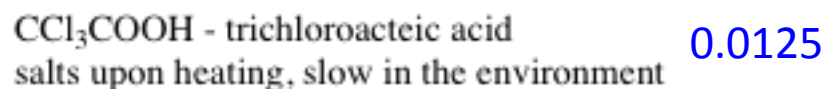
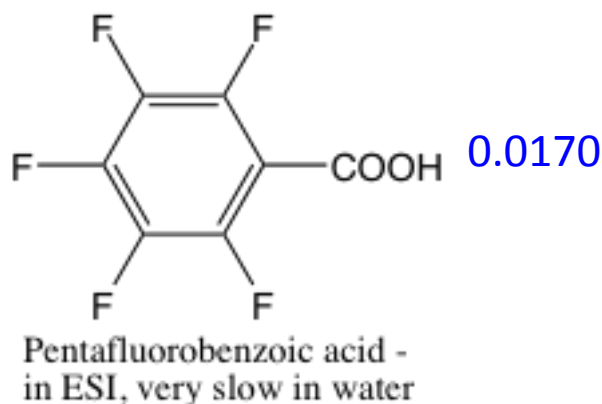
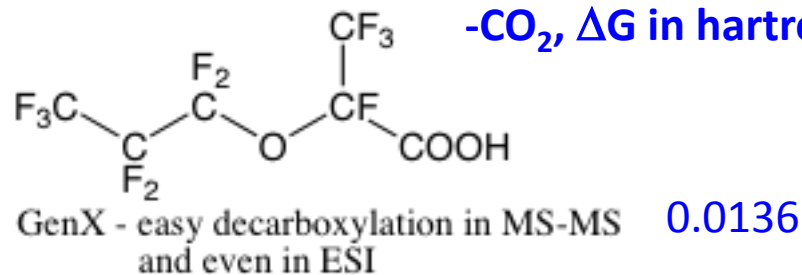
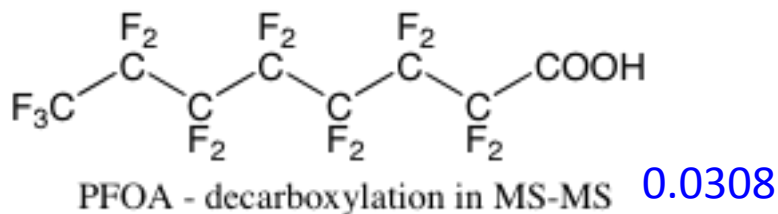
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Known facts from literature and DFT results: Easily decarboxylating acids/anions



DFT: Gaussian-09
RB3LYP/6-31+G(d,p)
-CO₂, ΔG in hartree

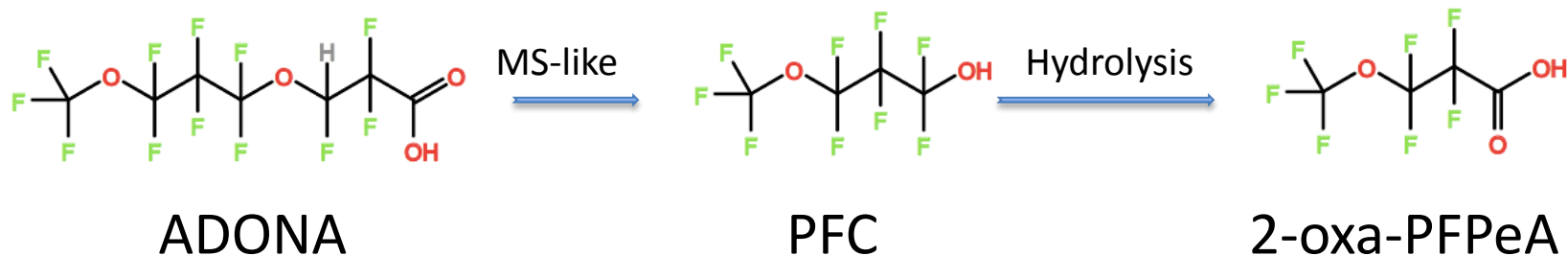
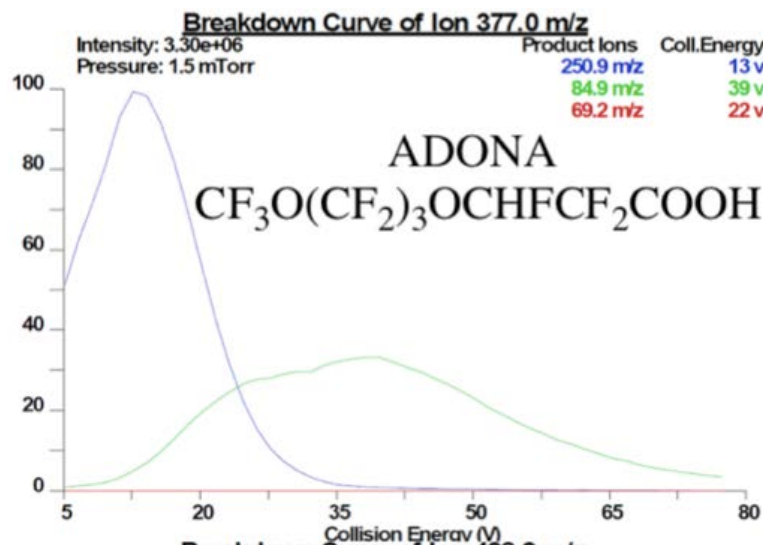


**A correlation between
DFT ΔG
and apparent stability**

Decarboxylation, Transformation, Degradation

1. Decarboxylation rate can be assessed through MS and DFT
2. Decarboxylation is just the first step
3. Decarboxylation is “not enough” $R_FCF_2COOH \rightarrow R_FCF_2H \rightarrow R_FCOOH$
4. Decarboxylation is not degradation
5. ADONA seems promising, as it degrades in MS “deeper”

Decarboxylation product of ADONA - $\text{CF}_3\text{O}(\text{CF}_2)_3\text{OCHF}_2\text{CF}_2^-$
 anion – unstable *in silico* –
 "decomposition" to $\text{CF}_3\text{O}(\text{CF}_2)_3\text{O}^-$ + CHF_2CF_2

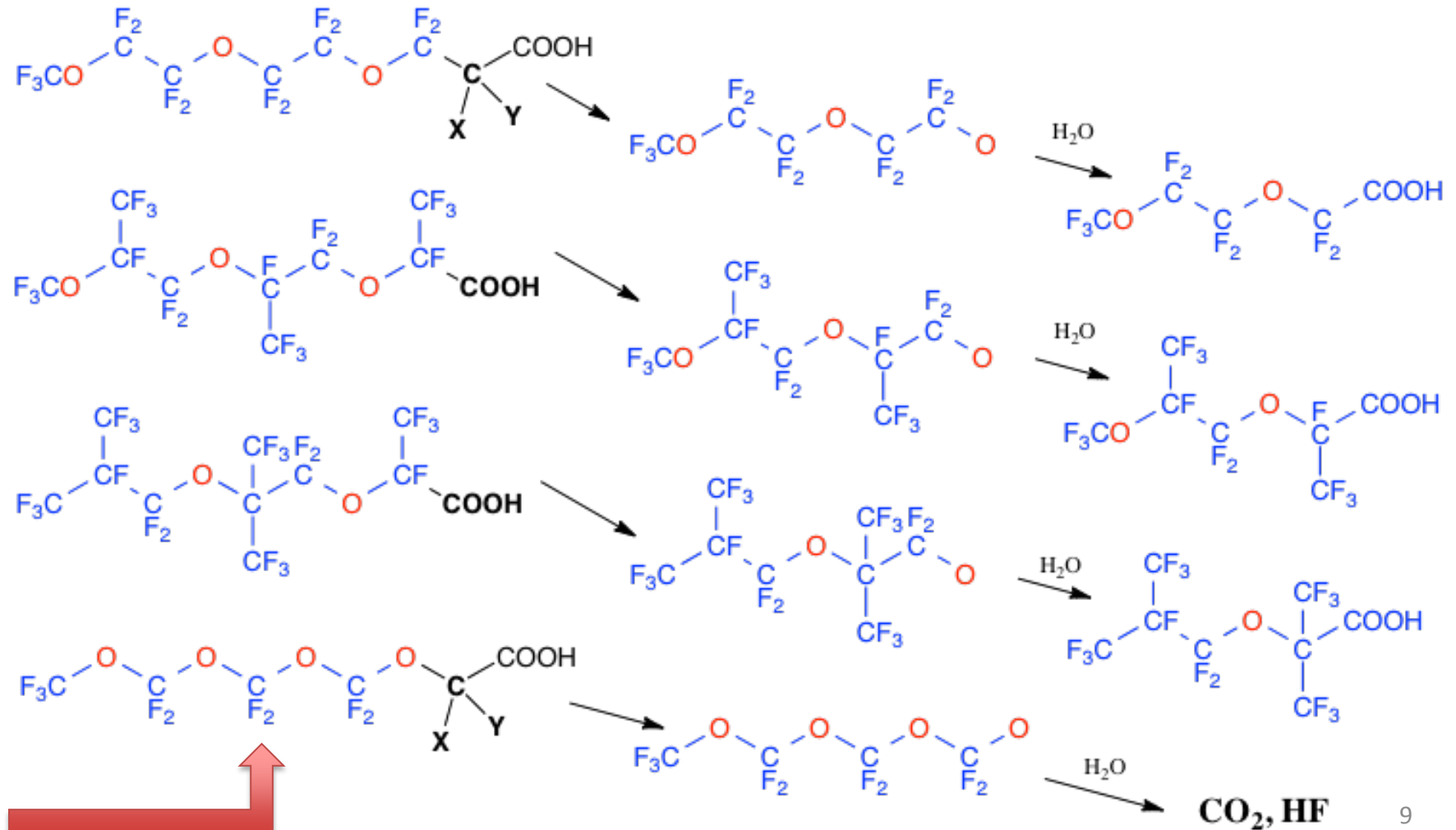


The rest of PF-chain must be degradable !

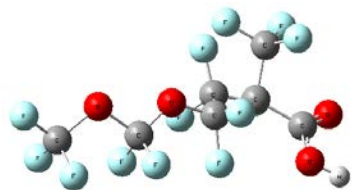
In addition, we need a degradable chain !!!

PFECA - PerFluoroEther Carboxylic Acids

A way to unchain PFC world?



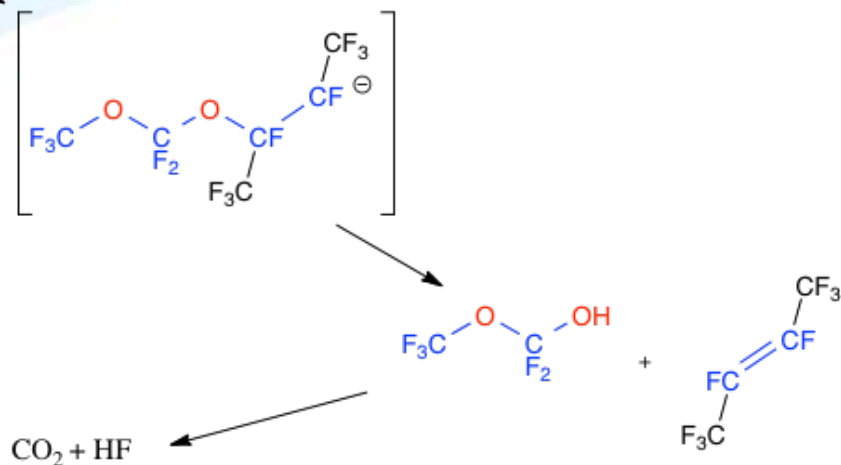
Design of a fully degradable: imagination + *in silico* DFT trials



Sorry, no room
for more DFT



Decarboxylation: better than TCA
Fragmentation: better than ADONA
Further degradation: complete



PFOA, stable: $\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-COOH}$

ADONA, fragmentation: $\text{CF}_3\text{O-CF}_2\text{-CF}_2\text{-CF}_2\text{-O-CHF-CF}_2\text{-COOH}$

Gen-X, decarboxylation: $\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-O-CF(CF}_3\text{)-COOH}$

PFE-CA, degradable chain: $\text{CF}_3\text{O-(CF}_2\text{O)}_n\text{-CF}_2\text{-O-CF}_2\text{-COOH}$

Designed ENVI-PFCA: $\text{CF}_3\text{O-(CF}_2\text{O)}_n\text{-CF}_2\text{-O-CF(CF}_3\text{)-CF(CF}_3\text{)-COOH}$

	Coll. E, V	Half-life	Decarboxylation, E_h	Fragmentation ?	End-products
ADONA	13	?	0.0765	yes	PFAS
PFECA	n.a.	?	0.0644	no	HF, CO ₂
PFOA	11	> 10 y	0.0604	no	PFAS
GEN-X	5	?	0.0506	yes/no	PFAS
TCA	n.a.	100 d*	0.0413	yes	HCl, CO ₂
NV-PFCA	n.a.	30 d**	0.0365	yes	HF, CO₂
PFPvA	n.a.	hours	0.0106	yes	PFAS

Final remarks

- Decarboxylation was a model Step 1
- Environment-dependent Step 1 is required (bio or UV)
- Every mass-spectrometrists, being attentive, can help unchain the world

Thank you for your attention!

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Thank you for your attention,

IN ADVANCE !!!