Direct dynamics simulation of prospective PFAS molecules dissociation after electron impact – PPVE and C4H3F7O isomers.

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QUANTEMOL WORKSHOP

10th May 2024

Motivation

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- Excerpt from the U.S-EU Joint Statement of the Trade and Technology Council – April 5th 2024[1]:

‘’ We plan to continue working to identify research cooperation opportunities on alternatives to the use of per- and polyfluorinated substances (PFAS) in chips.”

References: 1. https://www.whitehouse.gov/briefing-room/statements-releases/2024/04/05/u-s-eu-joint-statement-of-the-trade-and-technology-council-3/

Workflow

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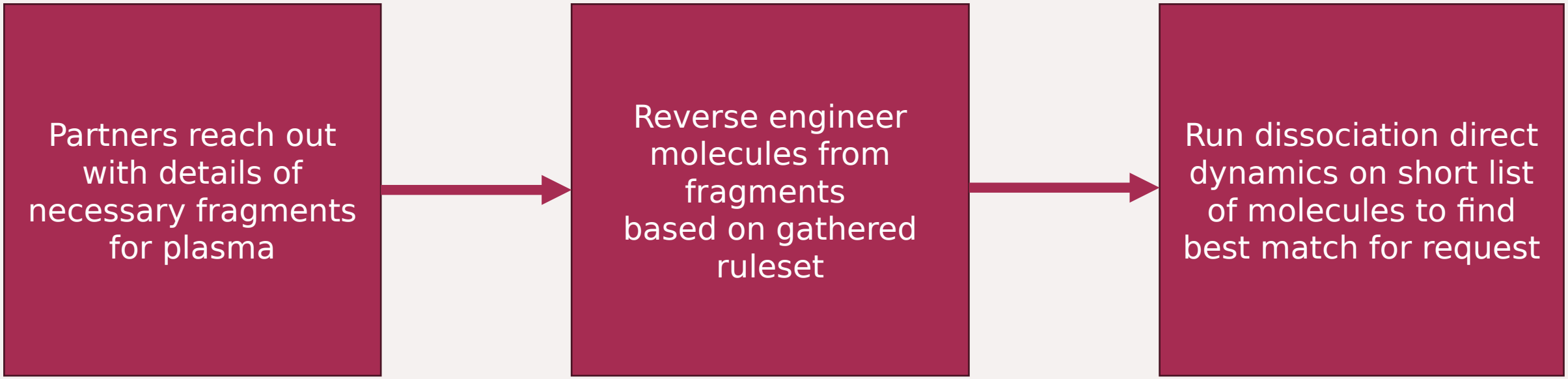

Triplet states

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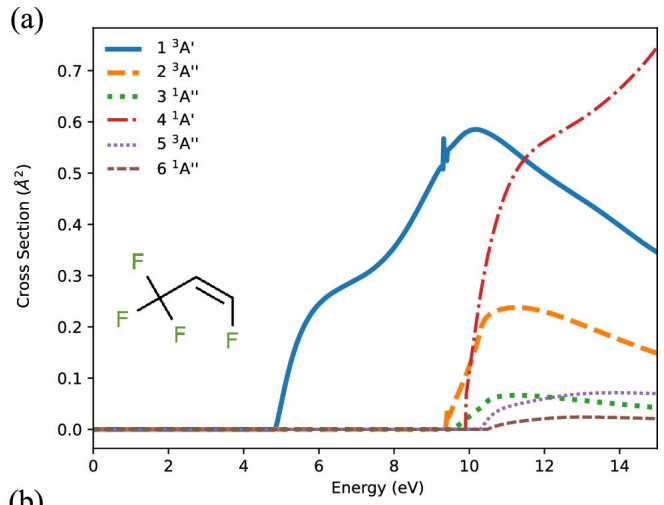
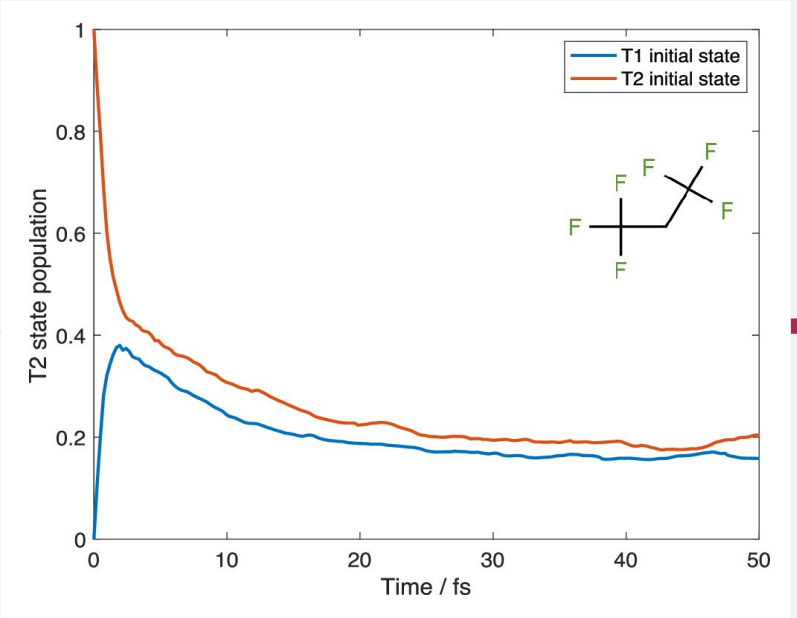


One clear lowest triplet state, can run dynamics on one state



Higher states quickly relax to lowest lying triplet state, can still run dynamics on one state

References: D. V. Makhov, et al, Journal of Physical Chemistry Letters **15** (12), 3404-3411

Ab Initio Multiple Cloning

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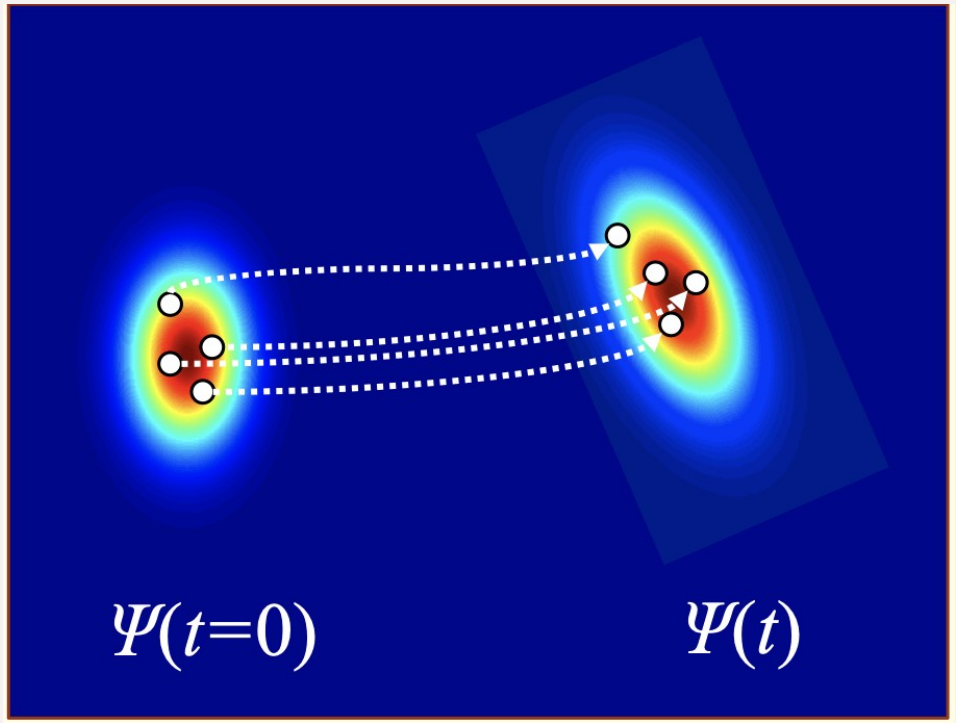
Previous group work focused on modelling photoexcitation with singlet states lead to the development of AIMC.



Using a randomly trajectory guided grid to move the nuclear parts, electronic energy then recalculated with SF-TDDFT (via QChem) at every timestep, making the method fully ‘on the fly’.

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Ehrenfest Trajectories

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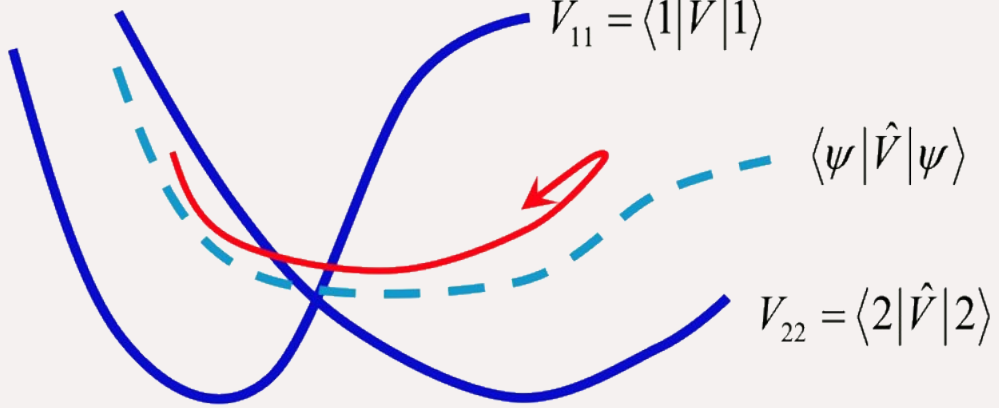
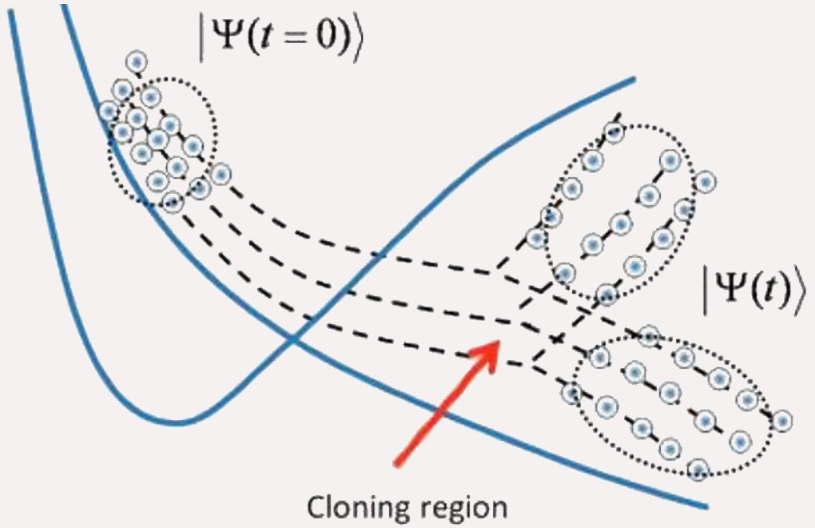
In order to guide the grid correctly, we employ the use of Ehrenfest trajectories which take the path of the average potential energy.

$$|\psi\rangle = \left(a_1|1\rangle + a_2|2\rangle\right)|\mathbf{z}\rangle$$





To combat a weakness of Ehrenfest trajectories, the cloning procedure was developed to capture the bifurcation
of the wavefunction.

Molecules

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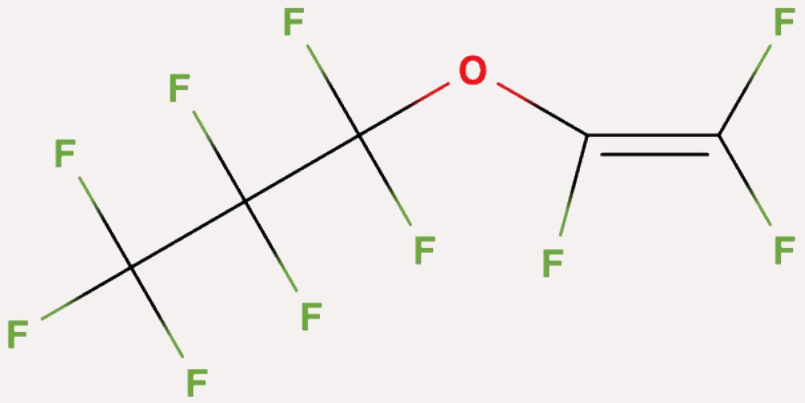
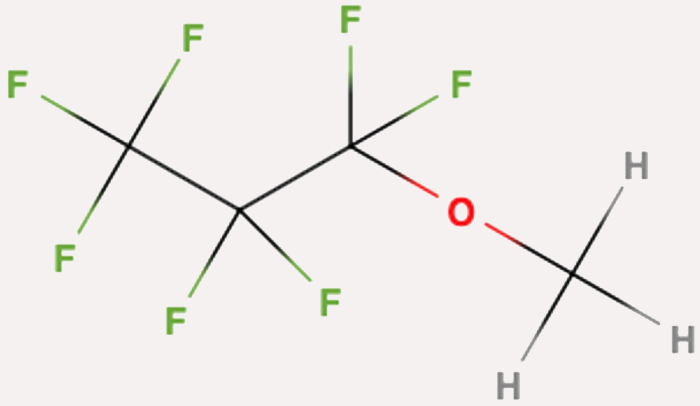
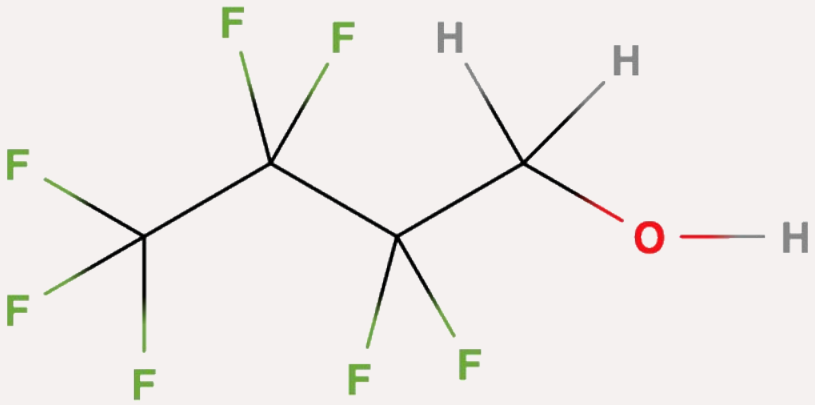
PPVE:



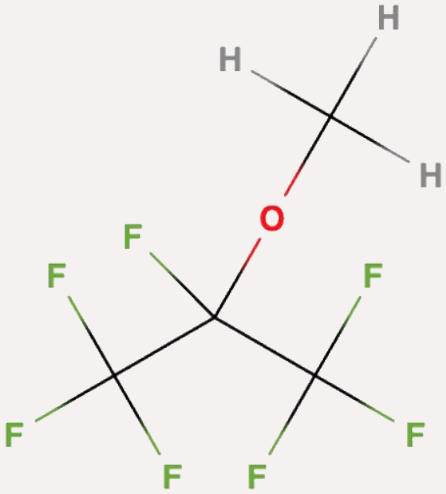
n-$C_4H_3F_7O$:



$C_4H_2F_7OH$:



i-$C_4H_3F_7O$:



$C_4H_2F_7OH$ – Overview

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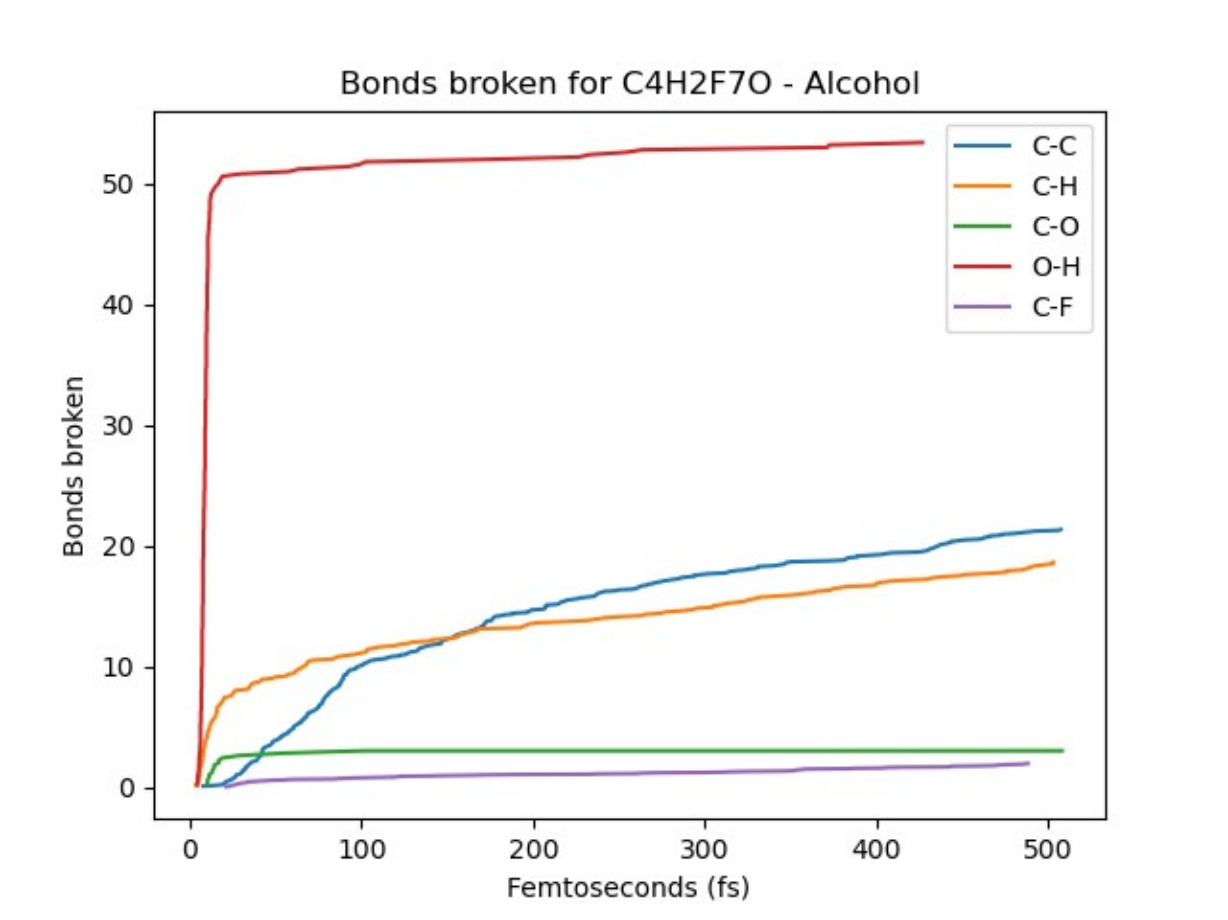

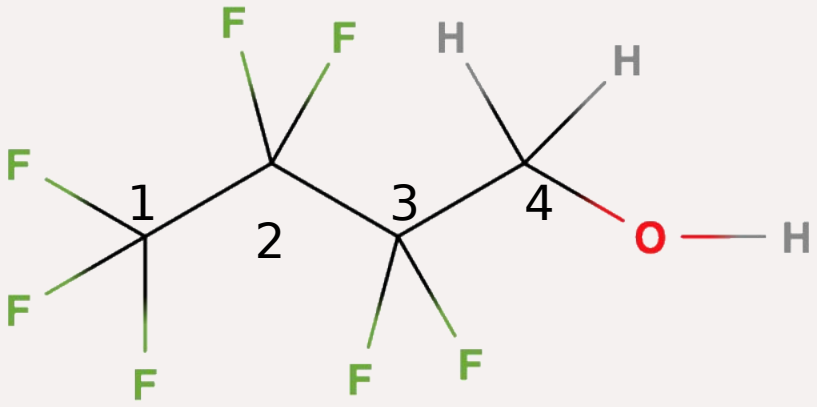

Notes:

- Bonds to H break very quickly, over 95% of O-H broken within 20fs
- C-O stops breaking after 100fs.

n-C4H3F7O – Overview

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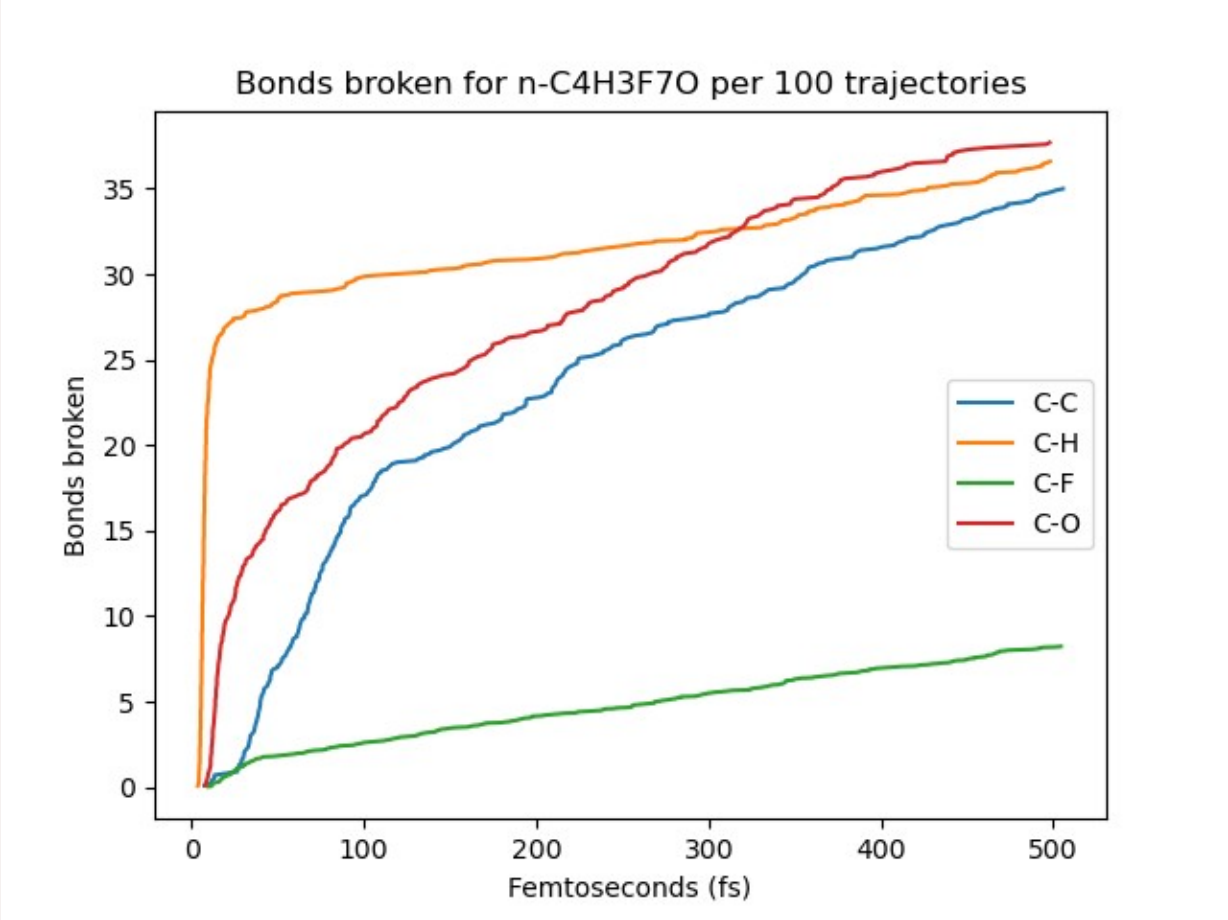

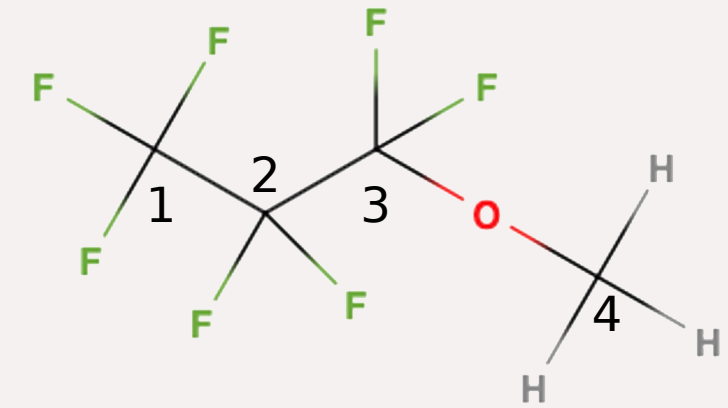

Notes:

- C-O bonds ends up breaking the most
- C-O behaviour completely different to the alcohol.

i-$C_4H_3F_7O$ – Overview

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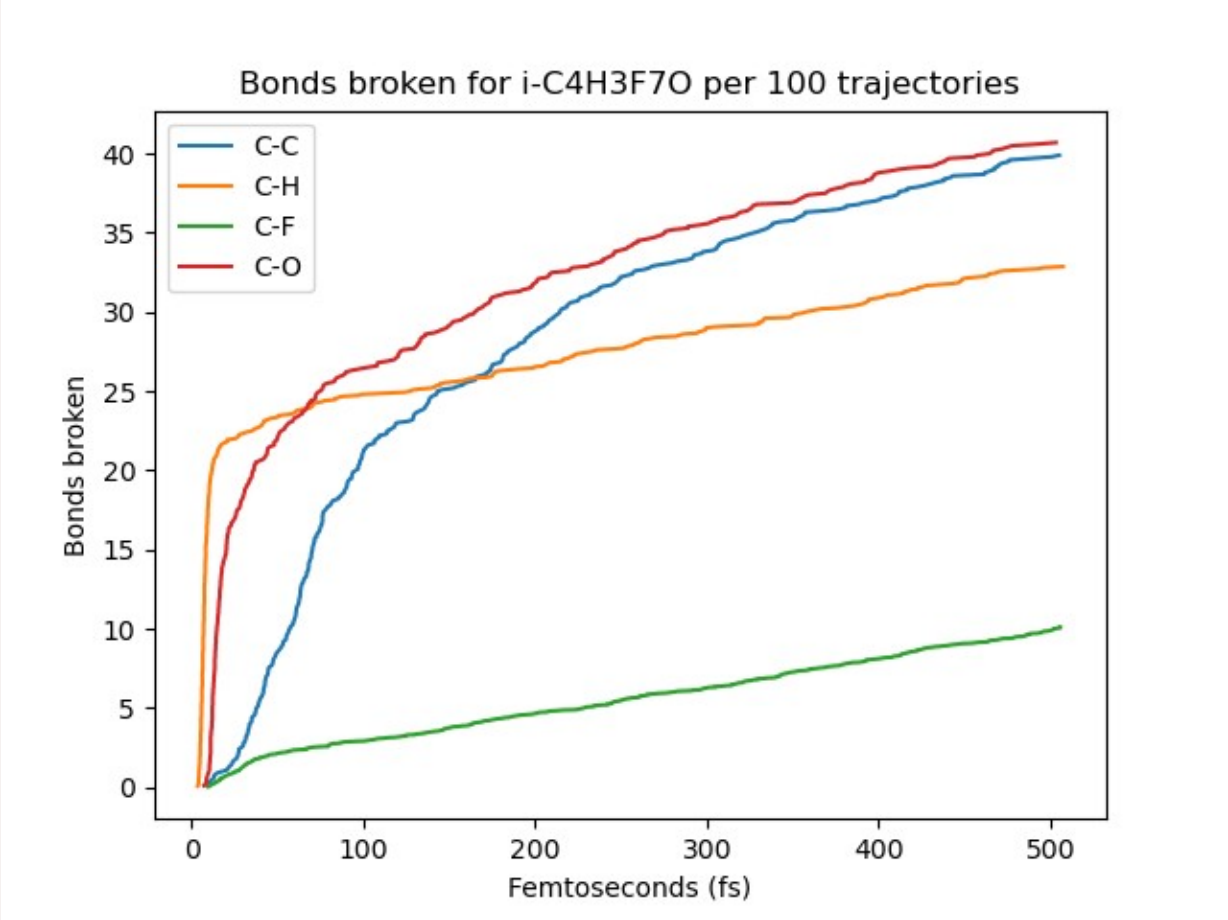

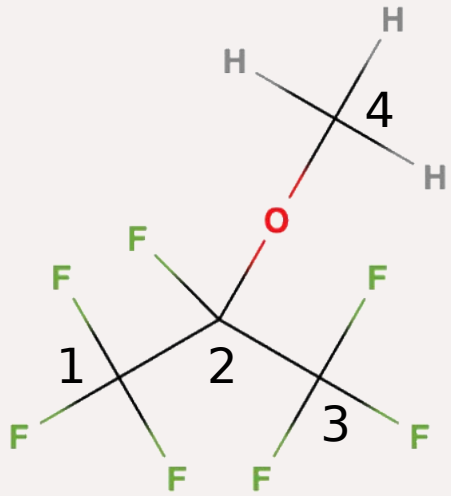

Notes:

- More C-C and C-O bonds broken than its positional isomer, and quicker.
- C-F bonds relatively unchanged, same overall trends.

Isomer comparison

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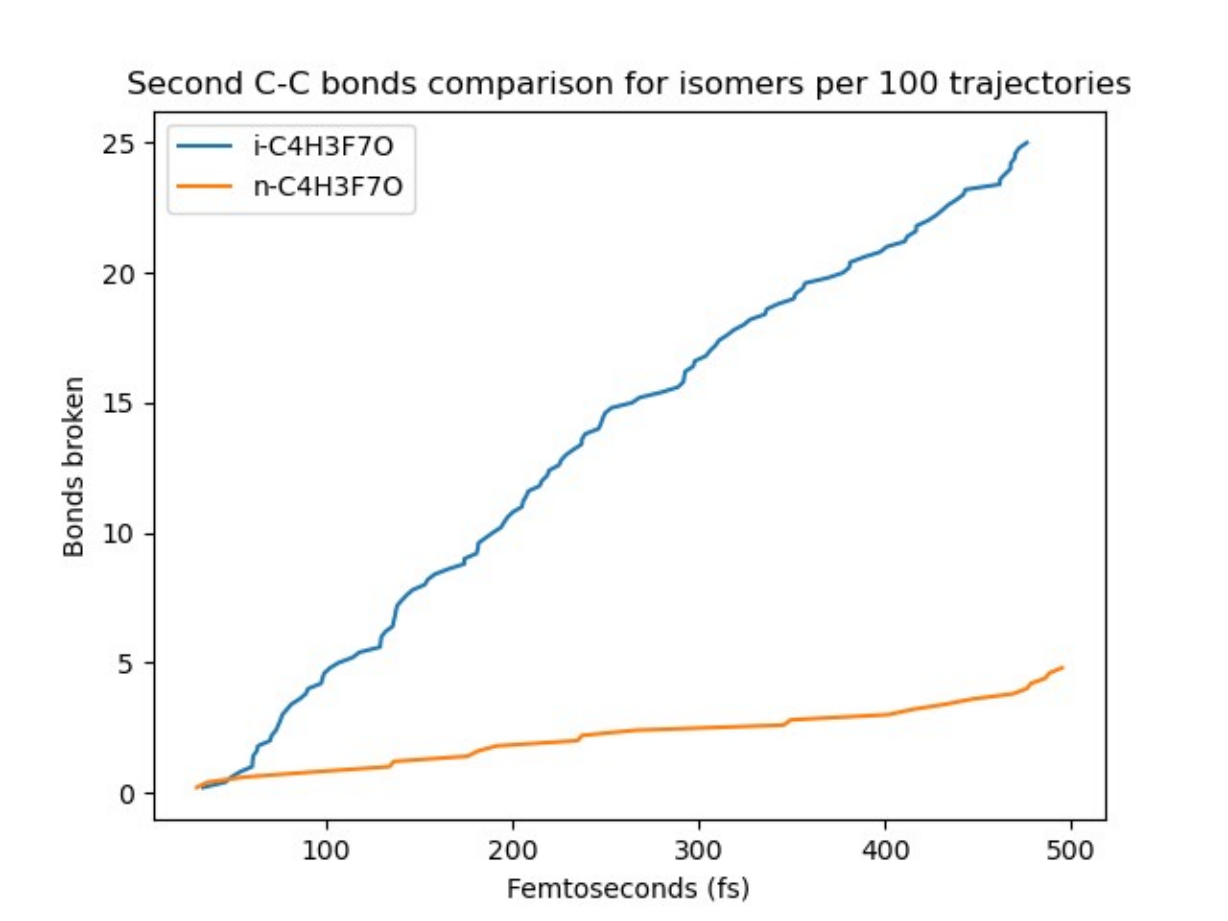

"…the electron- withdrawing methoxy group in the center of the [i-$C_4H_3F_7O$] molecule weakens the adjacent C−C bonds, resulting in smaller fragments of radicals than in [n-$C_4H_3F_7O$]…"

Molecule	2nd C-C broke n
n-$C_4H_3F_7O$	7.4%
i-$C_4H_3F_7O$	45.6%

References: . Kim, S. Kim et al, Acs Sustainable Chemistry & Engineering **10** (32), 10537-10546 (2022).

PPVE – Overview

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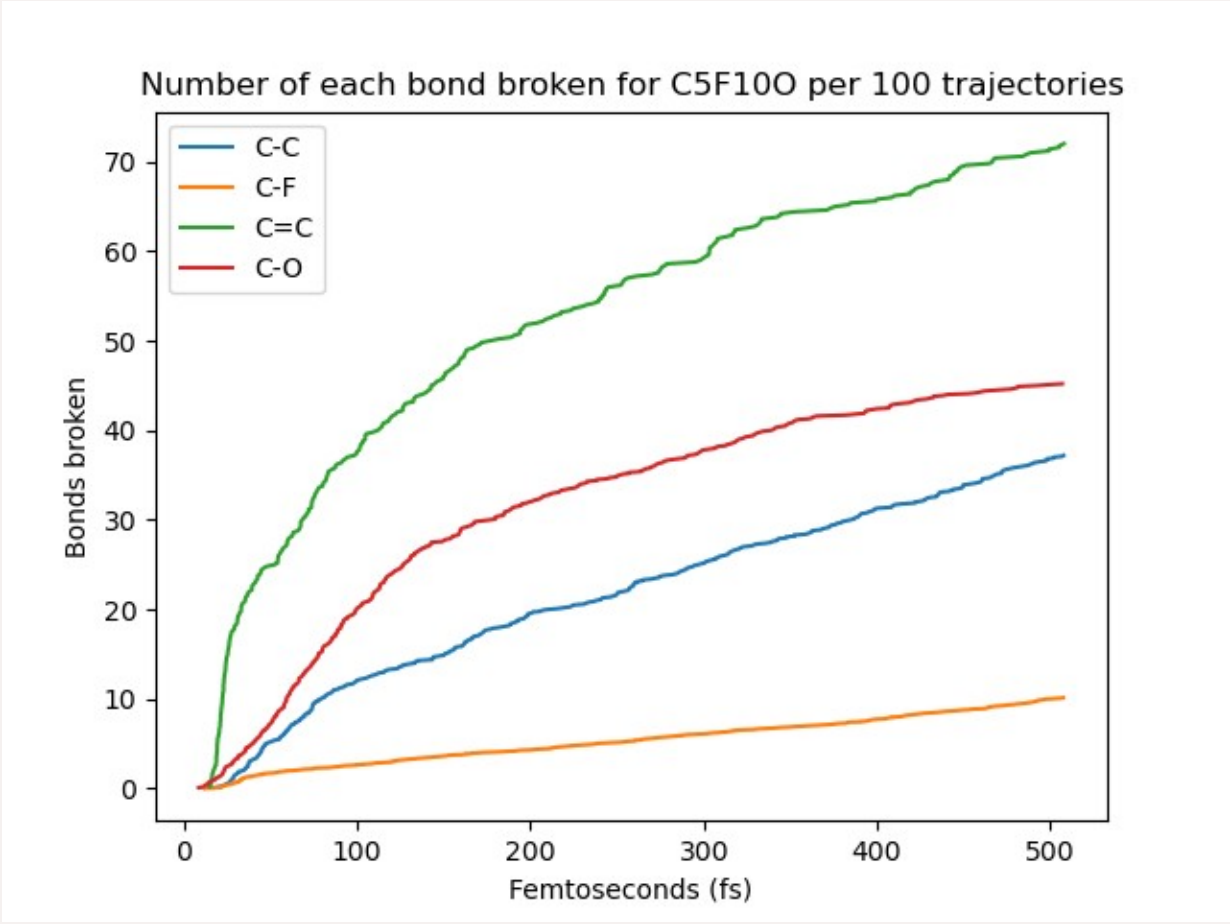

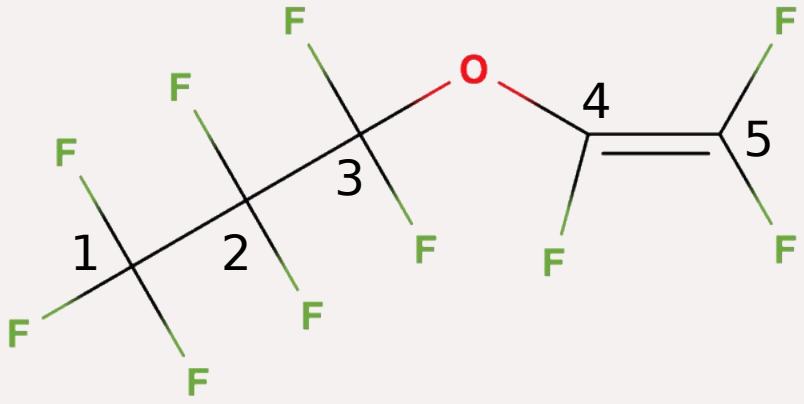

Notes:

- C=C & C-O breaks the most, suggesting location of localisation
- Fairly ‘standard’ bond breaking order

PPVE – Specific behaviour

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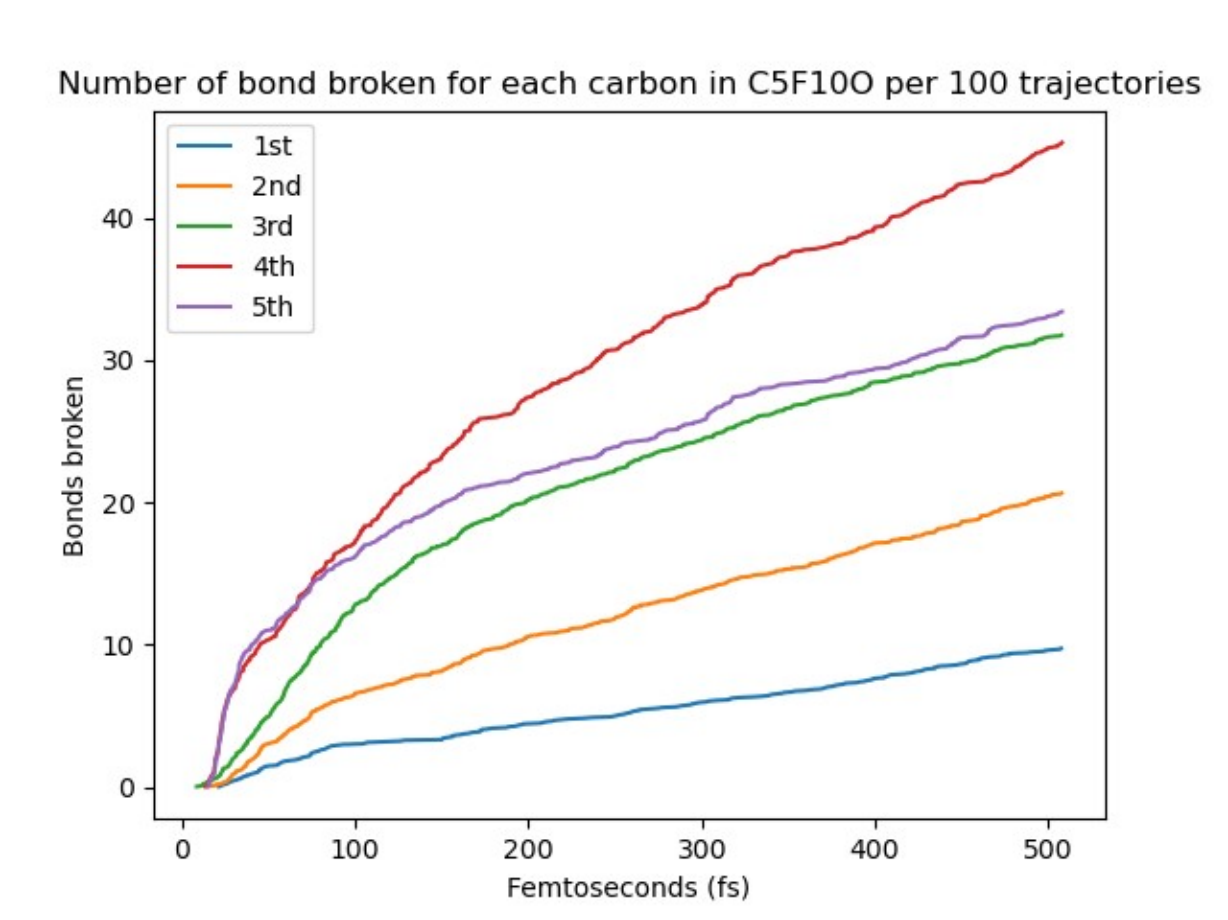

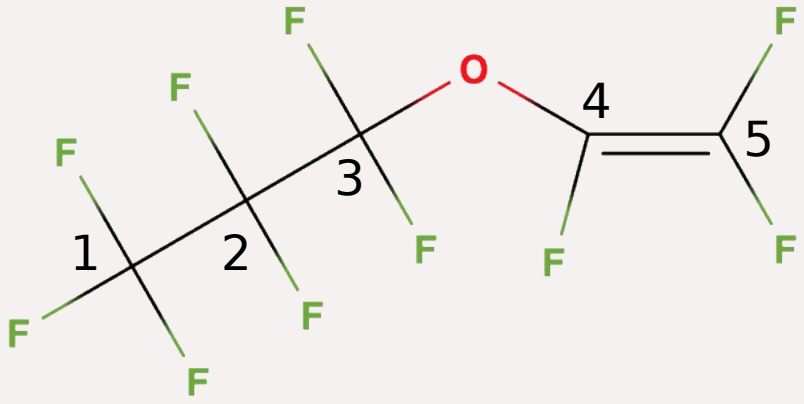

Notes:

- Trend is double bond & O > O > closest to O
- Big separation between different environments

PPVE – Specific behaviour

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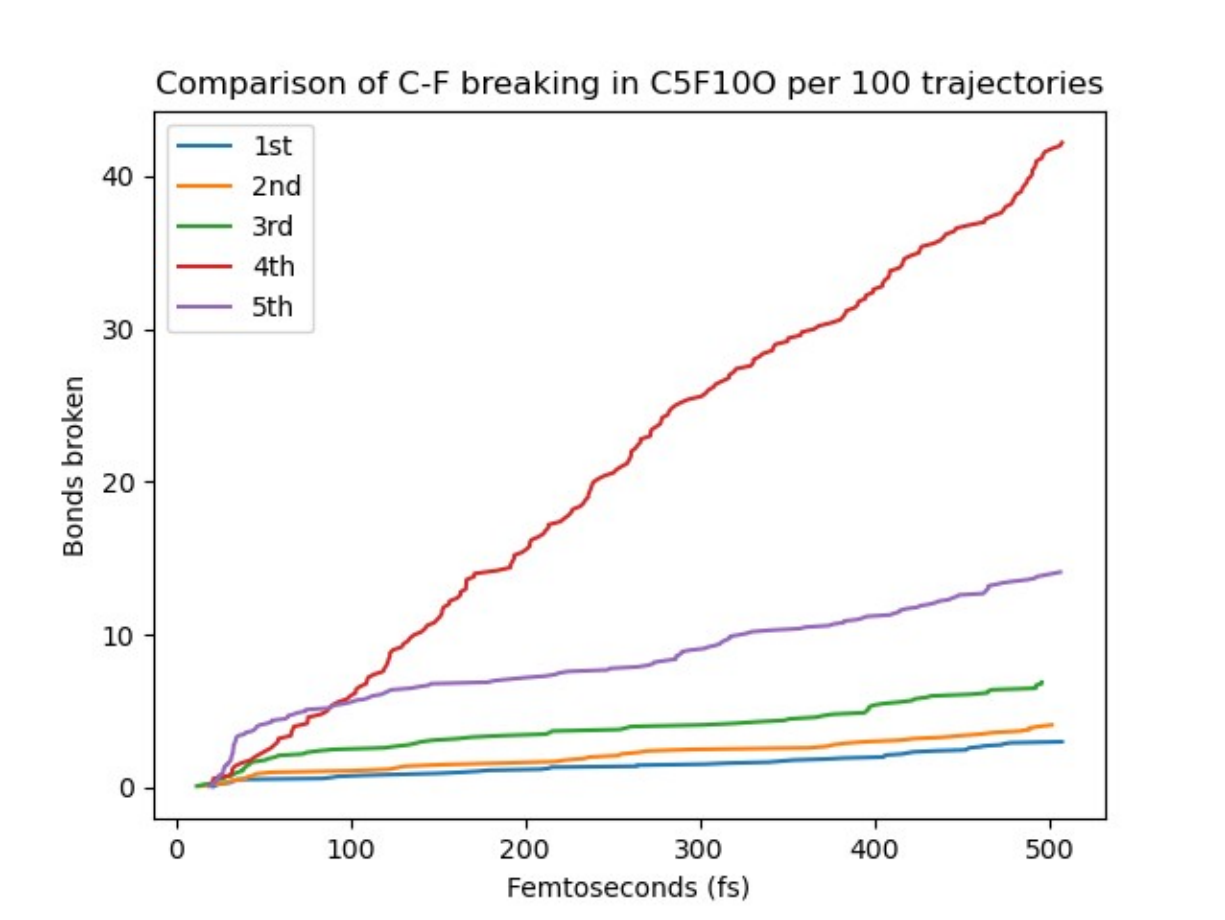

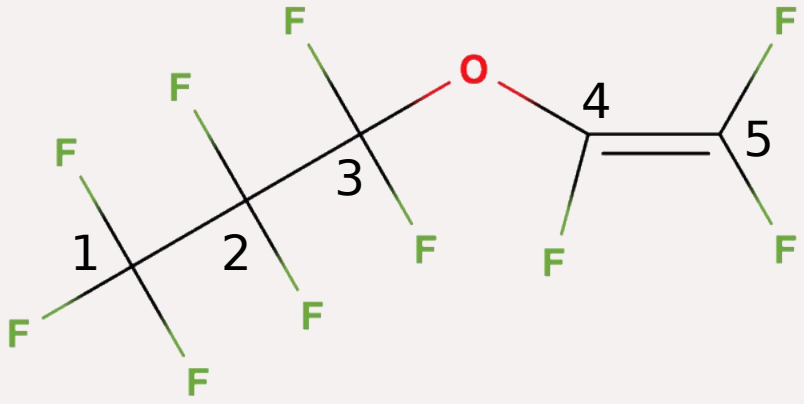

Notes:

- Even the least broken bond C-F follows the same trends.
- The double bond (or a combination of double bond and O) causes a drastic change in behaviour.

PPVE – Fragments

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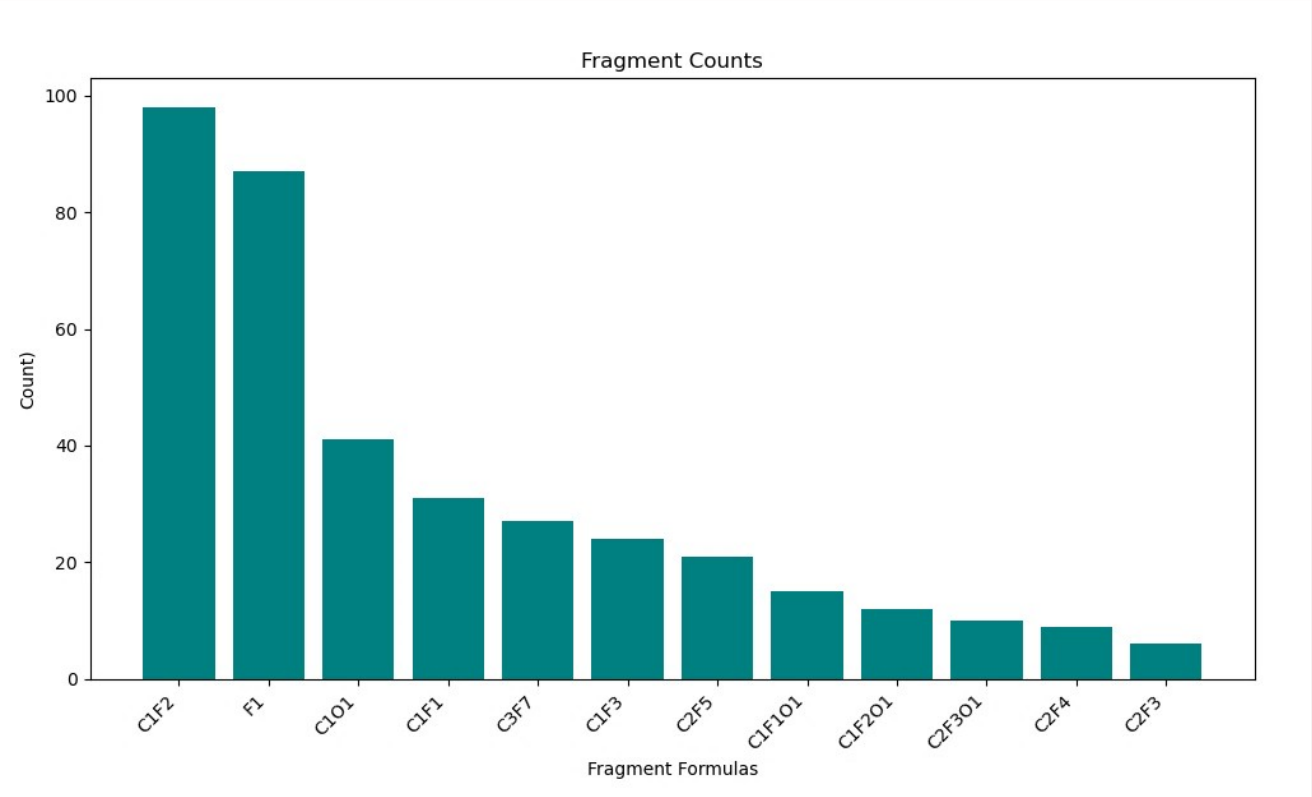

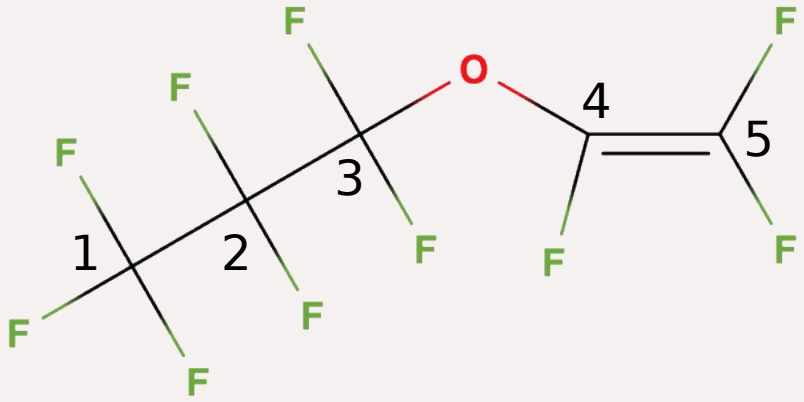

“a strong CO signal was observed with a weak COF signal attributing to the oxygen atoms in it”

“Low-mass fluorocarbons were predominant in PPVE…”

References: Y. Kim, et al, Acs Sustainable Chemistry & Engineering **11** (16), 6136-6142 (2023).

Fragments - Comparisons

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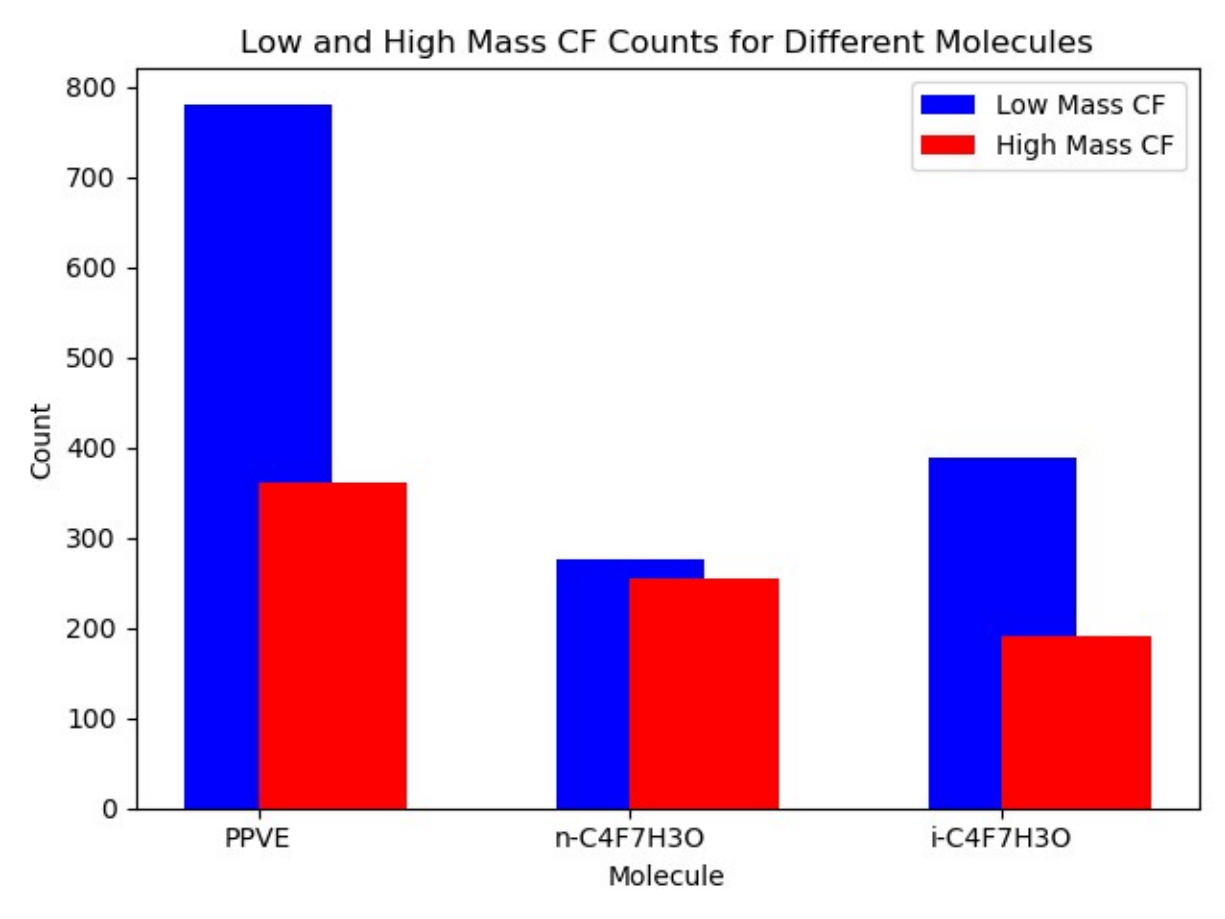

"[i-C4F7H3O] showed slightly higher F and low-mass fluorocarbon intensities than [n-C4F7H3O] ."

"[n-C4F7H3O] showed higher large-mass fluorocarbon intensity than [i-C4F7H30]."

"the intensity of the fluorocarbon peaks observed for the [n-C4F7H3O] and [i-C4F7H3O] plasmas was lower than that of the fluorocarbon peaks observed for the C4F8 and PPVE plasmas"

References: Y. Kim, et al, Acs Sustainable Chemistry & Engineering **11** (16), 6136-6142 (2023).

Rules for Fragmentation

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- Position of an Oxygen atom is very important due to hypothesised localisation
- Functional group of the oxygen atom is also important, e.g. an alcohol can be used to limit C-O breaking
- Hydrogen atoms have fairly consistent behaviour in terms of being ejected very quickly
- Double carbon-carbon bonds dissociate more rapidly than single carbon-carbon bonds
- Effect of proximity to carbon-carbon double bond and proximity to oxygen atom are cumulative

Future Work

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- Investigate the different electronic structure packages/theories available

- Investigate the temperature dependence of dissociation and the optimal temperature for simulations

- More molecules. But which ones?

Acknowledgements

- Dmitry Shalashilin

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