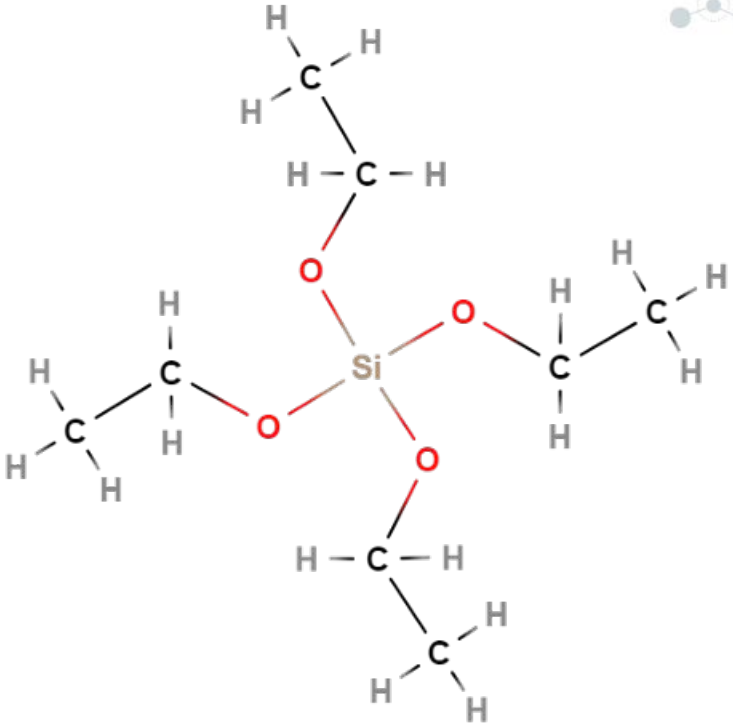
Calculating the dissociation of TEOS

Oliver Bramley

16.10.2024

TEOS

- TEOS is a precursor used for depositing layers of SiO_2
- Mechanism for its dissociation is not fully understood



General Motivation

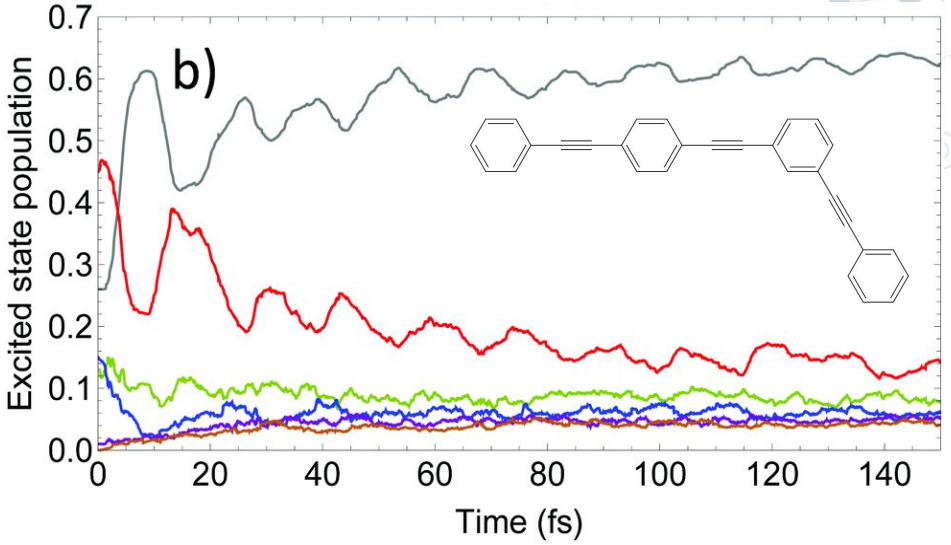
- Utilise direct dynamics simulations to better understand the dissociation process
- Understand how and which bonds break
- Predict intermediate and final products
- Design molecules starting with desired products

Ab initio Multiple Cloning

quantemol

UNIVERSITY OF LEEDS

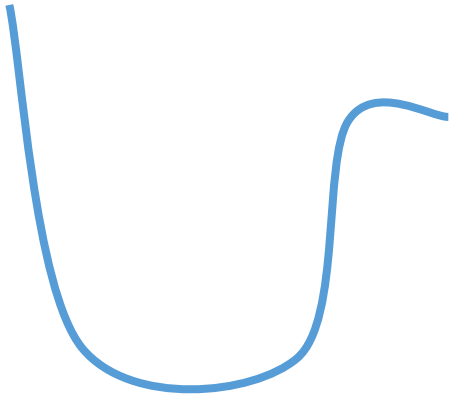
- Method developed at the University of Leeds by Dmitry Shalashilin and Dmitry Makhov
- Brings together *ab initio* Multiple Spawning (AIMS) and Multiconfigurational Ehrenfest (MCE)
- Used to model photoexcitation of singlet states



An ab initio multiple cloning approach for the simulation of photoinduced dynamics in conjugated molecules Phys. Chem. Chem. Phys., 2018, **20**, 17762-17772

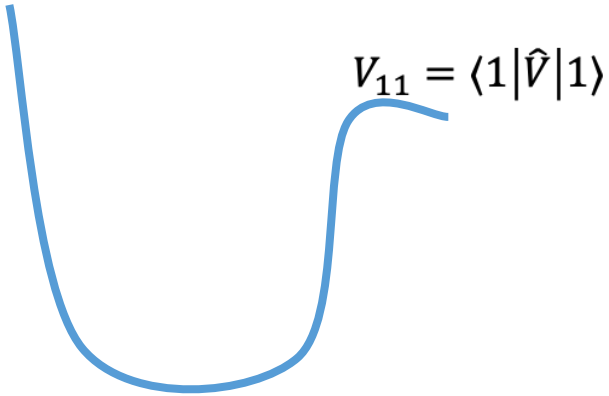
Ehrenfest Trajectories and Cloning

Ehrenfest Trajectories and Cloning



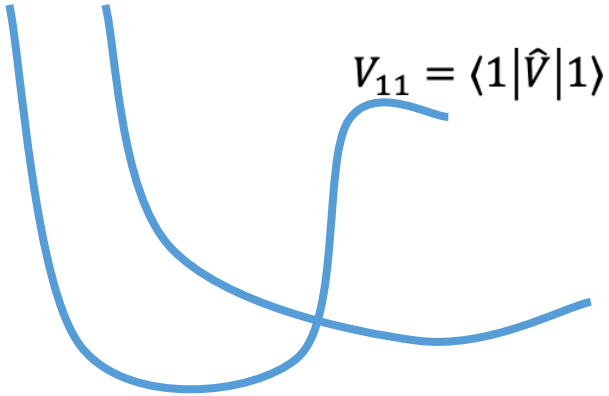
Potential energy surface

Ehrenfest Trajectories and Cloning



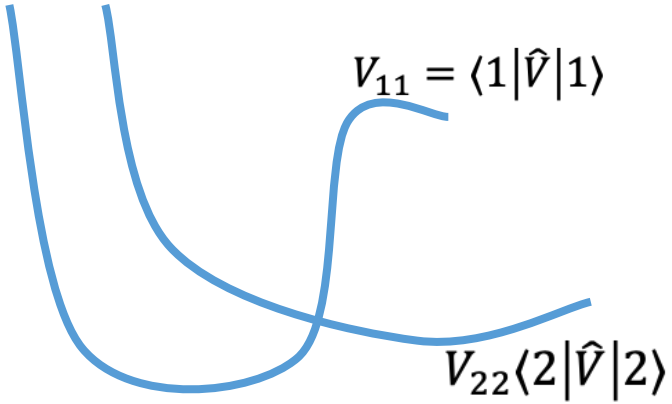
State 1

Ehrenfest Trajectories and Cloning



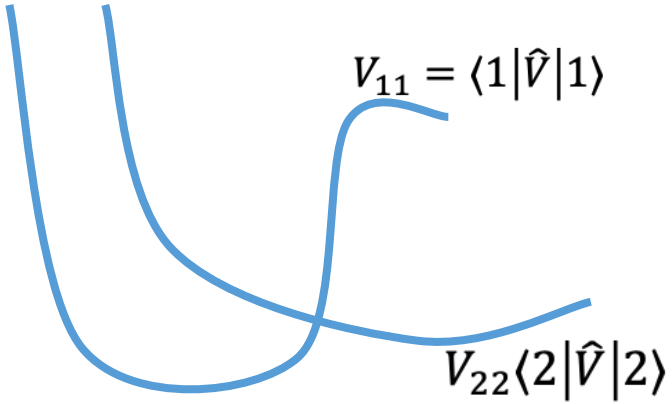
Add a second potential energy surface

Ehrenfest Trajectories and Cloning



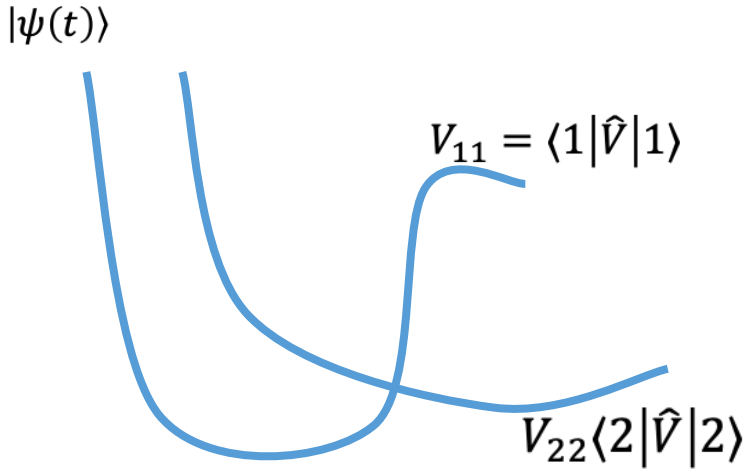
State 2

Ehrenfest Trajectories and Cloning



Construct a wavefunction

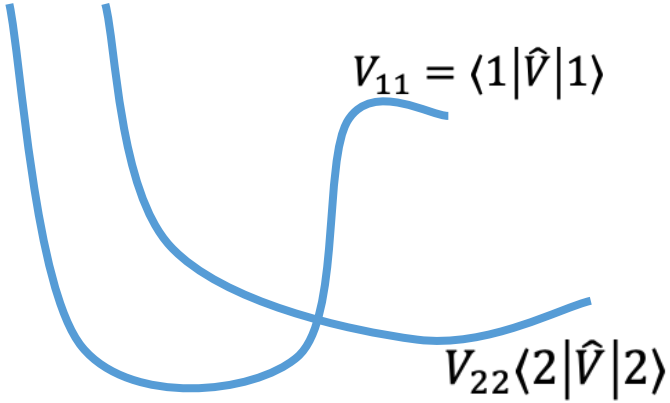
Ehrenfest Trajectories and Cloning



Construct a time-dependent wavefunction

Ehrenfest Trajectories and Cloning

$$|\psi(t)\rangle = (a_1(t)|1\rangle + a_2(t)|2\rangle)|\boldsymbol{z}(t)\rangle$$



$|z\rangle$ is a gaussian wave packet

Ehrenfest Trajectories and Cloning

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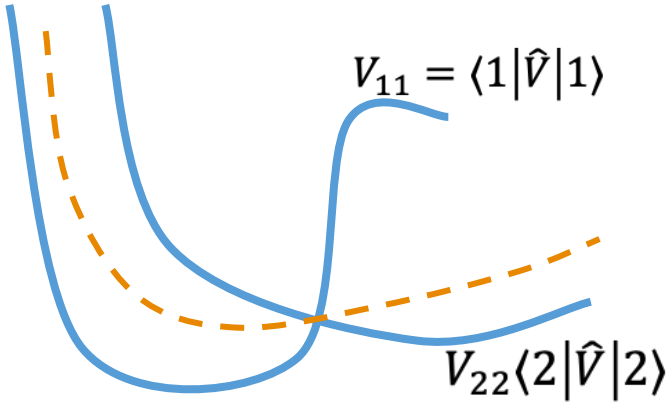

Ehrenfest trajectories follow the path of the average potential energy

Ehrenfest Trajectories and Cloning

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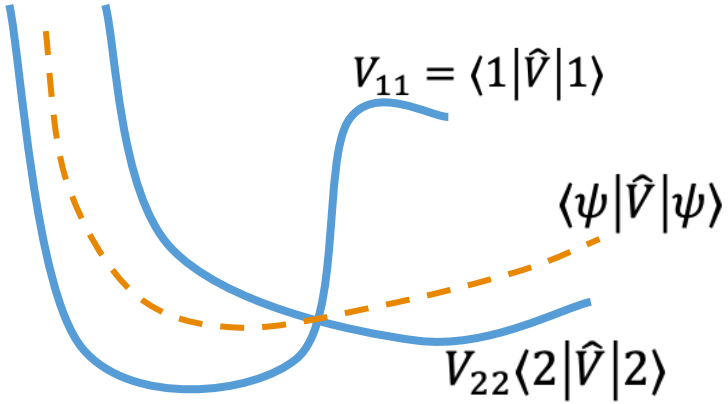

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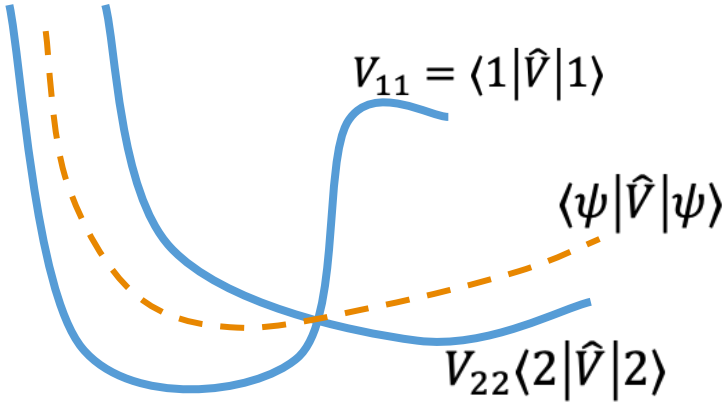

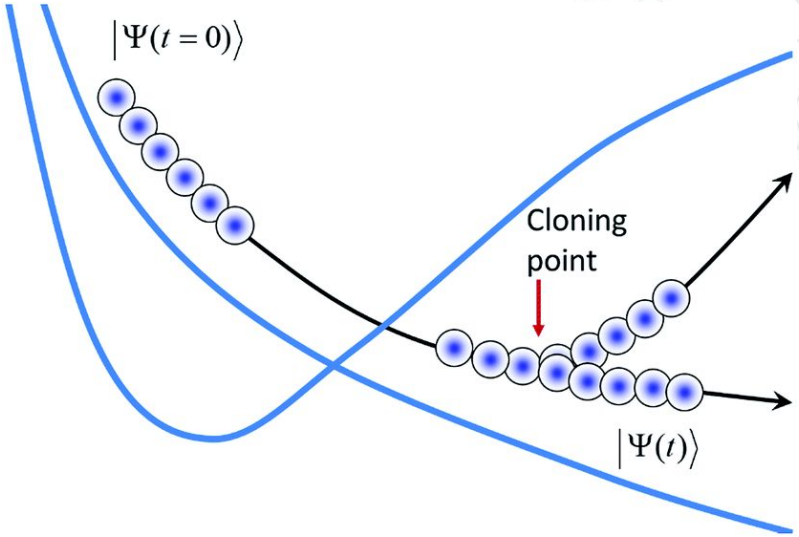

Cloning splits the wave function to combat the weakness of using Ehrenfest trajectories

Toward fully quantum modelling of ultrafast photodissociation imaging experiments. Treating tunnelling in the ab initio multiple cloning approach Faraday Discuss., 2016, **194**, 81-94

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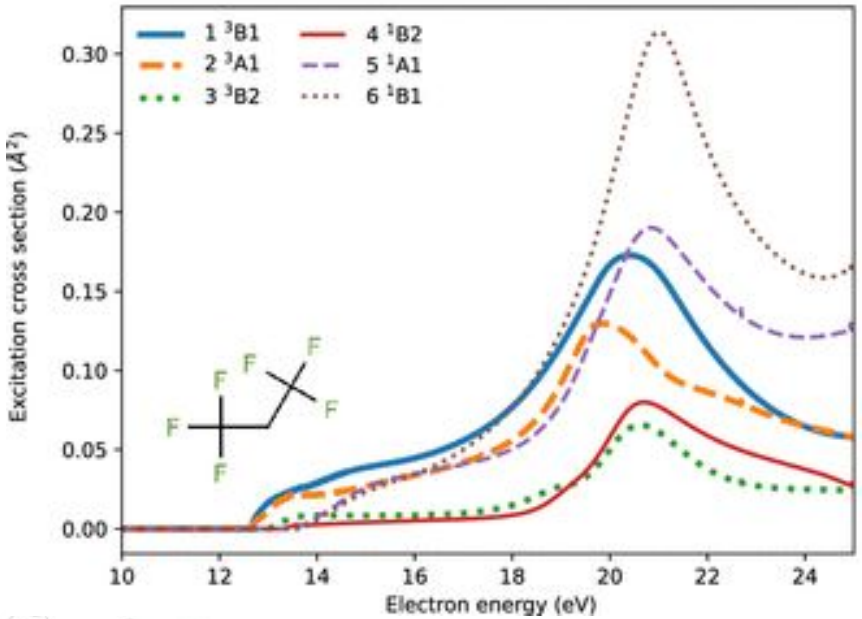
Method Overview

- Calculate electronic excitation cross sections using QEC
- AIMC method used to propagate an ensemble of trajectories
- Time Dependent Density Functional Theory used to calculate electronic energy

QEC
electron collisions

Q-CHEM™
A Quantum Leap Into the Future of Chemistry

Cross sections for $C_3H_2F_6$

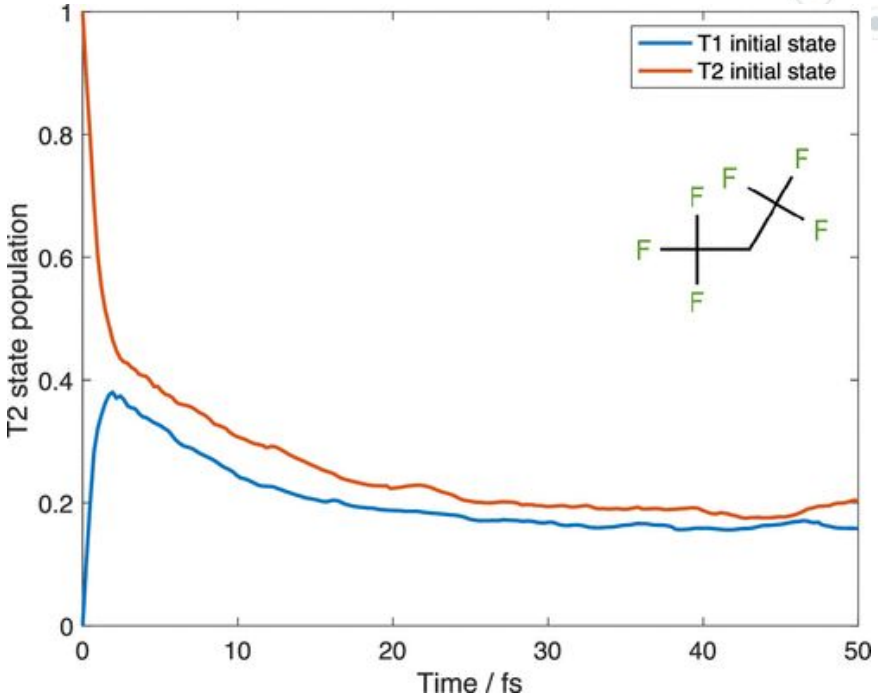


Electron impact electronic excitation cross sections for $C_3H_2F_6$ calculated using QEC

Lowest Triplet State

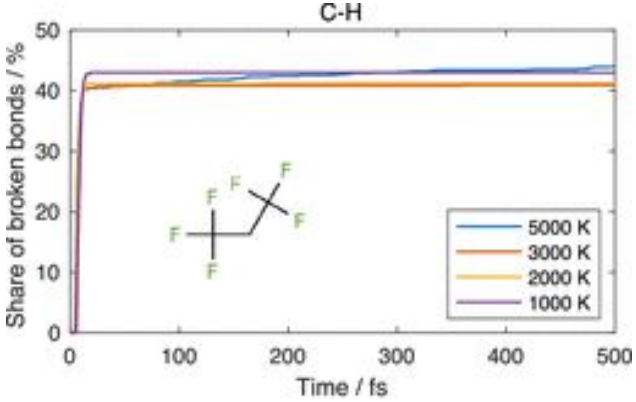
75% of the population is in the lower triplet state within a few femtoseconds

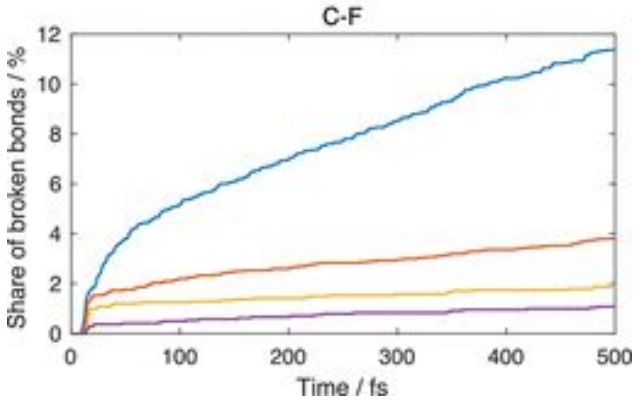
So proceed to use just the lowest triplet state

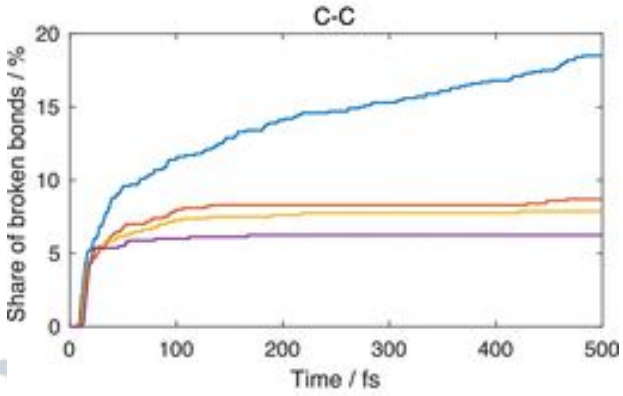


Dissociation of Hydrofluorocarbon Molecules after Electron Impact in Plasma J. Phys. Chem. Lett. 2024, 15, 12, 3404–3411

Dissociation of Hydrofluorocarbons



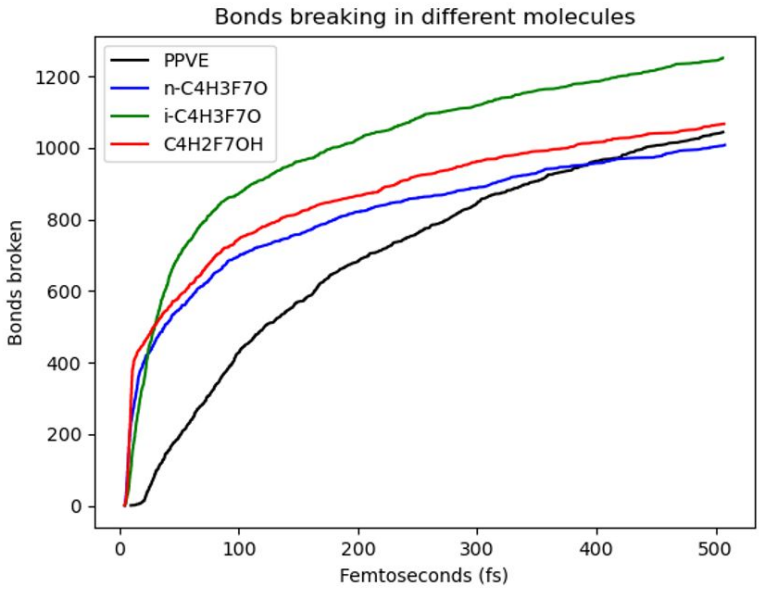


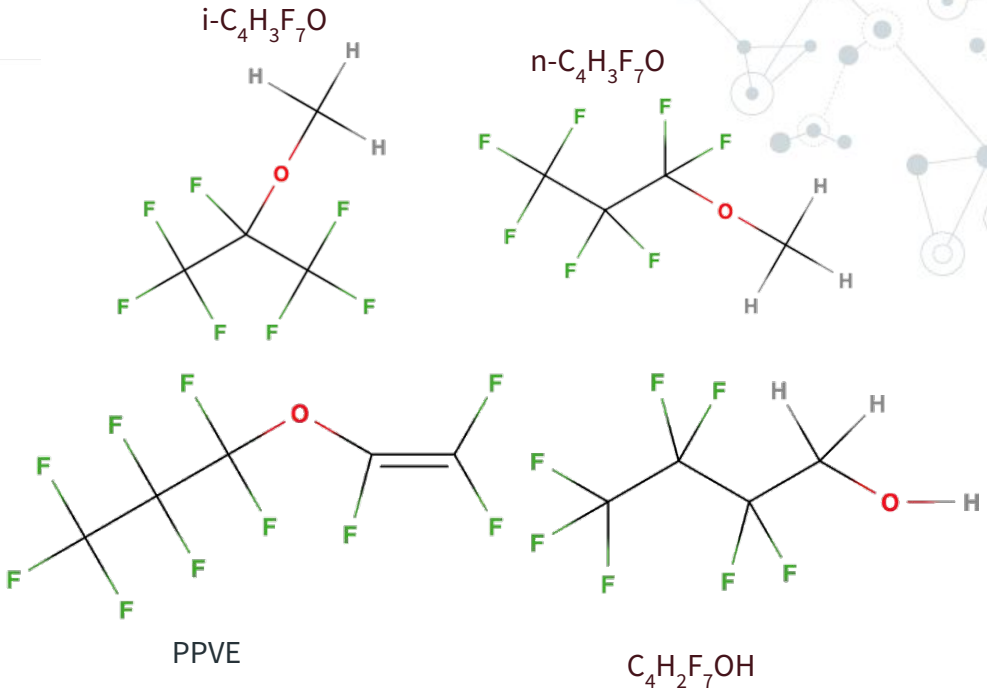


Number of bonds broken at different temperatures for $C_3H_2F_6$

Dissociation of Hydrofluorocarbon Molecules after Electron Impact in Plasma J. Phys. Chem. Lett. 2024, 15, 12, 3404–3411

Comparison



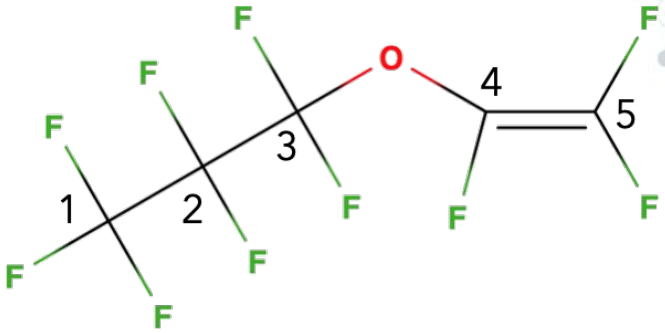


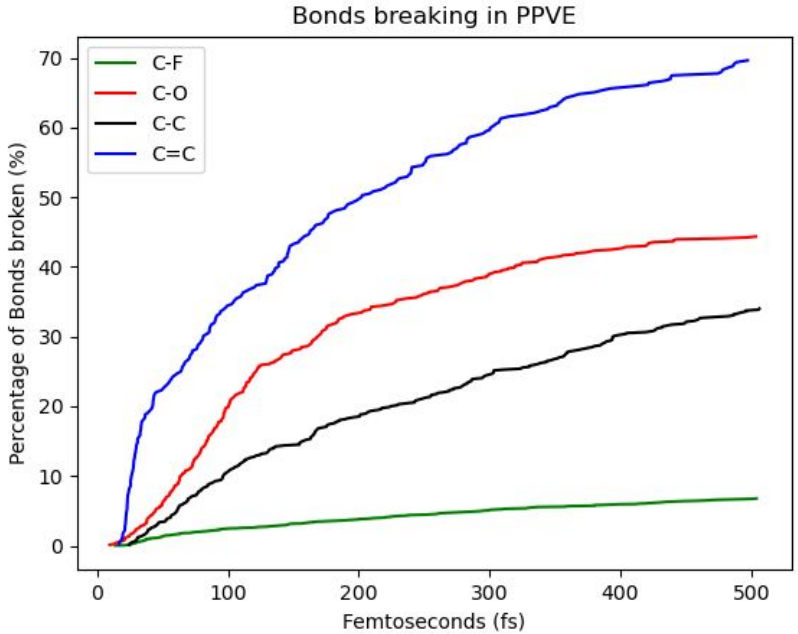
PPVE, n-$C_4H_3F_7O$ and $C_4H_2F_7OH$ all have approximately the same number of bonds broken after 500fs

As yet unpublished results from Ryan Brook

PPVE

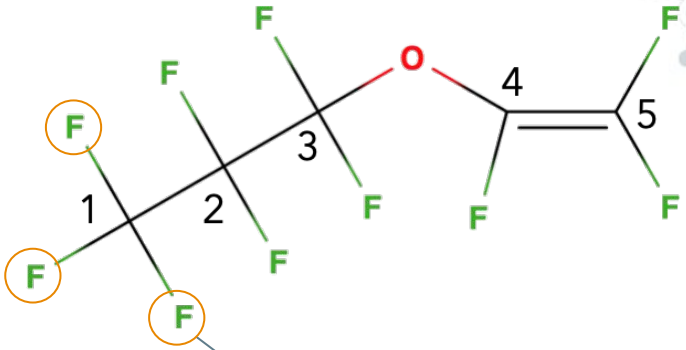
- Bond breaking starts comparatively slowly in PPVE due to lack of Hydrogen
- Perhaps surprisingly the 70% of the C=C bond breaks

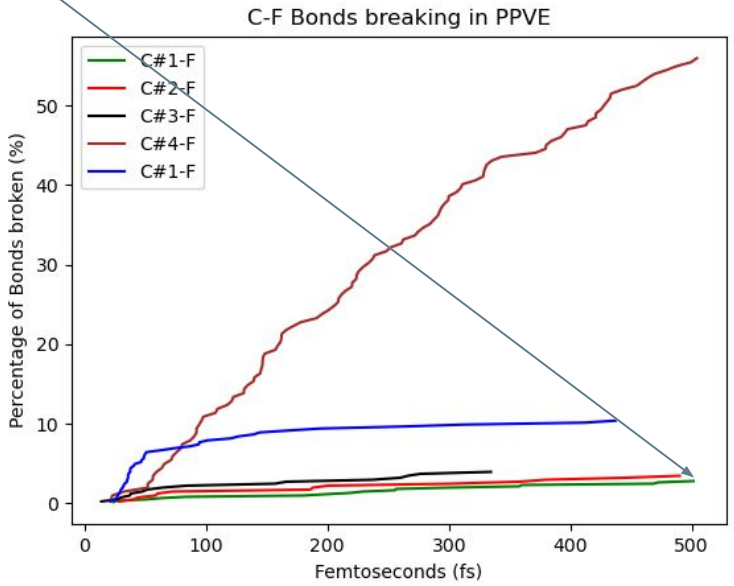




PPVE C-F Bonds

- Fluorines furthest away from the C-O and C=C bonds break least readily





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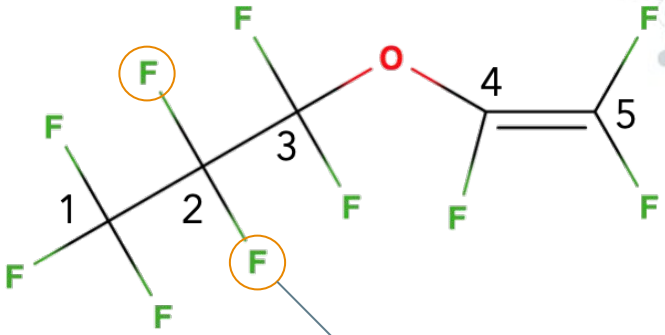

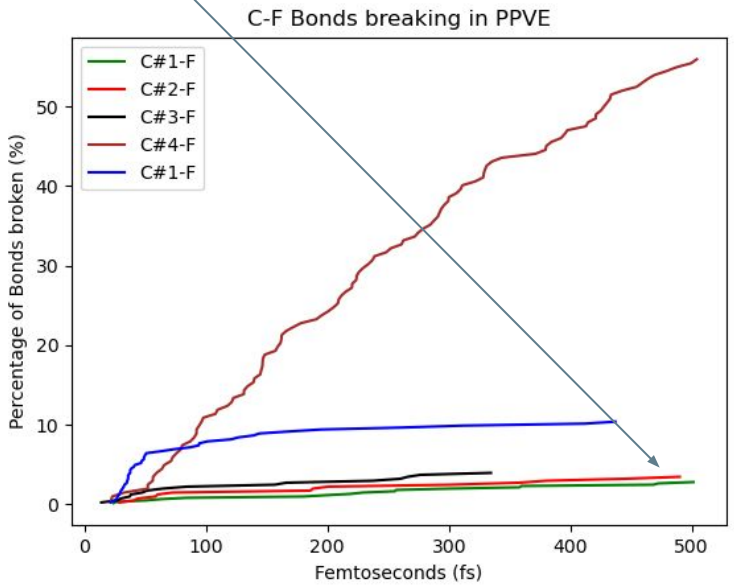

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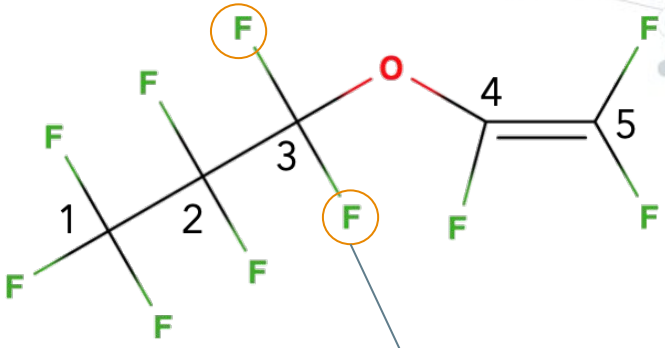
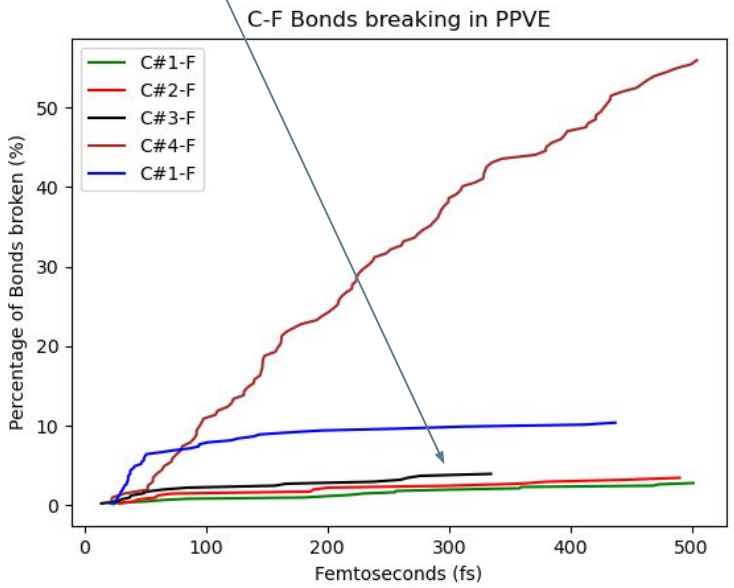
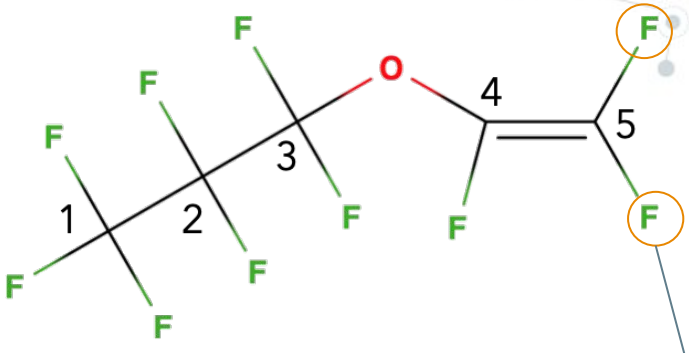
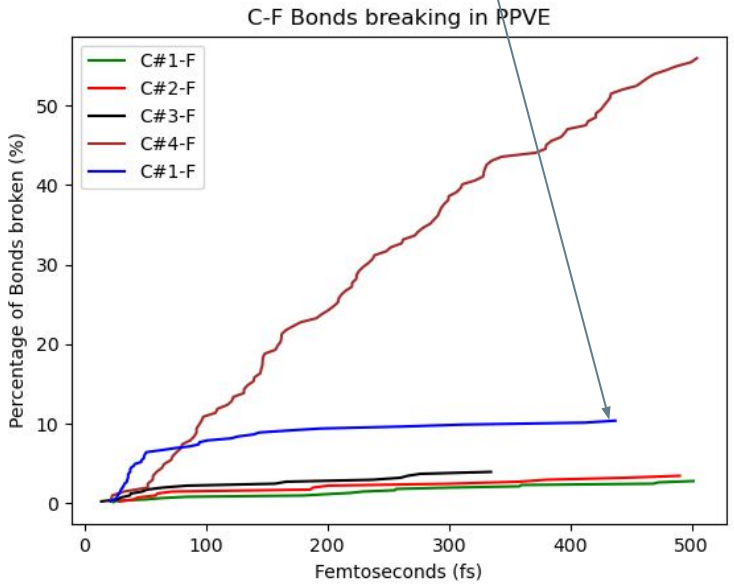




PPVE C-F Bonds

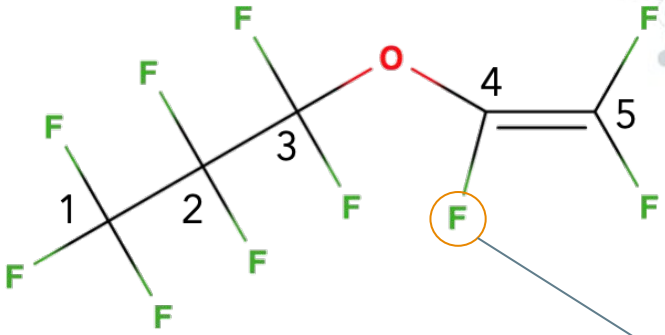
- Adjacent to C=C bond and close proximity to C-O still makes up small proportion of C-F bonds broken

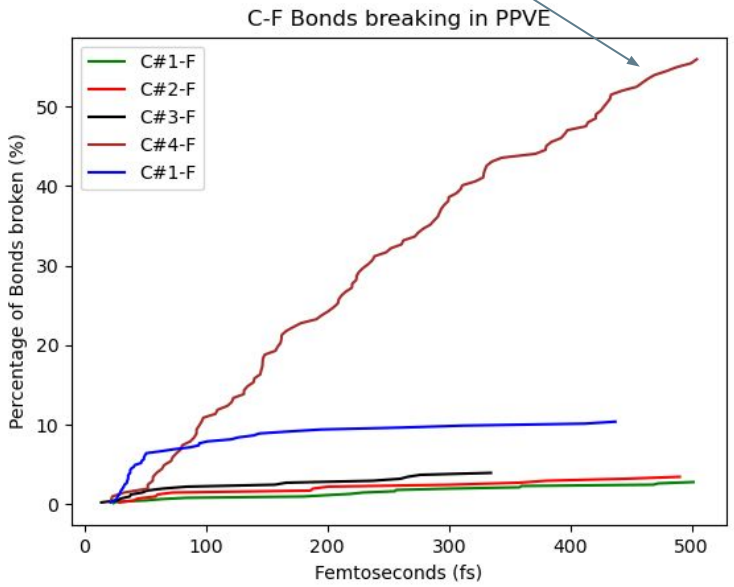




PPVE C-F Bonds

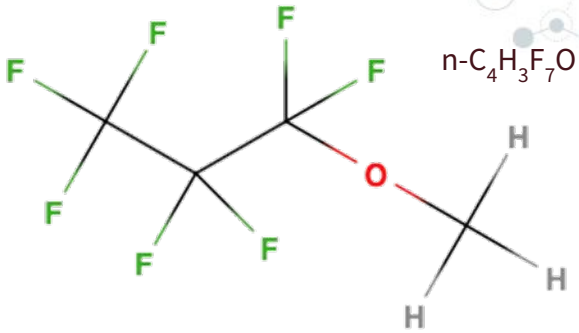
- Majority of C-F bonds broken are adjacent to the C-O and C=C bonds





n-$C_4H_3F_7O$ vs i-$C_4H_3F_7O$ isomer comparison

- Comparing bond breaking in isomers we can pinpoint which atoms affect bond breaking
- Can see the importance of proximity to oxygen
- Same molecular formula but different structure



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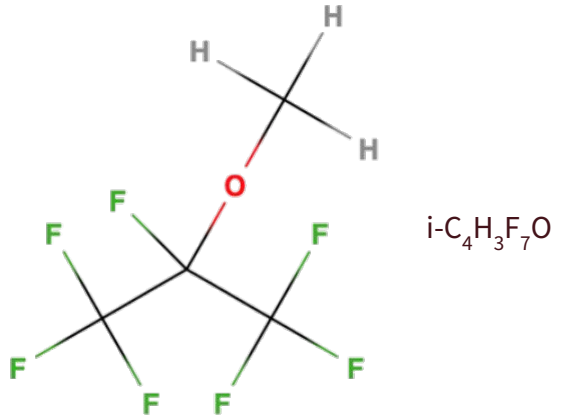
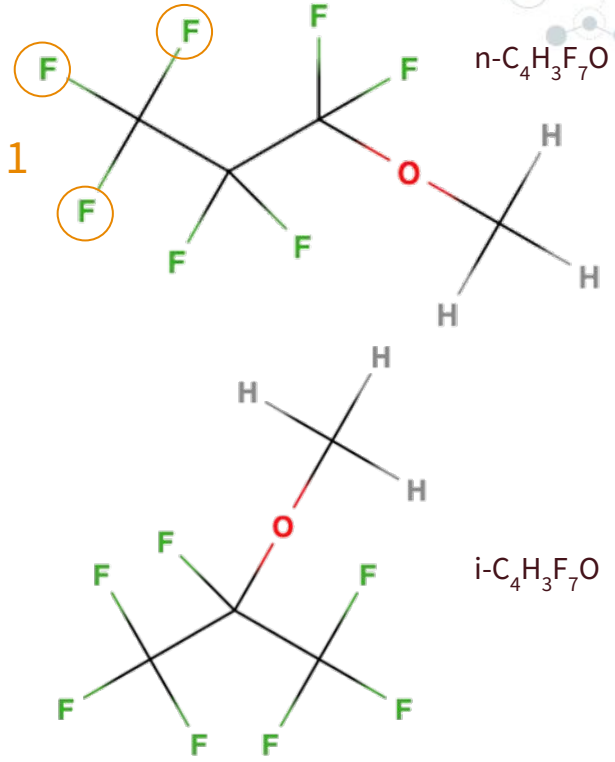


i-$C_4H_3F_7O$

n-$C_4H_3F_7O$ vs i-$C_4H_3F_7O$ isomer comparison

- Comparing bond breaking in isomers we can pinpoint which atoms affect bond breaking
- Can see the importance of proximity to oxygen
- Three different Fluorine environments



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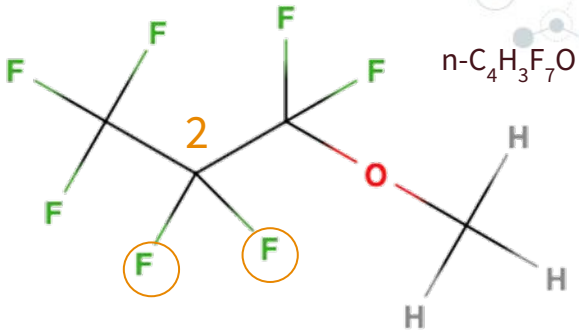

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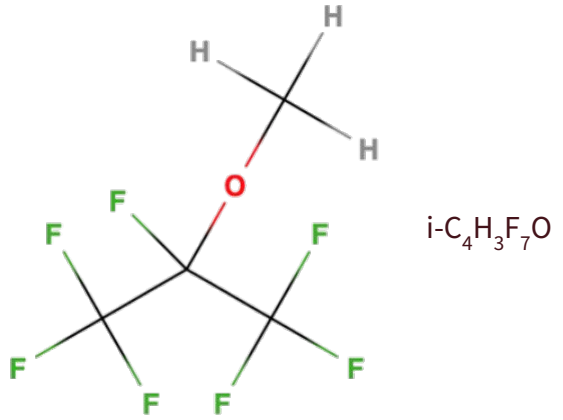

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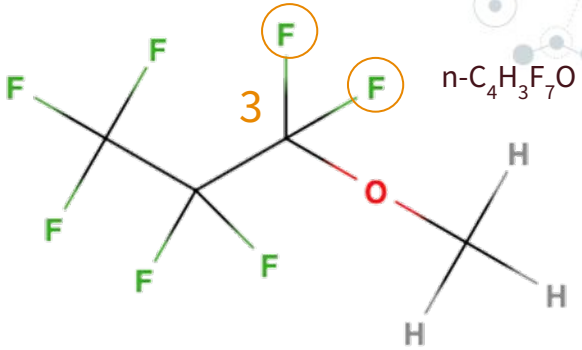
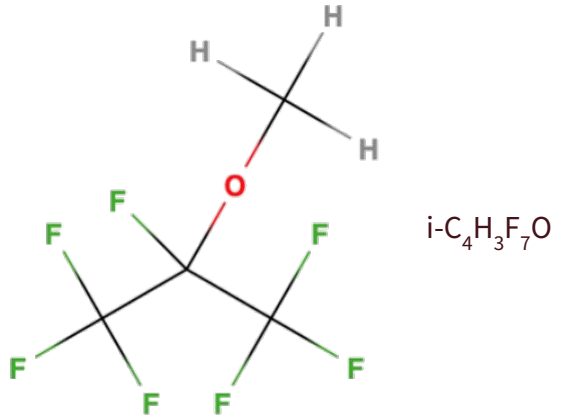


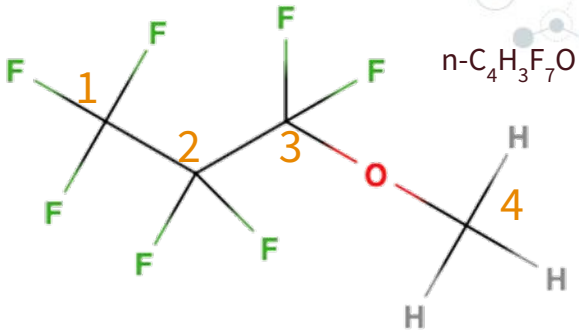
$n\text{-}C_4H_3F_7O$



$i\text{-}C_4H_3F_7O$

n-$C_4H_3F_7O$ vs i-$C_4H_3F_7O$ isomer comparison

- Comparing bond breaking in isomers we can pinpoint which atoms affect bond breaking
- Can see the importance of proximity to oxygen
- Four different carbon environments



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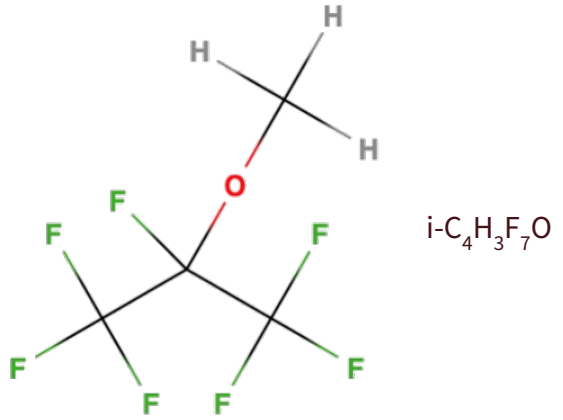

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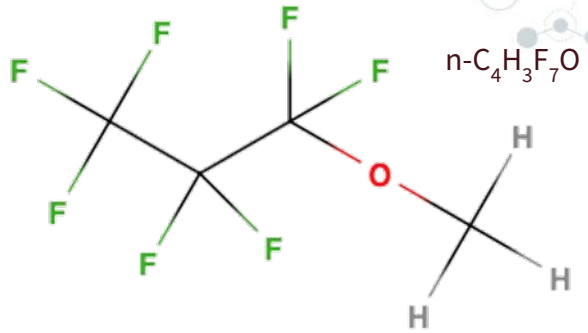

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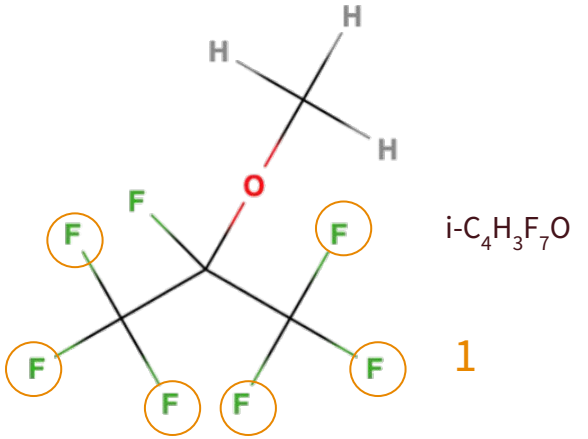

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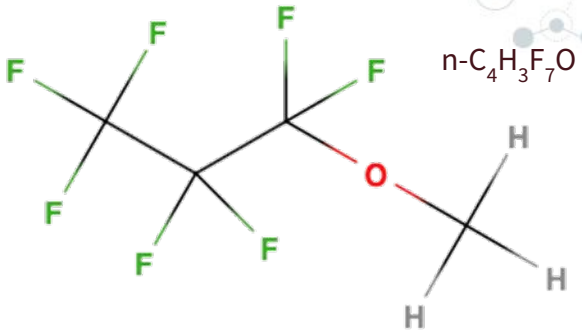
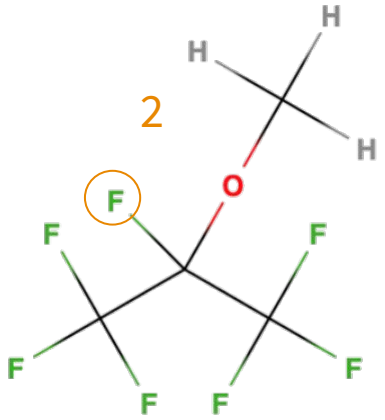


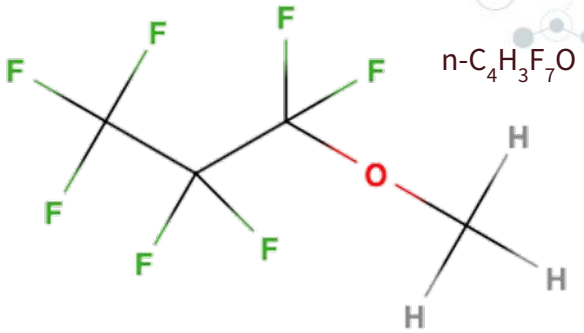
n-$C_4H_3F_7O$



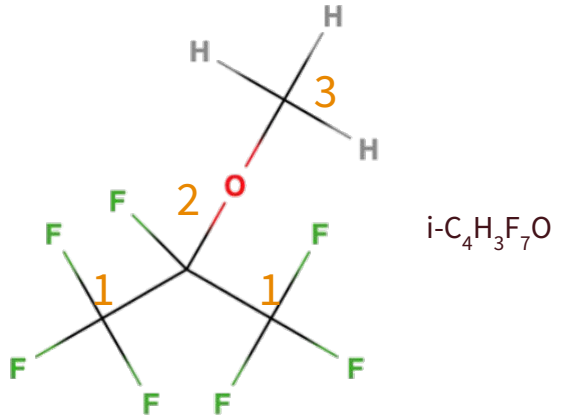
i-$C_4H_3F_7O$

n-$C_4H_3F_7O$ vs i-$C_4H_3F_7O$ isomer comparison

- Comparing bond breaking in isomers we can pinpoint which atoms affect bond breaking
- Can see the importance of proximity to oxygen
- Three different Carbon environments

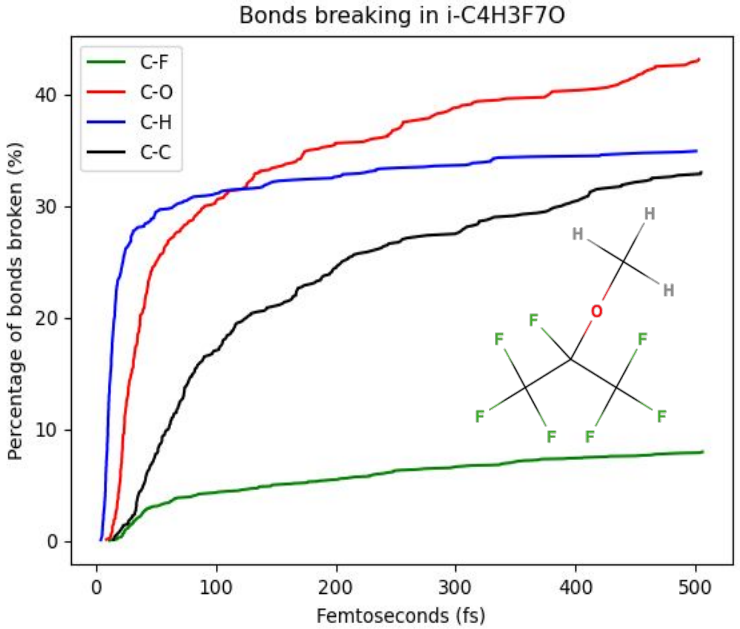


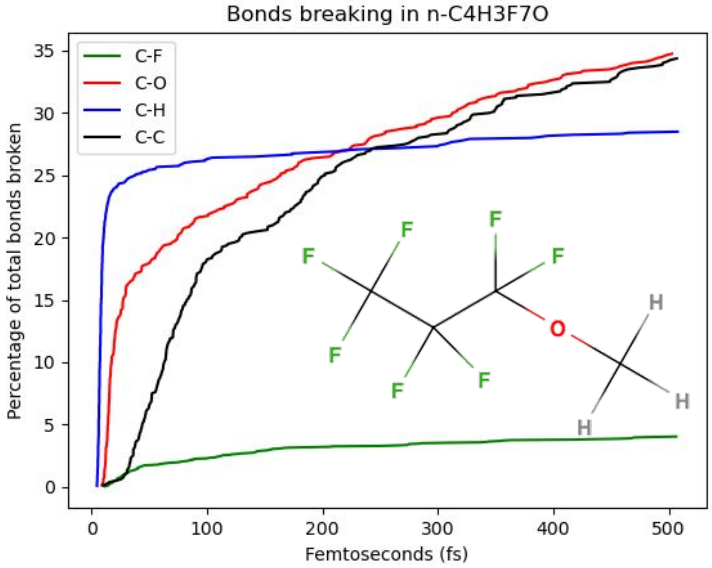
n-$C_4H_3F_7O$



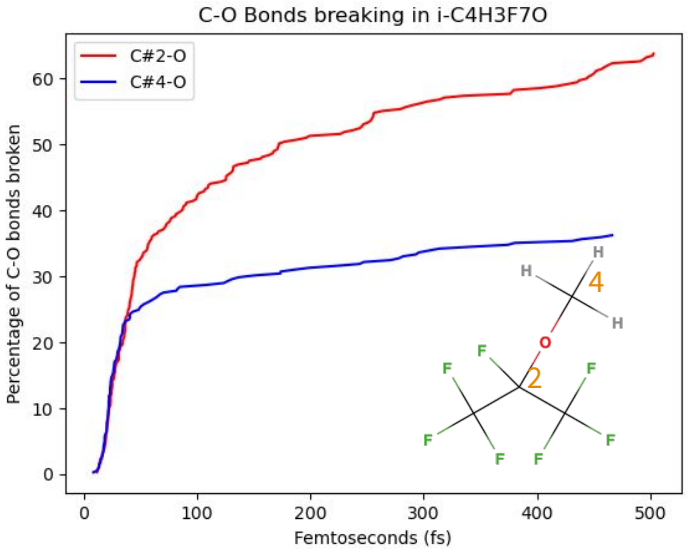
i-$C_4H_3F_7O$

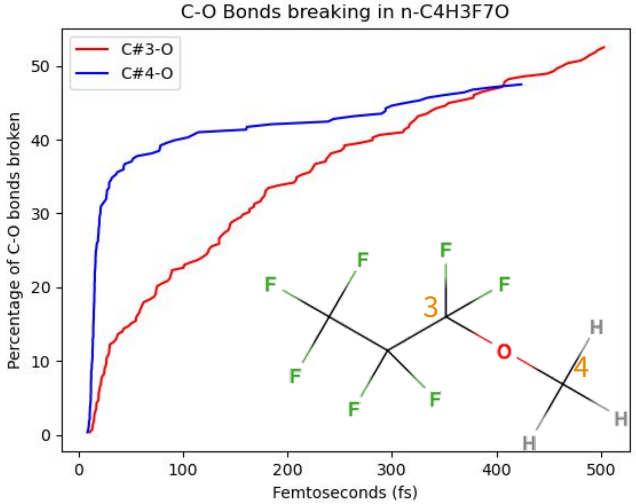
i-$C_4H_3F_7O$ vs n-$C_4H_3F_7O$ isomer comparison





i-$C_4H_3F_7O$ vs n-$C_4H_3F_7O$ isomer comparison





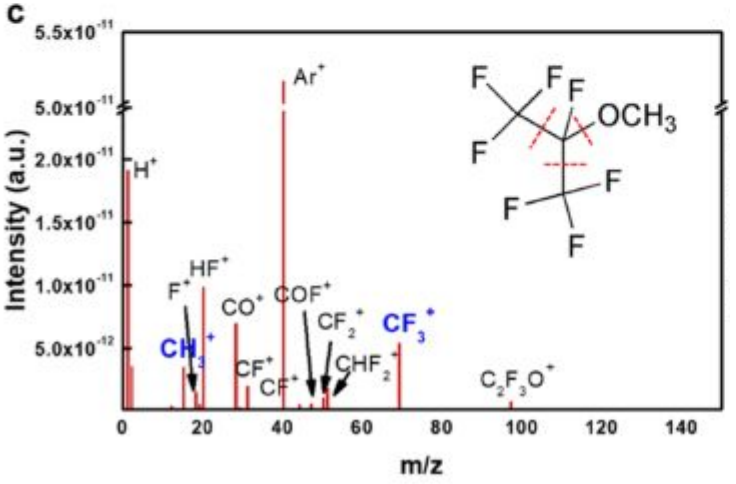
i-$C_4H_3F_7O$ vs n-$C_4H_3F_7O$ isomer comparison

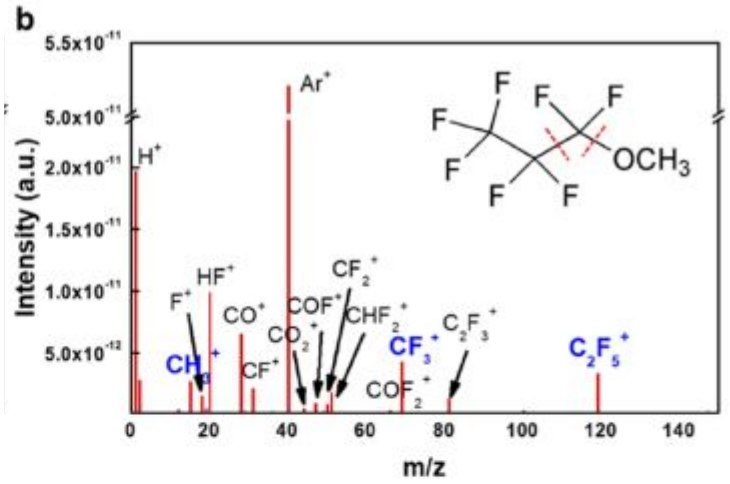
Bond Type	i-$C_4H_3F_7O$ (%)	n-$C_4H_3F_7O$ (%)
C-F	7.96	4.04
C-C	33.00	34.38
C-H	34.92	28.50
C-O	43.12	34.75

Final proportion of bonds broken for each isomer

$i\text{-}C_4H_3F_7O$ vs $n\text{-}C_4H_3F_7O$ isomer comparison

Bond Type	$i\text{-}C_4H_3F_7O$ (%)	$n\text{-}C_4H_3F_7O$ (%)
C-C	33.00	34.38
C-O	43.12	34.75





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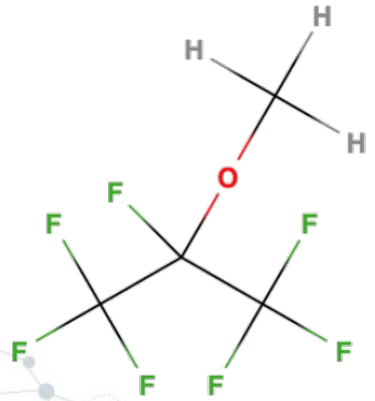
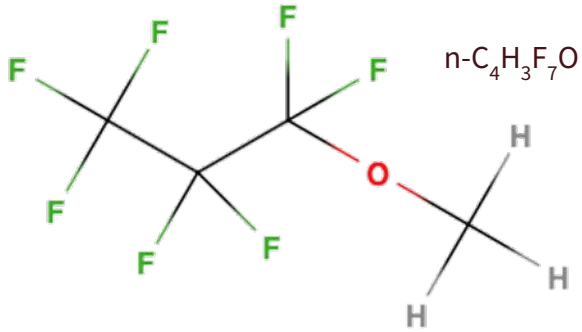
i-$C_4H_3F_7O$ vs n-$C_4H_3F_7O$ isomer comparison

- i-$C_4H_3F_7O$ has a great number of C-F bonds broken due to the proximity of the oxygen to more Fluorine atoms
- The oxygen in the n-$C_4H_3F_7O$ is mostly affecting closest carbon that contains C-F bonds.
- Oxygen position in i-$C_4H_3F_7O$ also gives a sharper peak

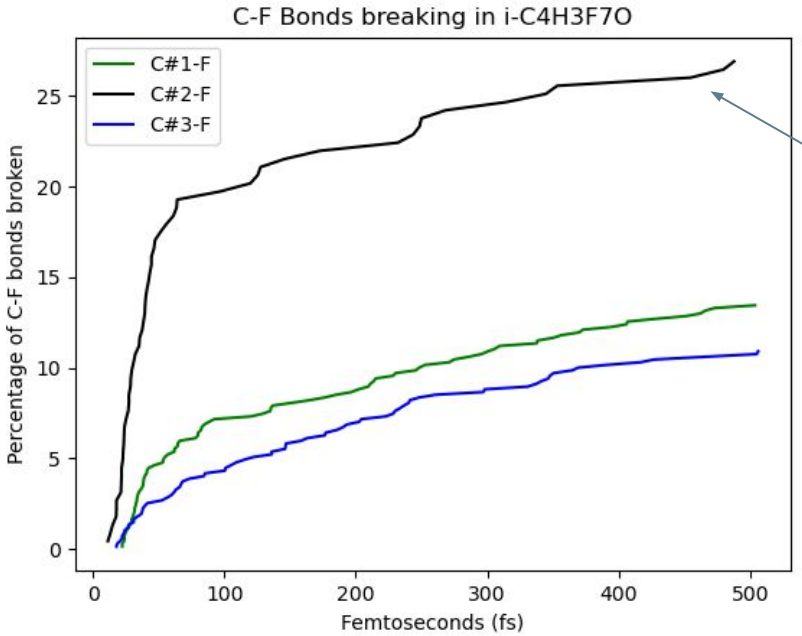


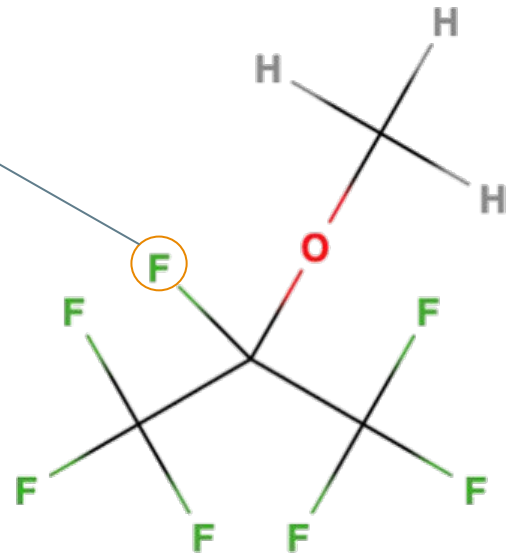
i-$C_4H_3F_7O$



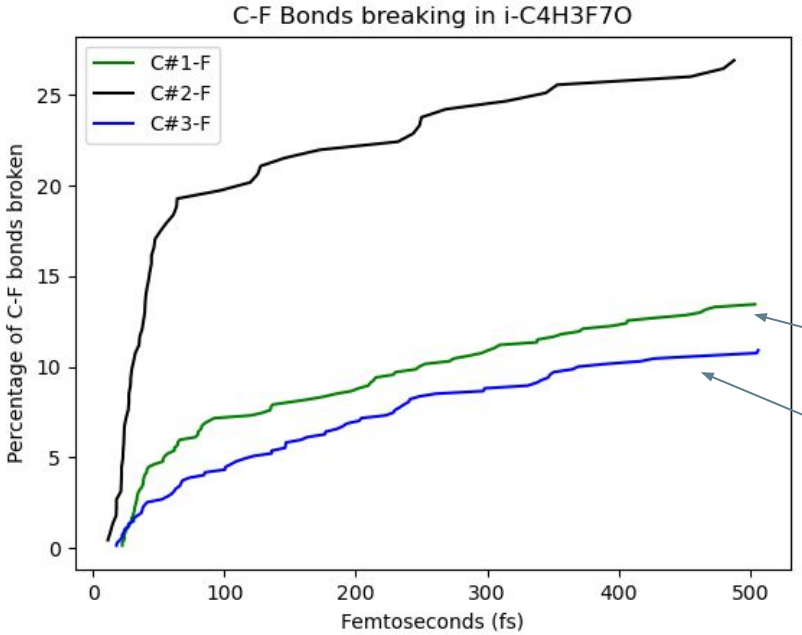
n-$C_4H_3F_7O$

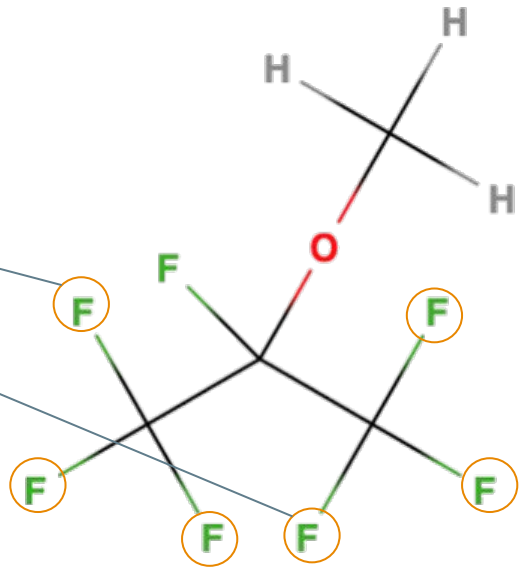
i-$C_4H_3F_7O$ vs n-$C_4H_3F_7O$ isomer comparison



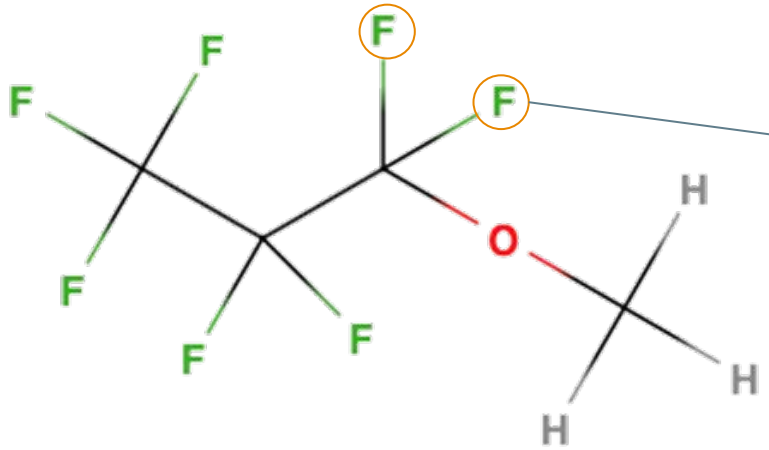


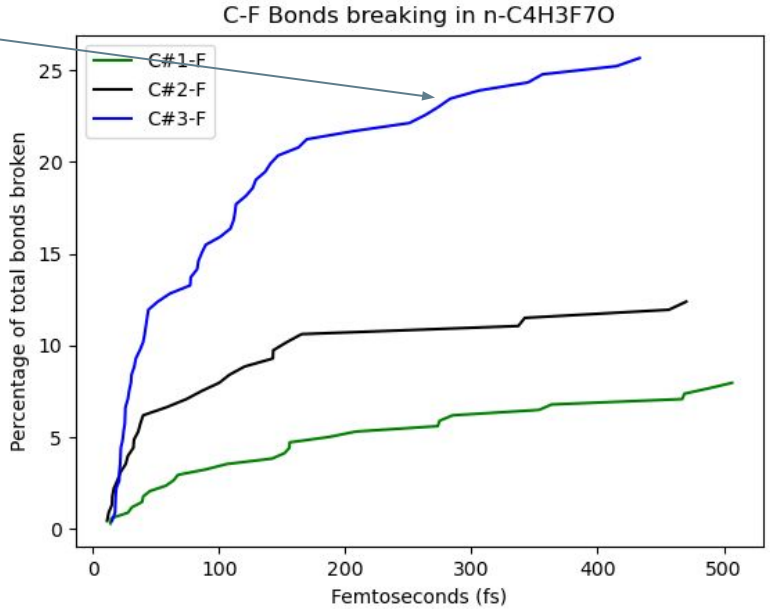
i-$C_4H_3F_7O$ vs n-$C_4H_3F_7O$ isomer comparison



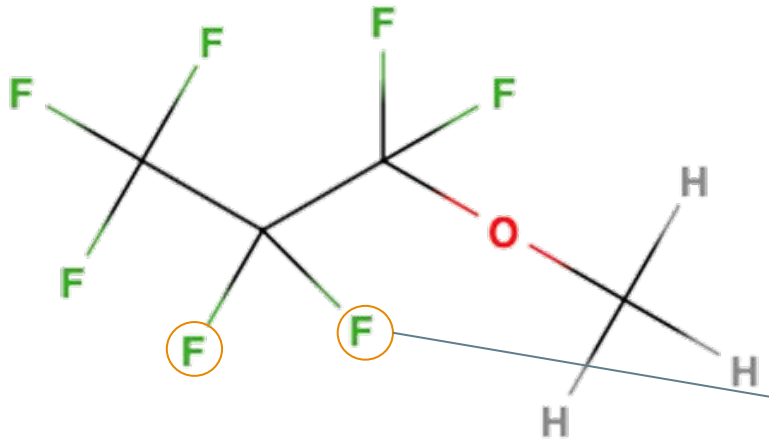


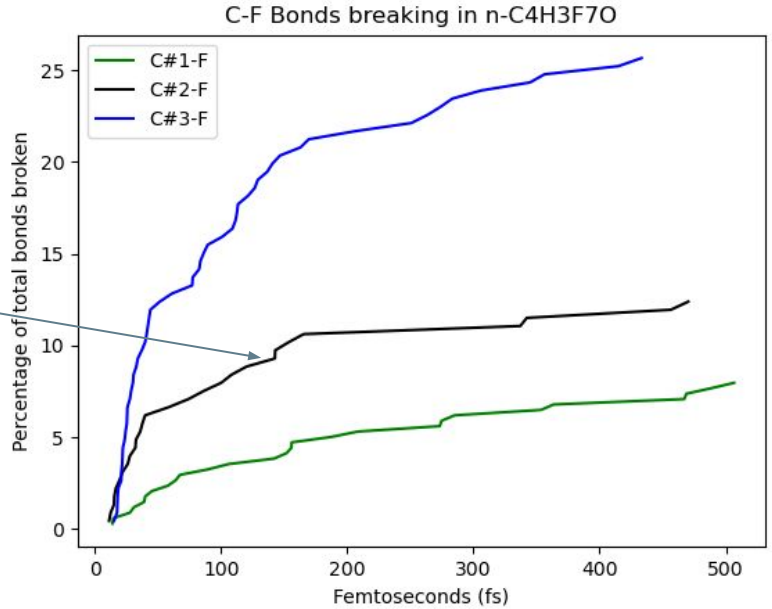
i-$C_4H_3F_7O$ vs n-$C_4H_3F_7O$ isomer comparison



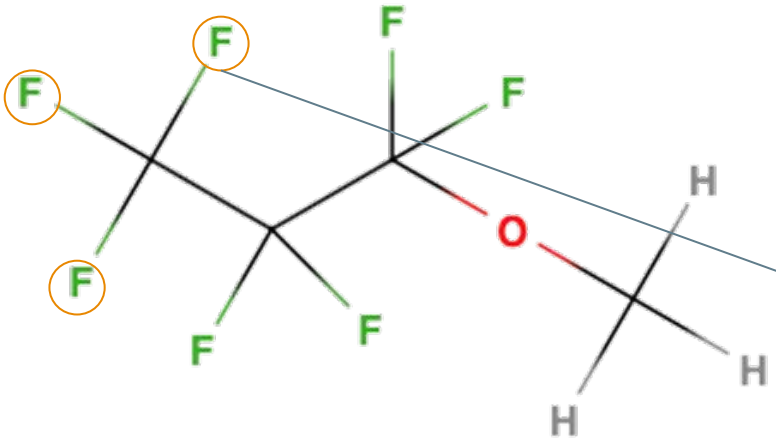


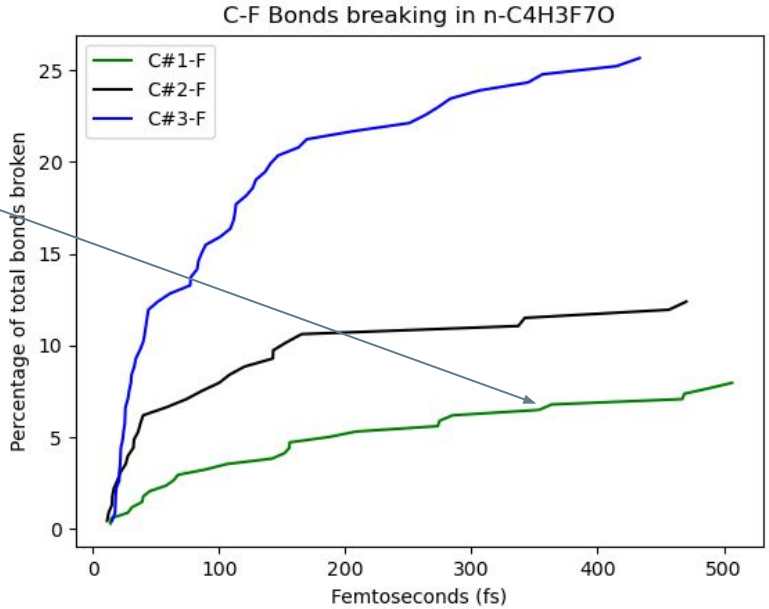
i-$C_4H_3F_7O$ vs n-$C_4H_3F_7O$ isomer comparison



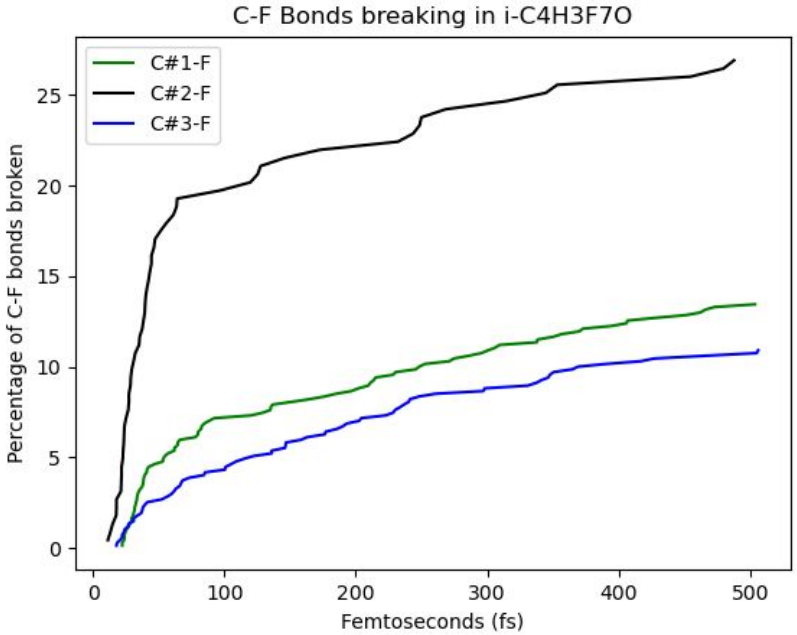


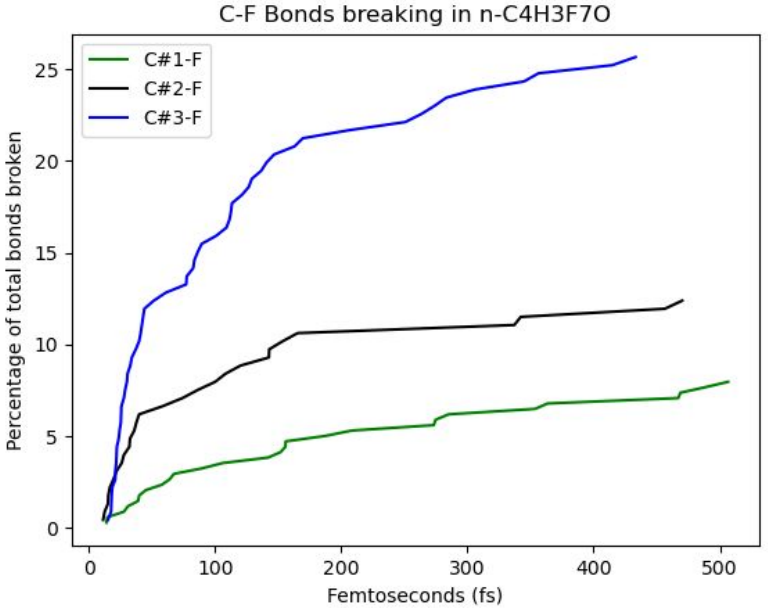
i-$C_4H_3F_7O$ vs n-$C_4H_3F_7O$ isomer comparison



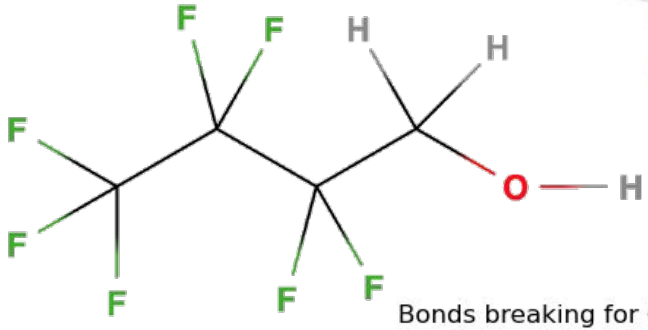


i-$C_4H_3F_7O$ vs n-$C_4H_3F_7O$ isomer comparison

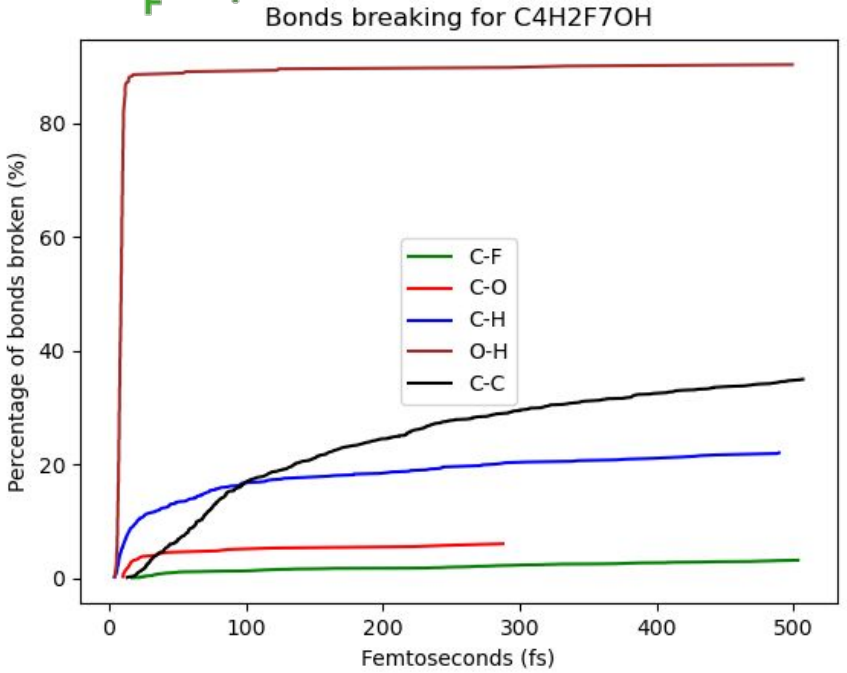




$C_4H_2F_7OH$



- 90% of all O-H bonds are broken
- Which is ⅓ of all bond breaking events
- $C_4H_2F_7OH$ has the lowest C-F bond breaking due to the ‘hydrogen buffer’ between the oxygen and the closest C-F bonds.

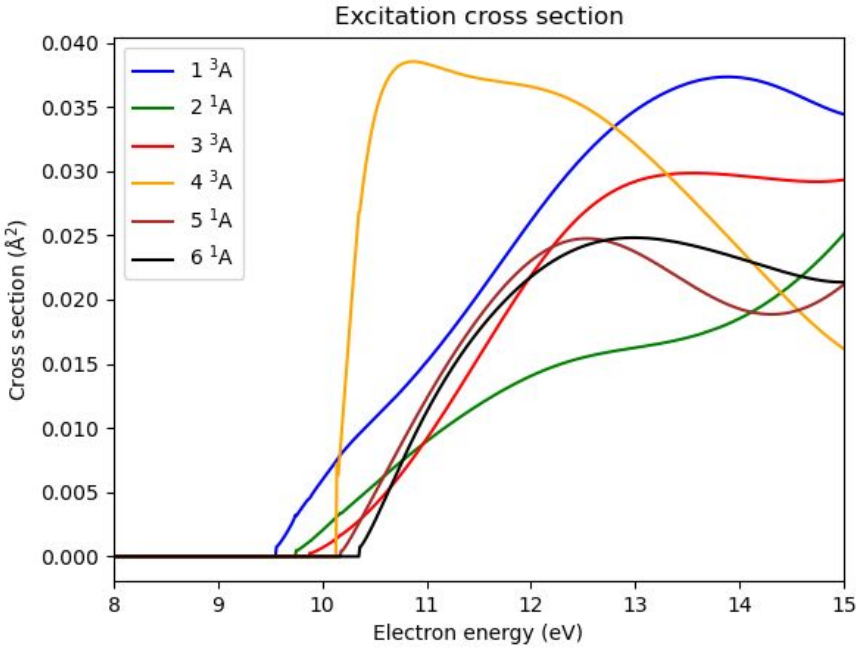


Fragmentation rules

- Oxygen atom position is 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 behaviour consistently – ejected quickly
- Double carbon-carbon bonds initially dissociate more rapidly than single carbon-carbon bonds
- Proximity effect to carbon-carbon double bond and oxygen atoms is cumulative

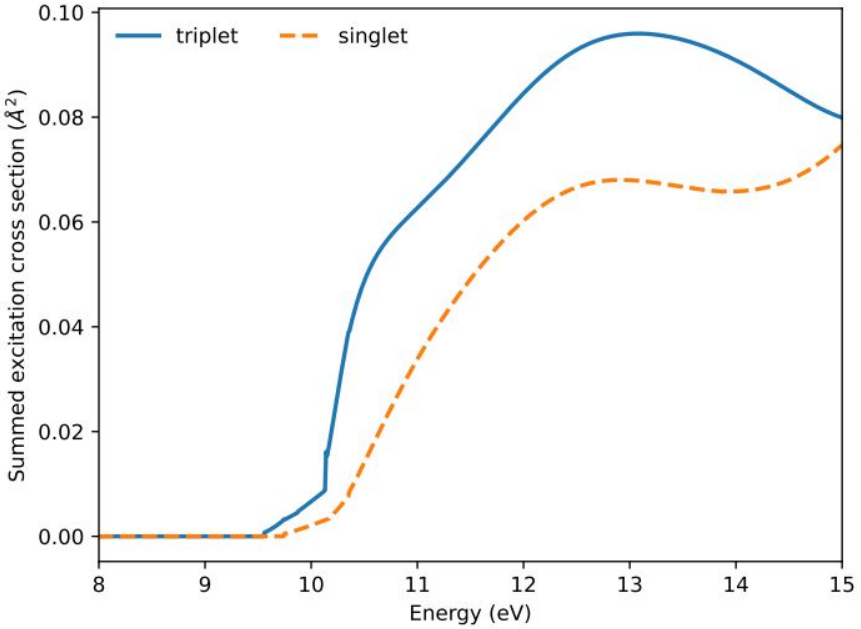
TEOS Electronic Excitation Cross Section

Cross section calculated using QEC

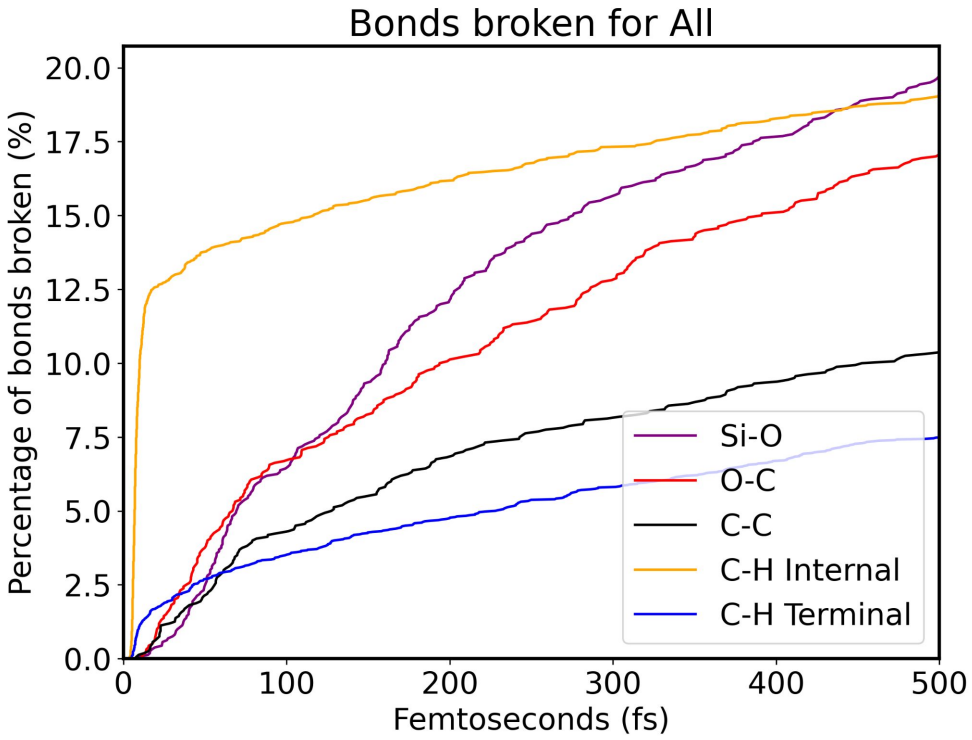


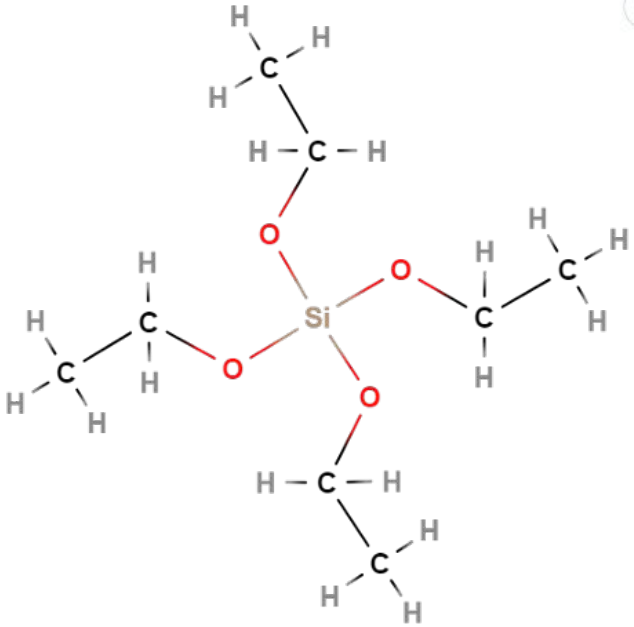
TEOS Electronic Excitation Cross Section

Triplet states dominate cross section

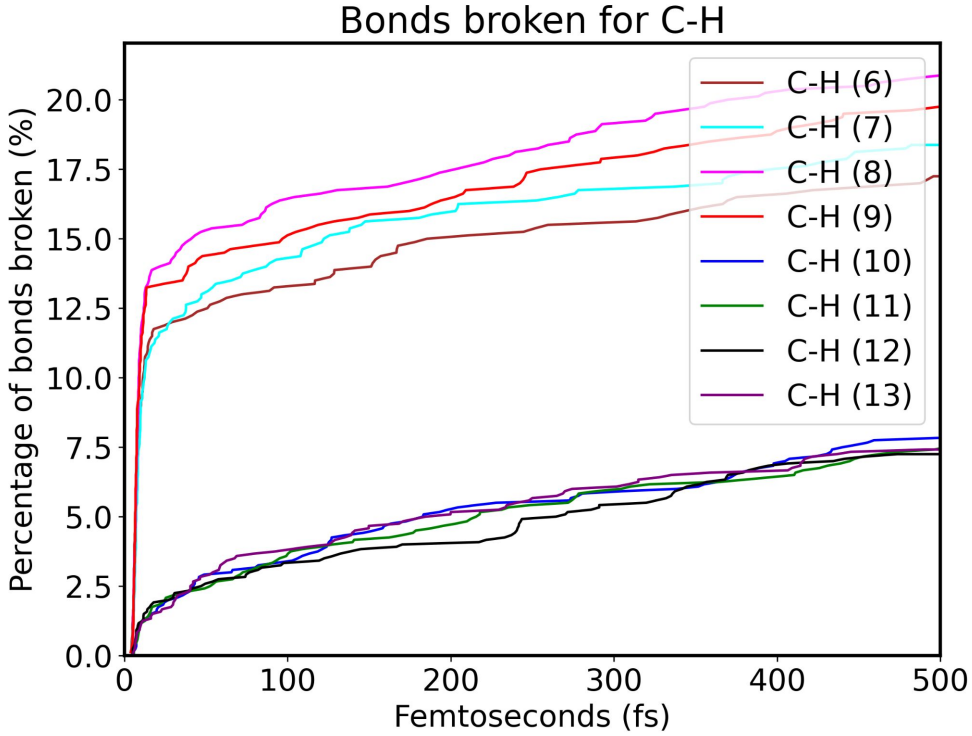


TEOS 5000K


Bonds broken for All
Percentage of bonds broken (%)
20.0
17.5
15.0
12.5
10.0
7.5
5.0
2.5
0.0
0
100
200
300
400
500
Femtoseconds (fs)
Si-O
O-C
C-C
C-H Internal
C-H Terminal


H
C
O
Si

TEOS 5000K



Hydrogens closer to oxygen are lost faster and in greater numbers than terminal hydrogens

Most Common Final Fragments TEOS

Fraction	Count	Fraction	Count	Fraction	Count
H1	573	C4H10O2Si1	22	C2H5O2Si1	10
C2H4O1	144	C2H6O3Si1	21	C1H2	10
C2H4	131	C7H16O4Si1	21	C2H3O1	9
C1H3	107	C2H2	19	C2H5O1	9
C2H5	81	C6H14O4Si1	19	C2H2O1	8
C4H10O3Si1	66	C2H3	17	C7H15O4Si1	8
C8H19O4Si1	60	C1H4	16	C2H6O1	8
H2	58	C6H15O4Si1	12	C8H17O4Si1	6
C1H2O1	43	C6H15O3Si1	12	C6H16O4Si1	6
C8H18O4Si1	38	C4H8O3Si1	10	C4H9O3Si1	5

Most Common Final Fragments TEOS

Fraction	Count	Fraction	Count	Fraction	Count
OC_2H_4	144	$Si(OC_2H_5)_3OCH$	21	OC_2H_3	9
C_2H_4	131	C_2H_2	19	OC_2H_5	9
CH_3	107	$Si(OC_2H_5)_2(OCH_2)_2$	19	OC_2H_2	8
C_2H_5	81	C_2H_3	17	$Si(OC_2H_5)_3C$	8
$Si(OC_2H_5)_2OH$	66	CH_4	16	OC_2H_6	8
$Si(OC_2H_5)_3OC_2H_4$	60	$Si(OC_2H_5)_3O$	12	$Si(OC_2H_5)_3OC_2H_2$	6
OCH_2	43	$Si(OC_2H_5)_3O$	12	$Si(OC_2H_5)_3OH$	6
$Si(OC_2H_5)_2(OC_2H_4)_2$	38	$Si(OCH_2)_2OC_2H_4$	10	$Si(OC_2H_5)(OCH_2)_2$	5
$Si(OC_2H_5)_2$	22	$Si(OCH_2)_2H$	10		
$Si(OC_2H_5)(OH)O$	21	CH_2	10		

Fragments

Many of the final fragments agree with products calculated using DFT calculations based on experimental results

No.	Reactants	Products	E, eV
1	$Si(OC_2H_5)_4 + e$	$Si(OC_2H_5)(OCH_2)H_2 + 2OC_2H_4O + CH_3 + e$	6.5
2		$Si(OC_2H_5)_3O + C_2H_5 + e$	3.7
3		$Si(OC_2H_5)_3OC_2H_4 + H + e$	4.2
4		$Si(OC_2H_5)_2OOH + C_2H_4 + C_2H_5 + e$	4.1
5		$Si(OC_2H_5)_3 + OC_2H_5 + e$	4.4
6		$Si(OC_2H_5)_3OCH_2 + CH_3 + e$	3.4
7		$Si(OC_2H_5)_2(OH) + C_2H_4 + OC_2H_5 + e$	4.9
8		$Si(OC_2H_5)_3CH_2 + OCH_3 + e$	4.7
9		$Si(OC_2H_5)(OCH_2)(OH)_2 + 2C_2H_4 + CH_3 + e$	4.3
10		$Si(OC_2H_5)_2(OCH_2)(OH) + C_2H_4 + CH_3 + e$	3.8
11		$Si(OC_2H_5)_2(OCH_2)H + OC_2H_4 + CH_3 + e$	5.0
12		$Si(OC_2H_5)(OCH_2)(OH)H + OC_2H_4 + C_2H_4 + CH_3 + e$	5.3
13		$Si(OC_2H_5)(OH)_2 + OC_2H_5 + 2C_2H_4 + e$	5.2
14		$Si(OC_2H_5)_2H + OC_2H_4 + OC_2H_5 + e$	5.9
15		$SiOH + OC_2H_4 + 2OC_2H_5 + C_2H_5 + e$	10.8
16		$Si(OH)_2H + OC_2H_4 + 2C_2H_4 + OC_2H_5 + e$	6.7
17		$Si(OC_2H_5)(OH)H + OC_2H_4 + OC_2H_5 + C_2H_4 + e$	6.3
18		$Si(OH)_3 + 3C_2H_4 + OC_2H_5 + e$	5.6

Computational study on silicon oxide plasma enhanced chemical vapor deposition (PECVD) process using tetraethoxysilane/oxygen/argon/Helium Hu Li et al 2019 Jpn. J. Appl. Phys. 58 SEED06

Conclusions

- Triplet dissociation can be simulated
- Find most common dissociation pathways
- Development of rules for fragmentation

Future Work

Short Term

- Optimise fragment calculation
- Introduce fragmentation during propagation
- Consider other triplet states of TEOS

Medium Term

- GPU - acceleration
- Machine learning to generate electronic structure

Long Term

- Use the method to generate large data sets so fragmentation rules can be used for generative AI

quantemol

People

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