

Electrophore model for dissociation of molecules after the electron impact in plasma

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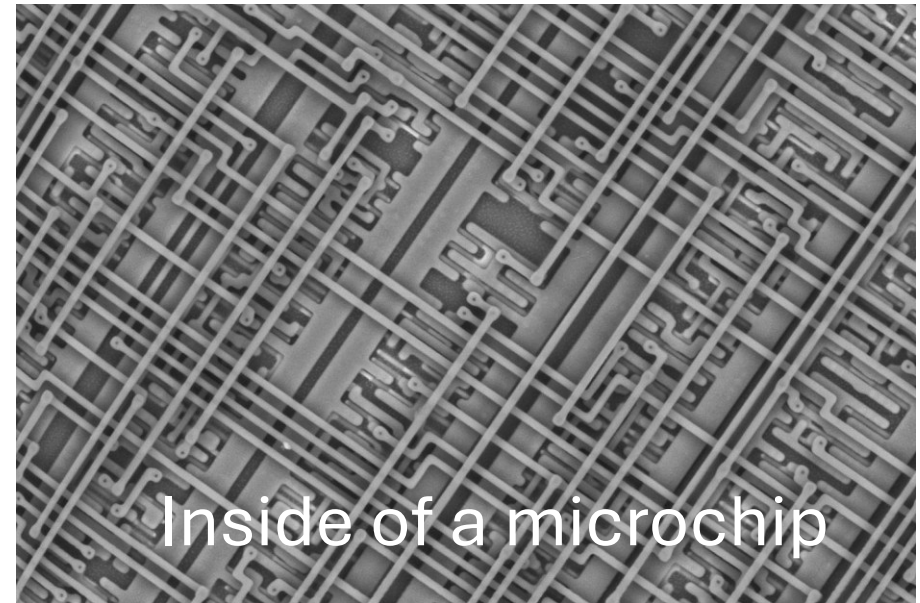
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Motivation and vision.

- Low temperature plasmas are essential to the manufacture of devices in the semiconductor industry.



Plasma Etching

Free radicals



Isotropic Etching

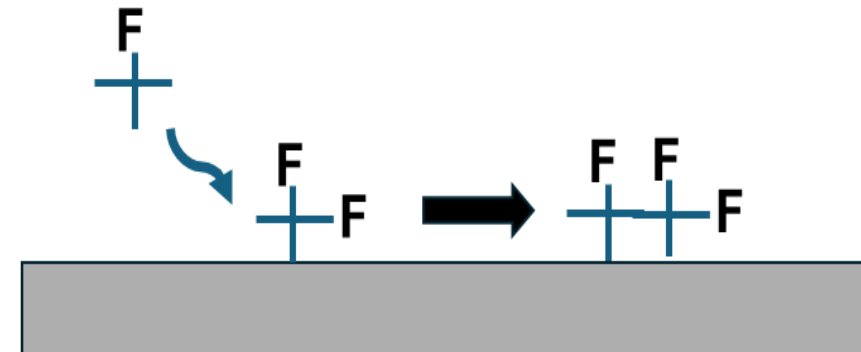
Ions



Anisotropic Etching

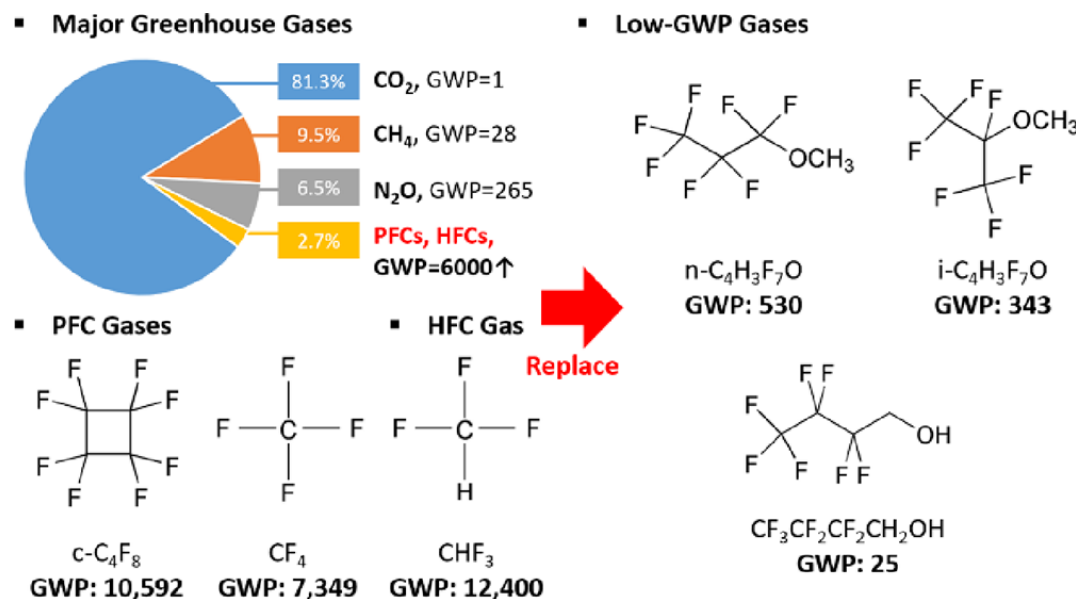
Plasma Deposition

Free Radicals



Motivation and vision.

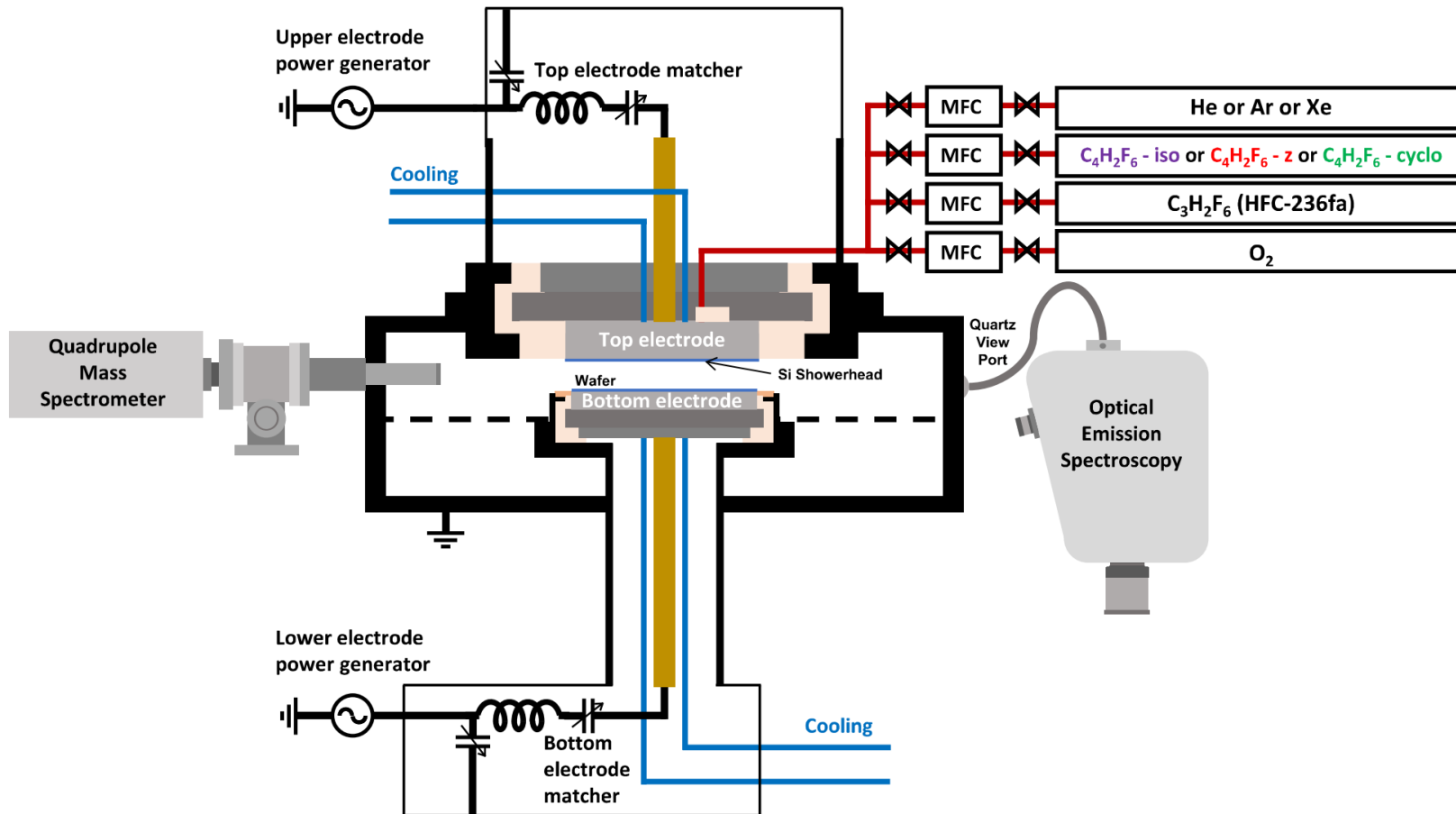
- The gases are fluorine-organic molecules which are not environmentally friendly and expected to be phased out of manufacturing.



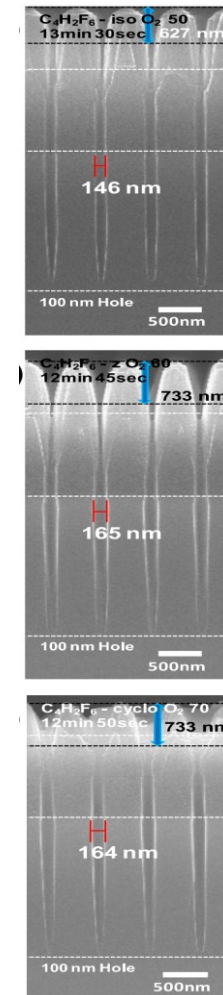
- Developing new plasma sources with new families of gases, which are efficient and environmentally friendly, is a high priority for the industry.

Experiment

- Real plasma etching device coupled to quadrupole Mass Spec.



Etching patterns



Theory

We run *ab initio* molecular dynamics (AIMC or AIMD) in order to identify:

1. The fragments formed
2. The kinetics of fragmentation
3. Give us a molecule and we tell you how it breaks. *In silico* design?

Plan of the talk

Molecular Dynamics we use

First simulations of dissociation of molecules after electron impact and Electrophore Model (EM)

<https://doi.org/10.1021/acs.jpcllett.4c00348>

Dmitry Makhov



Development of Electrophore Model and systematic simulations of the dynamics with a new code.

<https://doi.org/10.1116/6.0004454>

<https://etheses.whiterose.ac.uk/id/eprint/38227/>

Ryan Brook



More simulations of dissociation of hydrofluorocarbons and electronic structure confirmation of the Electrophore Model

Alfred Stonelake



Future developments and vision. Potential energy surfaces with Machine Learning and simulations at low T. Better comparison with mass spec.

Sourav Roy



Basics. Born-Oppenheimer Potential Energy Surfaces and Molecular Dynamics.

$$\Psi_e^{(m)}(\mathbf{r}_e, \mathbf{R})$$

Born-Oppenheimer electronic wave function of the m^{th} electronic state (Adiabatic states)

$$U^{(m)}(\mathbf{R})$$

m^{th} electronic energy

PES drives the motion of nuclei

But what are the surfaces involved in the dissociation in plasma?

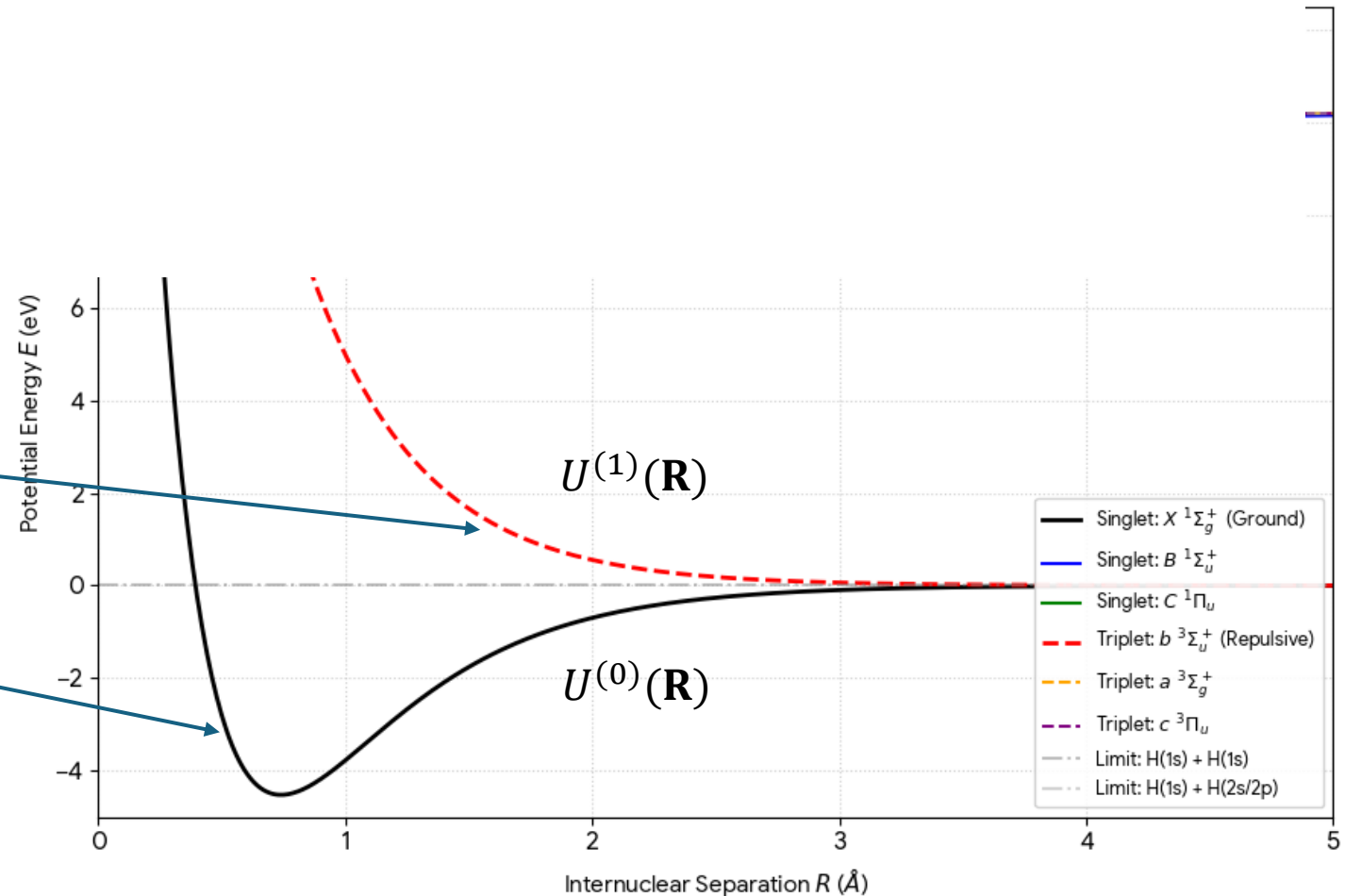
Basics. Born-Oppenheimer Potential Energy Surfaces and Molecular Dynamics.

In plasma molecules are excited to higher electronic states by electron impact.

Triplet state $\uparrow\uparrow$ more repulsion

Singlet state $\uparrow\downarrow$

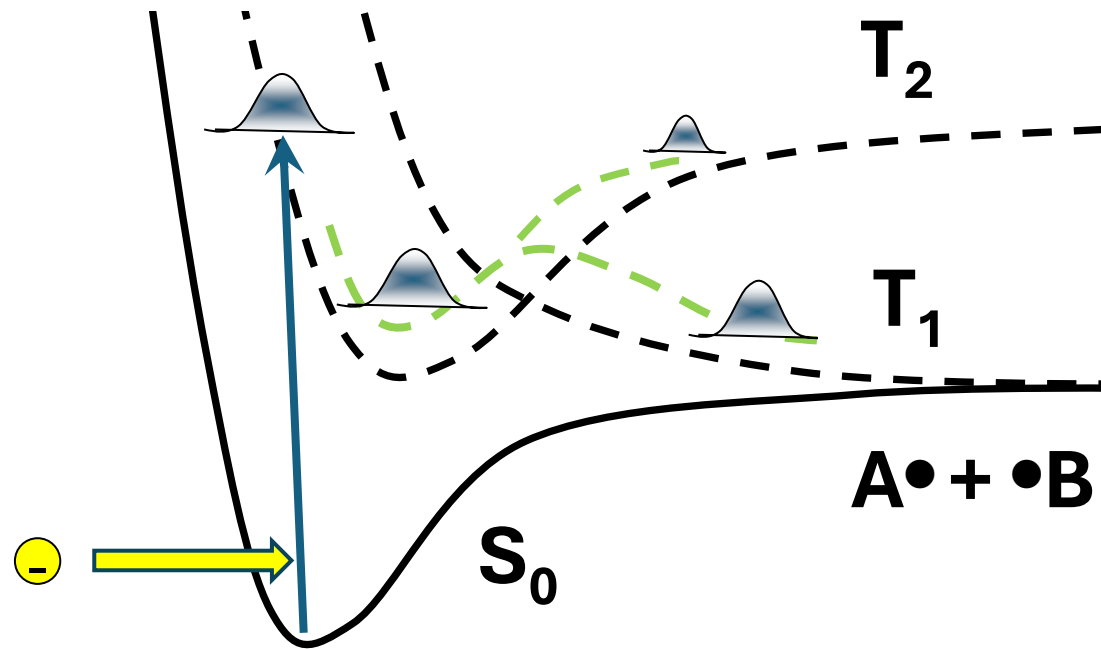
The lowest triplet electronic state plays crucial role in dissociation.



Basics. Born-Oppenheimer Potential Energy Surfaces and Mechanism of dissociation after electron impact

Several low electronic state both **triplet** and **singlet** can be excited by **electron impact**.

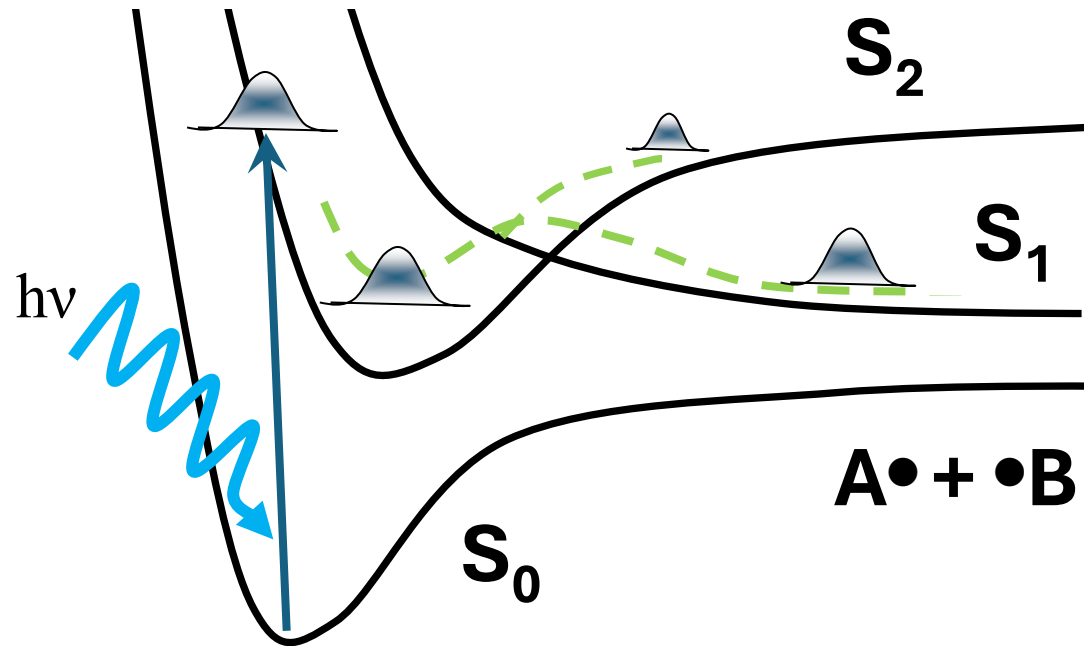
We expect that triplet states are most important as they are in general more repulsive and lower in energy



Basics. Born-Oppenheimer Potential Energy Surfaces and Mechanism of photo-dissociation

In photochemistry only **singlet** states are excited by **photons**.

However, all method developed in photochemistry can be applied to chemistry after electron impact



Non-adiabatic quantum dynamics

- We apply our own ***Ab Initio*** Multiple Cloning (AIMC) method.

$$|\Psi\rangle = \sum_{l=1,N} A_l \left(a_{l1}(t)|1\rangle + a_{l2}(t)|2\rangle + \dots \right) |z_l(t)\rangle$$

Electronic wave function

Amplitude

Ehrenfest configuration is a Gaussian CS dressed with Electronic wave function

Nuclear basis of Gaussian CSs

Sum of normalised Ehrenfest configurations

Non-adiabatic quantum dynamics

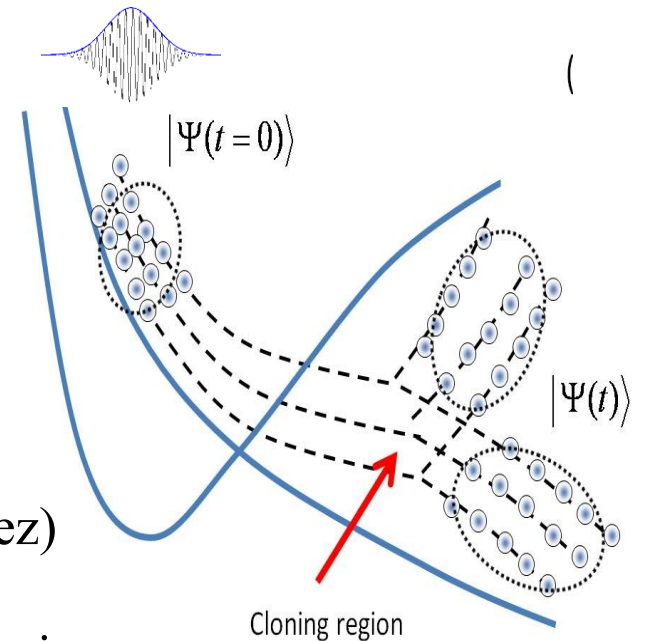
- We apply our own ***Ab Initio*** Multiple Cloning (AIMC) method.

Coherent State Samplings: Cloning

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

Cloning is a straightforward way to do spawning (Martinez)

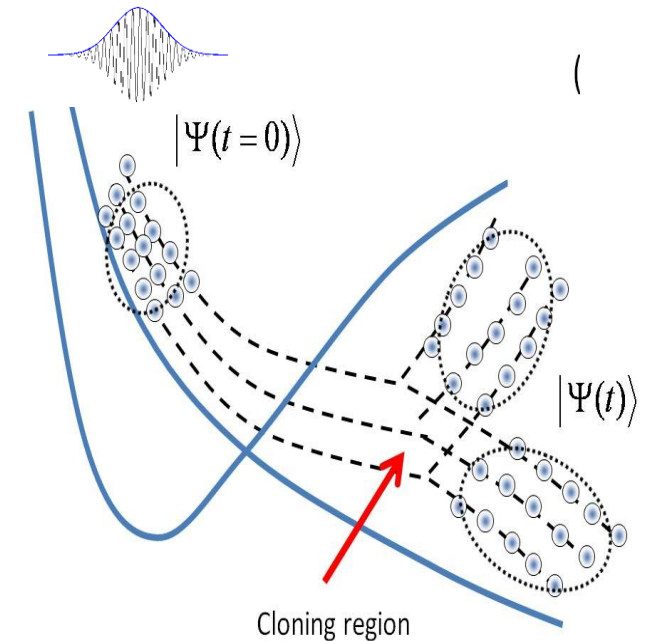
Cloning provides adoptive basis set for nonadiabatic dynamics



Non-adiabatic quantum dynamics

➤ We apply our own ***Ab Initio*** Multiple Cloning (AIMC) method.

- AIMC describes quantum motion of nuclei in terms of several coupled trajectory guided basis functions.
 - Cloning provides trajectory branching to account for wave-function bifurcation when there are transitions between electronic states.
 - Forces are calculated *Ab initio*
- If we use only one trajectory and one PES then AIMC becomes *Ab Initio* Molecular Dynamics AIMD.



First simulations of dissociation of molecules after electron impact and Electrophore Model (EM)

<https://doi.org/10.1021/acs.jpcllett.4c00348>

Dmitry Makhov



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Letter

Dissociation of Hydrofluorocarbon Molecules after Electron Impact in Plasma

Dmitry V. Makhov,* Gregory Armstrong, Hsiao-Han Chuang, Harin Ambalampitiya, Kateryna Lemishko, Sebastian Mohr, Anna Nelson, Jonathan Tennyson, and Dmitrii Shalashilin*



Cite This: *J. Phys. Chem. Lett.* 2024, 15, 3404–3411



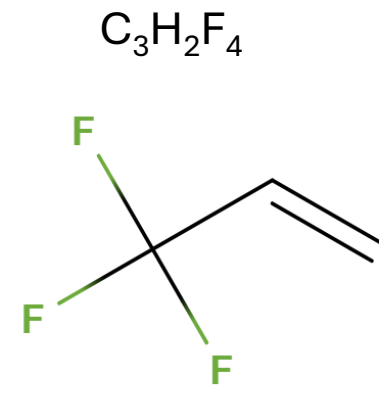
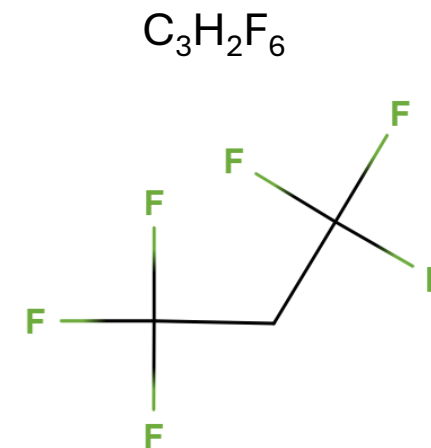
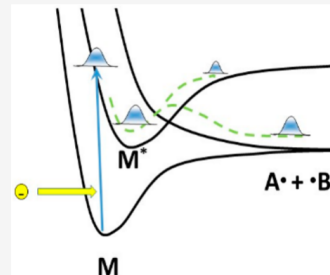
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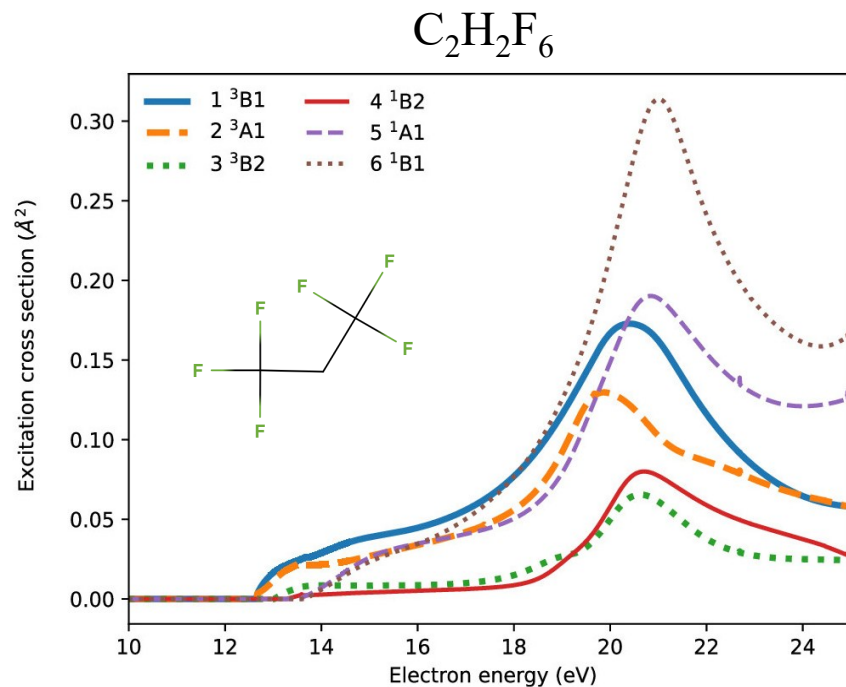
Article Recommendations

ABSTRACT: The process of dissociation for two hydrofluorocarbon molecules in low triplet states excited by electron impact in plasma is investigated by *ab initio* molecular dynamics (AIMD). The interest in the dissociation of hydrofluorocarbons in plasma is motivated by their role in plasma etching in microelectronic technologies. Dissociation of triplet states is very fast, and the reaction products can be predicted. In this work, it was found that higher triplet states relax into the lowest triplet state within a few femtoseconds due to nonadiabatic dynamics, such that the simplest *ab initio* MD on the lowest triplet state seems to give a reasonable estimate of the reaction channels branching ratios. We provide evidence of the existence of simple rules for the dissociation of hydrofluorocarbon molecules in triplet states. For molecules with a double bond, the bonds adjacent to the double bond dissociate faster than the other bonds.

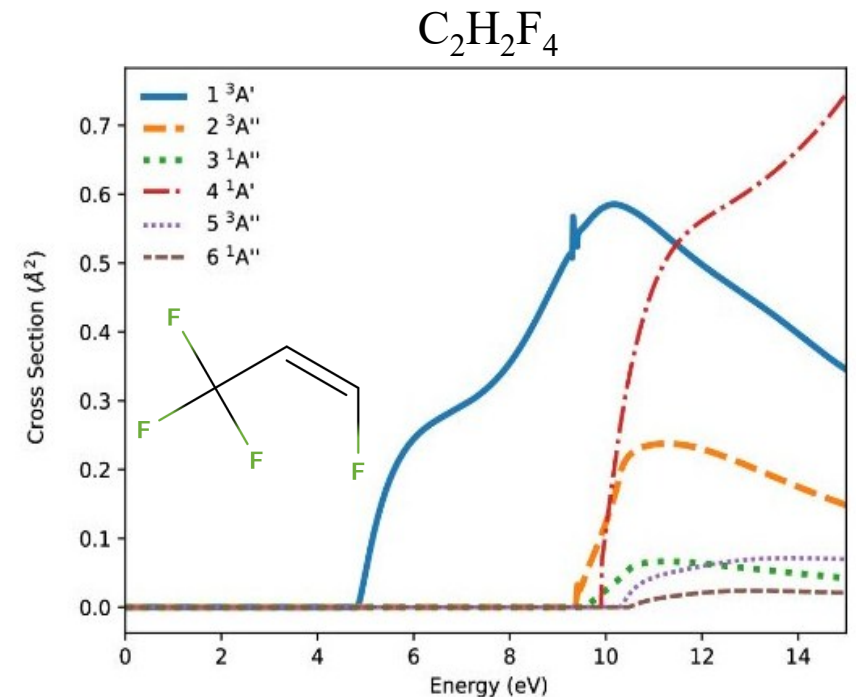


Molecules

➤ Two molecules has been chosen for the start, $\text{C}_2\text{H}_2\text{F}_4$ and $\text{C}_3\text{H}_2\text{F}_6$



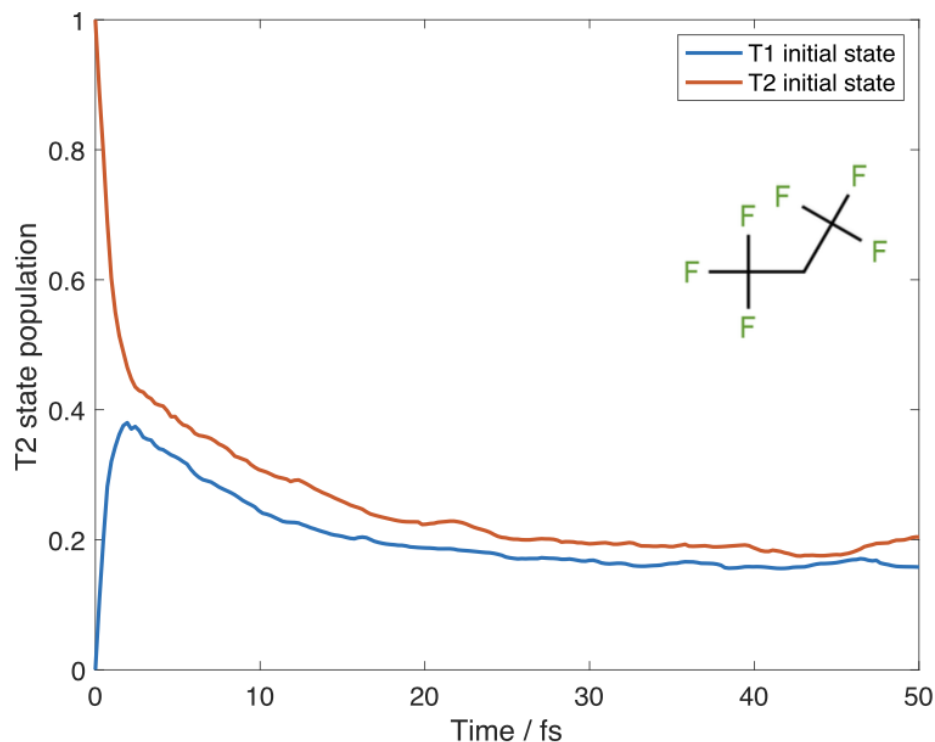
Electron impact excitation cross sections for $\text{C}_3\text{H}_2\text{F}_6$ and $\text{C}_3\text{H}_2\text{F}_4$



- No separation between two lowest excited states
- Non-adiabatic dynamics is needed

- One clearly separated lowest triplet state
- Can avoid expensive non-adiabatic dynamics

Non-adiabatic dynamics for C₂H₂F₆

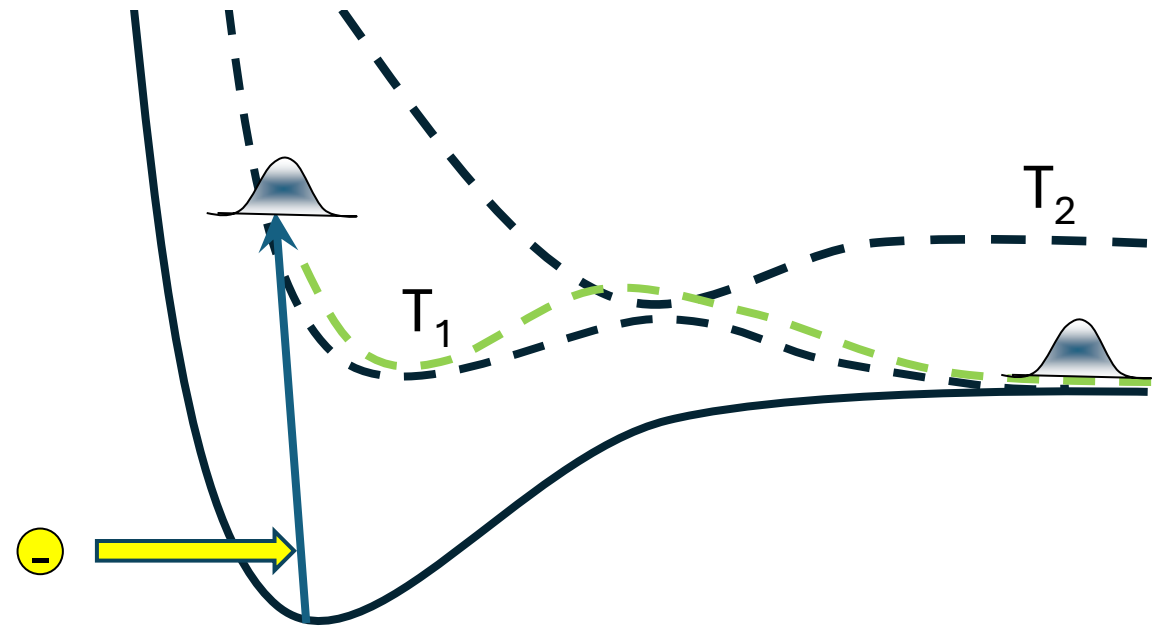
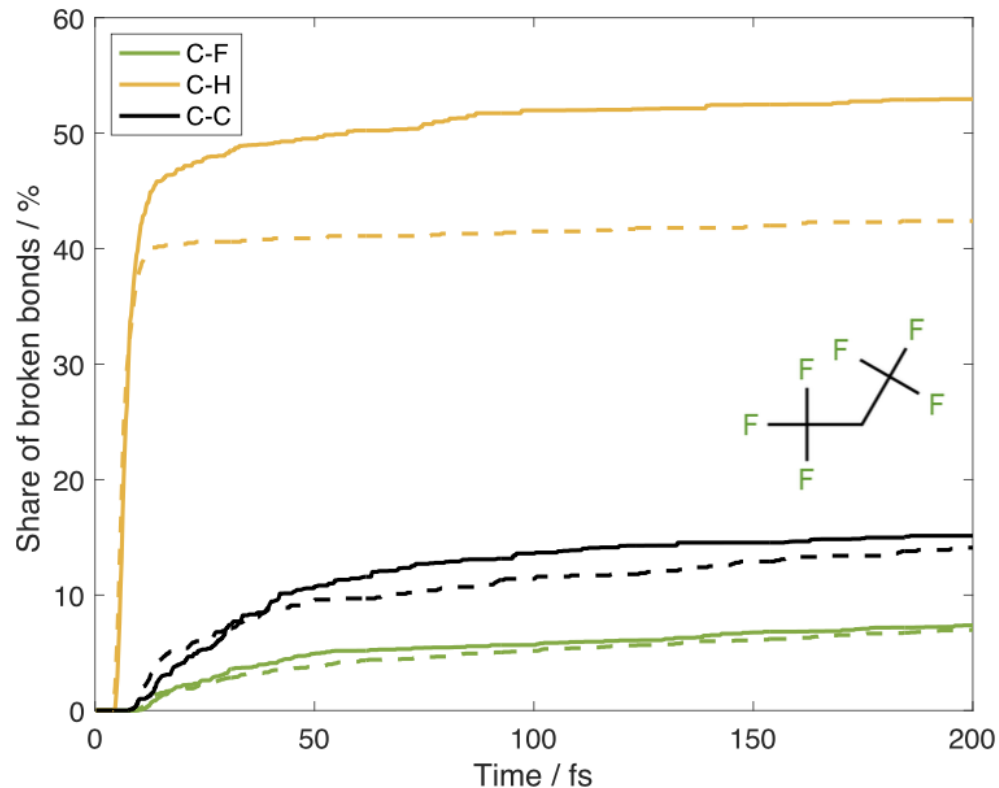


- Spin-flip TDDFT method implemented in Q-Chem quantum chemistry package (BH&HLYP, 6-31+G*)
- 500 trajectories with Boltzmann random initial conditions for 5000 K

Average populations of the upper triplet state of C₂H₂F₆ molecule as a function of time given by AIMC nonadiabatic dynamics calculations that use lower (blue) and upper (red) triplet states as the initial state.

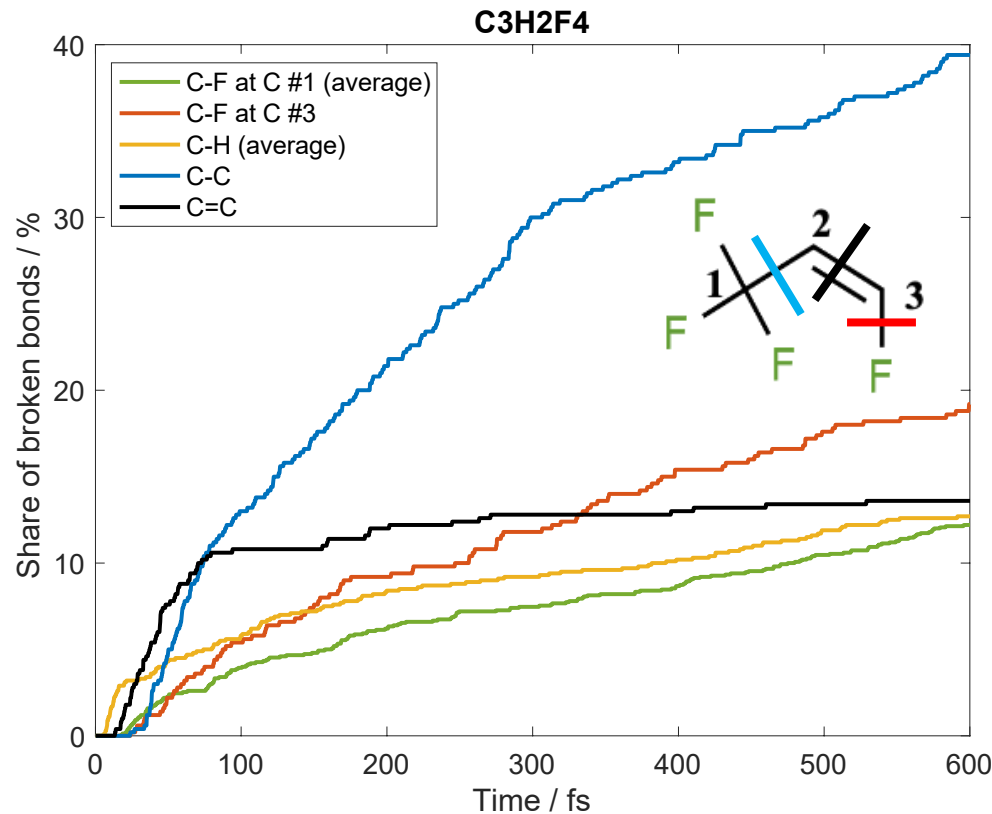
➤ Even when several triplet states are initially involved, in many cases higher triplet states quickly relax into the lowest triplet state.

Dissociation kinetics of $\text{C}_2\text{H}_2\text{F}_6$



- For all other molecules, we run molecular dynamics on a single T_1 potential energy surface.

Dissociation kinetics of $\text{C}_2\text{H}_2\text{F}_4$

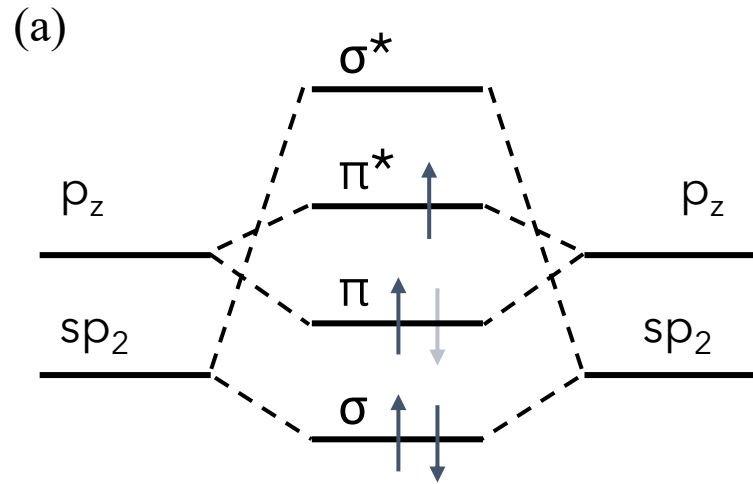


The number of broken bonds as a function of time for $\text{C}_3\text{H}_2\text{F}_4$ at 5000 K.

- C-C bond breaks efficiently
- C=C bond breaks very fast initially
- C-F bond at double-bonded C atom has significantly higher dissociation rate than other C-F bonds
- This can be explained by the localization of the initial T_1 excitation on the double bond.
- The double bond here can be called an electrophore, by analogy with the chromophore in photochemistry.

➤ The electrophore model can help to predict the dissociation channels

Electrophores



- Triplet excitation is localized in the region with a low energy gap between the highest occupied and the lowest unoccupied orbitals

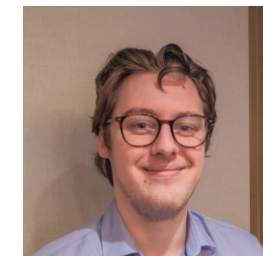
(a) The energy gap between π - and π^* -orbital is low, which makes C=C bond an electrophore

Development of Electrophore Model and systematic simulations of the dynamics with a new code.

<https://doi.org/10.1116/6.0004454>

<https://etheses.whiterose.ac.uk/id/eprint/38227/>

Ryan Brook



Rules of triplet state electron impact neutral dissociation in plasma from molecular dynamics simulations and an electrophore model

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Ryan Brook,^{1,a)} Oliver Bramley,² Dmitry V. Makhov,¹ Anna Nelson,² Gregory Armstrong,² Joseph Yong,¹ Ezri Saunders,¹ Johnny de Viggiani,¹ Jonathan Tennyson,^{2,3} and Dmitrii V. Shalashilin^{1,b)}

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ABSTRACT

Electron impact driven neutral dissociation of molecules that is important in low temperature plasma is investigated. Despite its importance for plasma technologies in microelectronics manufacturing, this process has received almost no attention from the computational chemistry community, which for decades has been focused on photodissociation. Simulations are performed for the dissociation of several fluorinate-organic molecules in their lowest triplet state, populated via electron impact excitation. Their dissociation in plasmas has recently been studied experimentally and their dissociation pathways have been shown to differ from those of the singlet ground state. Rules that determine the dissociation pathways in fluorinate-organic molecules are proposed and rationalized via analysis of an ensemble of trajectories, highlighting the common dissociation pathways. These rules can help to find new molecules for use in future plasma technologies, which produce a desired chemical composition of plasma, enhancing selectivity, etch rates, and environmental benefits.

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Classical and quantum molecular dynamics simulations of dissociation after electron impact in plasma



Ryan Brook

University of Leeds

School of Chemistry

Submitted in accordance with the requirements for the degree of

Doctor of Philosophy

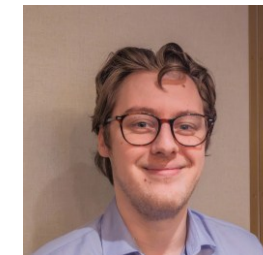
August, 2025

Development of Electrophore Model and systematic simulations of the dynamics with a new code.

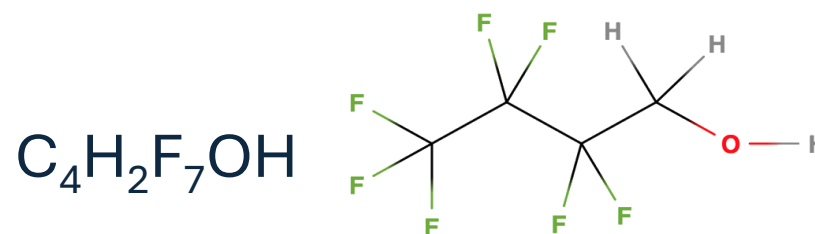
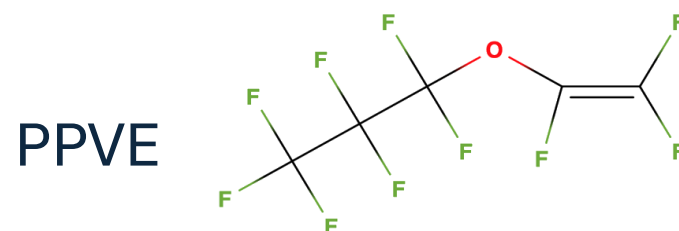
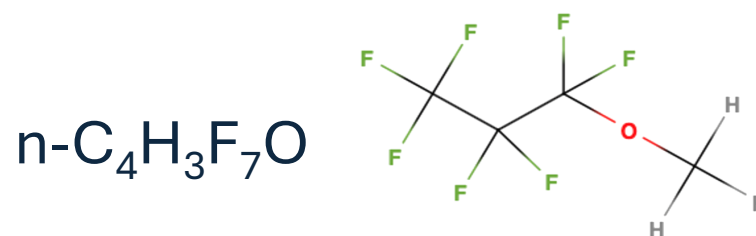
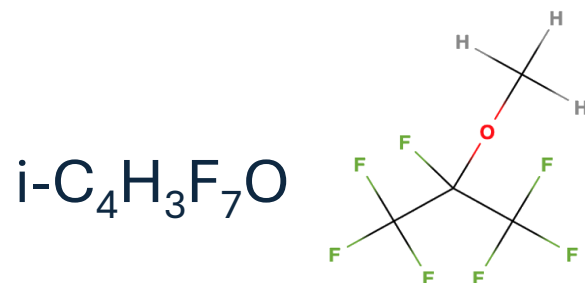
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<https://etheses.whiterose.ac.uk/id/eprint/38227/>

Ryan Brook



- We have chosen a new selection of fluorinated organic molecules, now with an oxygen atom.
- These molecules were investigated experimentally, and several key bonds were identified to be prominent in their neutral dissociation pathways.



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Research Article

Low Global Warming C₄H₃F₇O Isomers for Plasma Etching of SiO₂ and Si₃N₄ Films

Yongjae Kim,[#] Seoune Kim,[#] Hojin Kang, Sanghyun You, Changkoo Kim,^{*} and Heeyeop Chae^{*}

Cite This: ACS Sustainable Chem. Eng. 2022, 10, 10537–10546

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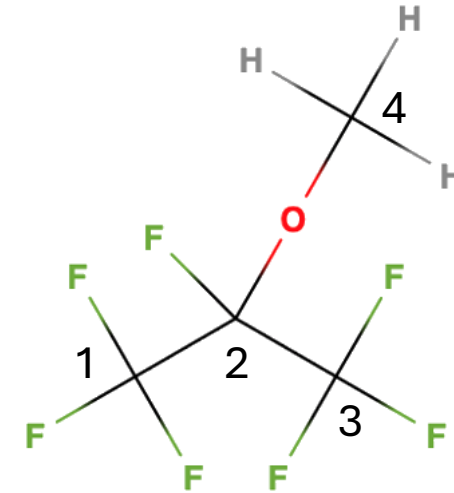
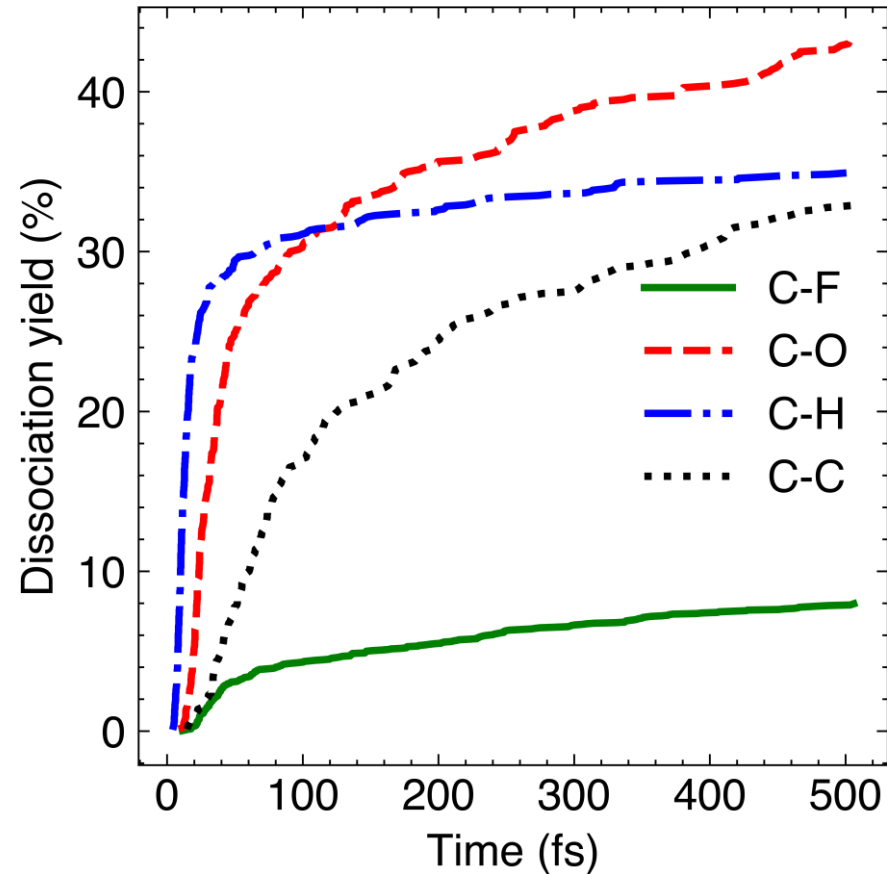
Article Recommendations

Supporting Information

ABSTRACT: In this study, the plasmas of C₄H₃F₇O fluoro-ether and fluoro-alcohol isomers of CF₃CF₂CF₂OCH₃ (HFE-347mcc3), (CF₃)₂CFOCH₃ (HFE-347mmy), and CF₃CF₂CF₂CH₂OH (PPC) with low global warming potentials (GWPs) were characterized for etching SiO₂, Si₃N₄, and poly-Si films. The C₄H₃F₇O isomers have a short lifetime (<5 years) and low GWP (<1000) compared to the widely used C₄F₈ with a lifetime of 3200 years and a GWP₁₀₀ of 10,592. Radicals in the plasma of C₄H₃F₇O fluoro-ethers and fluoro-alcohol isomers were analyzed by mass spectroscopy, and HF and CO peaks were identified as major gas-phase products in the plasma phase. The concentration of exhaust gases after plasma etching were analyzed, and the million metric tons of carbon equivalent (MMTCE) were determined relative to conventional perfluorocarbon (PFC), C₄F₈, HF, CO, and COF₂ were identified as the major reaction products in exhaust with C₄H₃F₇O isomer plasmas. The MMTCEs of HFE-347mcc3, HFE-347mmy, and PPC were lowered by 82, 74, and 85%, respectively, compared with that of C₄F₈. The chemical bonding of the steady-state fluorocarbon film on SiO₂, Si₃N₄, and poly-Si surfaces was analyzed during the etching process, and a lower F 1s/C 1s ratio was observed for C₄H₃F₇O isomers than for C₄F₈. A high etch selectivity of 170 was achieved for SiO₂ etching over poly-Si and 263 for Si₃N₄ etching over poly-Si with PPC plasma. This high selectivity is attributed to the higher carbon and lower fluorine contents in the steady-state fluorocarbon film. The C₄H₃F₇O isomer plasmas also generate a superior etch profile compared to the C₄F₈ plasma with an aspect ratio of 7:1 etch of 200 nm hole patterns. This study demonstrates that C₄H₃F₇O isomers can significantly reduce the global warming effect by replacing the conventional PFC in the etching processes of semiconductor device fabrication.

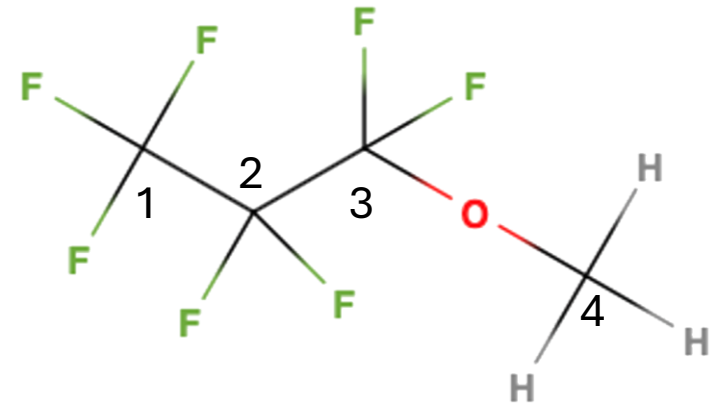
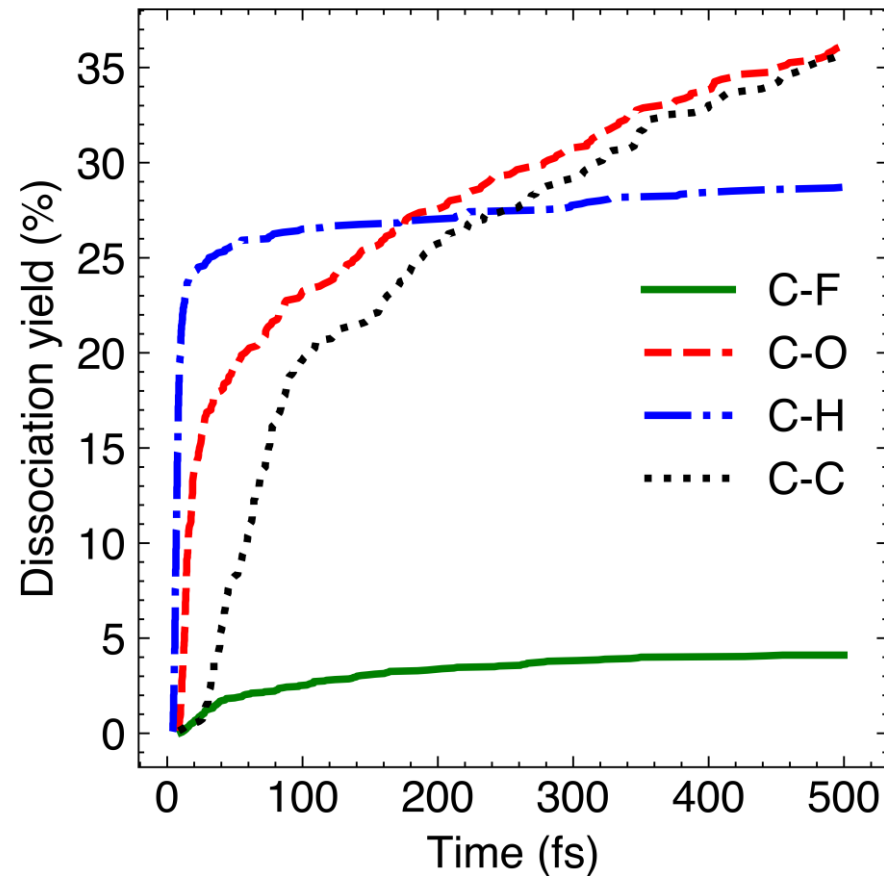
KEYWORDS: low GWP, MMTCE, PFC, plasma etching, etch selectivity

i-C₄H₃F₇O – Overview



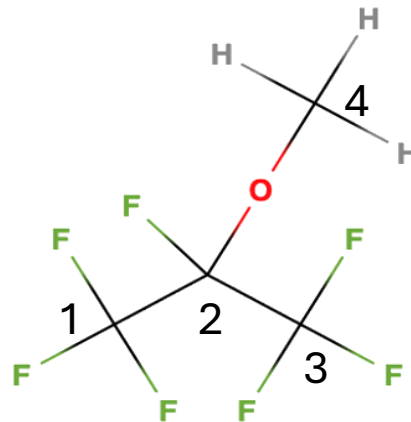
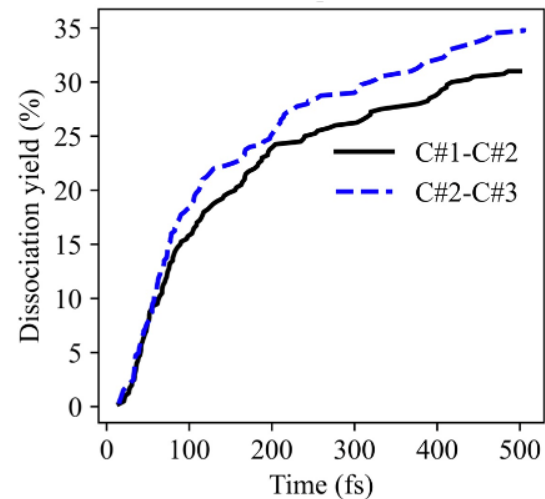
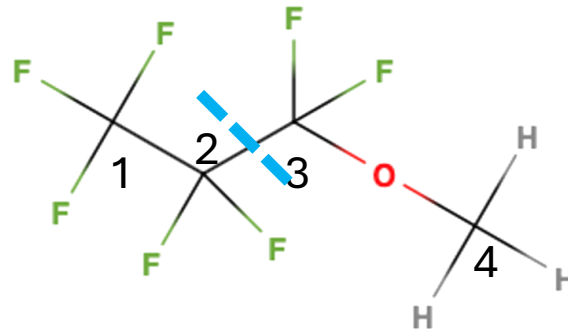
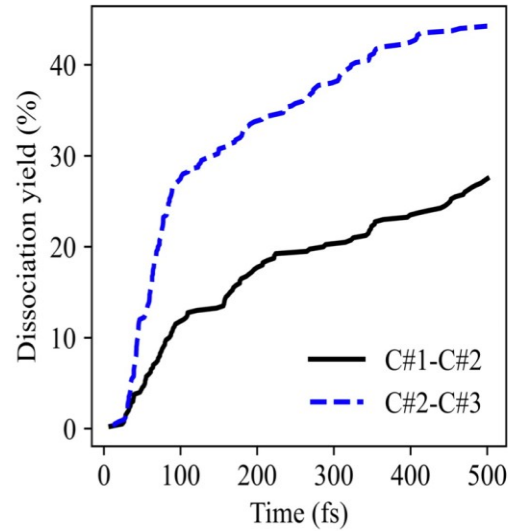
- C-O bonds break most
- One C-H bond breaks for every molecule
- C-F has the lowest number of bonds broken

$n\text{-C}_4\text{H}_3\text{F}_7\text{O}$ – Overview



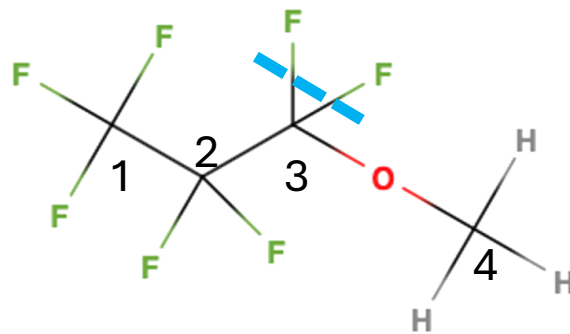
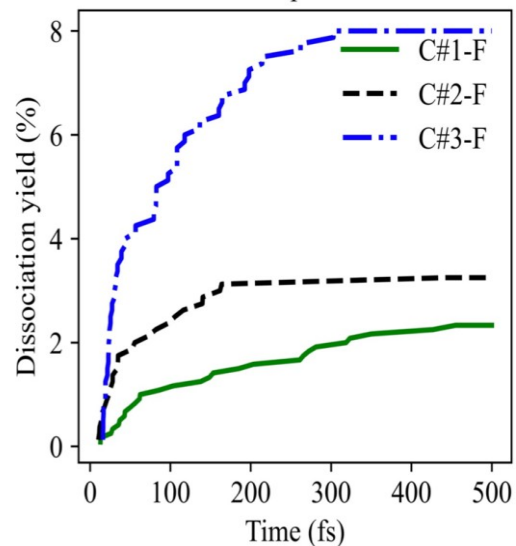
- C-C bonds break similar to the case of i-isomer, but other bonds break less frequently

n- vs i-isomer – C-C

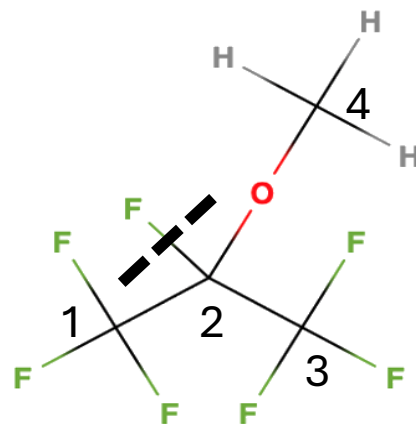
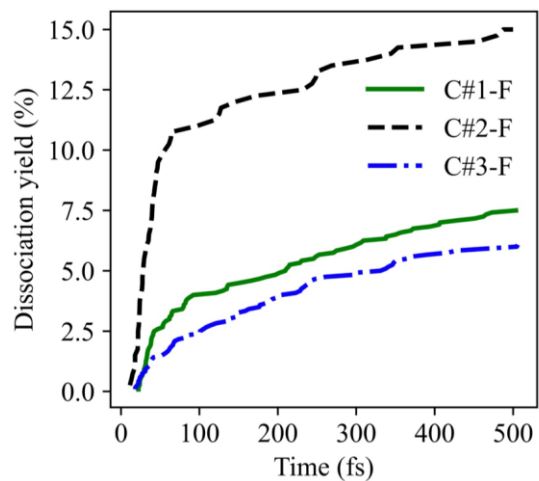


- The C#2-C#3 bonds in the n-isomer breaks much more often
- This can be explained by the proximity to the oxygen atom, which is an electrophore in this molecule
- The C-C bonds in the i-isomer breaks with the same rate, as to be expected from a symmetrical molecule.

n- vs i-isomer – C-F

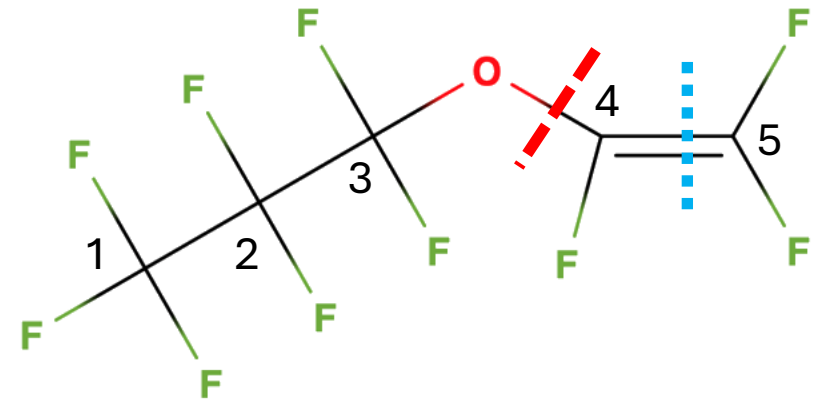
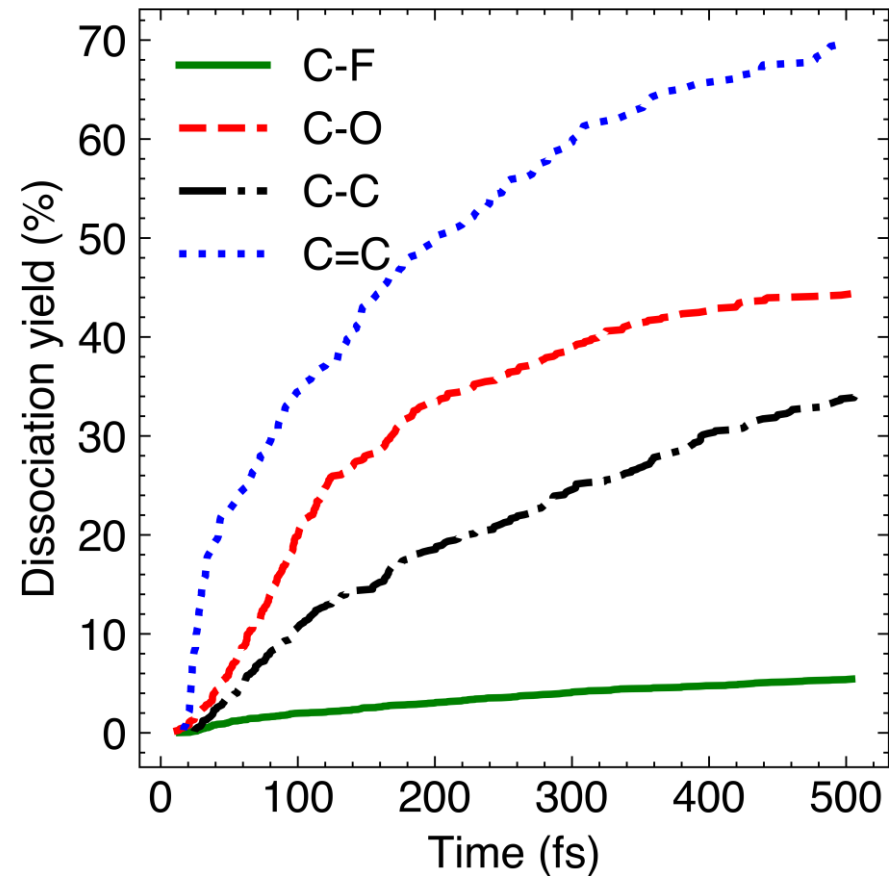


- The breaking rate of C-F bond in n-isomer greatly dependent on the proximity to the oxygen atom.
- For i-isomer, the C#2-F bond breaking rate is the highest.



➤ Oxygen atom is an electrophore

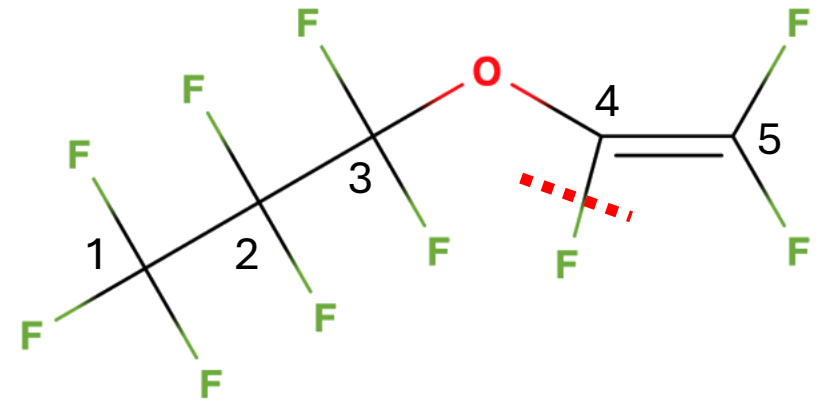
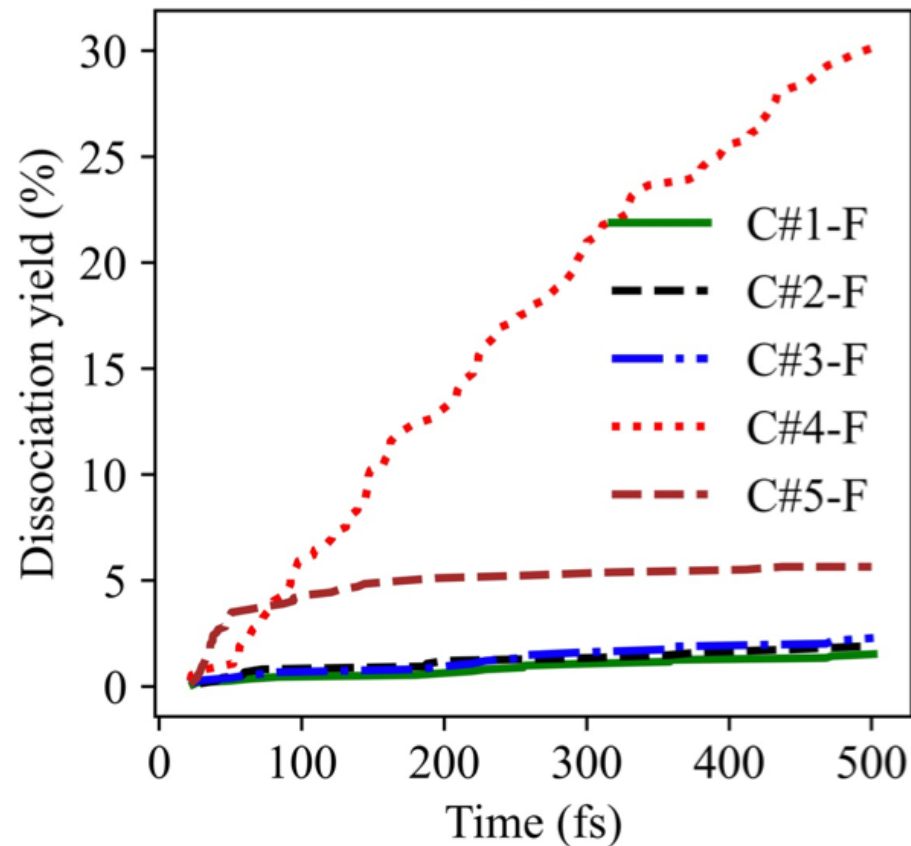
PPVE – Overview



- C=C & C-O bonds break the most, suggesting location of localization

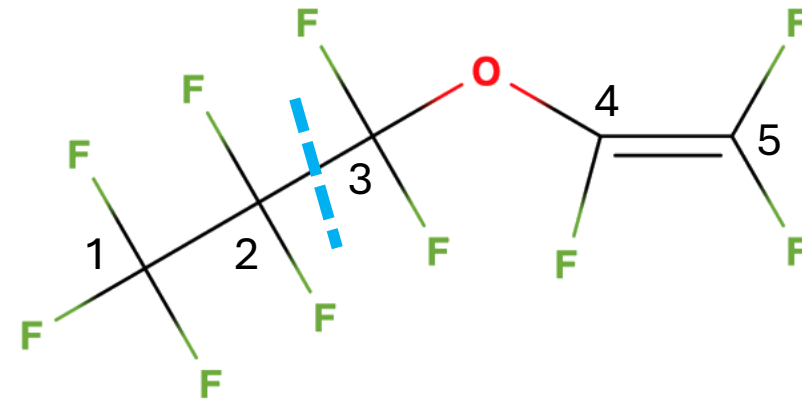
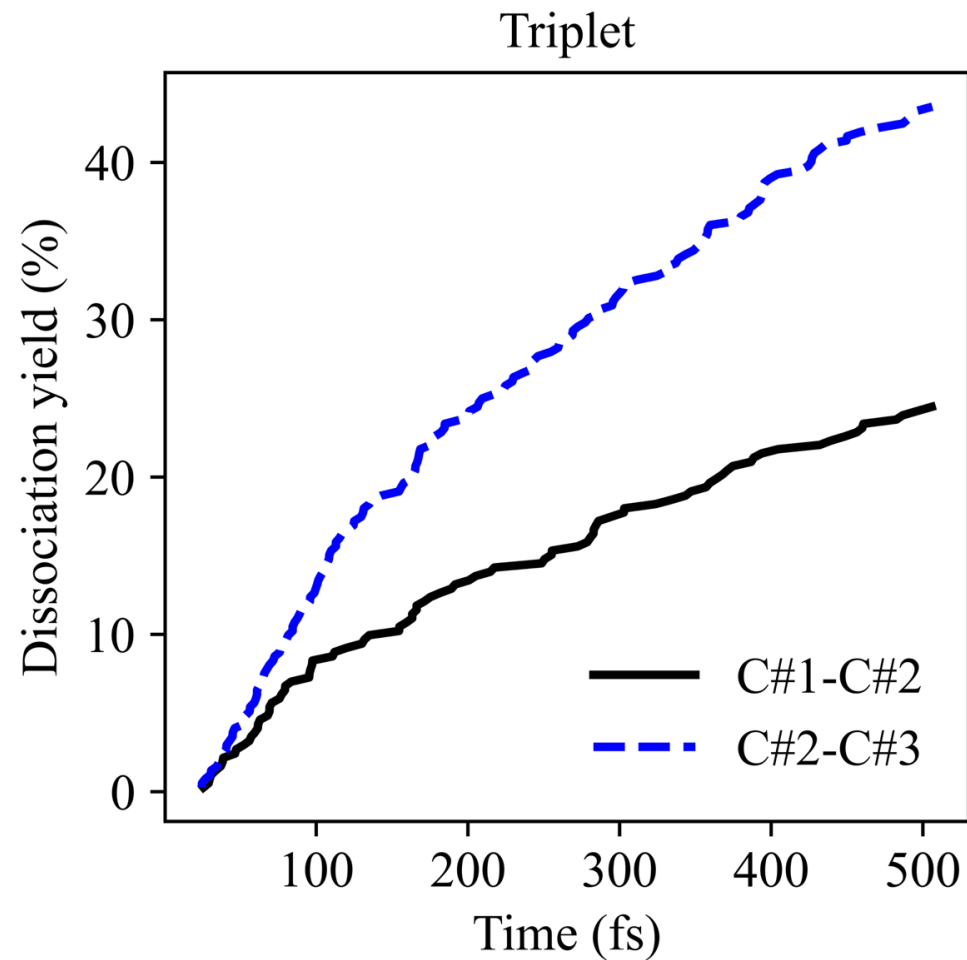
PPVE – C-F Bonds

- PPVE molecule has two electrophores – a double bond and an oxygen atom.



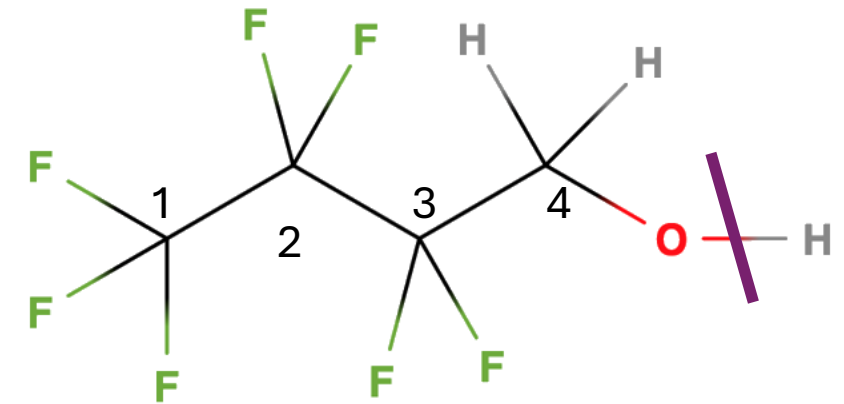
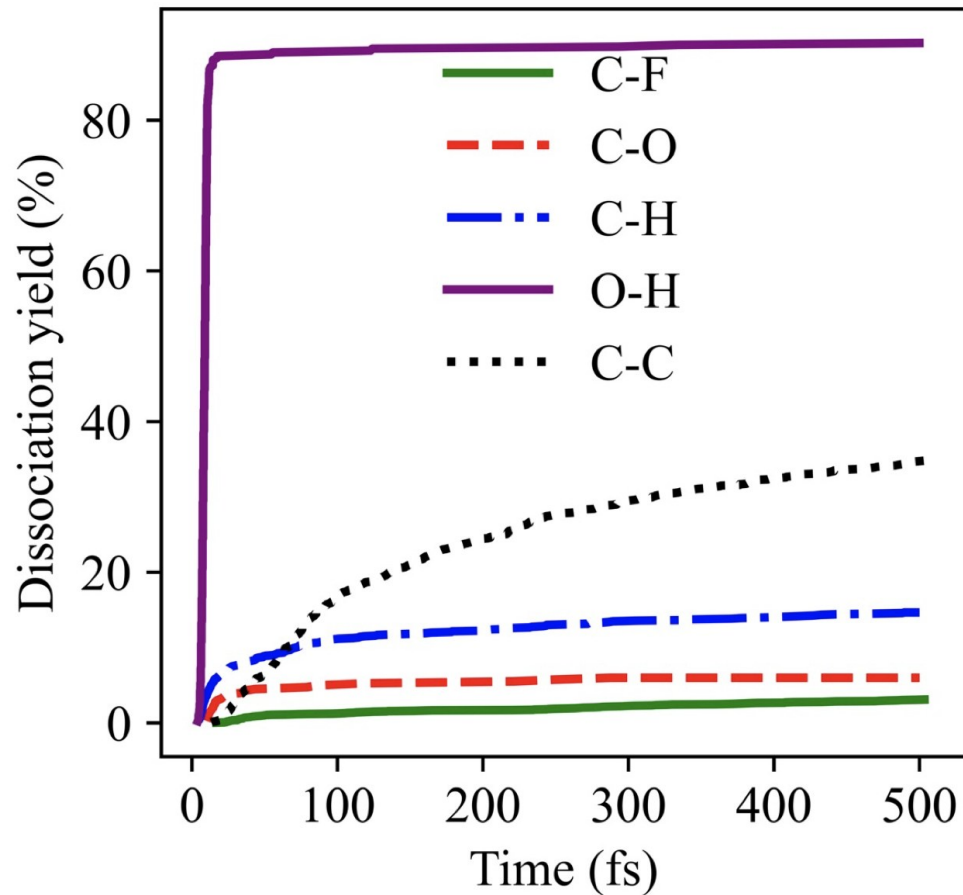
- Over 50% of all C-F bonds broken come from just one single C-F bond
- The effect of proximity to multiple electrophores is cumulative

PPVE – Low C#3-F Count



- C#3-O quickly breaks in 66% of the molecules due to the presence of the double bond.
- C#2-C#3 breaks in 40.5% of molecules
- Both of these factors combined limit the breaking of the C#3-F bonds, despite proximity to the oxygen atom.

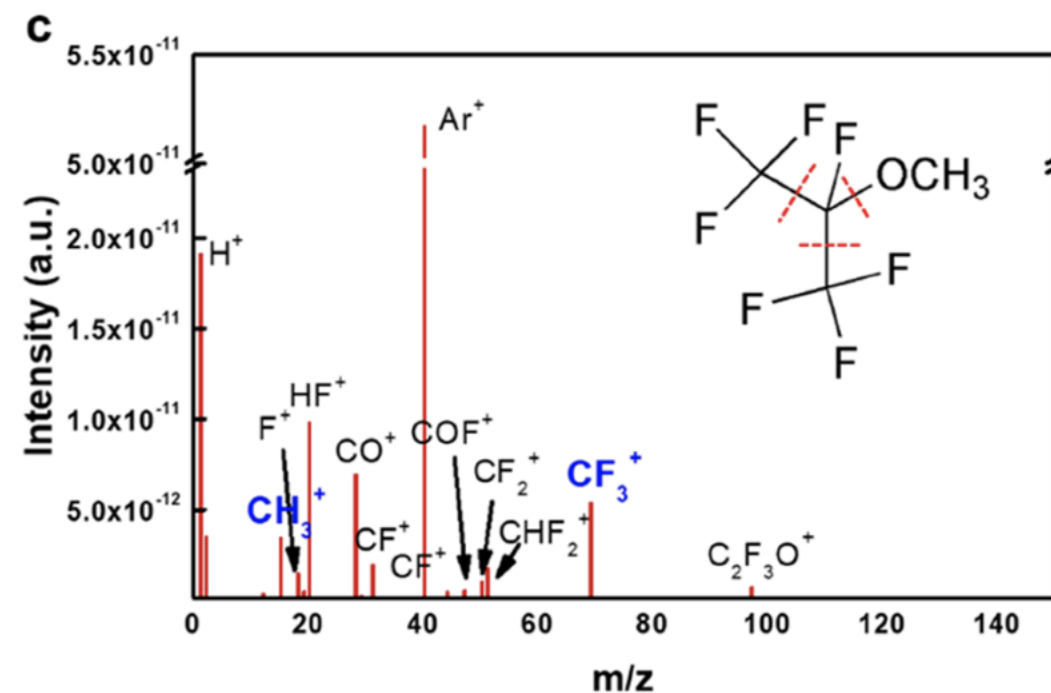
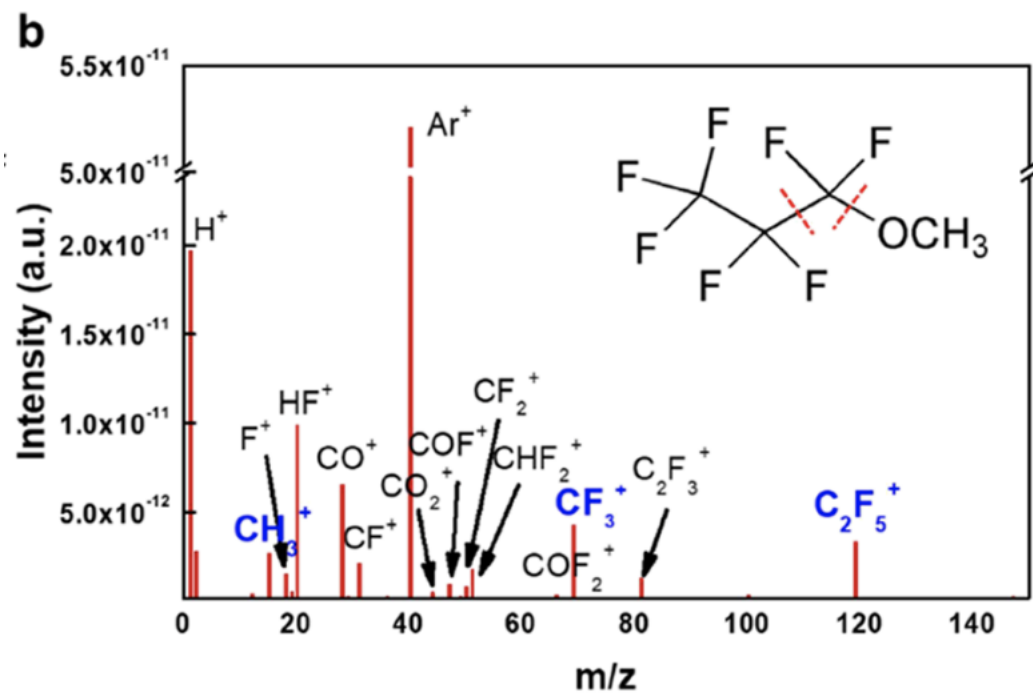
C₄H₂F₇OH – Overview



- O-H bond breaks almost immediately
- Probably this prevents C-O bond breaking

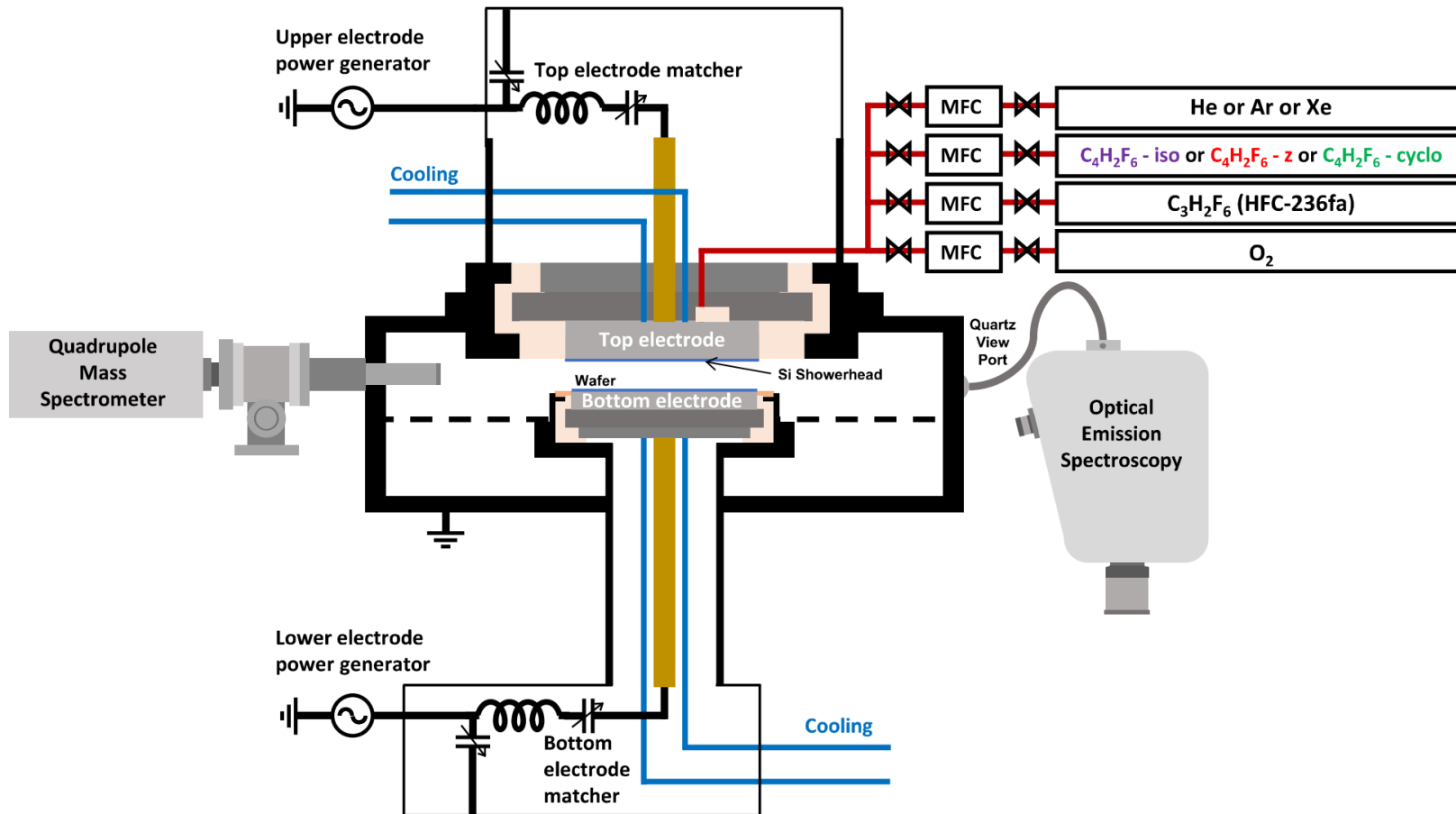
Experimental

- The molecules that we simulated were investigated experimentally to test whether they would be viable replacements for the C₄F₈ plasma precursor
- Several key bonds were identified to be prominent in their neutral dissociation pathways.
- These bonds correspond to the bonds most often dissociated in our simulations.

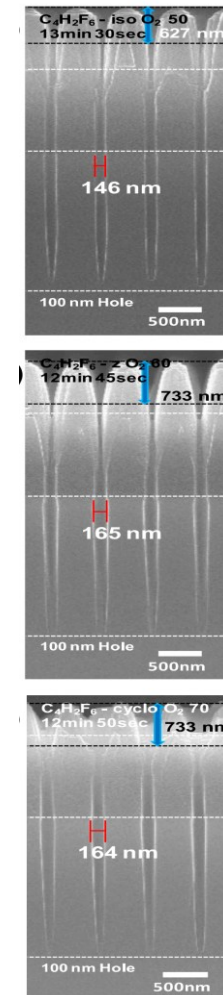


Experimental

- Real plasma etching device couple to quadruple Mass Spec.



Etching patterns



Dissociation rules

- Based on the results for all molecules, we have formulated a preliminary list of rules for triplet state dissociation

Selected rules:

- Double C=C bonds and an oxygen atoms are electrophores
- Bonds in the proximity of the electrophore dissociate more efficiently
- The effect of proximity to multiple electrophores is cumulative

Detailed list of rules is in our paper



JVST A
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ARTICLE

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Rules of triplet state electron impact neutral dissociation in plasma from molecular dynamics simulations and an electrophore model

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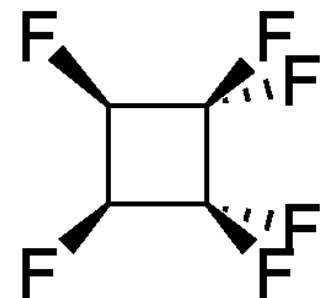
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ABSTRACT

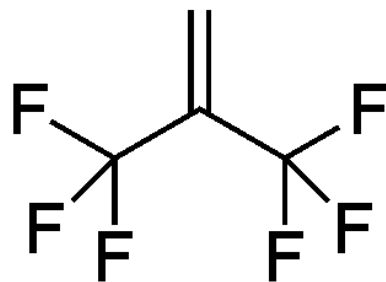
Electron impact driven neutral dissociation of molecules that is important in low temperature plasma is investigated. Despite its importance for plasma technologies in microelectronics manufacturing, this process has received almost no attention from the computational chemistry community, which for decades has been focused on photodissociation. Simulations are performed for the dissociation of several fluorinate-organic molecules in their lowest triplet state, populated via electron impact excitation. Their dissociation in plasmas has recently been studied experimentally and their dissociation pathways have been shown to differ from those of the singlet ground state. Rules that determine the dissociation pathways in fluorinate-organic molecules are proposed and rationalized via analysis of an ensemble of trajectories, highlighting the common dissociation pathways. These rules can help to find new molecules for use in future plasma technologies, which produce a desired chemical composition of plasma, enhancing selectivity, etch rates, and environmental benefits.

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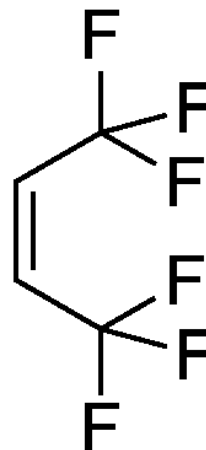
More simulations of dissociation of hydrofluorocarbons and electronic structure confirmation of the Electrophore Model



Cyclo



Iso



Z

Applied Surface Science 639 (2023) 158190

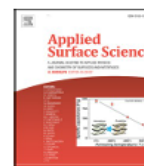


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Full Length Article

Characteristics of high aspect ratio SiO₂ etching using C₄H₂F₆ isomers

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Alfred Stonelake



Excited Triplet States during Organofluorine Molecular Dynamics upon Electron-Impact — A Study of Electronic Structure and Molecular Fragmentation

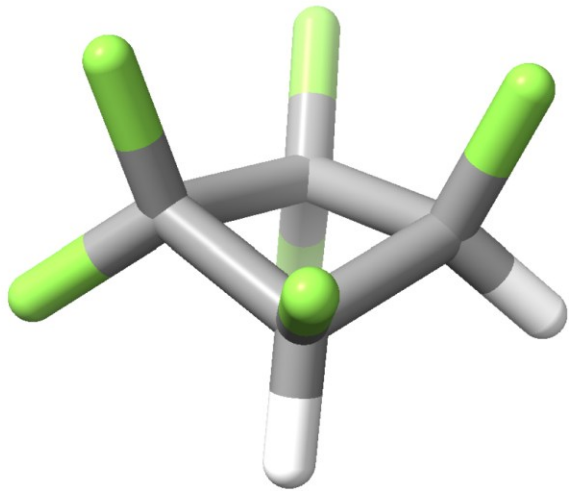
Supervisor: Prof. Dmitry Shalashilin

Submitted by:

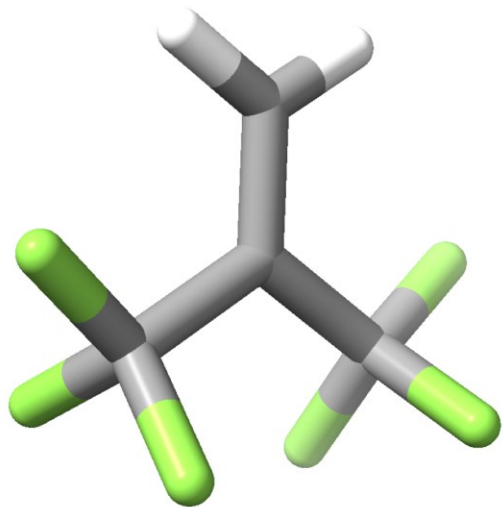
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Submission Date: 10.05.2026



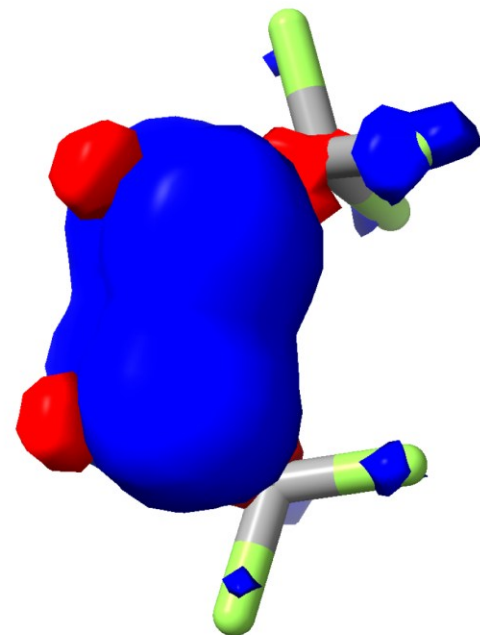
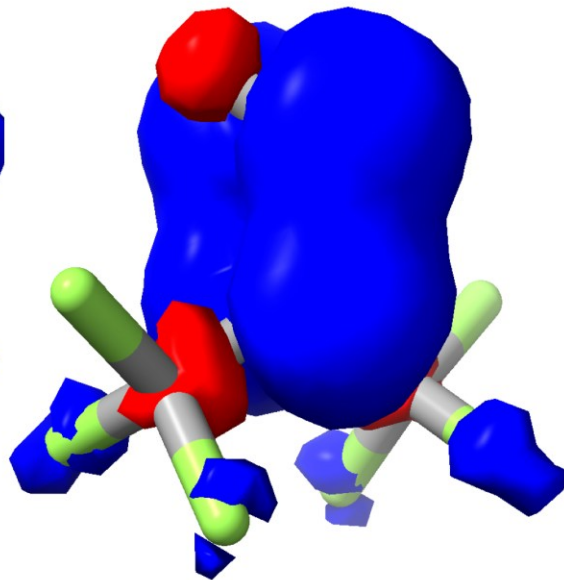
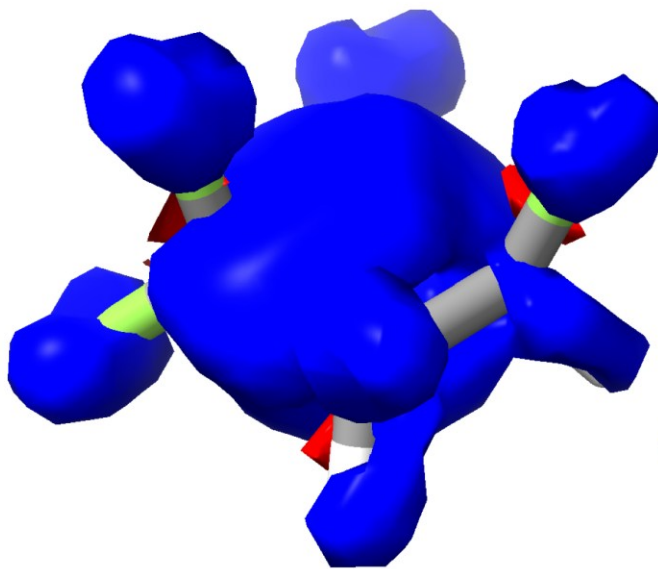
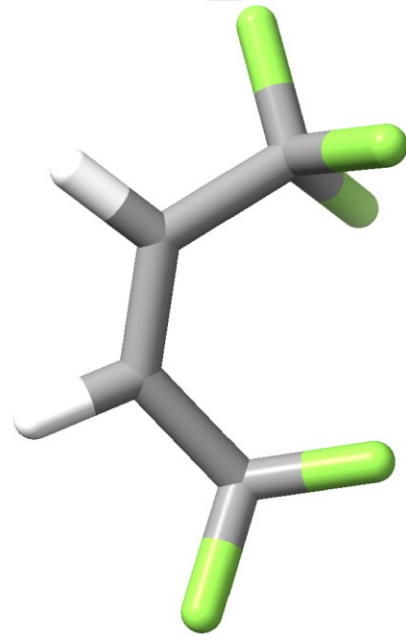
Cyclo

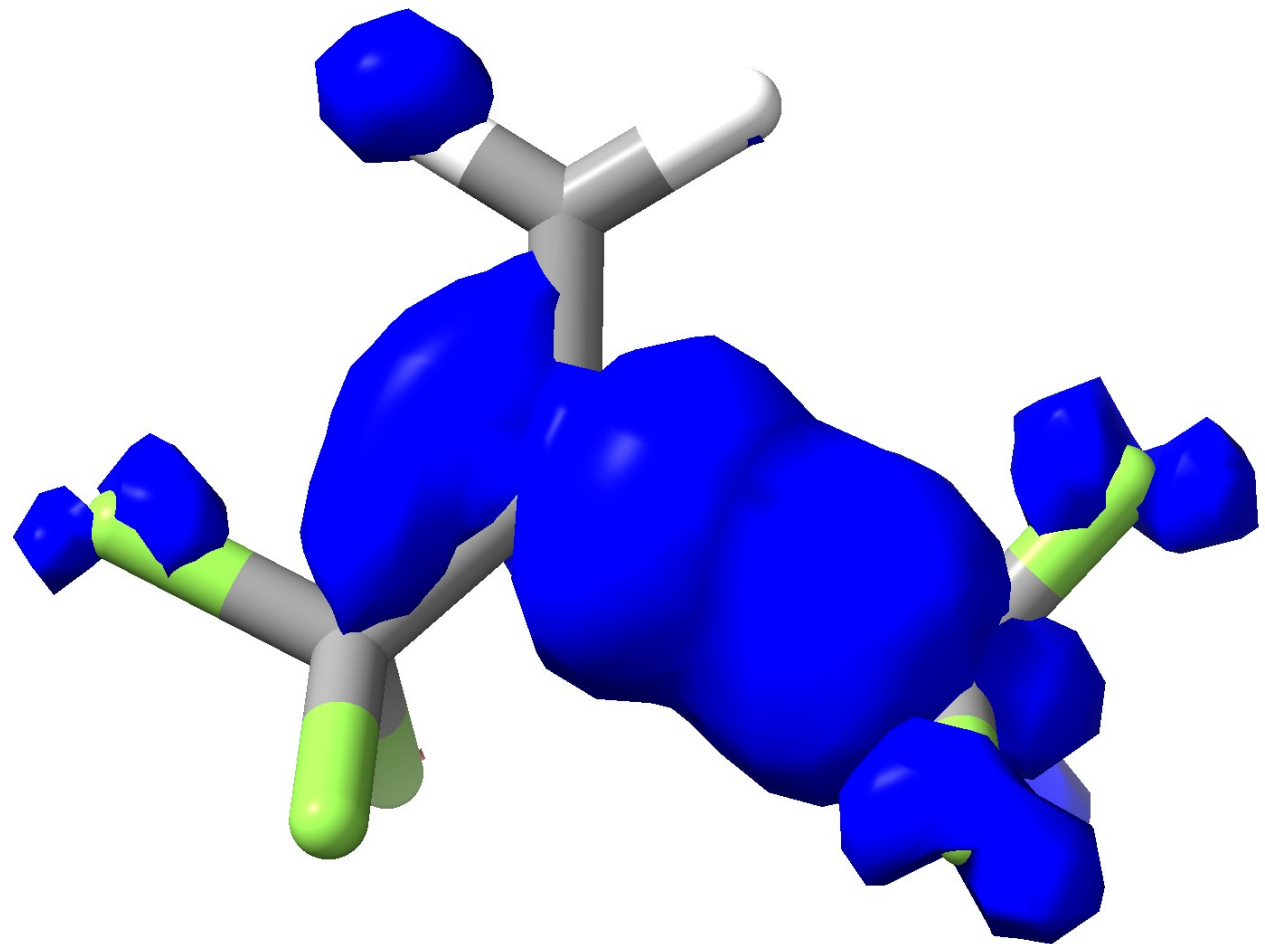
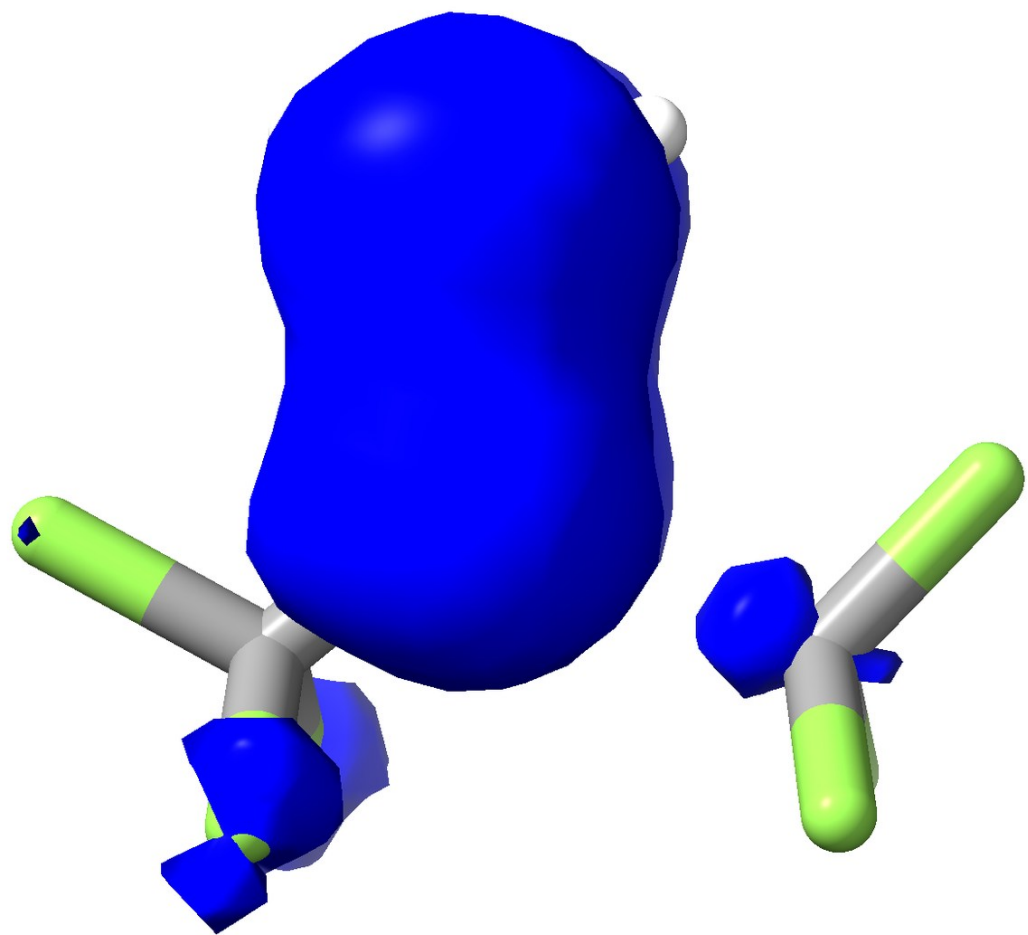


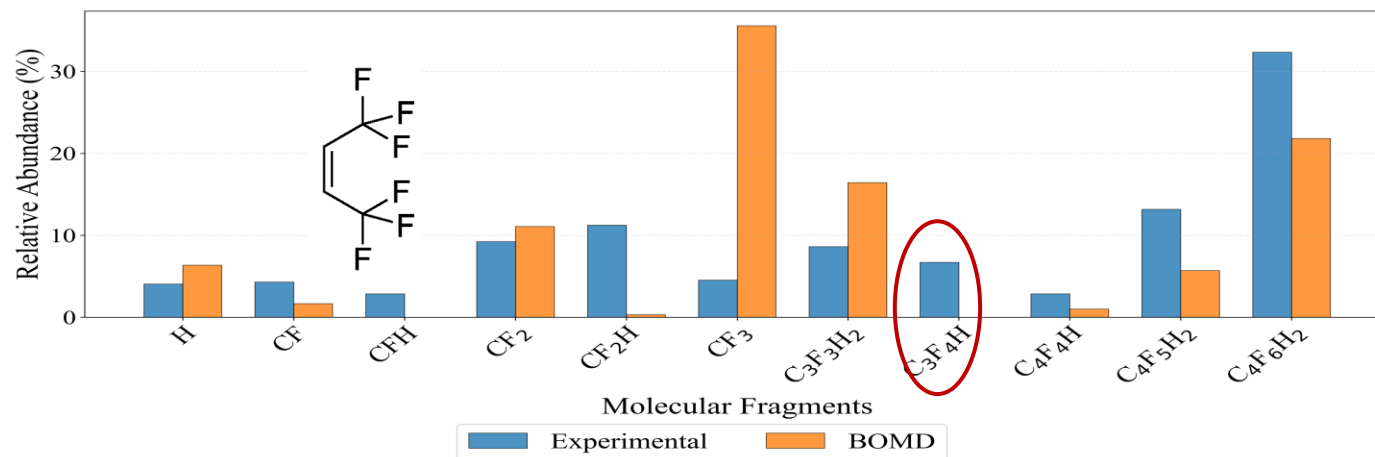
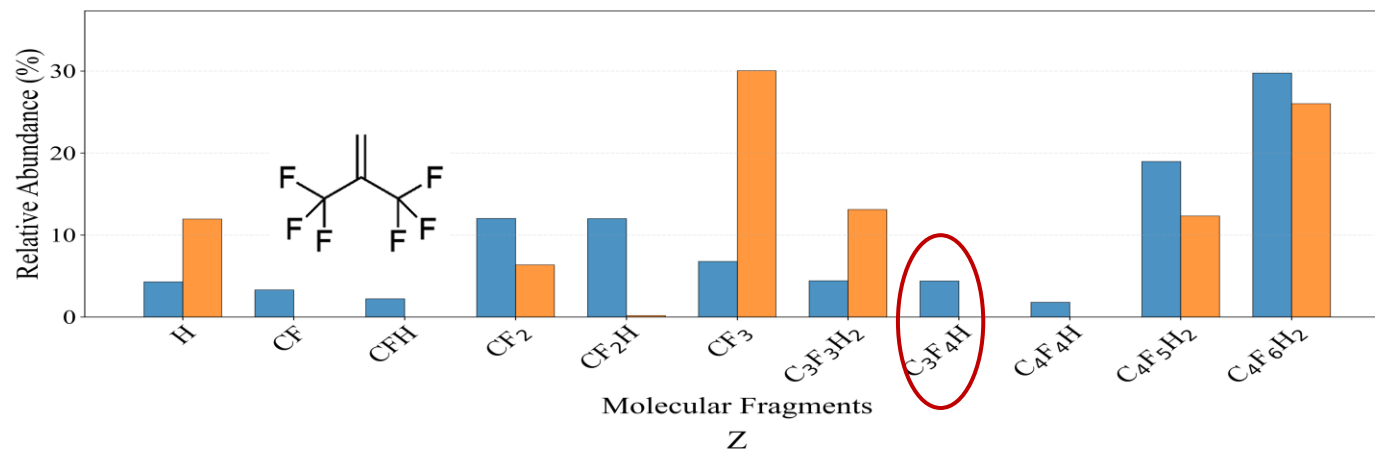
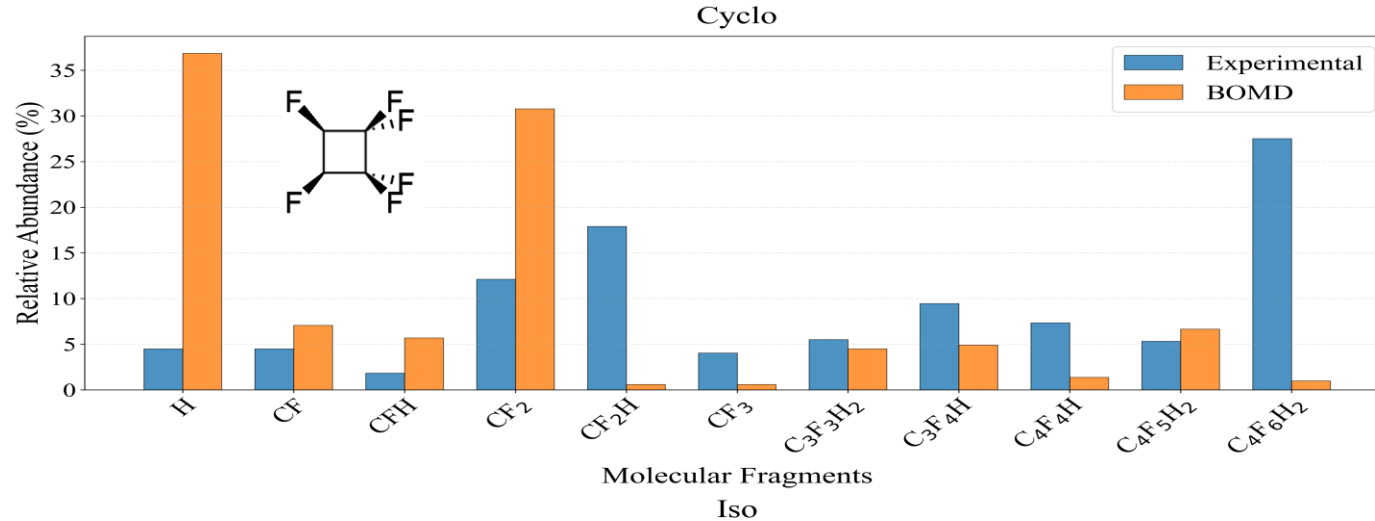
Iso



Z







Mass Spec (blue) at 300 K vs MD product distribution (red) at 5000 K

To make quantitative comparison we need :

- 1) To take into account dissociation of radicals after ionization
- 2) To take into account reactions in plasma
- 3) To reduce the temperature of the simulations to hundreds of K !!!

Future developments and vision. Potential energy surfaces with Machine Learning and simulations at low T. Better comparison with mass spec.

Sourav Roy



- 1) Machine Learning Force Field instead of *ab initio* dynamics will speed up calculations. Currently we can go down to 2000-3000 K
- 2) Better ways to compare with mass spec
- 3) More molecules, more types of electrophores.
- 4) Vision: Tell us the radicals you want, and we suggest molecules to put into your plasma

Summary

- Dissociation of lowest excited triplet state following electron impact excitation is important for industry but has been very little investigated.
- Electrophores, i.e., a small parts of the molecule that localize the initial triplet excitation, exist, such as C=C double bond or oxygen atom.
- The bonds containing the electrophore dissociate readily, and the proximity to the electrophore also affects the dissociation yield of other chemical bonds.
- For more details see the link from our group webpage:
<https://molecular-dynamics.leeds.ac.uk/neutral-dissociation-in-plasma/>

Thank you!