Theoretical Approach to Understanding Gas Phase Reactions in Hot Filament Chemical Vapor Deposition of Low ? Fluorocarbon Films

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Outline

Background on direct patterning of low ? FC films

Molecular design of low ? FC film architecture

Hot filament CVD of low ? FC films

Density functional theory methodology

CF_2 gas phase thermochemistry

Summary

Approach

Processing

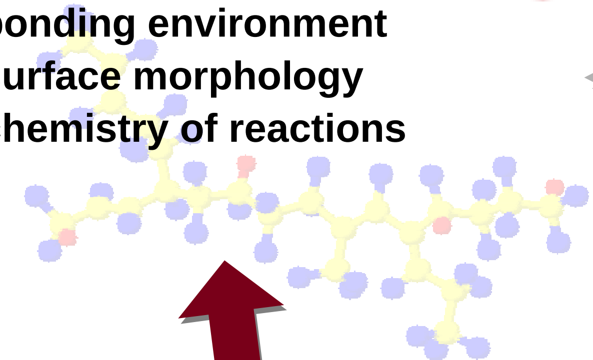
CVD parameters
precursor selection

Organosilicon
-$SiMe_2$-O-$SiMe_2$-

Fluorocarbon
-CF_2-CF_2-

Structure

bonding environment
surface morphology
chemistry of reactions



Properties

low dielectric constant
photo/e-beam sensitivity
supercritical CO_2 solubility

157-nm Lithography

MIT Lincoln Laboratory

E-Beam Direct Write

CORNELL UNIVERSITY

Supercritical CO_2 Development

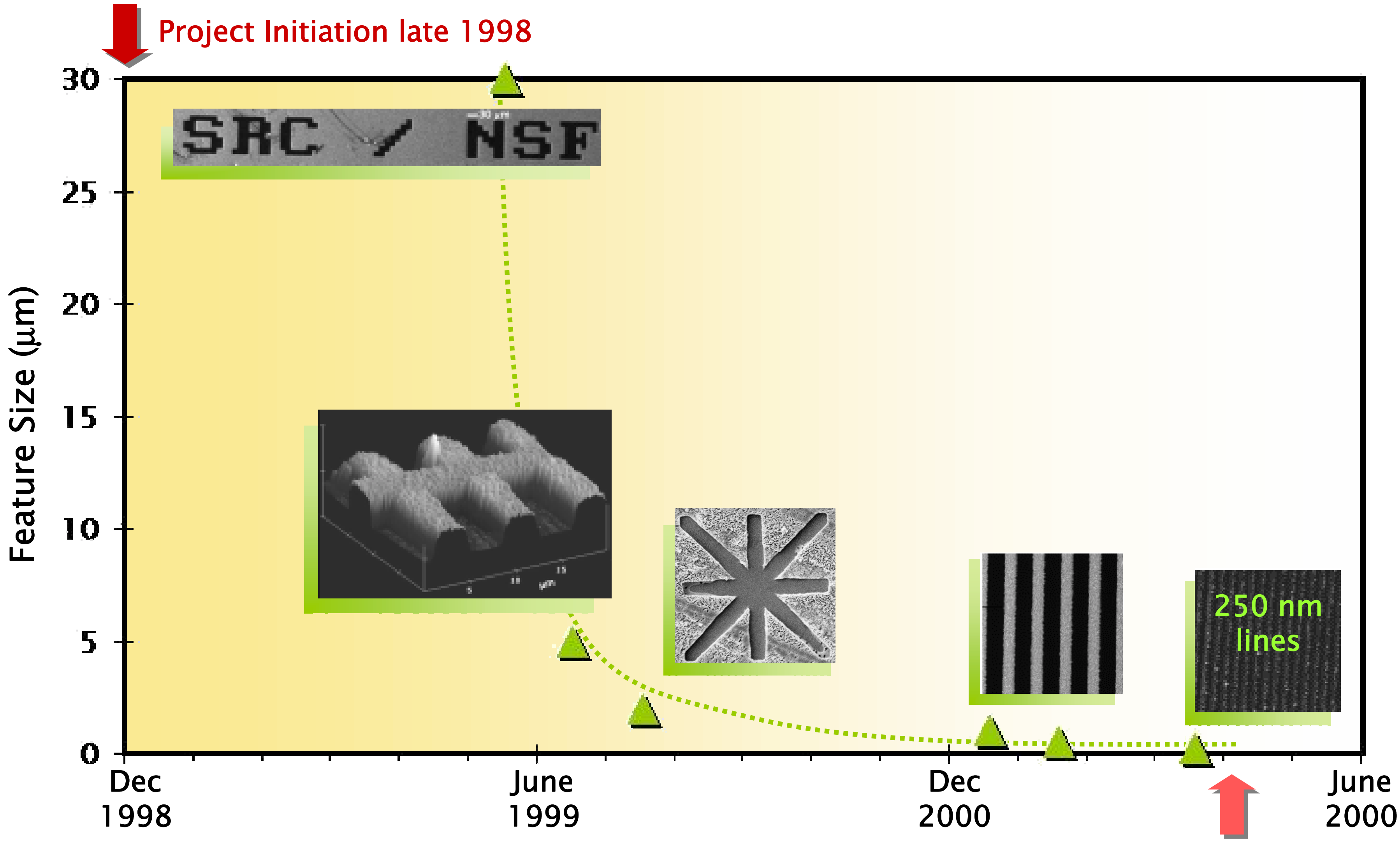
CORNELL UNIVERSITY

Film Characterization

XPS, FTIR, AFM, SEM
NMR, Raman, TGA

Progress in Patterning of HFCVD FC Films

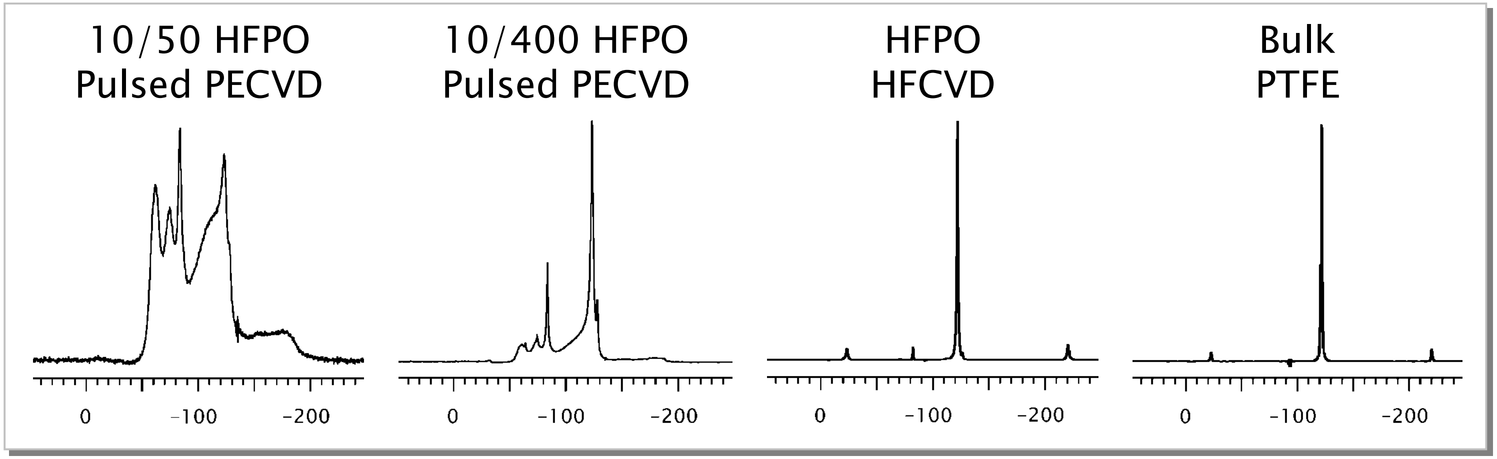
- ❑ deposition of fluorocarbon film
- ❑ e-beam exposure
- ❑ development in supercritical CO_2



Molecular Design of Film Architecture

Quantum Calculations

Experiment



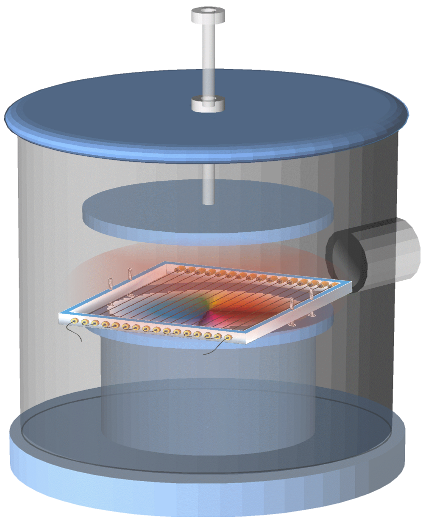
Reduce precursor fragmentation and breakdown

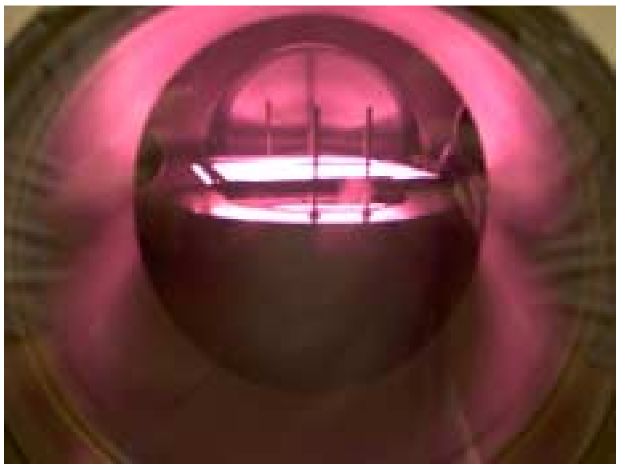
Higher CF_2 concentration and more CF_2 polymerization

More PTFE-like composition and structure

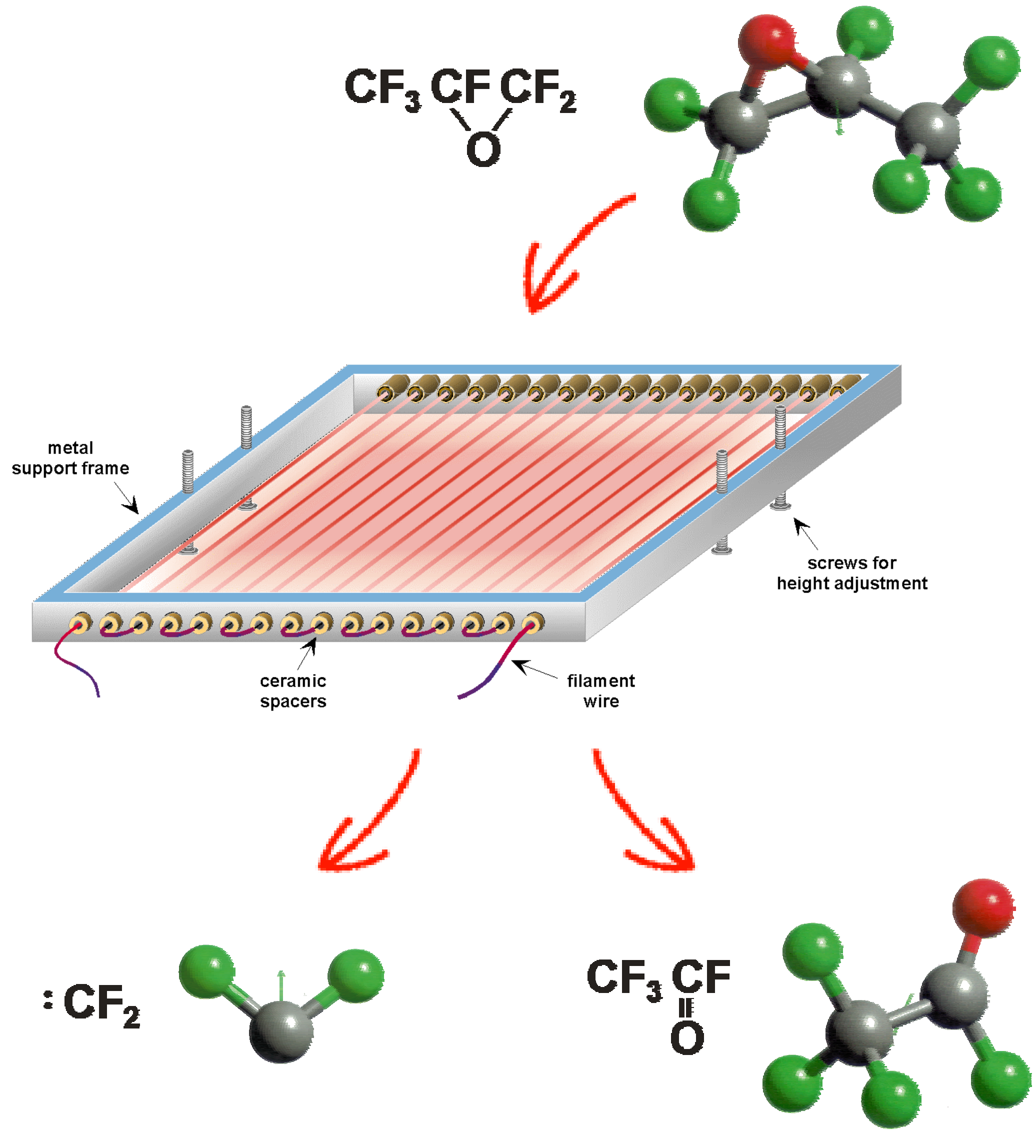
Hot Filament Chemical Vapor Deposition

CVD chamber setup



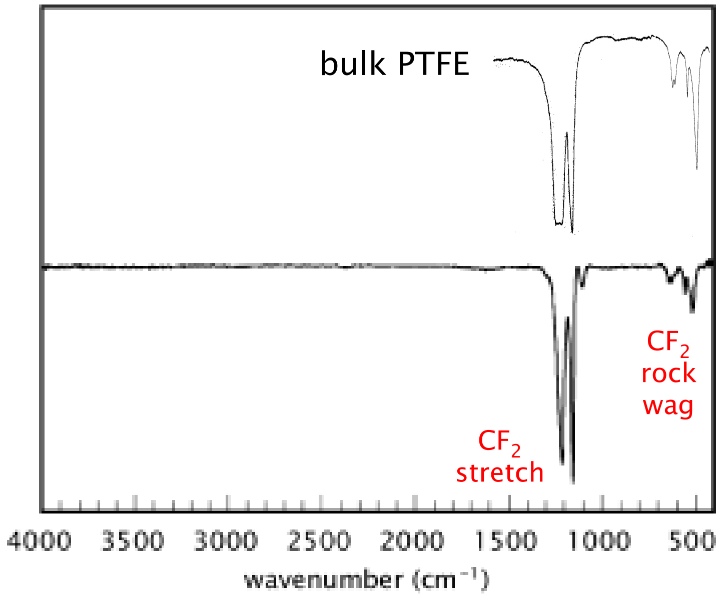


Pyrolysis of hexafluoropropylene oxide (HFPO)

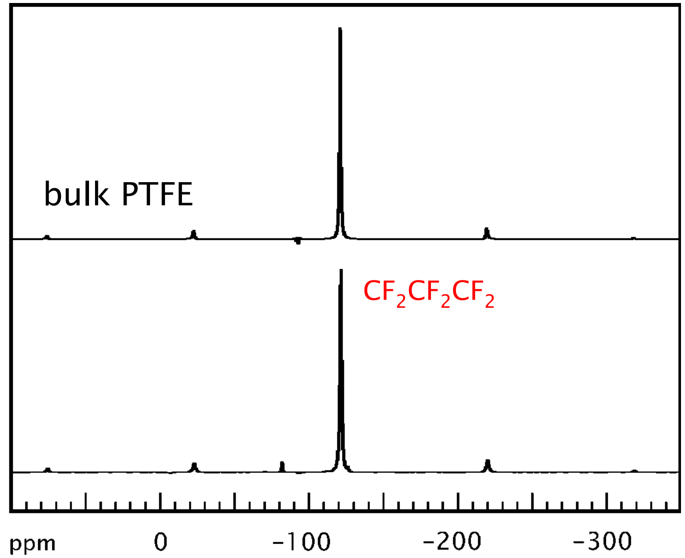


HFCVD Fluorocarbon Films

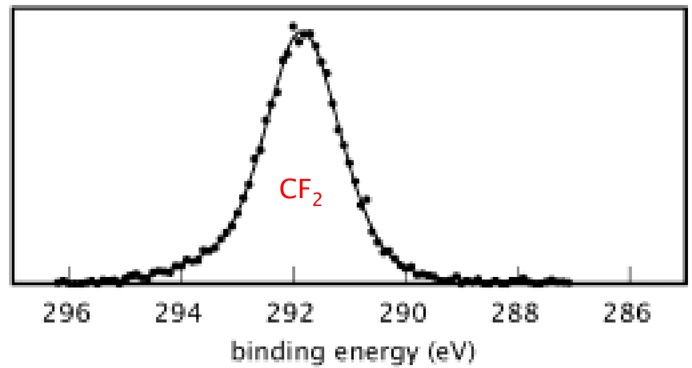
FTIR



^{19}F NMR

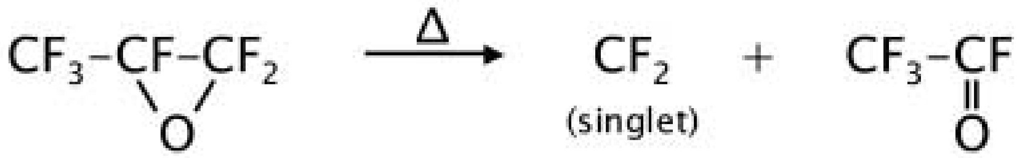


C1s XPS



CF_2 Reaction Pathways

Initiation



Recombination

$$CF_2 + CF_2 \longrightarrow CF_2{=}CF_2$$

Propagation

$$CF_2 + CF_2 \longrightarrow CF_2{-}CF_2$$

$$CF_2 + CF_2{-}CF_2 \longrightarrow CF_2{-}CF_2{-}CF_2$$

$$CF_2 + CF_2{-}CF_2{-}CF_2 \longrightarrow CF_2{-}CF_2{-}CF_2{-}CF_2$$

$$CF_2 + CF_2 \longrightarrow CF_2{-}CF_2$$

$$CF_2 + CF_2{=}CF_2 \longrightarrow CF_2{-}CF_2{-}CF_2$$

$$CF_2 + CF_3{-}CF{=}CF_2 \longrightarrow CF_2{-}CF_2{-}CF_2{-}CF_2$$

DFT Study: Methodology

HF / 3-21G
Geometry Optimization

↓

B3LYP / 3-21G
Geometry Optimization

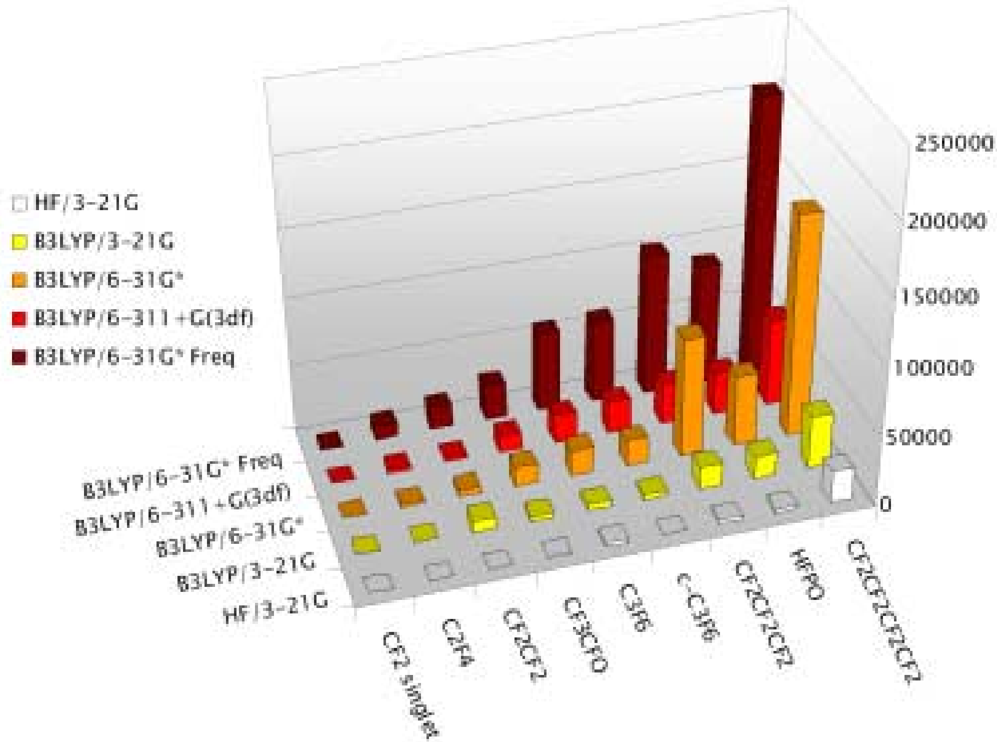
↓

B3LYP / 6-31G(d)
Geometry Optimization
Frequency Calculation

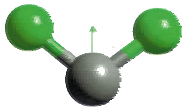
↓

B3LYP / 6-311+G(3df)
Single Point Energy Refinement

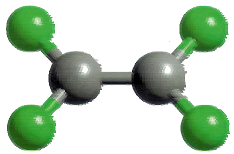
Computational Expenditure
(in seconds)



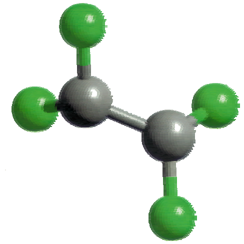
DFT Study: Optimized Geometries



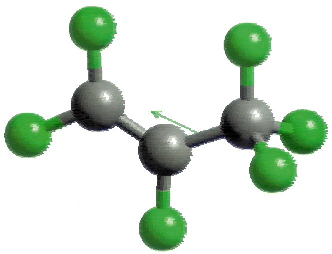
CF_2 (singlet)



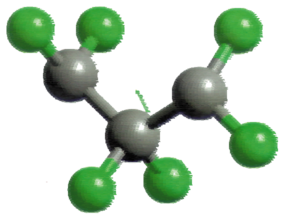
$CF_2{=}CF_2$



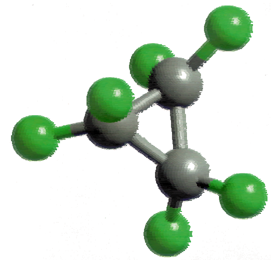
$\bullet CF_2{-}CF_2\bullet$



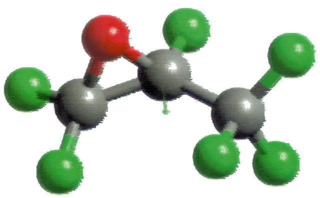
$CF_2{=}CF{-}CF_3$



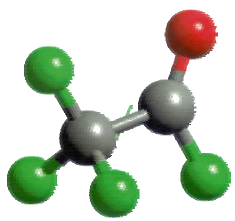
$\bullet CF_2{-}CF_2{-}CF_2\bullet$



$c{-}C_3F_6$



$CF_2{-}CF{-}CF_3$
$\quad \diagdown\ \diagup$
$\quad\ O$

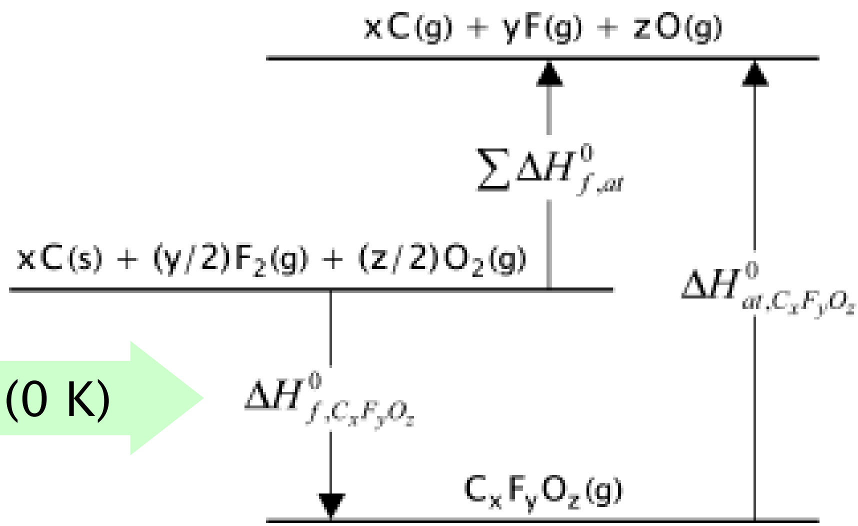


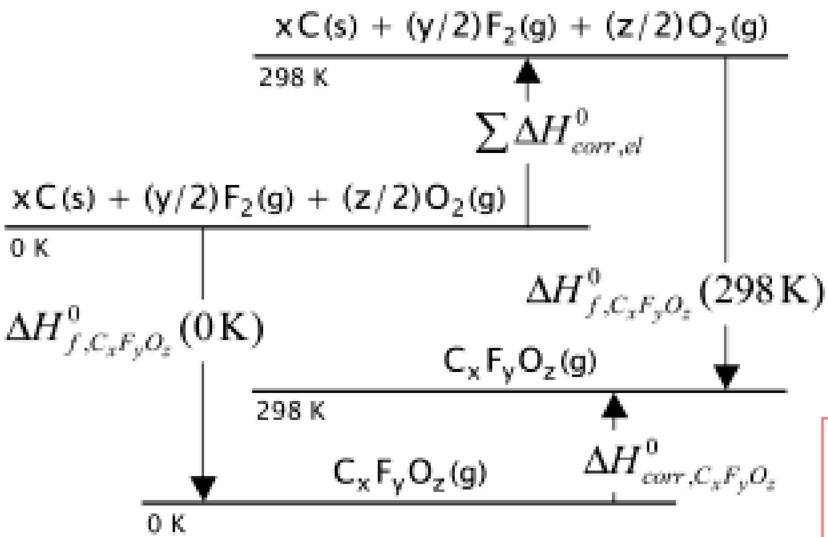
$CF_3{-}CF{=}O$

optimized at
B3LYP/6-31G(d)
level

DFT Study: Heat of Formation

Heat of Formation (0 K)





Heat of Formation (298 K)

$$\begin{aligned}\Delta H^0_{corr,C_xF_yO_z} &= PV + \Delta U^0_{translation} + \Delta U^0_{rotation} + \Delta U^0_{vibration} \\ &= RT + \tfrac{3}{2}RT + (\tfrac{3}{2}RT \text{ or } RT) + R\sum_i \frac{\frac{0.96\nu_i h}{k}}{\exp(\frac{0.96\nu_i h}{kT}) - 1}\end{aligned}$$

DFT Study: Methodology Validation

Total energies, zero point energies, enthalpic corrections and enthalpies of formation from B3LYP DFT.

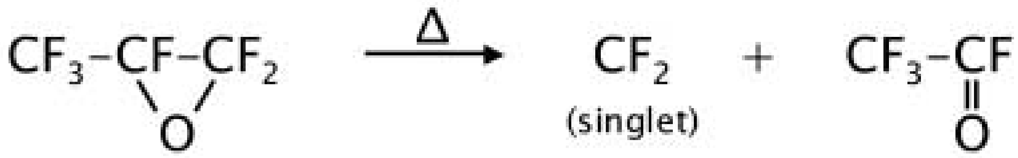
$C_xF_yO_z$ species	E_e (hartrees)	ZPE (hartrees)	ΔH^0_{corr} (hartrees)	ΔH^0_f (298 K) theory (kcal/mol)	ΔH^0_f (298 K) expt (kcal/mol)	Δ theory–expt (kcal/mol)
^3C	−37.857 47	0.000 00	0.002 36			
^2F	−99.761 68	0.000 00	0.002 36			
^3O	−75.090 87	0.000 00	0.002 36			
F_2	−199.581 02	0.002 43	0.003 34	2.2	0.0	2.22
$^1CF_2$	−237.790 29	0.006 95	0.003 96	−45.7	−43.5	−2.20
$^3CF_2$	−237.706 59	0.006 79	0.004 05	6.8		
$CF_2{=}CF_2$	−475.697 41	0.021 48	0.006 37	−161.1	−157.4	−3.71
$CF_3CF{=}CF_2$	−713.593 08	0.034 27	0.009 11	−270.2	−269.0	−1.19
$CF_2{-}CF_2$	−475.619 25	0.019 62	0.006 66	−113.0		
$CF_2{-}CF_2{-}CF_2$	−713.492 44	0.031 98	0.009 59	−208.1		
$CF_2{-}CF_2{-}CF_2{-}CF_2$	−951.363 26	0.044 37	0.012 41	−301.8		
CF_3CFO	−551.011 63	0.026 32	0.007 18	−239.9		
$CF_3CF(O)CF_2$ / HFPO	−788.843 36	0.038 94	0.009 52	−309.2		

$|\Delta|_{av}$ = 2.33

Heats of formation derived following approach by Curtiss et al, J. Chem. Phys., 95, 2433 (1991).

DFT Study: CF_2 Reaction Set

Initiation



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$$CF_2 + CF_2{-}CF_2 \longrightarrow CF_2{-}CF_2{-}CF_2$$

$$CF_2 + CF_2{-}CF_2{-}CF_2 \longrightarrow CF_2{-}CF_2{-}CF_2{-}CF_2$$

$$CF_2 + CF_2 \longrightarrow CF_2{-}CF_2$$

$$CF_2 + CF_2{=}CF_2 \longrightarrow CF_2{-}CF_2{-}CF_2$$

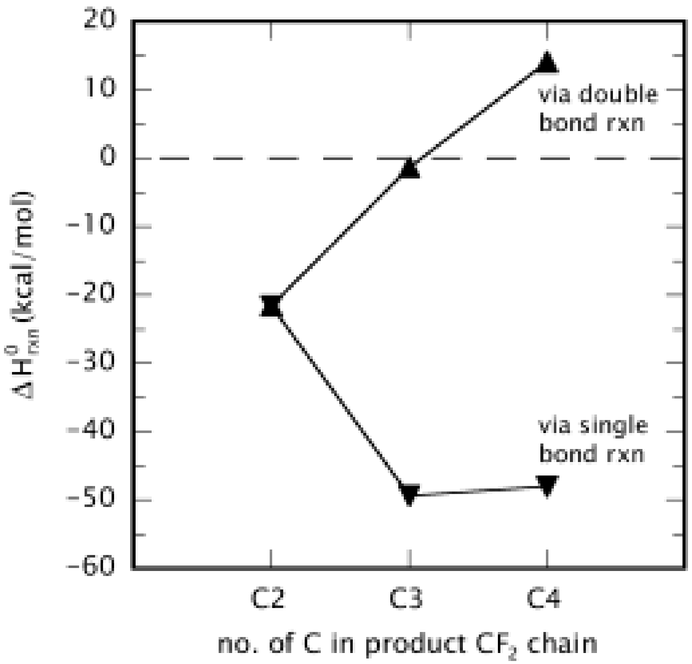
$$CF_2 + CF_3{-}CF{=}CF_2 \longrightarrow CF_2{-}CF_2{-}CF_2{-}CF_2$$

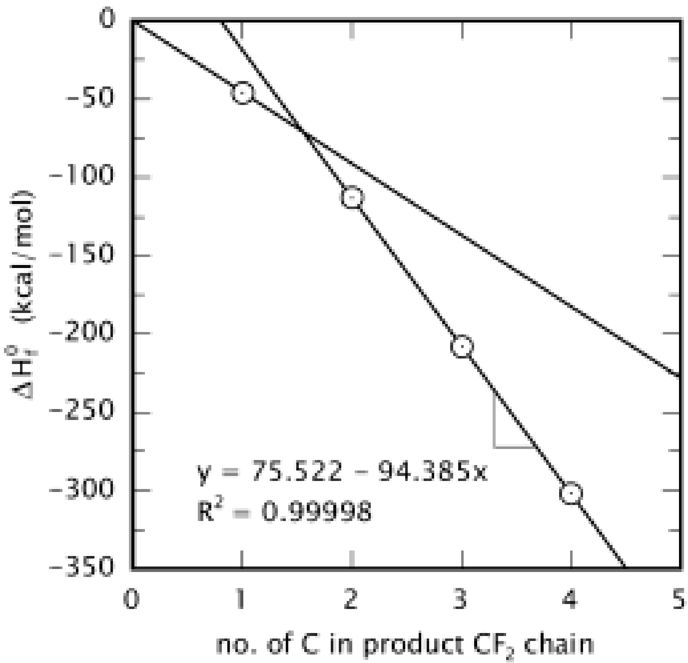
DFT Study: CF_2 Thermochemistry

Enthalpies of reactions from the B3LYP DFT method for a set of gas phase CF_2 reactions from HFPO pyrolysis.

$C_xF_yO_z$ reaction	ΔH^0_{rxn} (298 K) theory (kcal/mol)	ΔH^0_{rxn} (298 K) expt (kcal/mol)	Δ theory–expt (kcal/mol)
HFPO $\rightarrow$ CF_2 + CF_3CFO	23.6		
$CF_2{=}CF_2$ $\rightarrow$ CF_2 + CF_2	69.7	68.4	1.32
CF_2 + CF_2 $\rightarrow$ $CF_2\text{-}CF_2$	-21.6		
CF_2 + $CF_2\text{-}CF_2$ $\rightarrow$ $CF_2\text{-}CF_2\text{-}CF_2$	-49.4		
CF_2 + $CF_2\text{-}CF_2\text{-}CF_2$ $\rightarrow$ $CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2$	-48.0		
CF_2 + CF_2 $\rightarrow$ $CF_2\text{-}CF_2$	-21.6		
CF_2 + $CF_2{=}CF_2$ $\rightarrow$ $CF_2\text{-}CF_2\text{-}CF_2$	-1.3		
CF_2 + $CF_3\text{-}CF{=}CF_2$ $\rightarrow$ $CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2$	14.1		
CF_2 ($^3B_1$) $\rightarrow$ CF_2 ($^1A_1$)	-52.5	-54.0	1.52
		$\lvert\Delta\rvert_{av}$ =	1.42

DFT Study: CF_2 Propagation/Depropagation





$CF_2 \quad + \quad (CF_2)_{n-1} \qquad (CF_2)_n$

$? \, H^0_{rxn} = -48.7$ kcal/mol

$nC \quad + \quad nF_2 \qquad (CF_2)_n$

$? \, H^0_{f,n} = 75.5 - 94.4n \quad n=2,3,\ldots$

$(CF_2)_{n+m} \qquad (CF_2)_n \quad + \quad (CF_2)_m$

$? \, H^0_{rxn} = +75.5$ kcal/mol

Summary

Molecular design of low ? FC films

HFCVD reactions and reactive species

CF_2 thermochemistry

Potential CF_2 polymerization pathway