Institute of General and Physical Chemistry (IGPC), Belgrade, Serbia

Searching for Eco-friendly molecules producing ·F and F^- during the degradation in gaseous detectors by using quantum-chemical calculation

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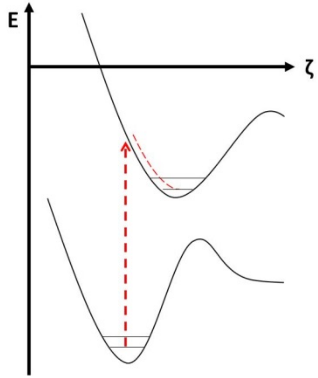
Molecule	Chemical formula	GWP (Global warming potential)	Hazards		
			Flammability	Health	Instability reactivity
freon	CF_4	6630	0	1	0
HFC-1234ze	CF_3CHCHF	< 1			
HFC-1336mzz	CF_3-CH=CH-CF_3	…	…	…	…
HCFC-1233zd	CHCl=CH-CF_3	…	…	…	…
HFE-143m	CF_3-O-CH_3	…	…	…	…
HFE-245mc	CF_3-CF_2-O-CH_3	…	…	…	…

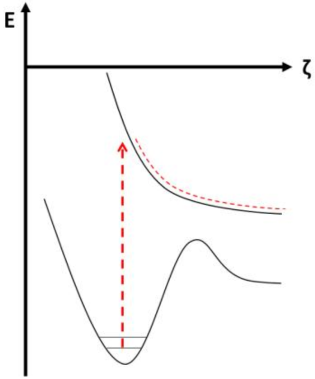
Examine and compare how three basic processes in plasma affect the stability of CF_4 and molecules from previous list

Examine ionization, excitation and electron attachment processes by calculations at Density-functional theory (DFT)(b3lyp and blyp) method with def2-tzvp basis set using Orca 5.0 quantum chemical package.

With minimum



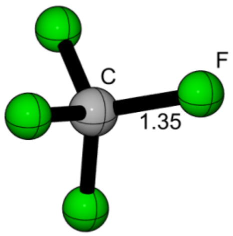
Vertical and Adiabatic energy

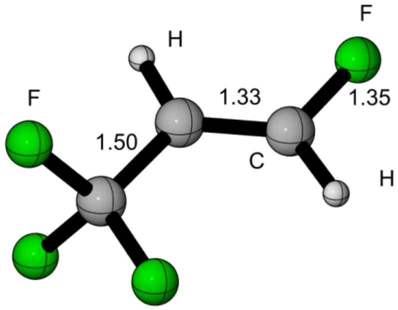


Without minimum

Ionization by losing electron

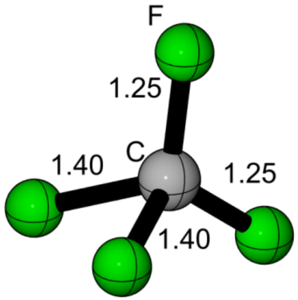
Ground state

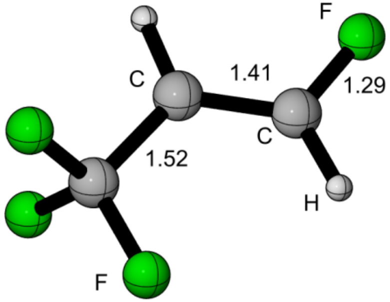




Ground state

Ionized state





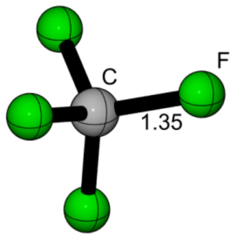
Ionized state

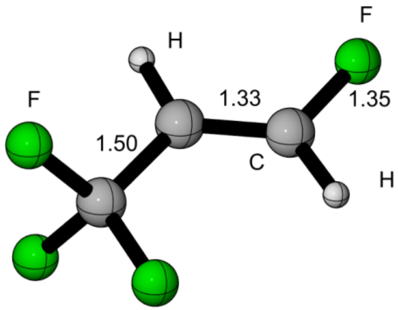
Vertical energy	(eV)	14.46
Adiabatic energy	(eV)	14.44

Vertical energy	(eV)	10.80
Adiabatic energy	(eV)	10.47

Electron excitation process

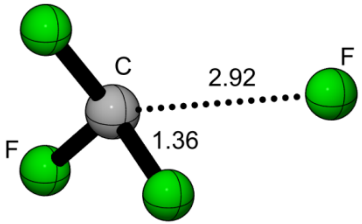
Ground state

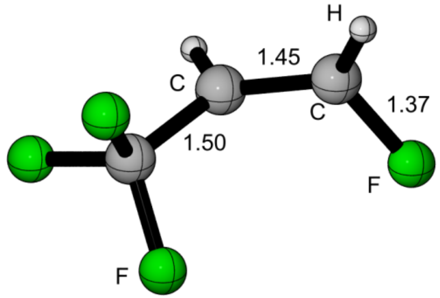




Ground state

Excited state





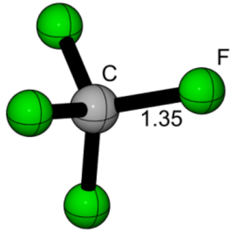
Excited state

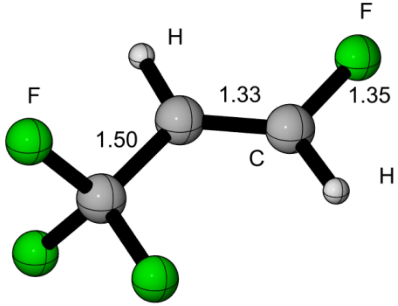
Vertical energy	(eV)	11.59
Adiabatic energy	(eV)	5.37

Vertical energy	(eV)	4.44
Adiabatic energy	(eV)	2.87

Ionization by attaching electron

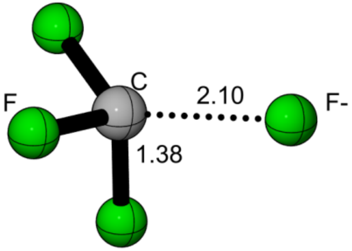
Ground state

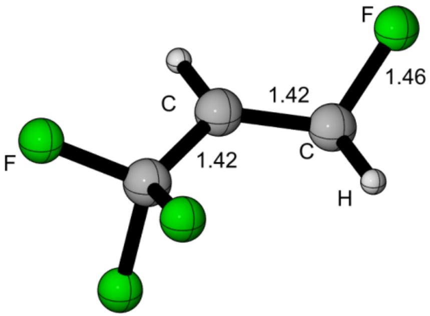




Ground state

electron attached
-abstracted state





electron attached
-abstracted state

Vertical energy (eV) 4.06
Adiabatic energy (eV) 1.12

Vertical energy (eV) 1.44
Adiabatic energy (eV) 0.44

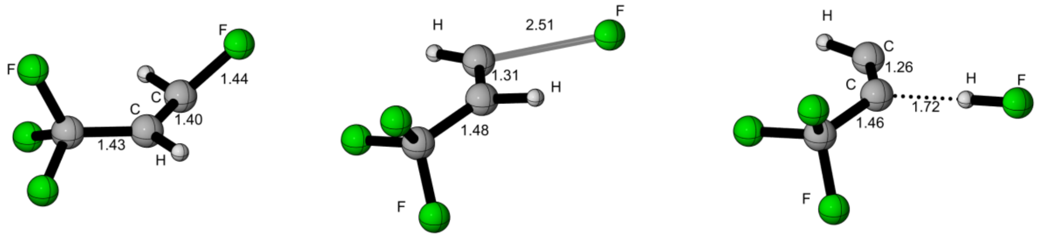
CF_4	HFO
$CF_4 + e^- \rightarrow CF_4^+ + e^- + e^-$	$HFO + e^- \rightarrow HFO^{+1} + e^- + e^-$
$CF_4 + e^- \rightarrow CF_4^* + e^- \rightarrow \cdot CF_3 + \cdot F$	$HFO + e^- \rightarrow HFO^* + e^-$
$CF_4 + e^- \rightarrow \cdot CF_4^- \rightarrow \cdot CF_3 + F^-$	$HFO + e^- \rightarrow HFO^{-1}$

$F^- + \text{Anode} \rightarrow \cdot F + e^- + \text{Anode}$

$\cdot F + e^- \rightarrow F^-$ spontaneous process primary ionization → avalanche → basic processes → additional degradation → time

start	TS	end structure

HFO^{-1}

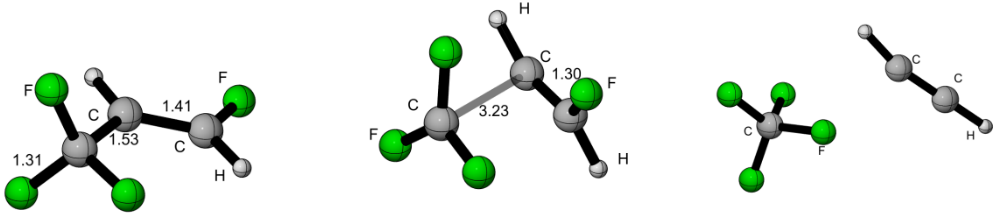


$[CHF{=}CH\text{-}CF_3]^{-1} \rightarrow TS \rightarrow [CH{=}C\text{-}CF_3]^{-1} + HF$

$E_a = 1.08$ eV

start	TS	end structure

HFO^{+1}

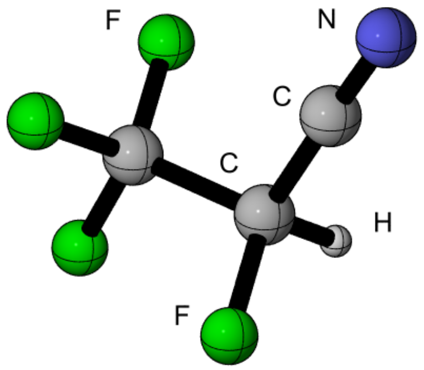


$[CHF{=}CH\text{-}CF_3]^{+1} \rightarrow TS \rightarrow CF_4 + C_2H_2^{+1}$

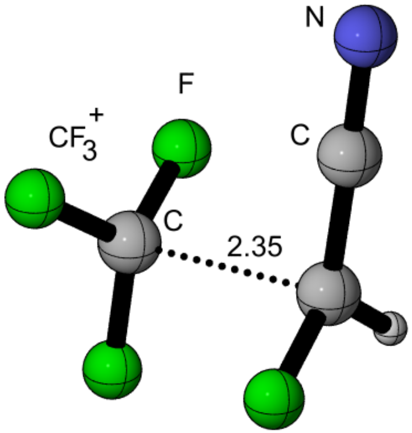
$E_a = 2.64$ eV

reaction	Activation energy E_a (eV)
$\cdot CF_4^+ \rightarrow TS \rightarrow CF_3^+ + F\cdot$	0.05
$CF_3^+ \rightarrow TS \rightarrow \cdot CF_2^+ + F\cdot$	6.26
$\cdot CF_2^+ \rightarrow TS \rightarrow CF^+ + F\cdot$	2.84
$CF^+ \rightarrow TS \rightarrow \cdot C^+ + F\cdot$	6.3

$CF_3^+ \rightarrow \cdot CF_2^+ + \cdot F$
$\cdot CF_2^+ \rightarrow CF^+ + \cdot F$
$CF^+ \rightarrow \cdot C^+ + \cdot F$



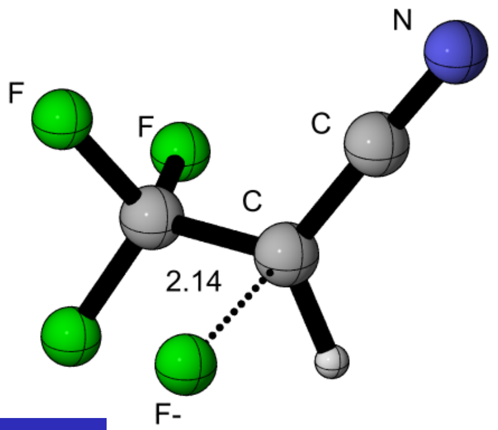
Ground state



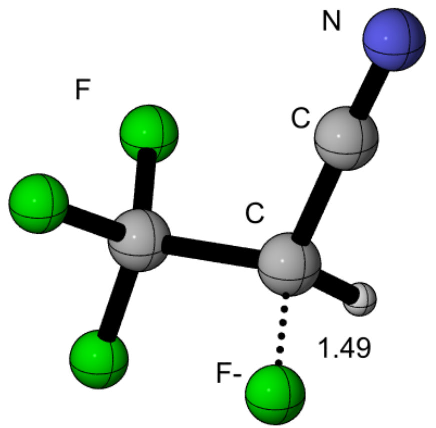
Ionized state

CF_3-CHF-CN

[CF_3-CHF-CN] + e^- → CF_3^+ + [CHF-CN]$^{\cdot}$



electron attached -abstracted state



Excited state

$[CF_3\text{-}CHF\text{-}CN] + e^- \rightarrow F^- + [CF3\text{-}CH\text{-}CN]^{\cdot}$

$[CF_3\text{-}CHF\text{-}CN] + e^- \rightarrow e^- + F^- + [CF3\text{-}CH\text{-}CN]^+$

$F^- + \text{Anode} \rightarrow {}^{\cdot}F + e^- + \text{Anode}$

${}^{\cdot}F + e^- \rightarrow F^-$ spontaneous process

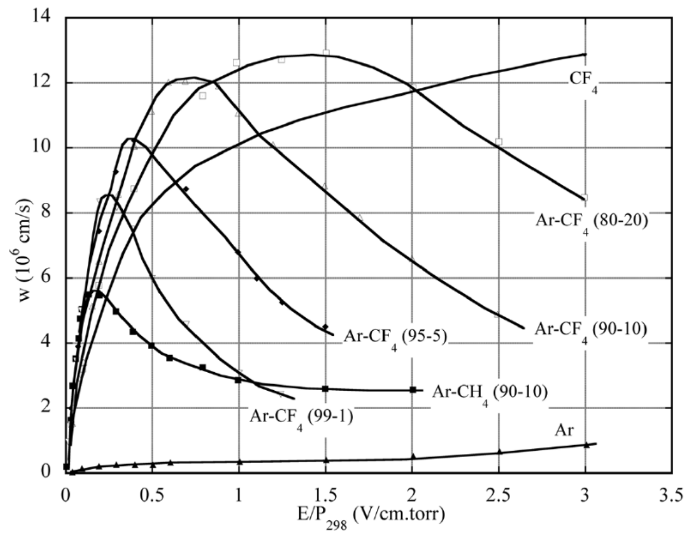


Figure 4.27 Electron drift velocity as a function of field in CF_4, pure and in mixtures with argon (Christophorou *et al.*, 1979). By kind permission of Elsevier.

Carbon tetrafluoride also has fast drift velocity and low diffusion, comparable to methane; CF_4-based gas mixtures for use in high-rate detectors have been studied extensively, Figure 4.27 (Christophorou *et al.*, 1979). Their main advantages for use in large volume detectors in particle physics are non-flammability and low sensitivity to neutrons; also, they do not form polymers in the avalanches, and even have etching properties capable of removing existing deposits on electrodes, as discussed in Chapter 16.

Processes on phase boundary