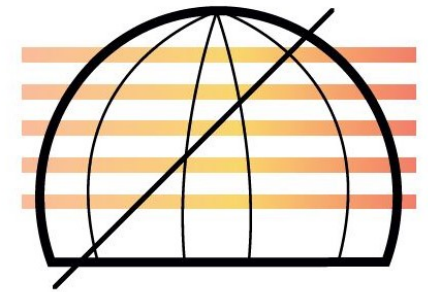




EP-DT  
Detector Technologies



RPC **2022**

# Possible alternatives to $\text{SF}_6$ for Resistive Plate Chambers

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Beatrice Mandelli, R. Guida, G. Rigoletti

CERN

The XVI Workshop on Resistive Plate Chambers  
CERN, 28<sup>th</sup> September 2022

# Outline

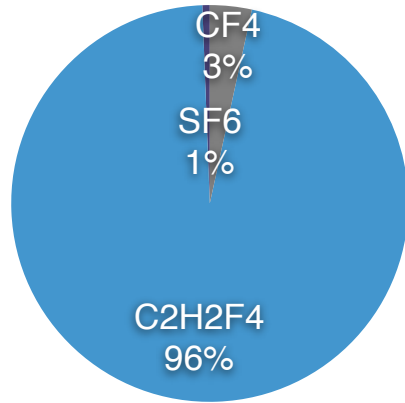
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**SF<sub>6</sub> impact on GHG emissions and possible alternatives**

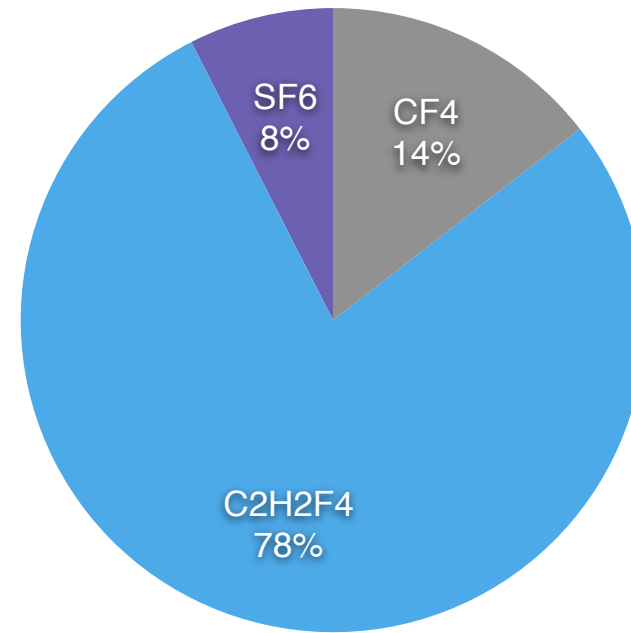
**RPC performance with new gases as substitutes of SF<sub>6</sub>**

**Thoughts and tests on properties of new gases**

# Use of SF<sub>6</sub> in RPC detectors at CERN



from kg to tCO<sub>2</sub>e



- CF4 **GWP 7390**
- C2H2F4 **GWP 1430**
- SF6 **GWP 22800**

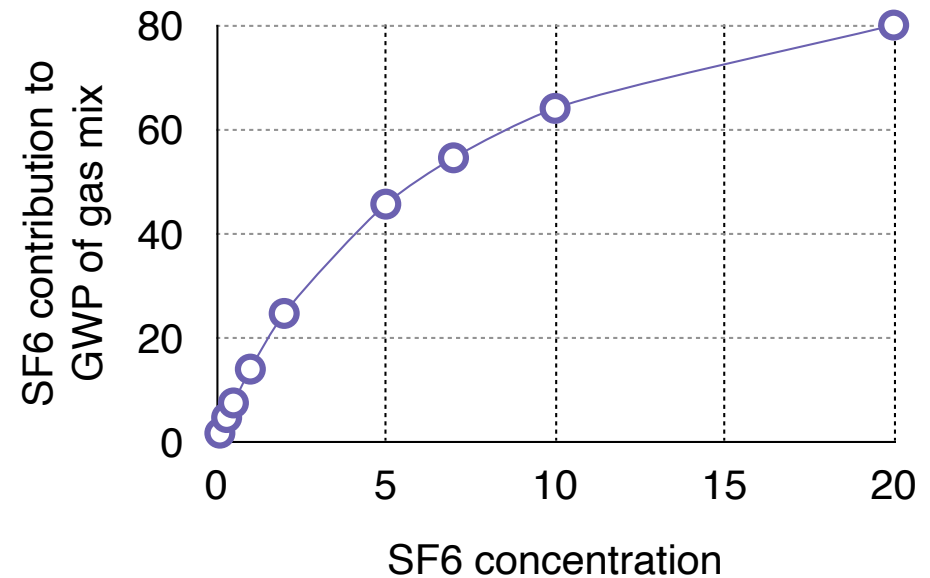
Impact of GHG in LHC Run 2 considering quantities used in **kg**

Impact of GHG in LHC Run 2 considering quantities used in **tCO<sub>2</sub>e**

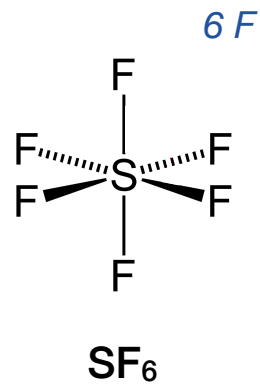
**SF<sub>6</sub> contributes for a high fraction in the GWP of RPC gas mixture even if it is used in small concentrations**

**HPL RPC: ~0.3%**  
**~5% of the GWP of the gas mixture**

**glass RPC: ~7%**  
**~50% of the GWP of the gas mixture**

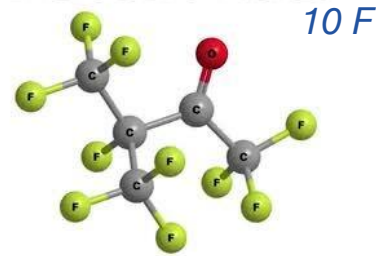


# Alternatives to SF<sub>6</sub>

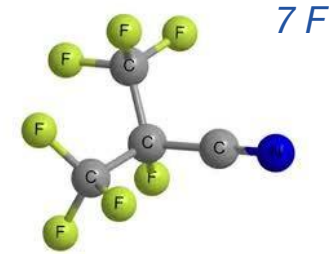


**GWP 23900**

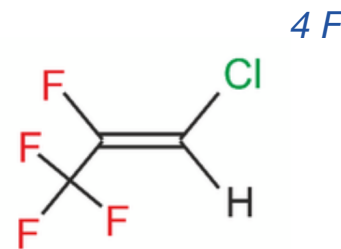
- Chemical inertness: extremely stable
- Exceptionally long lived in the atmosphere
- Excellent dielectric property
  - SF<sub>6</sub> x 2.5 than Air
- Non-flammable and toxic
- Gaseous form
- No major reactions
  - Ok with H<sub>2</sub>O, Cl and acids



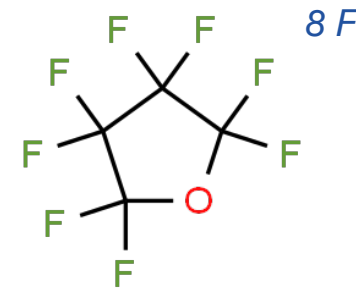
**3M™ Novec™ 5110**  
 (CF<sub>3</sub>C(O)CF(CF<sub>3</sub>)<sub>2</sub>)  
**GWP <1**  
 Atm. lifetime 15 days



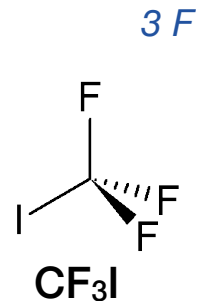
**3M™ Novec™ 4710**  
 ((CF<sub>3</sub>)<sub>2</sub>CFCN)  
**GWP 2100**  
 Atm. lifetime 30 years



**AMOLEA™ HFO-1224yd**  
 (CF<sub>3</sub>-CF=CHCl)  
**GWP <1**  
 Atm. lifetime 20 days

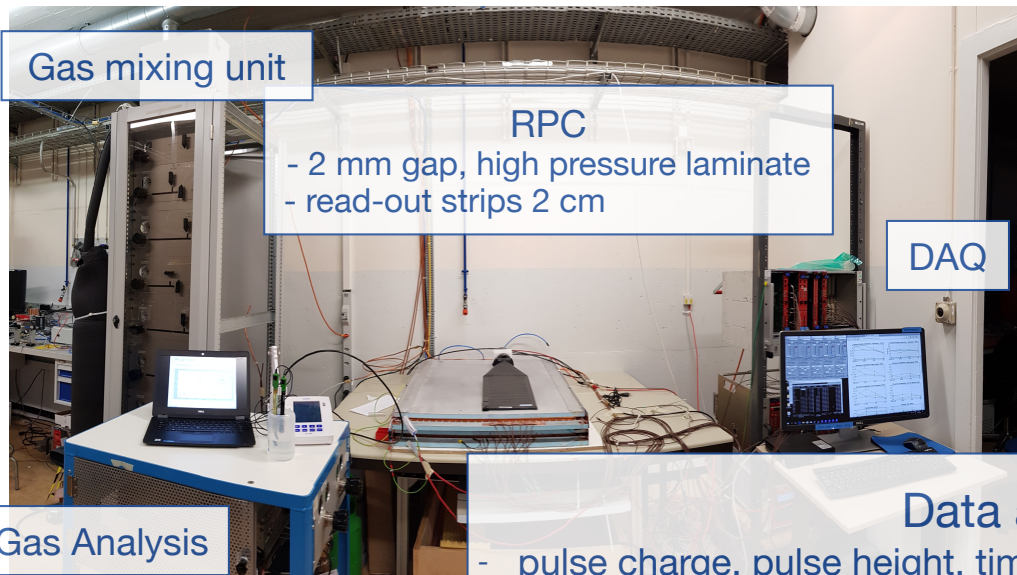


**C<sub>4</sub>F<sub>8</sub>O**  
**GWP 8700**  
 Atm. lifetime >3000 years



**CF<sub>3</sub>I**  
**GWP 0.4**  
 Atm. lifetime 6 days

# Set-ups: laboratory and GIF++



## Laboratory

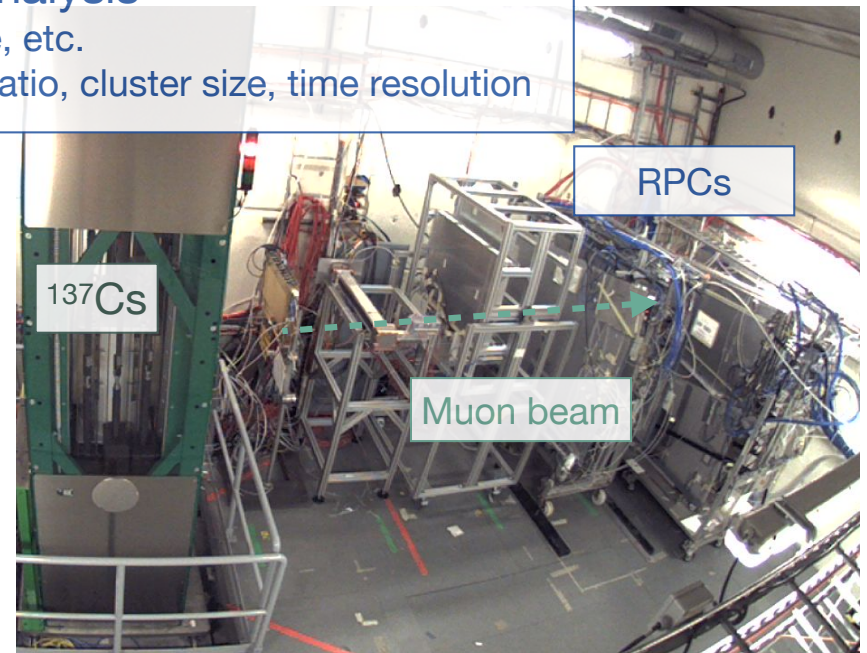
- Gas mixing unit
  - Gas mixture up to 6 components
- DAQ
  - CAEN Digitizer V1730: resolution 0.122 mV, sampling 500 MS/s
- Gas analysis
  - GC, MS and ISE

## Data analysis

- pulse charge, pulse height, time, etc.
- efficiency, avalanche/streamer ratio, cluster size, time resolution

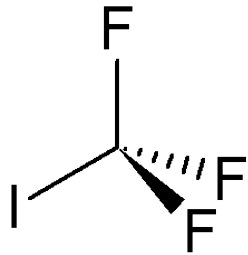
## Gamma Irradiation Facility (GIF++)

- Gamma source
  - $^{137}\text{Cs}$  of 12 TBq  $\rightarrow$  662 keV gamma
  - Lead filters to allow attenuation factors (ABS) between 1 and 46000
- Muon Beam
  - 100 GeV and  $10^4$  muons/spill ( $10 \times 10 \text{ cm}^2$ )
- Detectors tested up to to  $\sim \text{kHz/cm}^2$
- Very similar DAQ, gas system and gas analysis of laboratory



**$\text{SF}_6$  alternatives were tested in different concentrations as substitute of  $\text{SF}_6$  in RPC standard gas mixture**

# CF<sub>3</sub>I

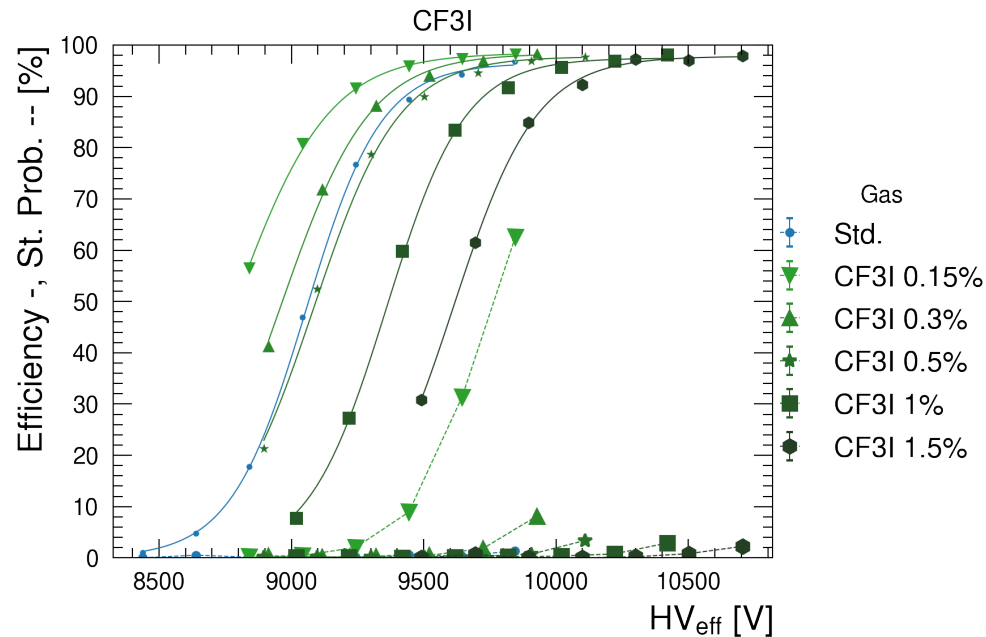


## PRO

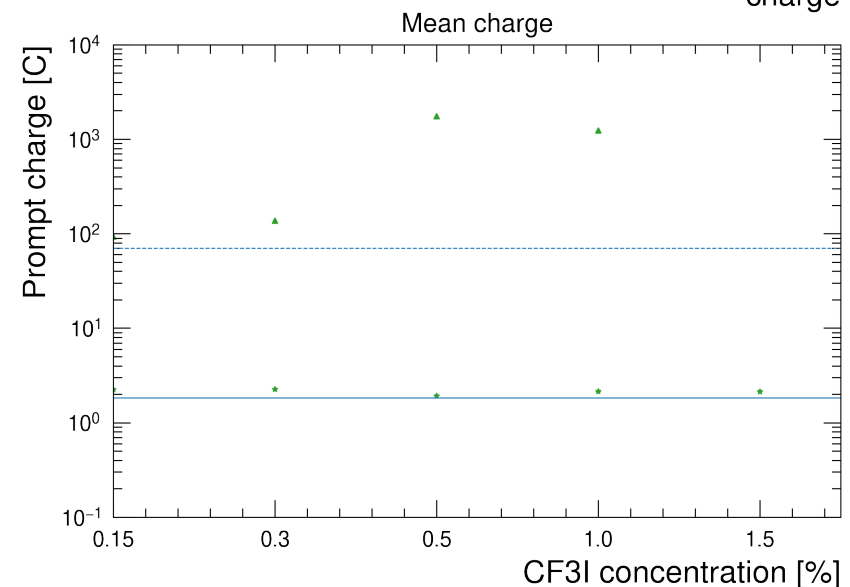
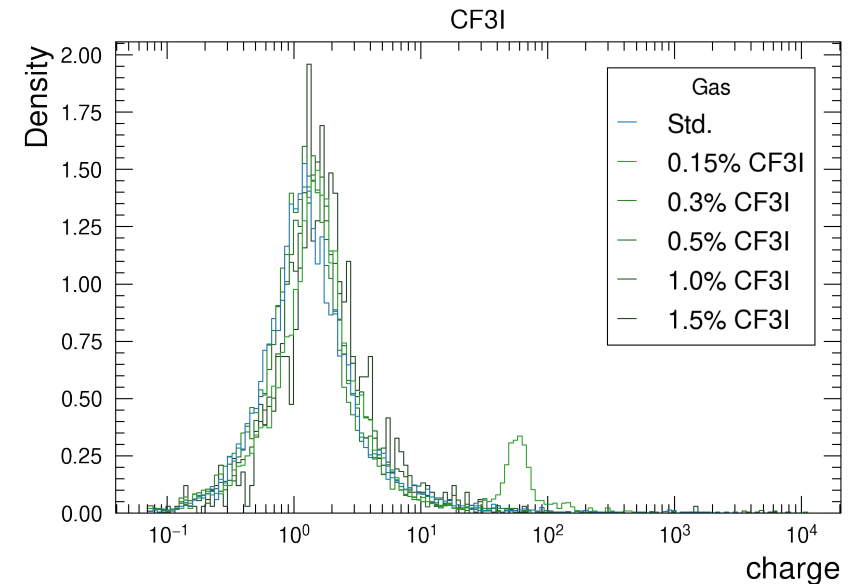
- Very low GWP: 0.4
- Application in industry

## CONS

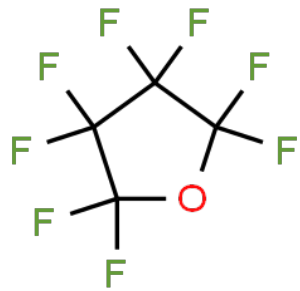
- Toxic (inhalation), low human genotoxic risk
- May react with H<sub>2</sub>O



- Low concentration (0.3-0.5%) enough for good streamer suppression
- Working point similar to std gas mixture with 0.3-0.5% of CF<sub>3</sub>I
- Avalanche charge similar to std gas mixture
  - Streamer charge much affected by error due to low statistics



# C<sub>4</sub>F<sub>8</sub>O

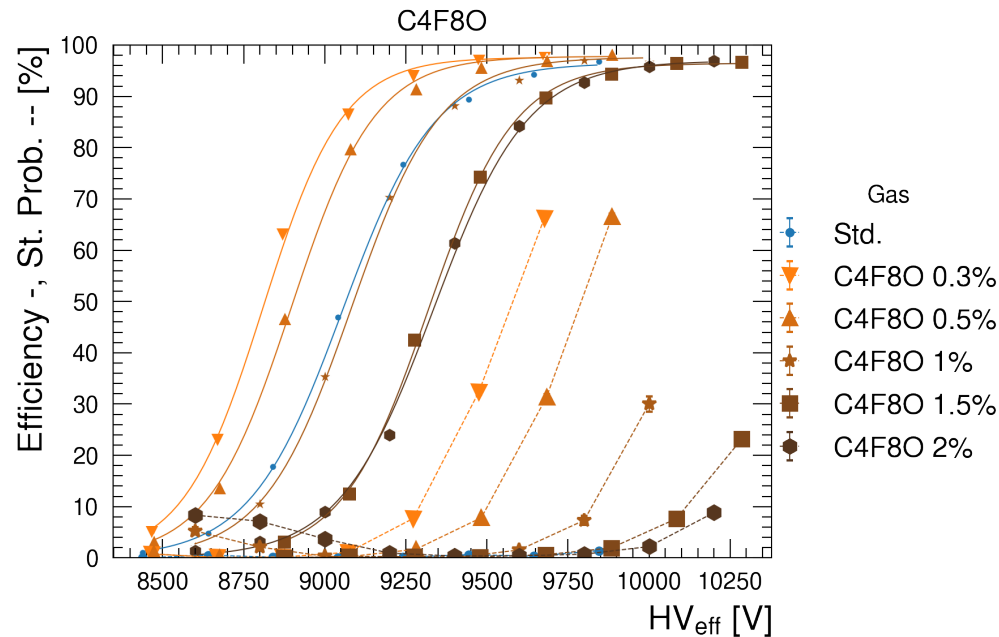


## PRO

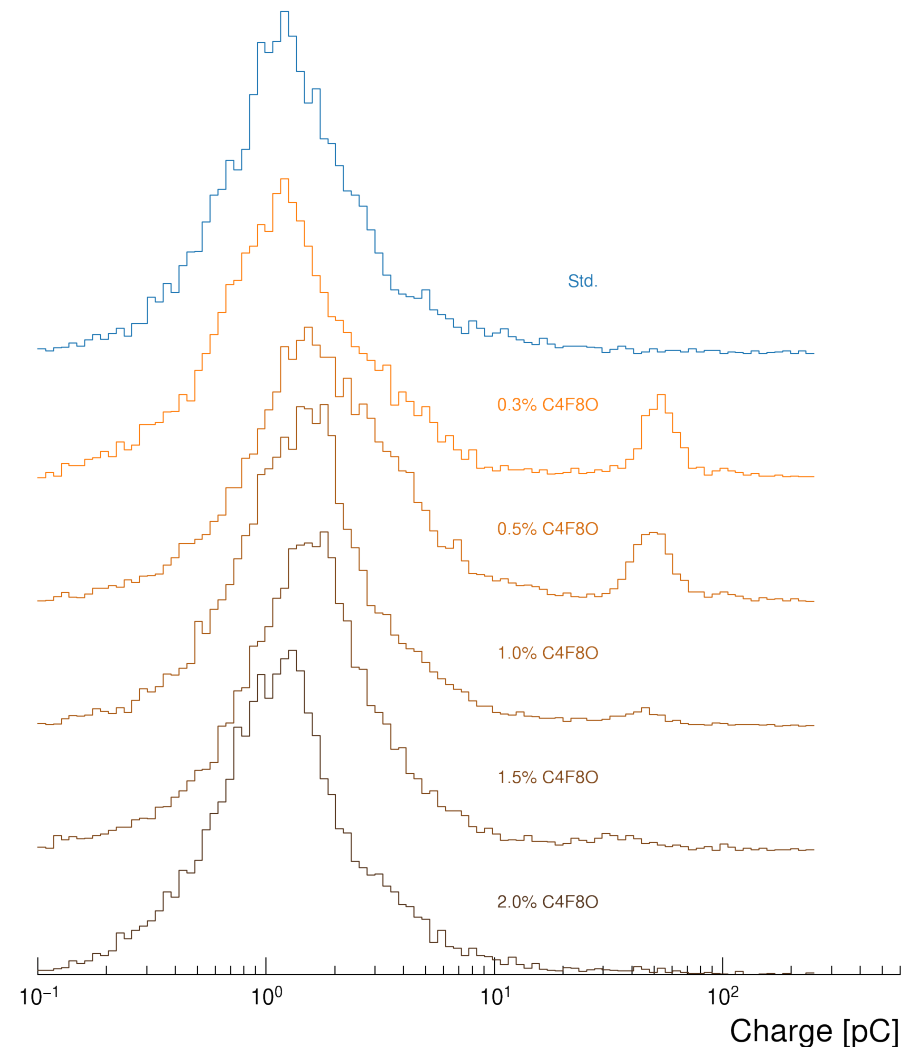
- Good quantity of F atoms
- Easy to use in gas form

## CONS

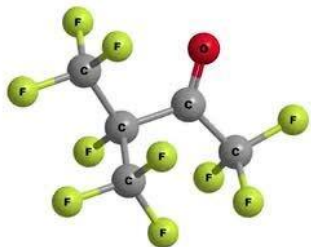
- High GWP: 8000
- When used as alternative to SF<sub>6</sub>, a large fraction is needed



- 1.5% needed for good performance
- GWP contribution therefore similar to SF<sub>6</sub> in std gas mixture
- At 1.5%-2% similar streamer probability of SF<sub>6</sub>
- Higher working point for concentration >1%
- Avalanche charge a bit higher than std gas mixture
- Streamer charge similar



# Novec 5110

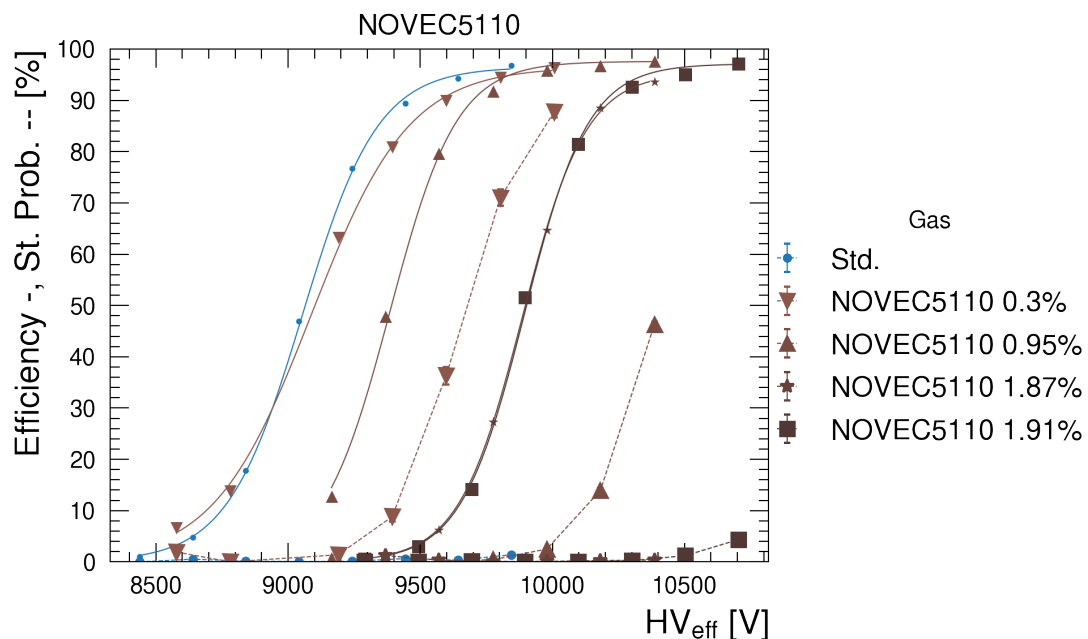


## PRO

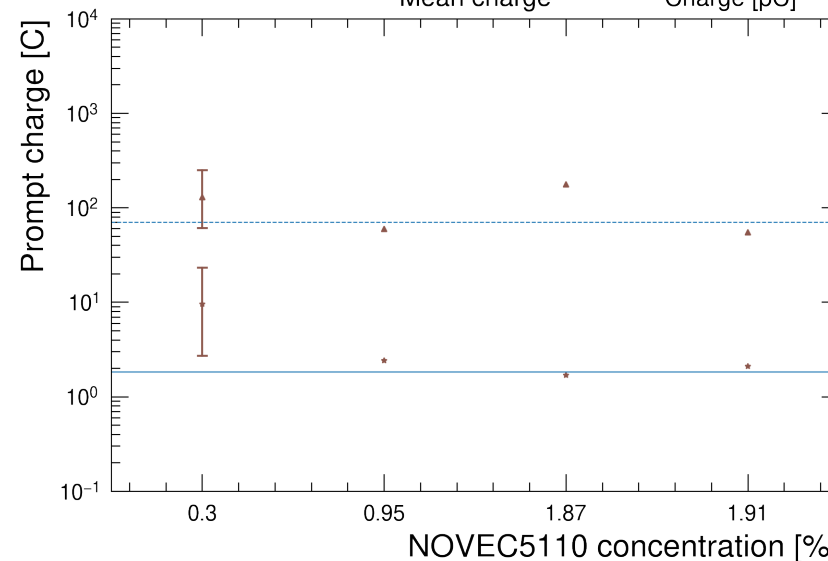
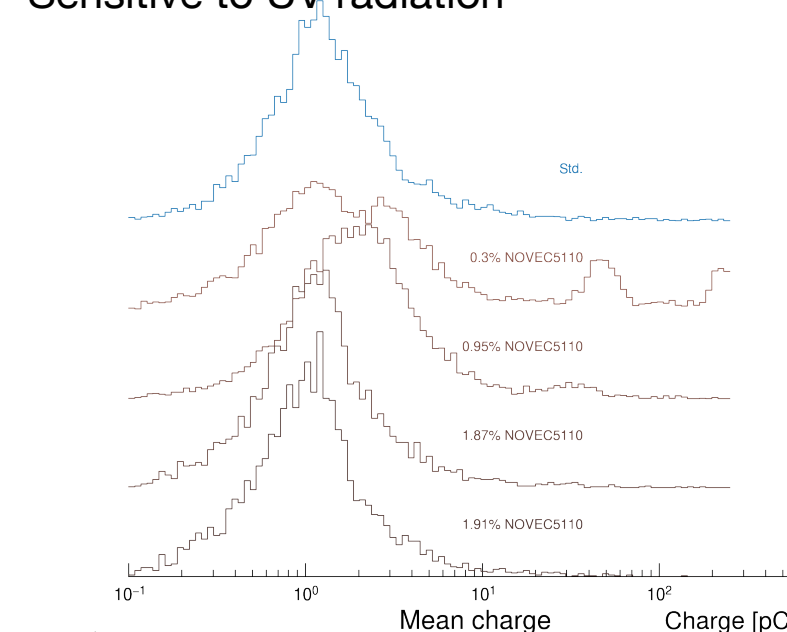
- Very low GWP: <1
- Application in industry
- High dielectric strength

## CONS

- High boiling point: 27 C
- Sensitive to UV radiation

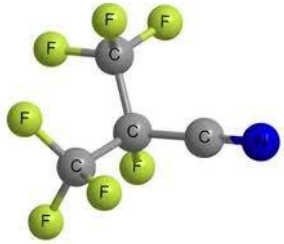


- High concentration (~2%) of NOVEC 5110 needed to obtain good streamer suppression
  - Suspect that NOVEC 5110 breaks inside the RPC
- Higher working point for concentrations > 0.3%
- Avalanche and streamer charge similar of std gas mixture from 0.9%
  - At 0.3% very large avalanche signals





# Novec 4710

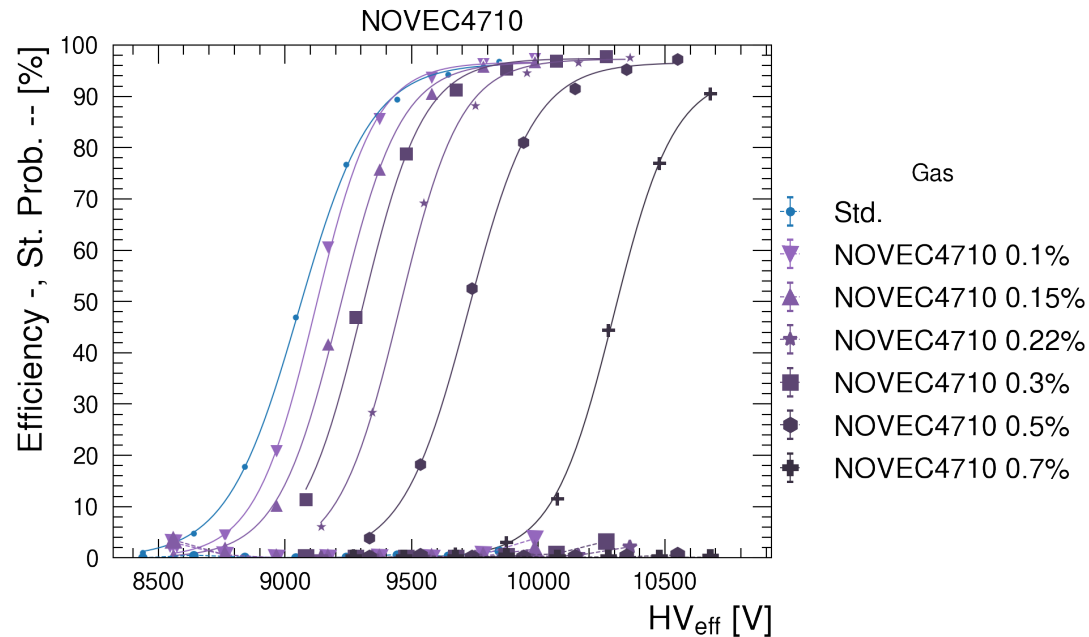


## PRO

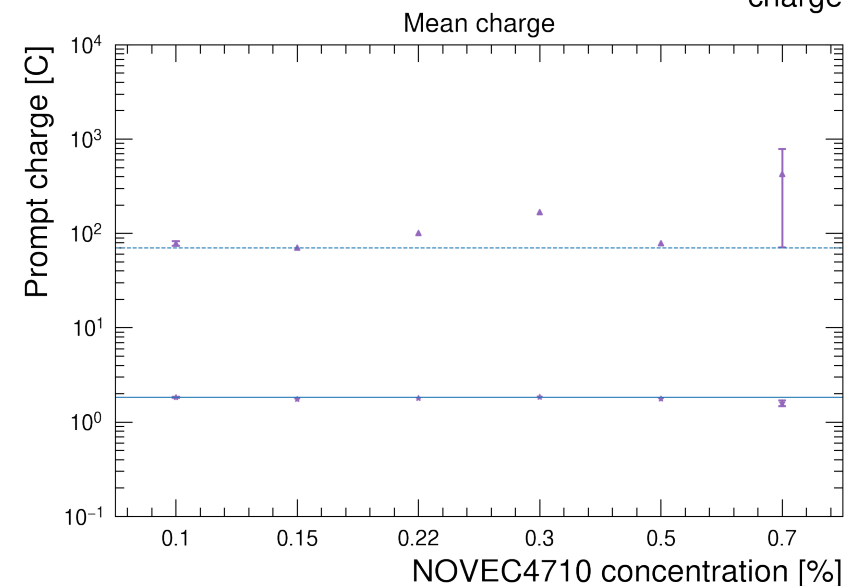
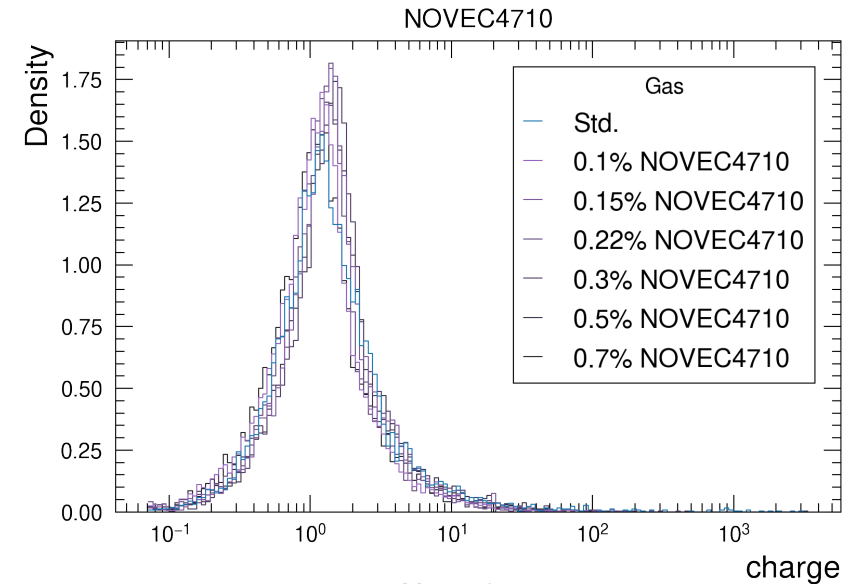
- Good vapour pressure
- Application in industry
- High dielectric strength

## CONS

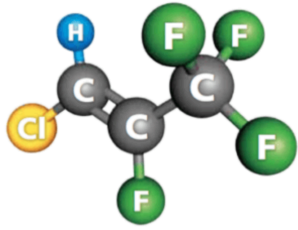
- GWP of 2200
- It may react with H<sub>2</sub>O



- Streamer probability always lower than std gas mixture
  - 0.1% of NOVEC 4710 already enough!
- Avalanche charge and cluster size lower than std gas mixture
- Higher working point for concentrations > 0.1%



# HFO-1224yd

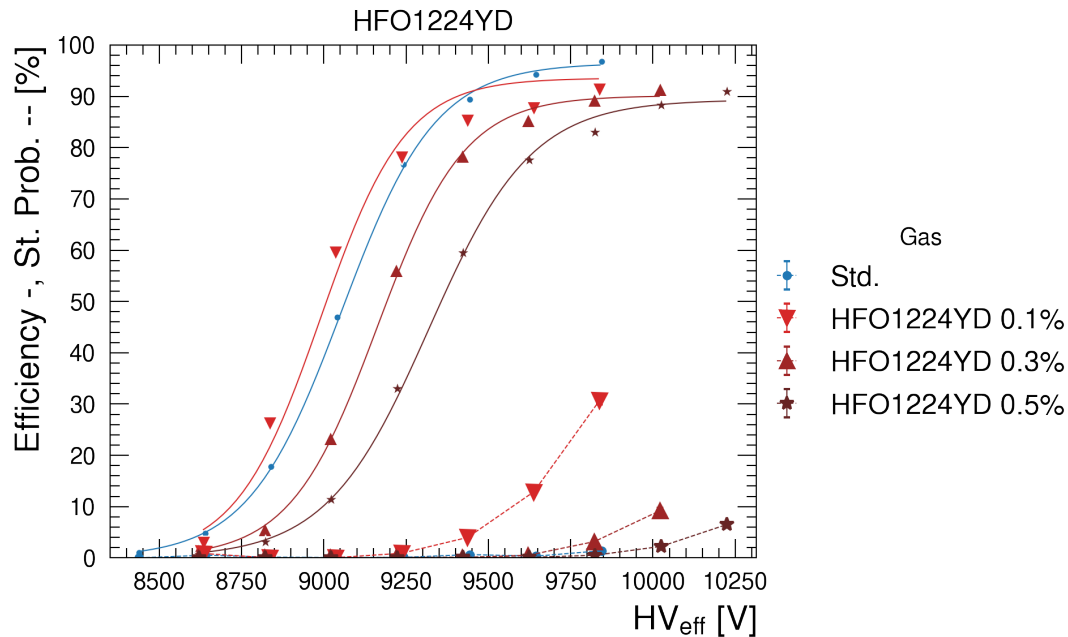


## PRO

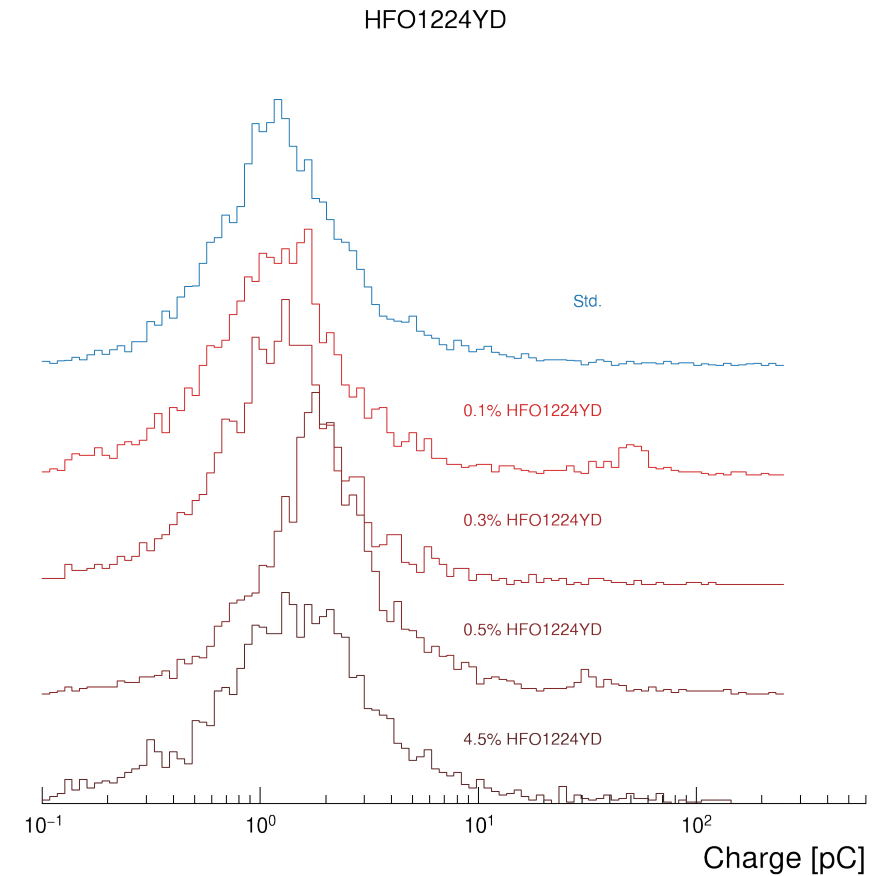
- Very low GWP: 1
- Application in industry

## CONS

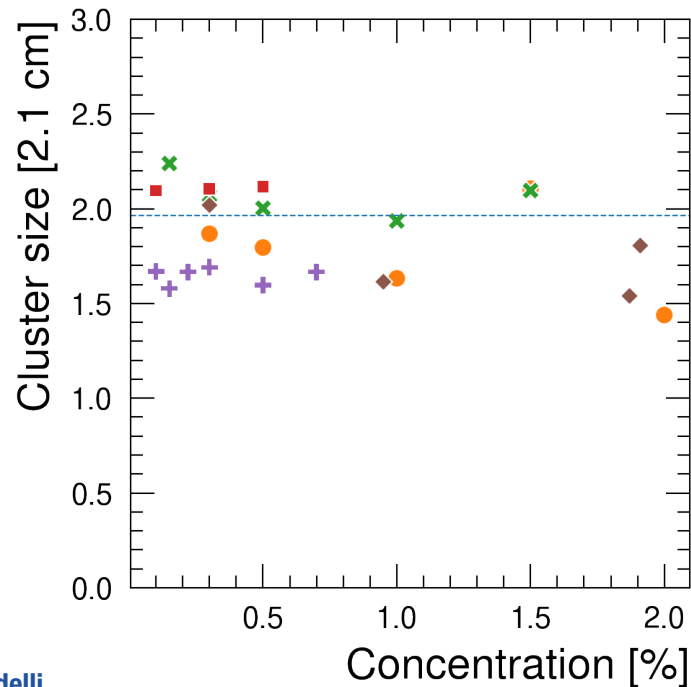
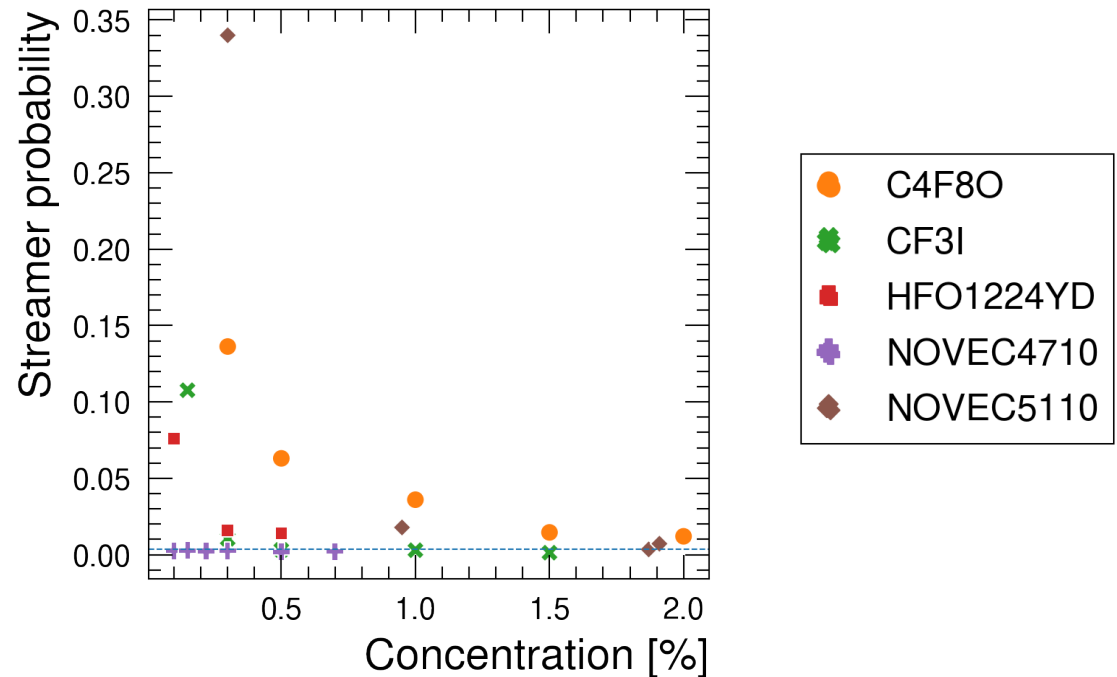
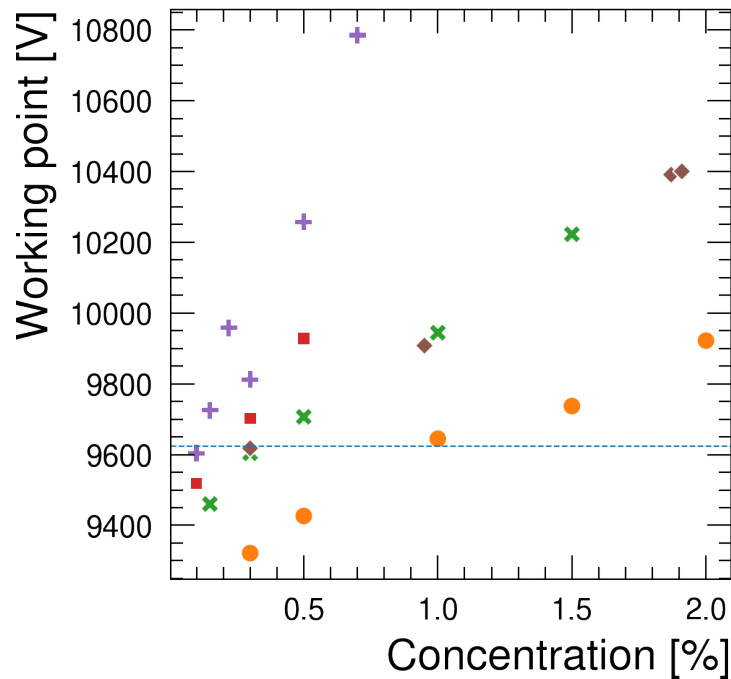
- Presence of Cl



- Lower efficiency than std gas mixture
- Under investigation
- Streamer probability acceptable from 0.5%
- Avalanche charge a bit higher than std gas mixture
- Higher working point for concentrations > 0.3%

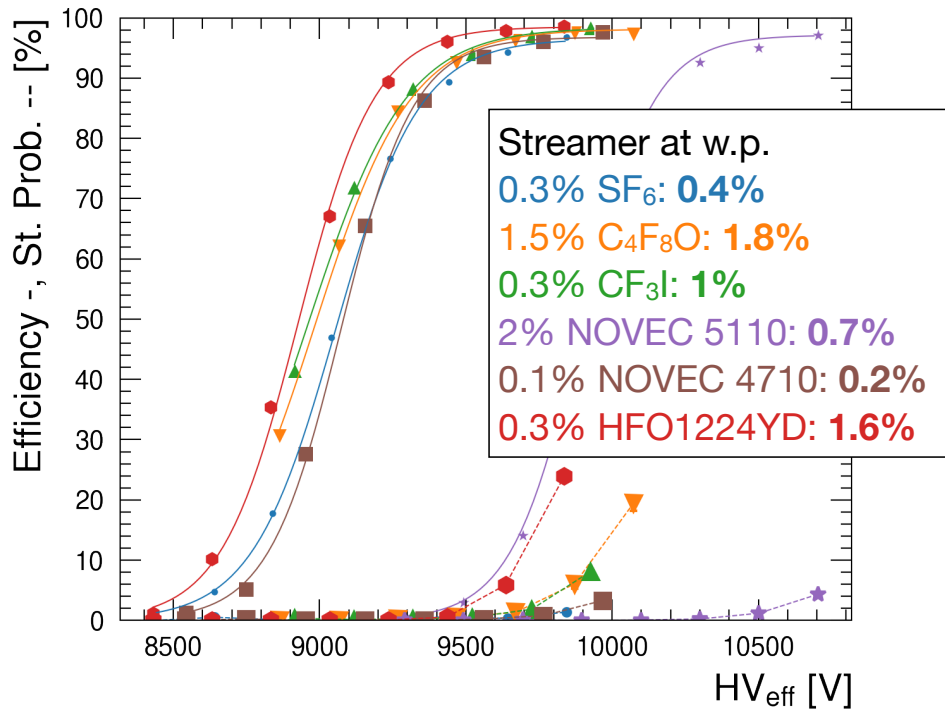


# Comparison of all tested gases



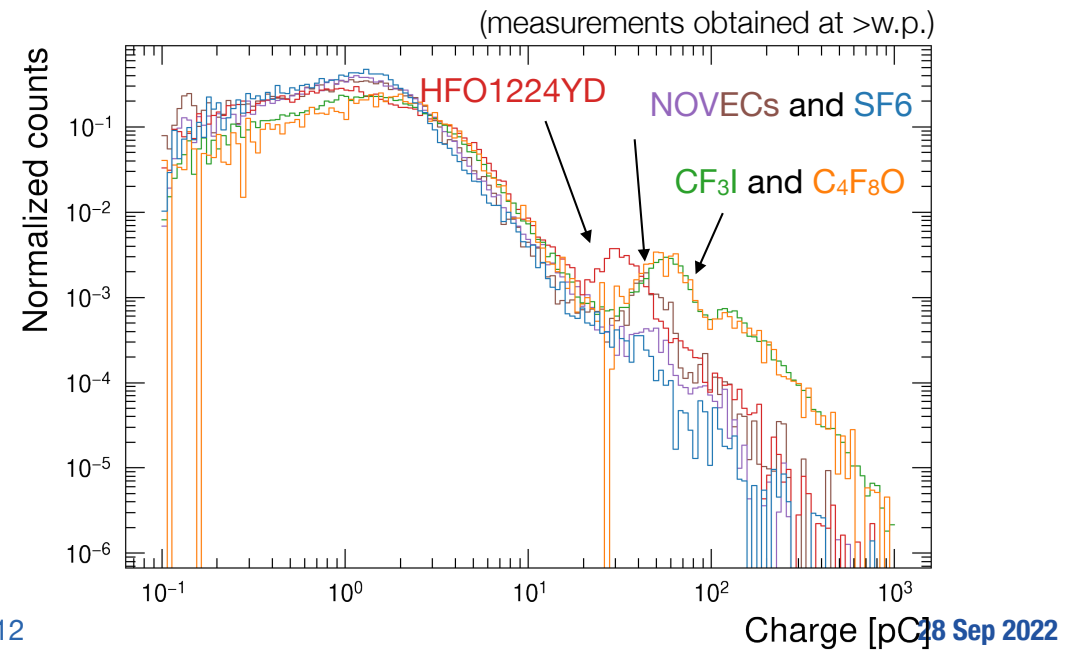
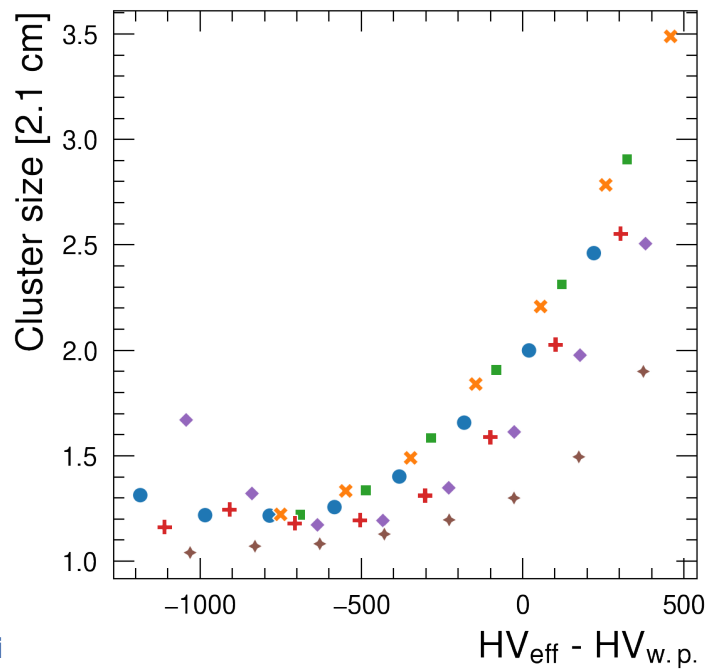
- Working point
  - Increasing with different slopes depending on gas
- Streamer probability
  - Decreasing with increase of concentration except for NOVEC4710 where it is stable
- Charge
  - Avalanche charge very similar for all gases tested at all concentrations
- Cluster size
  - Lower for NOVECs and C<sub>4</sub>F<sub>8</sub>O
- Time resolution
  - Very similar for all gases tested at all concentrations

# Comparison between best concentration



For each SF<sub>6</sub> alternative the best concentration has been selected

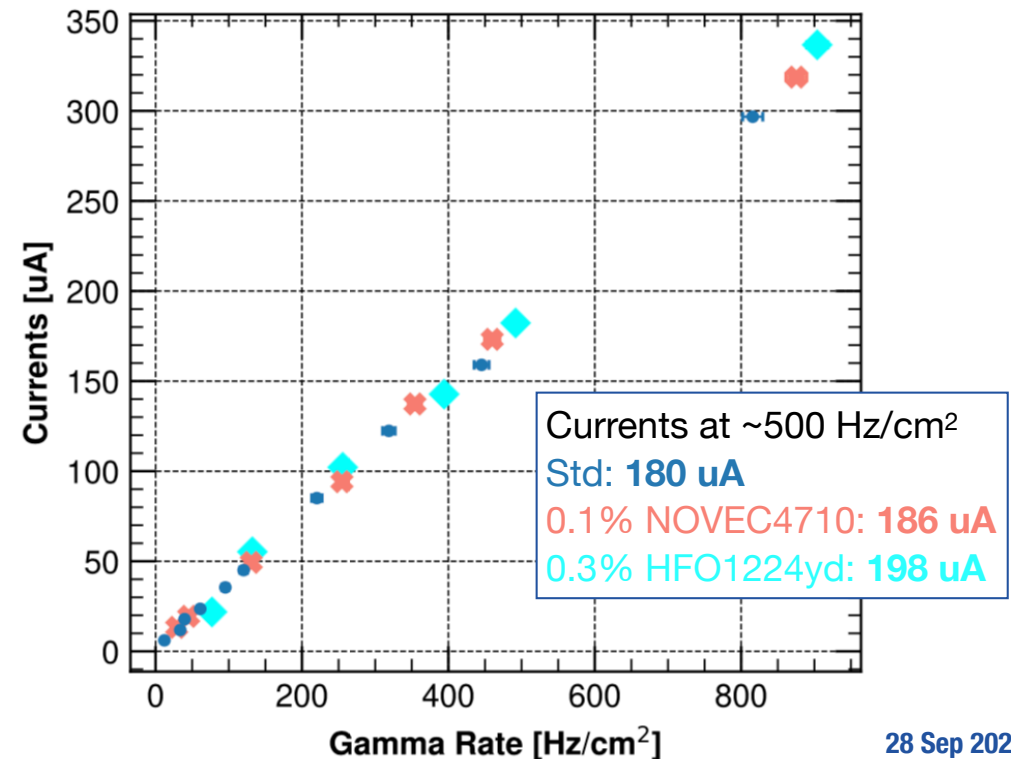
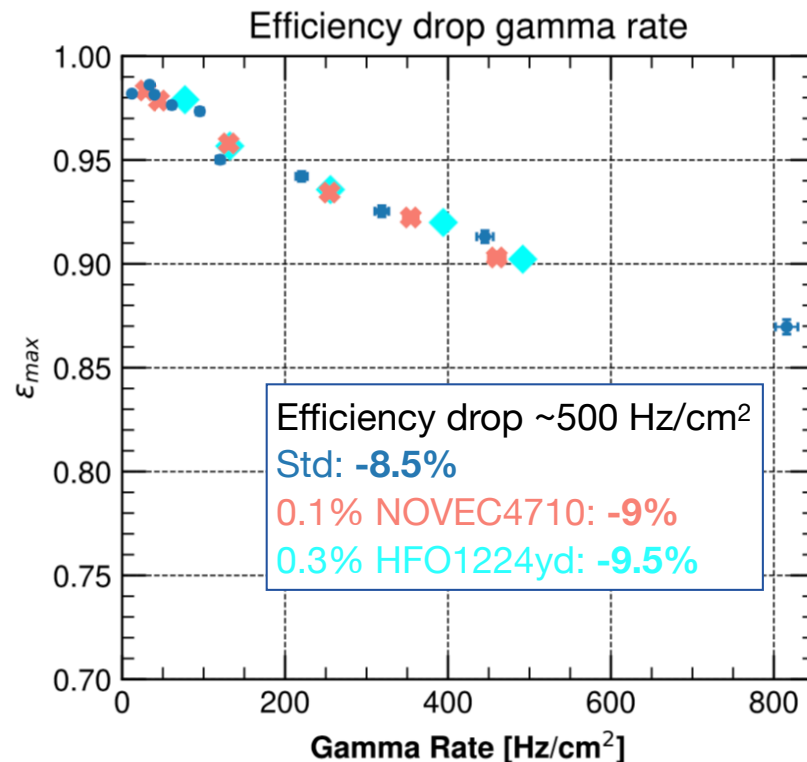
- Very small concentration of NOVEC 4710, Amolea and CF<sub>3</sub>I are enough to obtain satisfactory performance
  - But CF<sub>3</sub>I now discarded
- Working point very similar to std gas mixture except for NOVEC 5110
- Best streamer probabilities obtained with NOVEC gases
  - Excellent dielectric strength
- NOVEC gases also improve the cluster size
- Three different streamer population depending on the gas



# Testbeam with best candidates at GIF++

## RPC tested at high gamma background rate and muon beam

- Selection of 0.1% NOVEC4710 and 0.3% AMOLEA HFO1224yd for testing at GIF++
  - Best compromise between streamer probability, working point and avalanche and streamer charge
  - NOVEC5110 to further test
- Small increase of currents and efficiency drop at high gamma rates
  - A bit worse for HFO1224yd
- Best option seems NOVEC4710 but undergoing studies since it reacts with H<sub>2</sub>O
- HFO1224yd is also very promising
  - Streamer probability still a bit higher



# Not only detector performances....

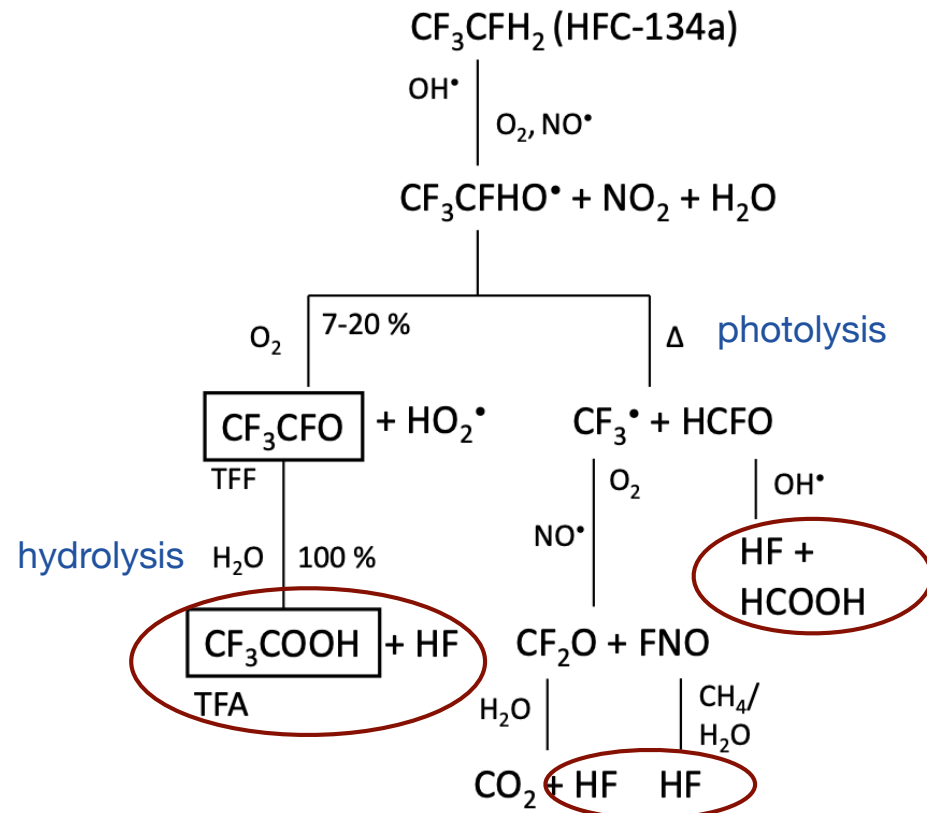
Two factors identify the greenhouse gases and their effects on climate:  
the radiative efficiency and lifetime in the atmosphere

*The lower are the GWP and the lifetime, the easier is the creation of sub-products*

***Do these sub-products have an impact on detector lifetime?***

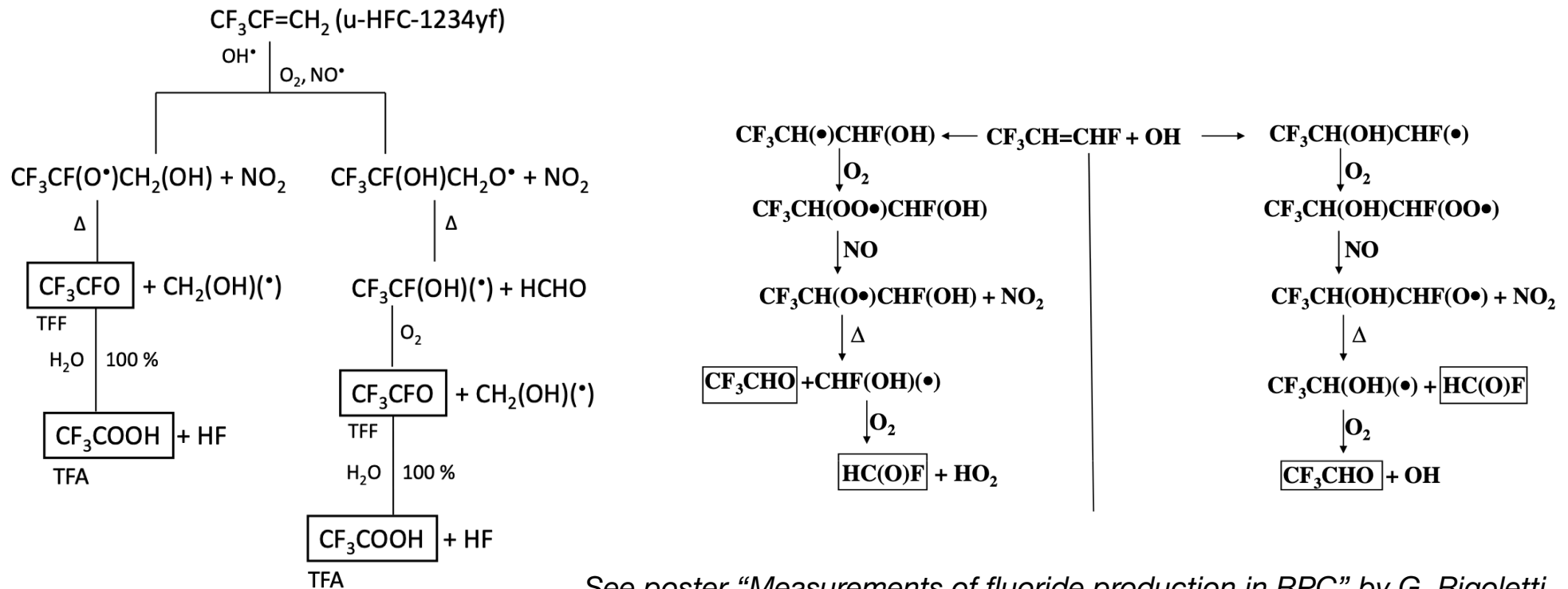
Three factors determine  
the atmospheric lifetime

- Rain out → Water solubility
- Oxidation → Reactivity with OH
- Photolysis → UV absorbance



# HFO degradation

Atmospheric lifetime of HFO1234yf is 11 days  
 Atmospheric lifetime of HFO1234ze is 18 days ↔ Atmospheric lifetime of R134a is 500 years



See poster "Measurements of fluoride production in RPC" by G. Rigoletti

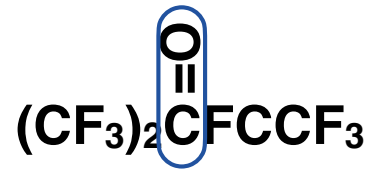
## Hydrofluoric Acid (HF)

- It has already been measured that HFO produces much more HF than R134a in RPC detectors

## Trifluoroacetic acid (TFA)

- HFO1234ze is estimated to break down into TFA at less than 10%, whereas R-1234yf will break down into TFA at 100% (R134a at 21%)
- TFA highly soluble: no formation of insoluble salts
- Phytotoxic

# NOVEC 5110

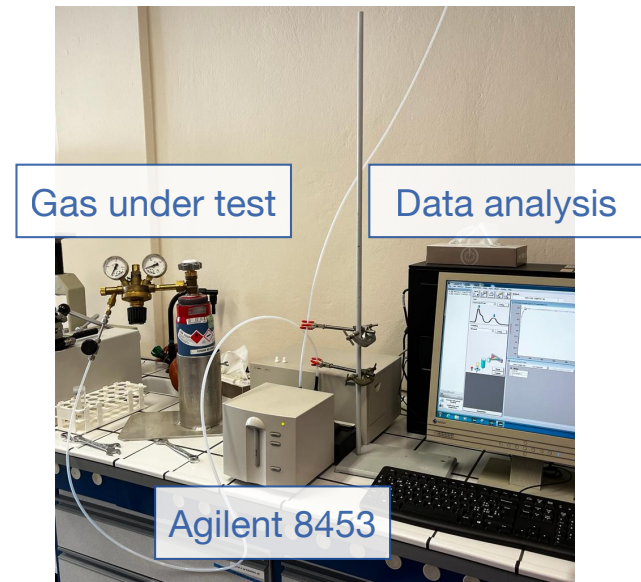


Rain out → water solubility (1ppmw)

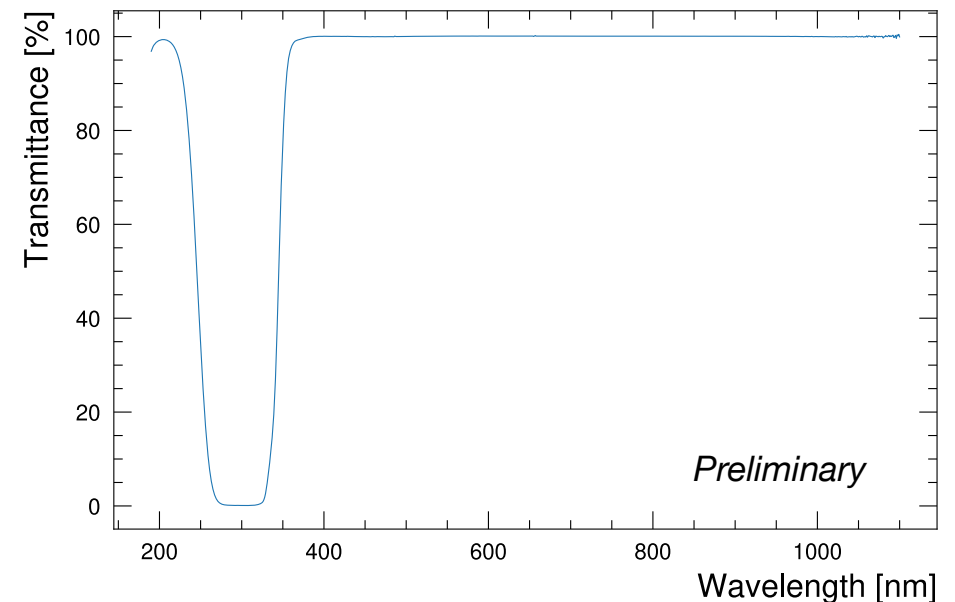
Oxidation → unreactive with OH

**Photolysis** → **strong absorbance in near UV**  
(wavelength > 300 nm)

- Several gases tested: NOVEC 5110, NOVEC 4710, iC<sub>4</sub>H<sub>10</sub>, HFO, N<sub>2</sub>, CO<sub>2</sub>
- Agilent 8453 UV-visible Spectroscopy system
  - Wavelength range: 190-1100 nm
- First measurements in agreement with 3M company
- Works on-going to go to lower wavelengths
  - No commercially available instruments (custom made from companies >500 kCHF)



*Thanks to B. Teissandier for helping in the measurements and providing the instrument*





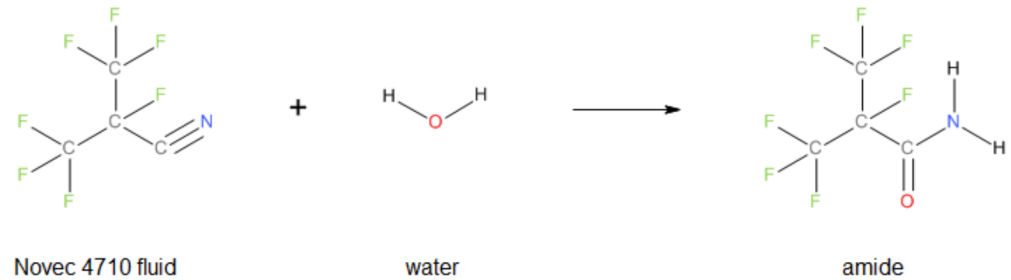
# NOVEC 4710



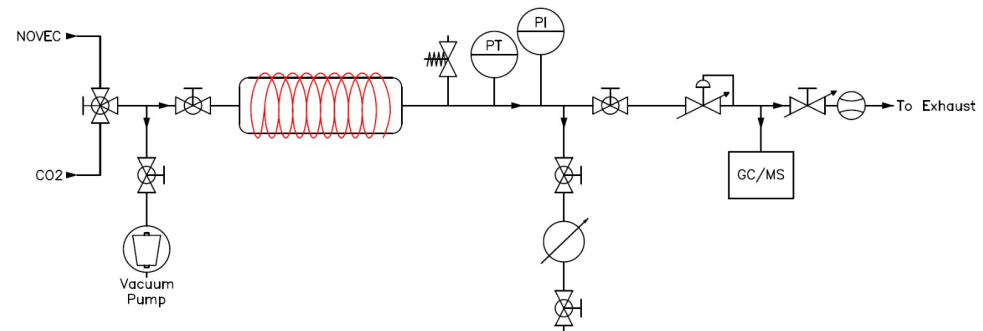
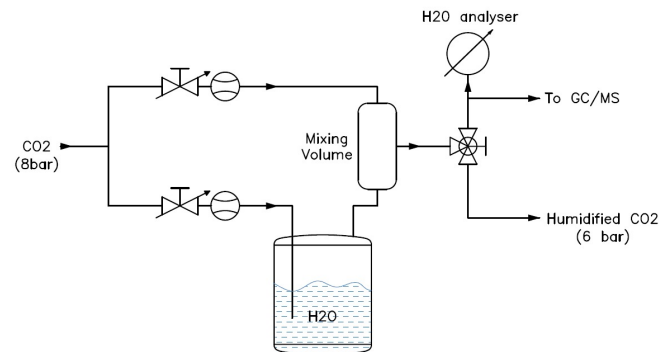
Rain out → Water solubility (272 ppbw)

Oxidation → reactivity with OH radicals

Photolysis → transparent in near UV

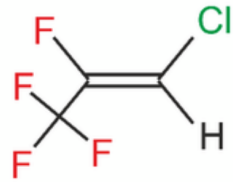


## Set-up for studies of NOVEC 4710 water solubility



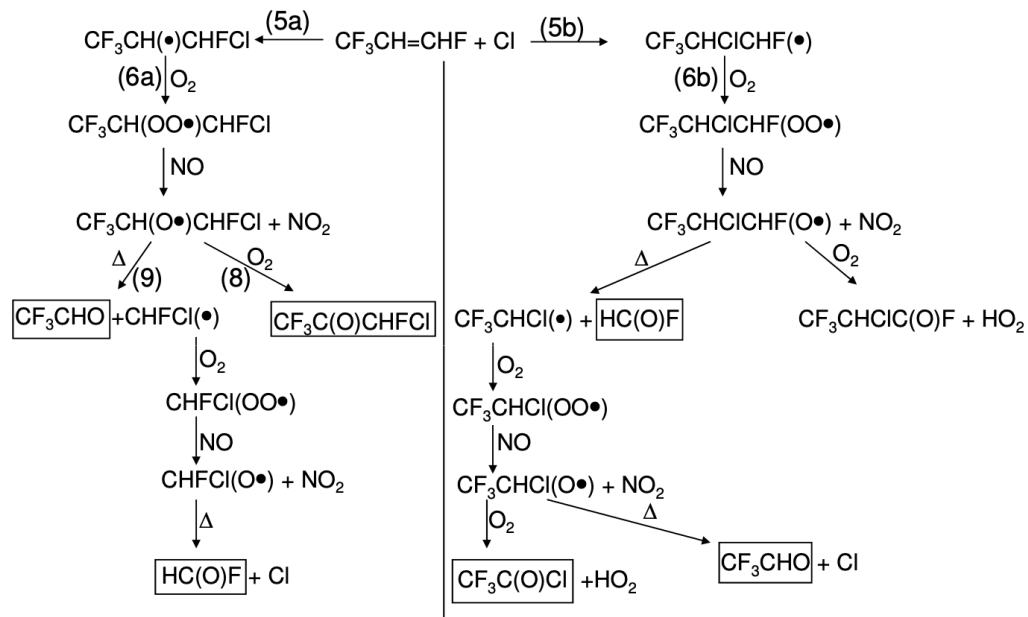
- Bakelite RPCs use 40% relative humidity
  - Already a concern for the creation of HF
- 3M recommend to use NOVEC gases in a dry environment
- Production of an amide from NOVEC 4710 + H<sub>2</sub>O
  - Sub-products in the order of ppb
  - Solid at room T with a melting point of 49°C
  - The amide has appreciable vapor pressure at 60°C, it remains in gas phase at low concentrations
- Tests on-going in laboratory
  - Try to reproduce 3M tests
  - Analysis at the output of an RPC

# HFO-1224yd

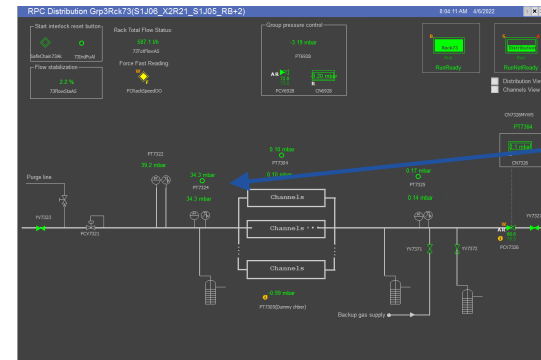


Degradation products:  $\text{CF}_3\text{C}(\text{O})\text{OH}$ ,  $\text{CO}_2$ ,  $\text{HF}$ ,  $\text{HCl}$   
 TFA yield from atmospheric degradation very low

## Reactions of HFO with Cl



## The Cl case of CMS RPC system



Increase of input pressure

presence of white dust at detector input!



Float balls		
Element	Ball #1	Ball #2
C	5.3	6.1
O	4.6	7.9
F	0.0	0.0
Na	0.0	0.1
Al	0.0	0.0
Si	0.7	1.8
Cl	53.0	28.1
Cr	0.0	8.6
Fe	36.5	47.2
Ni	0.0	0.3

# Conclusions

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## Search for alternatives to SF<sub>6</sub>

- It has a very high GWP and even if used in small quantities it accounts for a large fraction of the gas mixture GWP
- Not yet a problem as in industry SF<sub>6</sub> is largely employed for HV insulating plants but new alternatives start to be used

## Detector performance

- Several alternatives were tested in concentrations from 0.1% to 2% in the standard RPC gas mixture
- Very promising candidates with excellent streamer suppression
- Test performed in laboratory and at GIF++

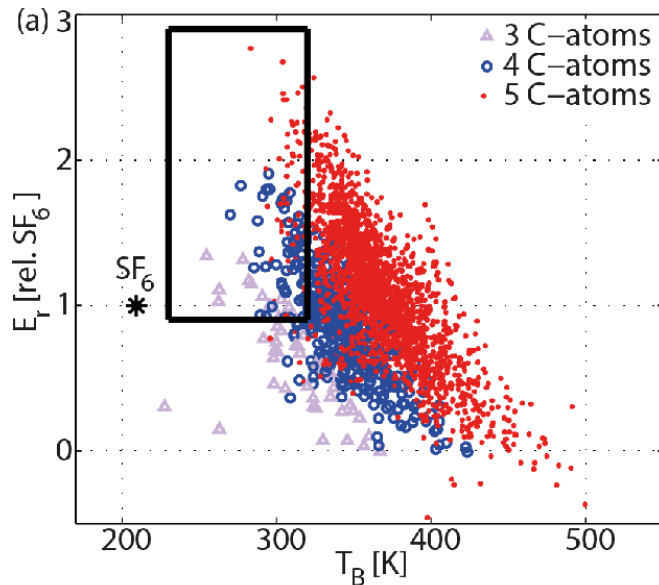
## Properties of new gases

- The new low-GWP gases can easily breaks in well-defined conditions (UV radiation, presence of OH, presence of humidity)
- Studies on-going to characterise these gases
- Detailed studies needed to understand possible effects on RPC long-term operation

# Back-up slides

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# Alternatives to SF<sub>6</sub>: search in HV industry



	Dielectric Strength	GWP	Lifetime (year)	T <sub>b</sub> (°C)
<b>SF<sub>6</sub></b>	1	23900	3200	-63.8
<b>N<sub>2</sub></b>	0.36	0	-	-198
<b>CO<sub>2</sub></b>	0.3	1	300-1000	-78
<b>CF<sub>4</sub></b>	0.4	6300	50000	-128
<b>CF<sub>3</sub>I</b>	1.2	0.4	6 days	-21.8
<b>C<sub>4</sub>F<sub>8</sub>O</b>	1.2	8000	>3000	-
<b>C<sub>4</sub>F<sub>7</sub>N (Novec 4710)</b>	2	1490	30	-4.7
<b>C<sub>5</sub>F<sub>10</sub>O (Novec 5110)</b>	1.5 - 2	1	15 days	27
<b>C<sub>3</sub>F<sub>4</sub>HCl (HFO1224yd)</b>	-	0.88	20 days	15

group	<E <sub>r</sub> > [rel. SF <sub>6</sub> ]	<T <sub>B</sub> > [K]	<Z>	n
C <sub>3</sub> -Ketones	0.39	319	2.00	17
C <sub>3</sub> -Aldehydes	0.56	320	1.89	18
C <sub>3</sub> -Acyl Fluorides	0.98	293	3.15	13
C <sub>4</sub> -Ketones	0.69	352	2.58	138
C <sub>4</sub> -Aldehydes	0.77	345	2.39	117
C <sub>4</sub> -Acyl Fluorides	1.14	326	3.36	110
C <sub>5</sub> -Ketones	0.94	375	3.30	923
C <sub>5</sub> -Aldehydes	1.00	370	2.91	685
C <sub>5</sub> -Acyl Fluorides	1.35	356	3.85	590
SF <sub>6</sub>	1	209 [18]	6	1

Nr	SMILES	E <sub>r</sub>	T <sub>B</sub>	T <sub>B</sub> <sup>L</sup>
<b>C<sub>3</sub>-compounds</b>				
(1)	FC(=O)C(C(F)F)F	1.34	255	280
(2)	O=C(C(F)F)C(F)F	1.03	262	280
(3)	FC(C(=O)F)F	1.11	263	288
(4)	FC(=O)C(F)F	1.31	278	302
<b>C<sub>4</sub>-compounds</b>				
(5)	FC(=O)C(C(F)F)C(F)F	1.63	270	317
(6)	FC(C(C(F)F)C(=O)F)F	1.82	277	
(7)	FCC(C(F)F)C(=O)F	1.91	295	
<b>C<sub>5</sub>-compounds</b>				
(8)	FC(=O)C(C(F)F)C(C(F)F)C(F)F	2.77	283	303
(9)	O=C(C(C(F)F)C(F)F)C(F)F	1.93	293	310
(10)	FC(C(C(C(F)F)F)C(=O)F)F	2.28	296	
(11)	O=C(C(C(C(F)F)F)F)C(F)F	2.01	302	322
(12)	FC(=O)C(C(C(F)F)C(F)F)F	2.67	304	

M. Rabie, C. Franck, predicting the electric strength of proposed sf6 replacement gases by means of density functional theory

# By-products under Arcing Conditions

Data provided by 3M Company

## SF<sub>6</sub>

Compound	CAS no.	Molecular formula
Bispentafluorosulfur oxide	42310-84-9	S <sub>2</sub> OF <sub>10</sub>
Carbon tetrafluoride	75-73-0	CF <sub>4</sub>
Carbonyl fluoride	353-50-4	COF <sub>2</sub>
Fluorine	7782-41-4	F <sub>2</sub>
Hydrogen fluoride	7664-39-3	HF
Hydrogen sulfide	7783-06-4	H <sub>2</sub> S
Nitrogen trifluoride	7783-54-2	NF <sub>3</sub>
Oxygen difluoride	7783-41-7	F <sub>2</sub> O
Silicon tetrafluoride	7783-61-1	SiF <sub>4</sub>
Sulfur dioxide	7446-09-5	SO <sub>2</sub>
Sulfur fluoramide fluorine	81625-84-5	(SF <sub>5</sub> ) <sub>2</sub> NF
Sulfur fluoride fluorosulfate	81439-35-2	S <sub>2</sub> O <sub>3</sub> F <sub>6</sub>
Sulfur fluoride peroxide	12395-41-4	S <sub>2</sub> O <sub>2</sub> F <sub>10</sub>
Sulfur pentafluoride	5714-22-7	S <sub>2</sub> F <sub>10</sub>
Sulfur tetrafluoride	7783-60-0	SF <sub>4</sub>
Sulfur tetrafluoride oxide	13709-54-1	SOF <sub>4</sub>
Sulfuryl fluoride	2699-79-8	SO <sub>2</sub> F <sub>2</sub>
Thionyl fluoride	7783-42-8	SOF <sub>2</sub>
Trifluoromethyl sulfur pentafluoride	373-80-8	SF <sub>5</sub> CF <sub>3</sub>

## 3M NOVEC 4710

Compound	Concentration (ppm)
CO <sub>2</sub>	935018
(CF <sub>3</sub> ) <sub>2</sub> CFCN (Novec 4710)	40600
CO	24000
CF <sub>2</sub> =CFCN	130
CNCN	65
C <sub>2</sub> F <sub>5</sub> CN	60
CF <sub>3</sub> CN	58
(CH <sub>3</sub> ) <sub>2</sub> SiF <sub>2</sub>	52
COF <sub>2</sub>	14
(CF <sub>3</sub> ) <sub>2</sub> CHCN	1.9
(CF <sub>3</sub> ) <sub>2</sub> C=CF <sub>2</sub>	1.3

Calculated LC<sub>50</sub> value for arced-gas mixture = 39000 ppmv

## 3M NOVEC 5110

Compound	Concentration (ppm)
CO <sub>2</sub>	61000
CO	6200
HF	690
CF <sub>4</sub>	100
(CF <sub>3</sub> ) <sub>2</sub> CFC(O)CF <sub>3</sub> (Novec 5110)	39
C <sub>3</sub> F <sub>8</sub>	19
C <sub>3</sub> F <sub>7</sub> H	<15
C <sub>3</sub> F <sub>6</sub>	14
C <sub>2</sub> F <sub>6</sub>	<10
C <sub>4</sub> F <sub>8</sub> O	5
C <sub>4</sub> F <sub>10</sub>	2

Calculated LC<sub>50</sub> value for arced-gas mixture = 122000 ppmv