



dRICH Office

September 10th, 2025

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Studies of C_2F_6 - CO_2 separation via membranes

Studies of C_2F_6 scintillation and chemical properties



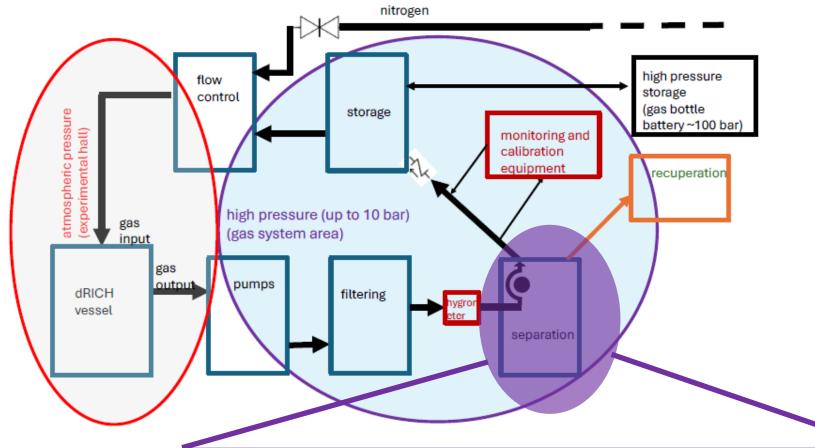


Studies of C_2F_6 - CO_2 separation via membranes



Block diagram of the dRICH gas system



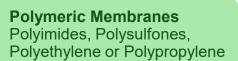


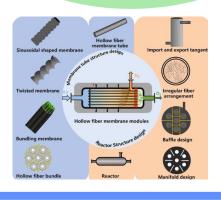
Studies for a possible separation system



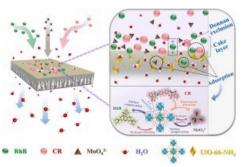
Selective permeability



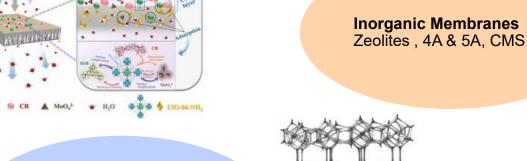


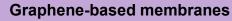


Nanocomposite Membranes

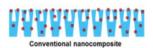


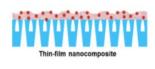
Mixed Matrix Membrane Composite Membranes Polymer & inorganic

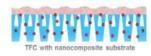




- 1. Monolayer Graphene Membranes
- 2. Graphene Oxide (GO)
- 3. Graphene-Based Composite Membranes
- 4. Graphene Nanopore Membranes











UBE membranes





Module Structure - CO₂ Separator

History of UBE's Membrane Business

Jointed MITI's C1 Project (National Project)

Field Tests at Ammonia Plant for H2 Recovery

Started R&D Work

First Membrane for H₂

Organized Membrane Dept.

3rd Hollow Fiber Line in Ube.

4th Hollow Fiber Line in Ube.

Supply First H₂ Recovery Unit

First Membranes for CO₂ & Dryer

First Membrane for Dehydration

First Membrane for N₂/O₂ Separation

Improving Membranes and Modules

2nd Hollow Fiber Line in Ube City facility Module Assembly Line in Sakai.

Expansion in the Module Assembly facility in Sakai.

CS-001E_REV.K_250717

· 1978

· 1981 · 1983

· 1985

· 1986

· 1989

· 1989

· 1992

2007

2008

2025



Polyimide Hollow Fiber Membranes



200 to 500 µm in outer diameter of	Skin lay	Porous layer		
fiber				
	`\			

BPDA-based polyimide

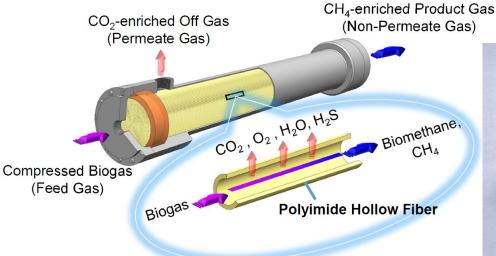
Permeation rate to gases in polyimide membrane

Benefits of BPDA-based polyimide as material for hollow fiber membrane

H₂O High permeation CO2 H₂S solubility and 0, CO Ar **Equilibrium** N₂ CH₄ C₂H₅OH C₂H₆

dependent on molecule size + Kinetic Separ. Low C₃+ Hydrocarbons

- 1) Good balance for permeability and selectivity
- 2) Good mechanical property
- 3) Excellent heat resistance
- 4) Good chemical resistance
- 5) Excellent lifetime
- 6) Easy to make fiber and thin skin layer







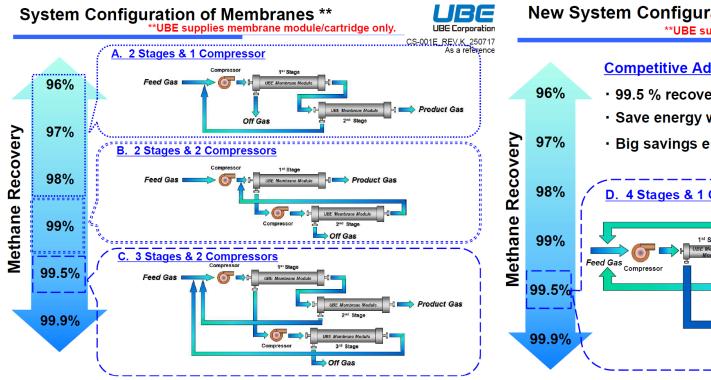
Product Specification and Features

Hollow Fiber	Polyimide Resin	
Housing	Aluminum	
Operating Pressure	Housing type - Max. 1.4 MPaG Cartridge type - Max. 2.4 MPaG	
Operation Temperature	up to 60°C	
H₂S resistance up to 3 vol %		



Biogas applications





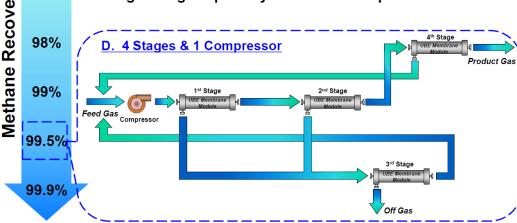


**UBE supplies membrane module/cartridge only.



Competitive Advantages

- 99.5 % recovery & 99.0 % purity CH₄, all in one go.
- Save energy with just one compressor.
- Big savings especially for small scale plants.





Feed Gas Flow Rate : 600 Nm³/h (at 0 °C, 1013 mbara)

Feed Gas Composition : CO₂ 40 %, CH₄ 60 % Operating Temperature: 25 °C (77 °F)*

Product Gas Purity : CO₂ < 1 % *Maximum allowable temperature is 60 °C (140 °F).



UBE membranes



UBE CO₂ Separator Lineup



CS-001E_REV.K_250717 As a reference

		Model				Weight	Dimensions			
_		High Permeability Membrane	High Selectivity Membrane	Classification	Operating Conditions	(kg)	(mm)			
	ng type	CO-0302NFS (1)	CO-0302SES (1)	Art. 4 par. 3	60 °C 24 barg	1.7	Ф L 380mm			
		CO-C07F	CO-C07FS	Art. 4 par. 3	60 °C 16 barg	4.2	P R 800mm			
	with housi	CO-510F	CO-510FS	Category I (CE Mark)	60 °C 16 barg	16	θ L 1,080mm			
		CO-710F CO-710FS Category I 10.4 barg(60 °C 10.4 barg(CO-710F) 9.6 barg(CO-710FS)	33	D 1,080mm				
	without housing type (2) (cartridge type)	CC-1610NFH	CC-1610SEH	N/A (w/o housing)	60 °C 24 barg	19	Φ L 1,030mm Φ 1,75m			
		CO-810FC	CO-810FSC	N/A (w/o housing)	60 °C 24 barg	23	Ф 249mm Ф 249mm			
		CC-2015NFH	-	N/A (w/o housing)	60 °C 24 barg	30	Ф 539mm Ф 239mm Ф 239mm			

(1) Mainly for testing purpose

7

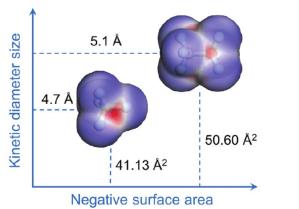
⁽²⁾ Customer needs to procure the housing. UBE supports a design of the housing.



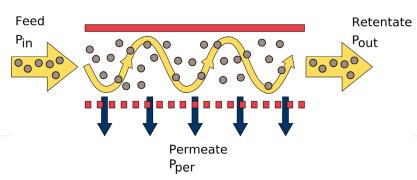
C_2F_6 - CO_2 permeability separation







use of membranes optimized for CO₂

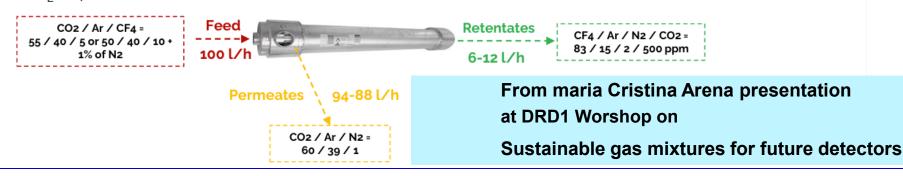




EP-DT Detector Technologies

CMS CSC recovery system for CF4

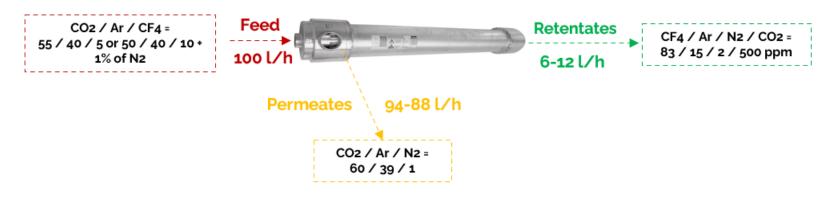
Phase 1 → CO₂ separation





Tests with C₂F₆





Example from Cristina Arena measurement using an UBE membrane also available for our tests:

Composition input flow I/h				Compositon retentates flow I/h					
	,	, i							
CF4	CO2	Ar	02	N2	CF4	CO2	Ar	02	N2
21	214	157	0.6	7.920	15	0.06	1	0.000	0.1

We plan a first test in October-November at CERN with C_2F_6 (and then purchasing new membranes for ePIC)





Studies of C_2F_6 scintillation and chemical properties



Collaboration with Belgrade



Letter of Agreement

for the study of C₂F₆ and C₄F₁₀ molecular properties

BETWEEN

the "Trieste Section of INFN"

AND

the "Institute of General and Physical Chemistry, Belgrade University",

1. Scope of the agreement

On request of the Trieste team participating in the ePIC experiment at BNL (USA), the Trieste Section of INFN and the Institute of General and Physical Chemistry, Belgrade University, will perform a joint investigation of the properties of hexafluoro-ethane and perfluoro-butane molecules to determine their:

- excitation states, light emission and absorption probabilities, in particular the scintillation probability in the visible range,
- kinetic diameter of the molecules, and other chemical properties relevant for the selective permeability of membranes,
- the refractive index for the wavelength range between 200 nm and 900 nm,
- the properties of gas mixtures of hexafluoroethane and nitrogen.
- the properties of gas mixtures of hexafluoroethane and carbon dioxide.



Molecule chemical simulation study



Jelena Jovanovic and Nebojsa Begovic have performed dedicated calculations for C_2F_6

Photon interaction with C₂F₆ calculate by XCOM program (National Institute of Standards and Technology)

J.J. & N.B. IOFH (GIPC)

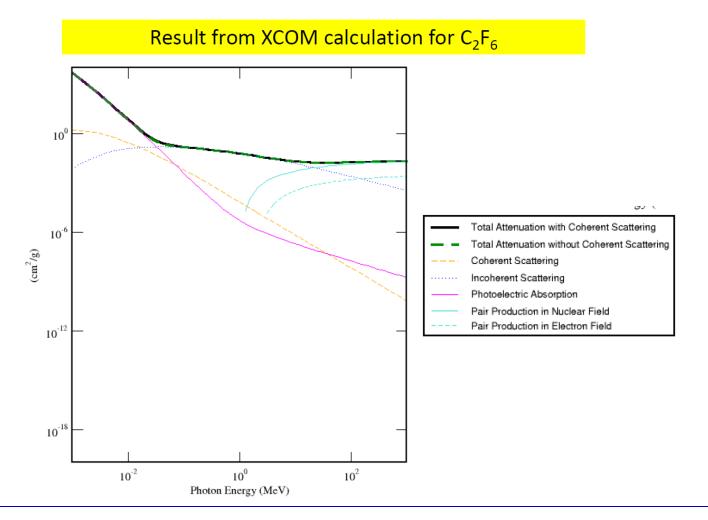
A computer program and data base can be used to calculate, on a personal computer, photon cross sections for scattering, photoelectric absorption and pair production, as well as total attenuation coefficients, in any element, compound, or mixture, at energies from 1 keV to 100 GeV.



Cross sections: photons



Cross-section for photons on C_2F_6



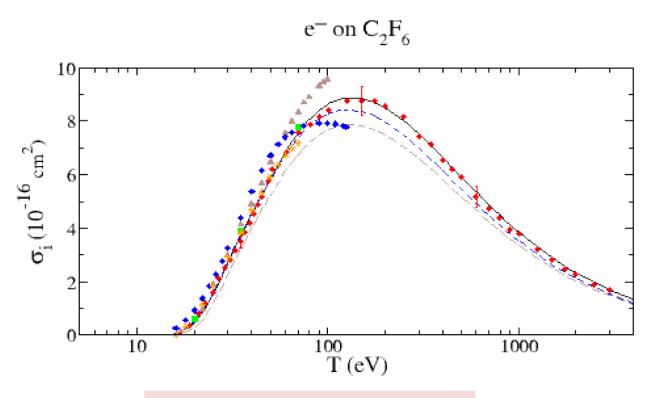


Cross sections: electrons



Cross-section for low-energy electrons on C2F6

Data from NIST data base for cross section for ionization end excitation



* Black curve could be calculated by **QC**

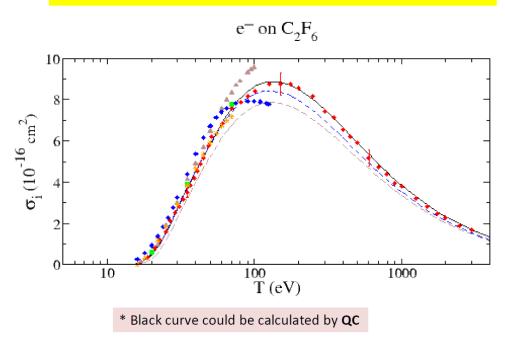


Cross sections: electrons

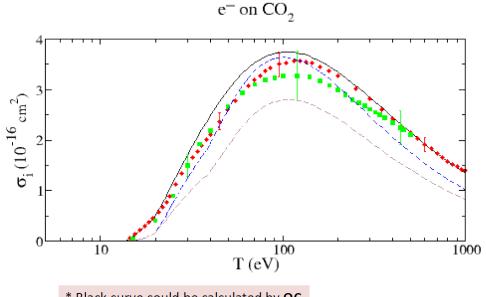


Cross-section for low-energy electrons on C_2F_6 and CO_2

Data from NIST data base for cross section for ionization end excitation



Comparison of experimental (points) and calculated (curve) values



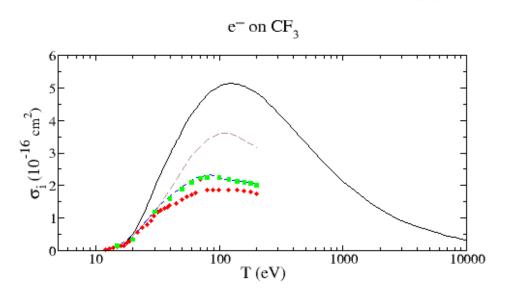
* Black curve could be calculated by QC

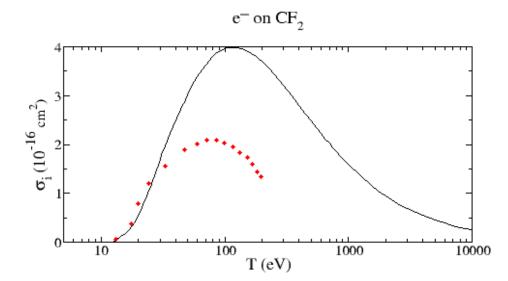


Cross sections: electrons on fragments



Cross-section for low-energy electrons on CF3 and CF2







C_2F_6 excitation and ionization



Evaluation of C2F6 degradation applying QC calculations

NB & JJ; IOFH

For all calculations used *ORCA* package, with *aug-cc-pvdz* basis set and perform calculation at *B2PLYP* double-hybrid theoretical level (combination of *DFT* and *MP2* methods)

We recheck all calculations presented in previous presentation: Three main processes:

IP ionization

EA electron abstraction

EXC excitation



C₂F₆ excitation and ionization



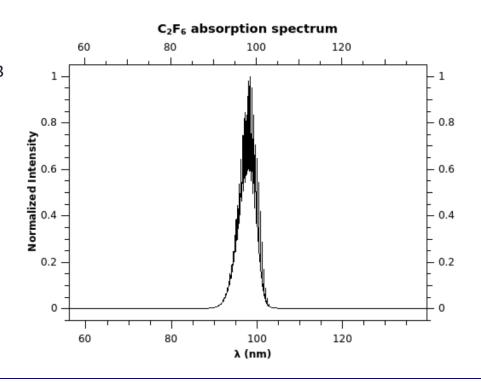
Reaction schema for C₂F₆ molecule degradation

$$[C_2F_6] \rightarrow IP \rightarrow CF_3^{1/2} + CF_3^{1/2} => CF_3^+ + CF_3^-$$

$$[C_2F_6] \rightarrow EA \rightarrow C_2F_5 + F^-$$

$$[C_2F_6] \rightarrow EXC \rightarrow CF_3 + CF_3$$

[C₂F₆] absorption spectra





C₂F₅ excitation and emission



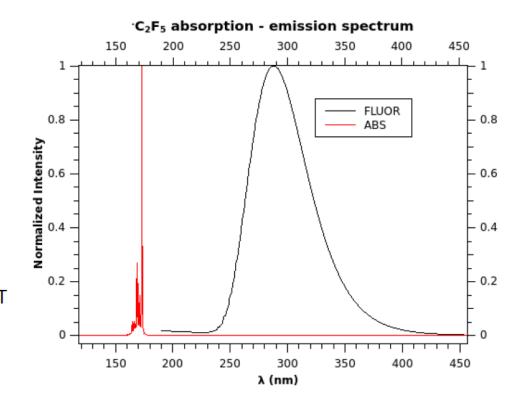
Reaction schema for C₂F₅ molecule degradation

$$[\cdot C_2F_5] \rightarrow IP \rightarrow [C_2F_5]^+$$

$$[\cdot C_2F_5] \rightarrow EA \rightarrow [C_2F_5]$$

$$[\cdot C_2F_5] \rightarrow EXC \rightarrow [\cdot C_2F_5]^*$$

The calculated fluorescence rate constant is 3.926436e+07 s-1 with 24.73% from FC and 75.27% from HT



Tau=2.55E-08 s



CF₃⁺ excitation and emission

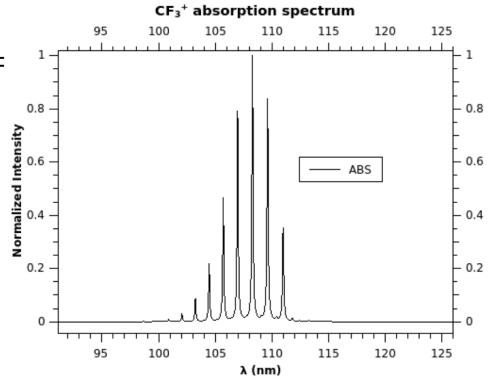


Reaction schema for CF₃⁺ molecule degradation

$$[CF_3^+] \rightarrow IP \rightarrow [CF_3]^{2+}$$

$$[CF_3^+] \rightarrow EA \rightarrow [CF_3]$$

$$[CF_3^+] \rightarrow EXC \rightarrow CF_2^+ + F$$

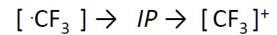




· CF₃ excitation and emission

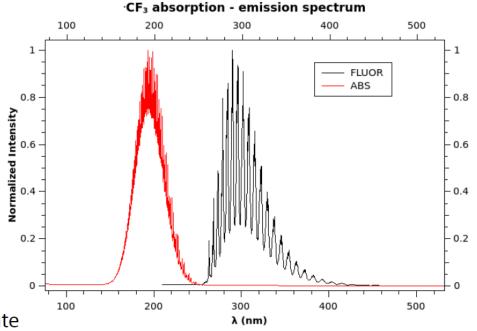


Reaction schema for CF₃ molecule degradation



$$[\cdot CF_3] \rightarrow EA \rightarrow [CF_3]$$

$$[\ \cdot \mathsf{CF}_3\] \to \mathit{EXC} \to [\ \cdot \mathsf{CF}_3\]^*$$



The calculated fluorescence rate constant is 1.097213e+07 s-1 with 66.77% from FC and 33.23% from HT

Tau= 9.11E-08 s



C₂F₅⁺ excitation



Reaction schema for [C₂F₅]⁺ molecule degradation

$$[C_{2}F_{5}^{+}] \rightarrow IP \rightarrow [C_{2}F_{5}]^{2+} \rightarrow F + C_{2}F_{4}^{2+}$$

$$[C_{2}F_{5}^{+}] \rightarrow EA \rightarrow [C_{2}F_{5}]$$

$$[C_{2}F_{5}^{+}] \rightarrow EXC \rightarrow CF_{2} + CF_{3}^{+}$$

100

150

λ (nm)

200



C_2F_5 excitation and emission



Reaction schema for $[C_2F_5]$ molecule degradation

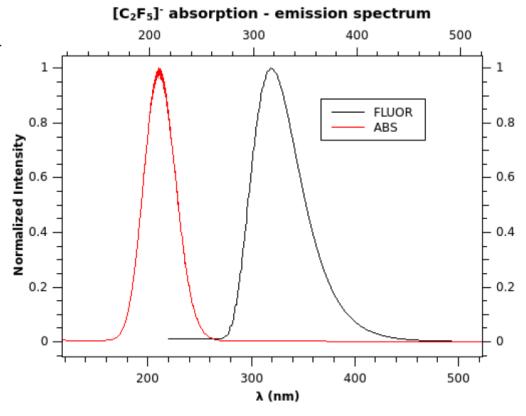
$$[C_2F_5] \rightarrow IP \rightarrow [C_2F_5]$$

$$[C_2F_5^-] \rightarrow EA \rightarrow F + C_2F_4^{2-}$$

$$[C_2F_5^-] \rightarrow EXC \rightarrow [C_2F_5^-]^*$$

The calculated fluorescence rate constant is 3.064903e+07 s⁻¹ with 98.10% from FC and 1.90% from HT

Tau = 3.26E-08 s





·CF2⁺ excitation and emission



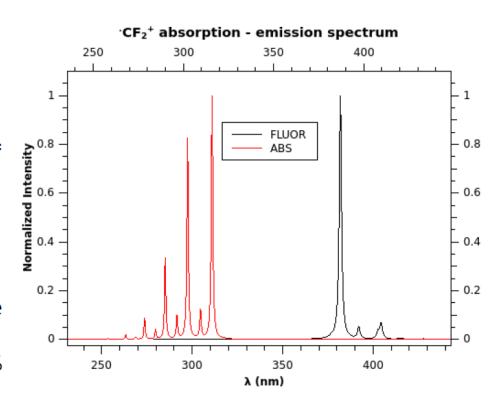
Reaction schema for [·CF₂⁺] molecule degradation

$$[\,\cdot\mathsf{CF_2}^{\,+}\,] \to \ \mathit{IP} \to [\,\mathsf{CF_2}\,]^{2+}$$

$$[\cdot CF_2^+] \rightarrow EA \rightarrow [CF_2]$$

$$[\ \cdot \mathsf{CF_2}^+\] \to \mathit{EXC} \to [\ \cdot \mathsf{CF_2}^+\]^*$$

The calculated fluorescence rate constant is 4.043094e+06 s-1 with 98.65% from FC and 1.35% from HT



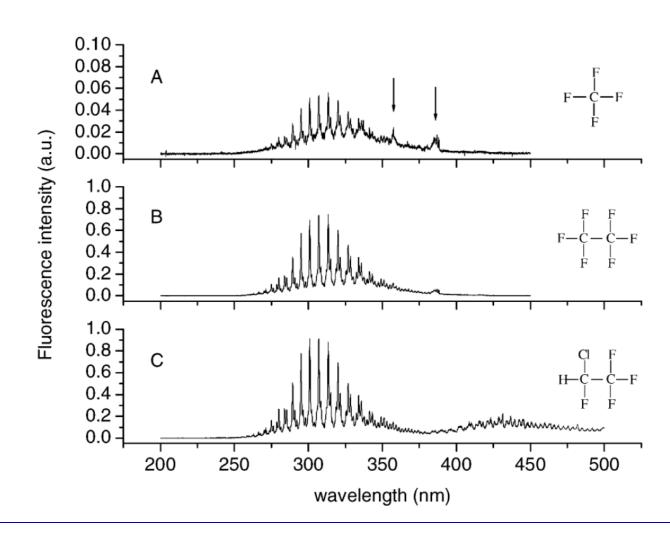
Tau = 2.47E-07 s



Very large fluorescence! (10×CF₄)



Experimentally obtained spectra





LHCb quenching of CF₄ scintillation



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journal homepage: www.elsevier.com/locate/nima

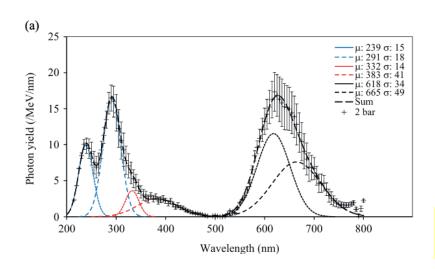


Quenching the scintillation in CF₄ Cherenkov gas radiator

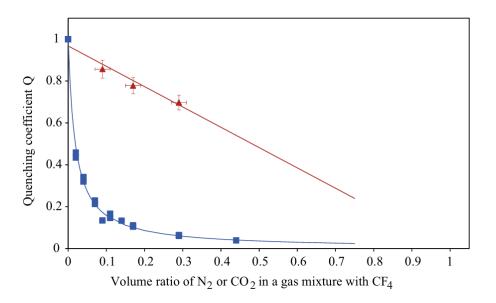
T. Blake ^f, C. D'Ambrosio ^b, S. Easo ^{g,b}, S. Eisenhardt ^h, C. Fitzpatrick ^c, R. Forty ^b, C. Frei ^b, V. Gibson ^e, T. Gys ^b, N. Harnew ^j, P. Hunt ^j, C.R. Jones ^e, R.W. Lambert ^d, C. Matteuzzi ^a, F. Muheim ^h, A. Papanestis ^{g,b,*}, D.L. Perego ^{a,k,1}, D. Piedigrossi ^b, R. Plackett ⁱ, A. Powell ^j, S. Topp-Joergensen ^j, O. Ullaland ^{b,k}, D. Websdale ⁱ, S.A. Wotton ^e, K. Wyllie ^b



similar results [5]. The estimated total scintillation photon yield per MeV of energy deposited in CF_4 was about 1200 photons/MeV $\times 4\pi$ [4]. About 75% of these photons were estimated to be emitted at wavelengths in the range 220–600 nm. The scintillation in C_4F_{10} is, in comparison to CF_4 , only a minor effect [5]. Our



... in 2010 the charged particle rate was higher than expected and the background became unsustainable for data taking ...



LHCb decided to add few% of CO2 to CF4



Conclusions



Membranes for C_2F_6 - CO_2 separation expected to be very effective

Test at CERN with UBE membrane on Oct-Nov. foreseen

Studies of C_2F_6 scintillation and chemical properties ongoing

Scintillation expected to be a potentially serious problem!

Scintillation measurement to be organized.