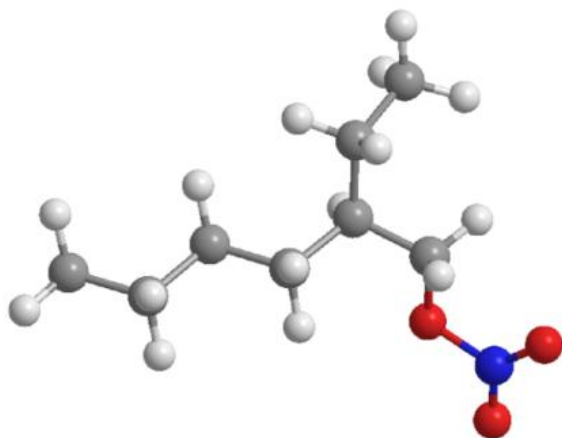


# Vibrational spectroscopy of a cetane improver for biodiesel

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<https://www.veryone.com/fr/cetane-improver-fr/>

Biofuels Comprehensive Study by Type (Wood, Biogas, Biodiesel, Ethanol, Others), Sources (Animal Fat, Sugarcane, Rice, Beet, Wood Chippings) Players and Region - Global Market Outlook to 2027

Introduction

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Experimental setup

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Calculations

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Results

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Conclusion

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## 2-Ethylhexyl nitrate :

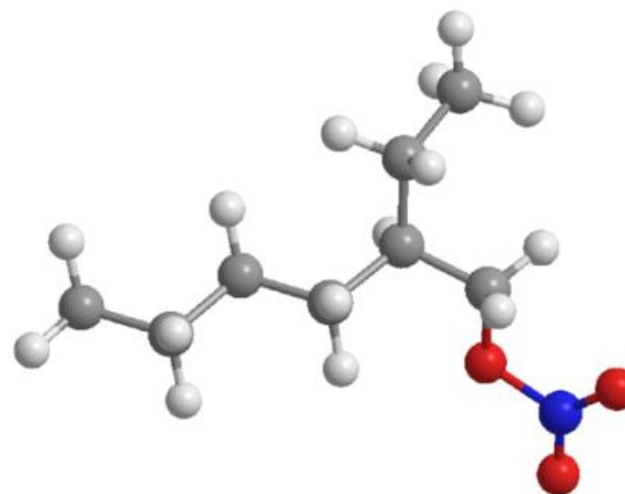
**Formula:**  $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{ONO}_2$

**M=** 175.2 g.mol<sup>-1</sup>

**Psat(20 °c)=** 0.27 Mbar

**Liquid at room Temp**

**T<sub>decomp</sub> =** 130 °C ( $\Delta\text{rH}<0$ )



-incorporated into diesel/biodiesel at a level of 0.3 to 1 g.L<sup>-1</sup>



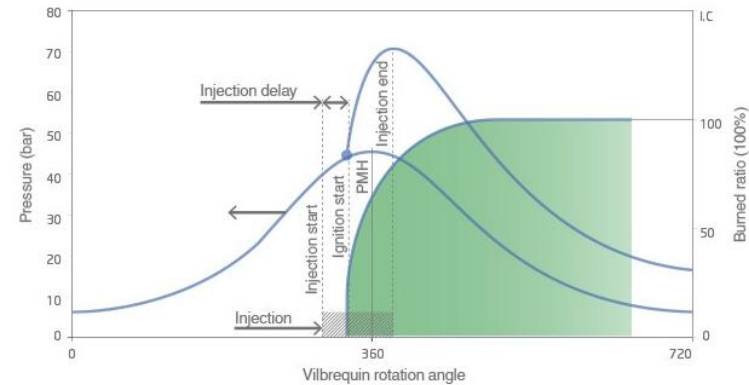
-acute toxicity :

H302 "harmful if swallowed"

H312 "harmful in contact with skin"

H332 "harmful by inhalation"

EUH066 "repeated exposure may cause skin dryness or cracking", EUH044 "danger of exposure if heated in a confined space" and H411 "toxic to aquatic organisms, causing long-term adverse effects".

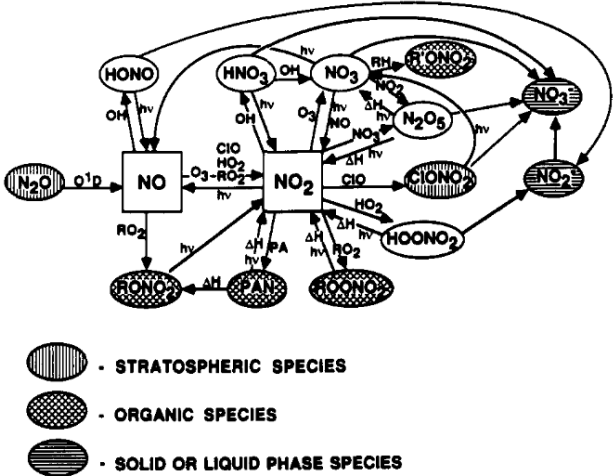


- Cetane improver
- Decrease of fuel consumption
- reduce the emissions of unburned hydrocarbons, particulates, carbon monoxide and nitrogen oxides

<https://www.veryone.com/fr/cetane-improver-fr/>



Double-Face in "Batman : The Animated Serie"



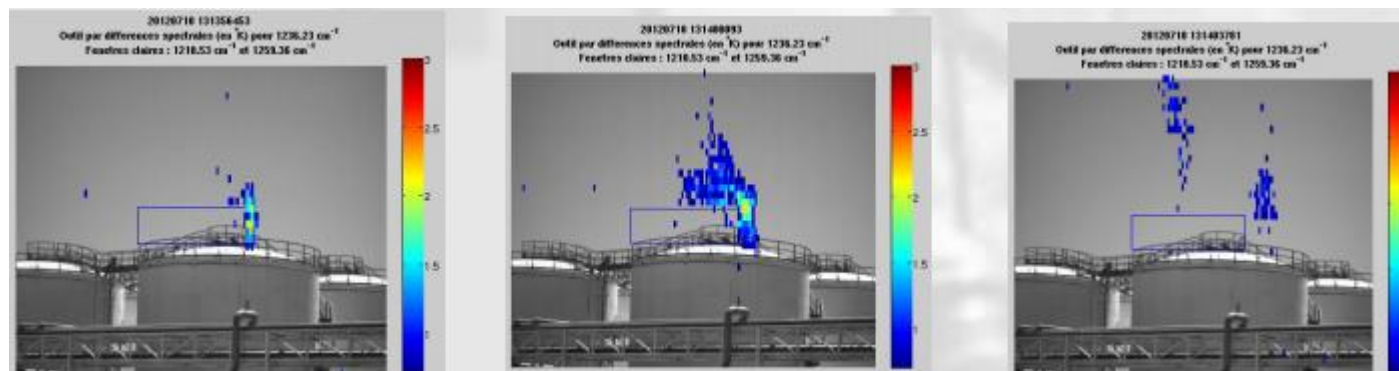
- Atmospheric pollutant
- involved in atmospheric chemistry,
- not easily biodegradable
- long term pollution

Fig. 1. Tropospheric and stratospheric odd-nitrogen cycle. [4]

[1]Ickes, A. M., Bohac, S. V., & Assanis, D. N. (2009). Effect of 2-ethylhexyl nitrate cetane improver on NO x emissions from premixed low-temperature diesel combustion. Energy & Fuels, 23(10), 4943-4948. Qian, [2]W., Huang, H., Pan, M., Huang, R., Tong, C., Guo, X., & Yin, J. (2020). Effects of 2-ethylhexyl nitrate and post-injection strategy on combustion and emission characterizes in a dimethyl carbonate/diesel blending engine. Fuel, 263, 116687.  
 [3]Roberts, J.M., 1990. The atmospheric chemistry of organic nitrates. Atmospheric Environment Part A e General Topics 24, 243e287  
 [4]Atkinson, R., 1997. Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and alkenes. Journal of Physical and Chemical Reference Data 26, 215e290.  
 [5]Solano-Serena, F., Nicolau, E., Favreau, G., Jouanneau, Y., & Marchal, R. (2009). Biodegradability of 2-ethylhexyl nitrate (2-EHN), a cetane improver of diesel oil. Biodegradation, 20(1), 85-94.

## Collaboration LATMOS/MONARIS

### Gas detection on an industrial site using hyperspectral imaging[1]



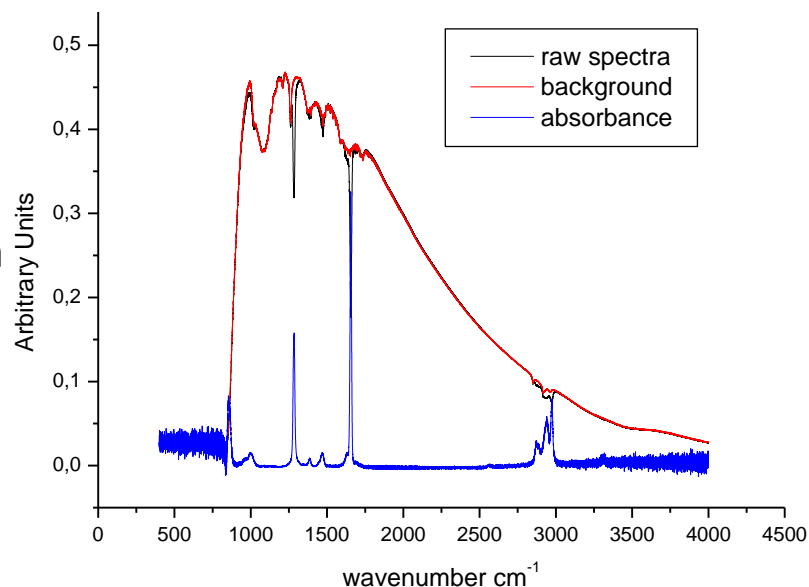
Successive infrared images superimposed on corresponding visible images. A tank degassing 1-2 dichloro-ethylene through a valve.

Measurements also done over a storage area of large 2-EHN tanks

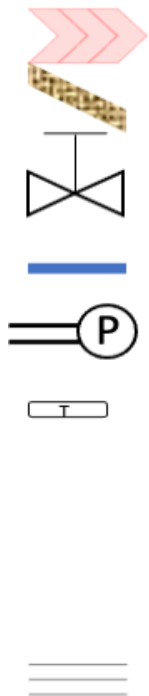
no data available for the phase gas in the mid-IR domain

*MONARIS, de la Molécule aux Nano-Objets : Réactivité, Interactions et Spectroscopies*  
*LATMOS, Laboratoire Atmosphères Milieux Observations Spatiales*

- Bruker IFS 120 HR :
- Resolution  $0.5 \text{ cm}^{-1}$  (+tests at  $2 \times 10^{-3} \text{ cm}^{-1}$ )
- Globar source / KBr beam splitter
- Stainless steel cells of 68.8 cm and 31.8 cm
- KBr windows



- coadditions of 20 scans/white spectrum (45 sec)
- Pressure  $0.025 \rightarrow 0.181 \text{ mbar}$
- capacitive gauge (0.25%)
- Temperature (298K  $\rightarrow$  318 K) (PT100)
- 2-EHN at 98%



FTIR Light

Heating cord

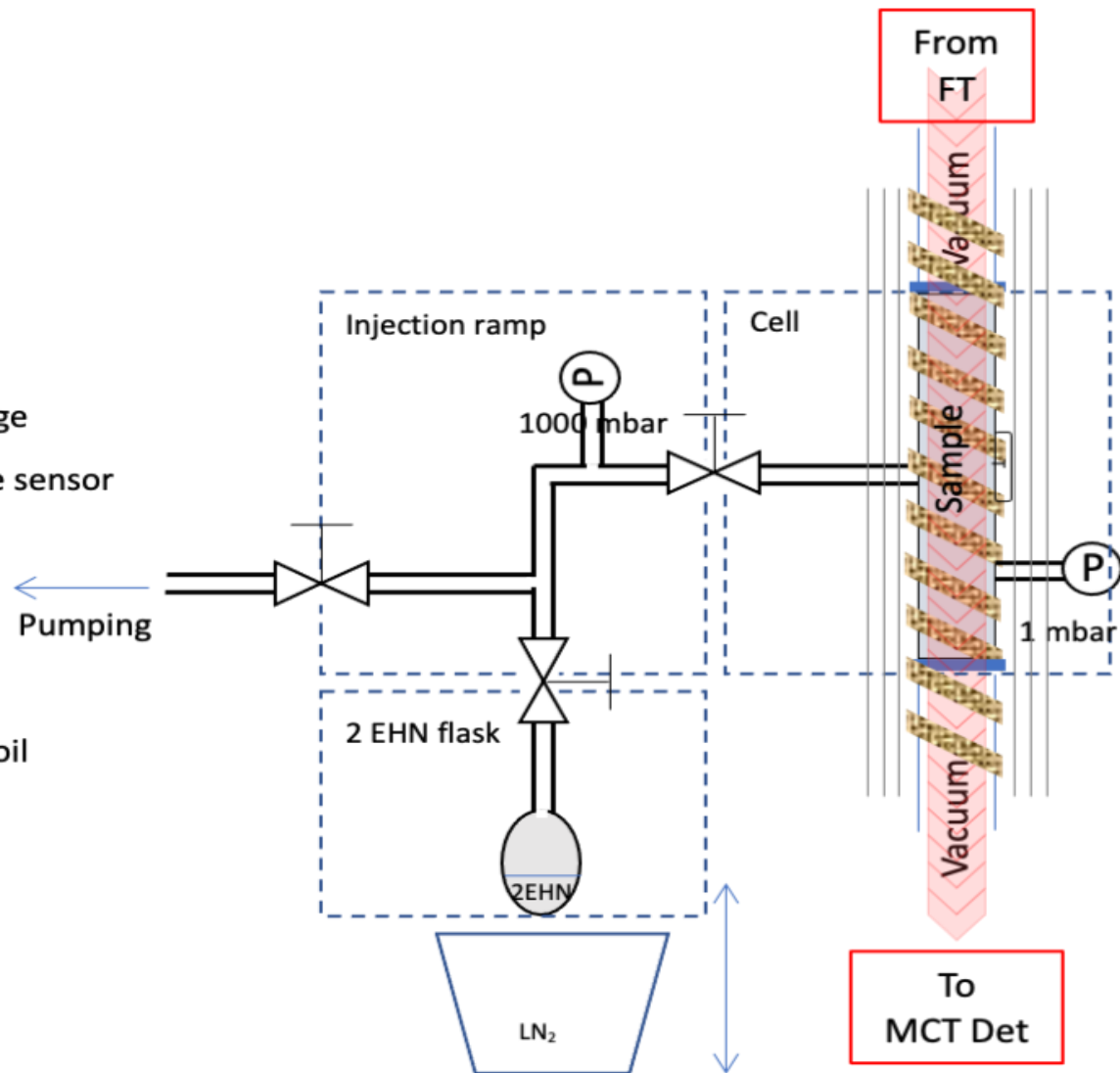
Valve

KBr Window

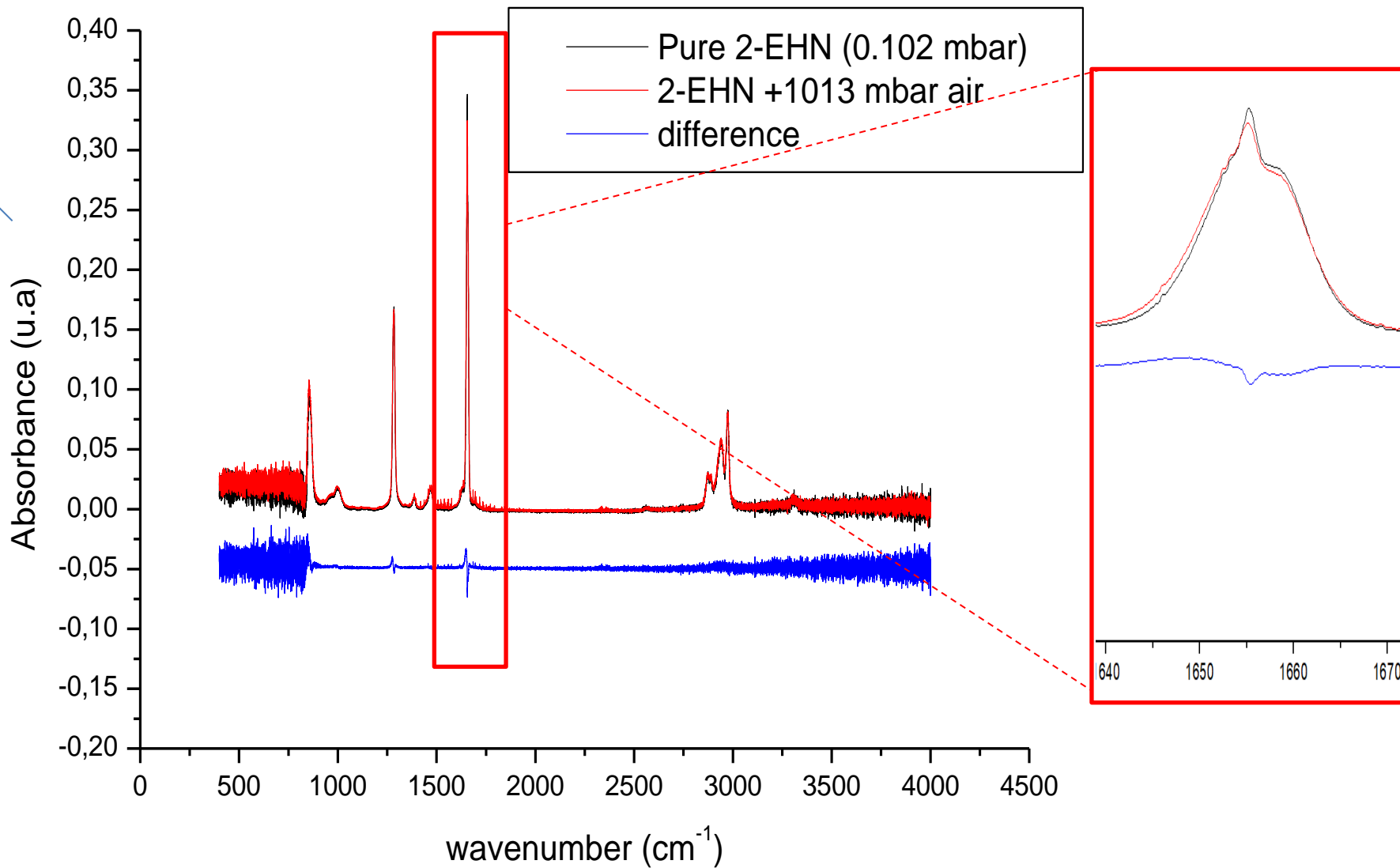
Pressure gauge

Temperature sensor

Aluminum foil

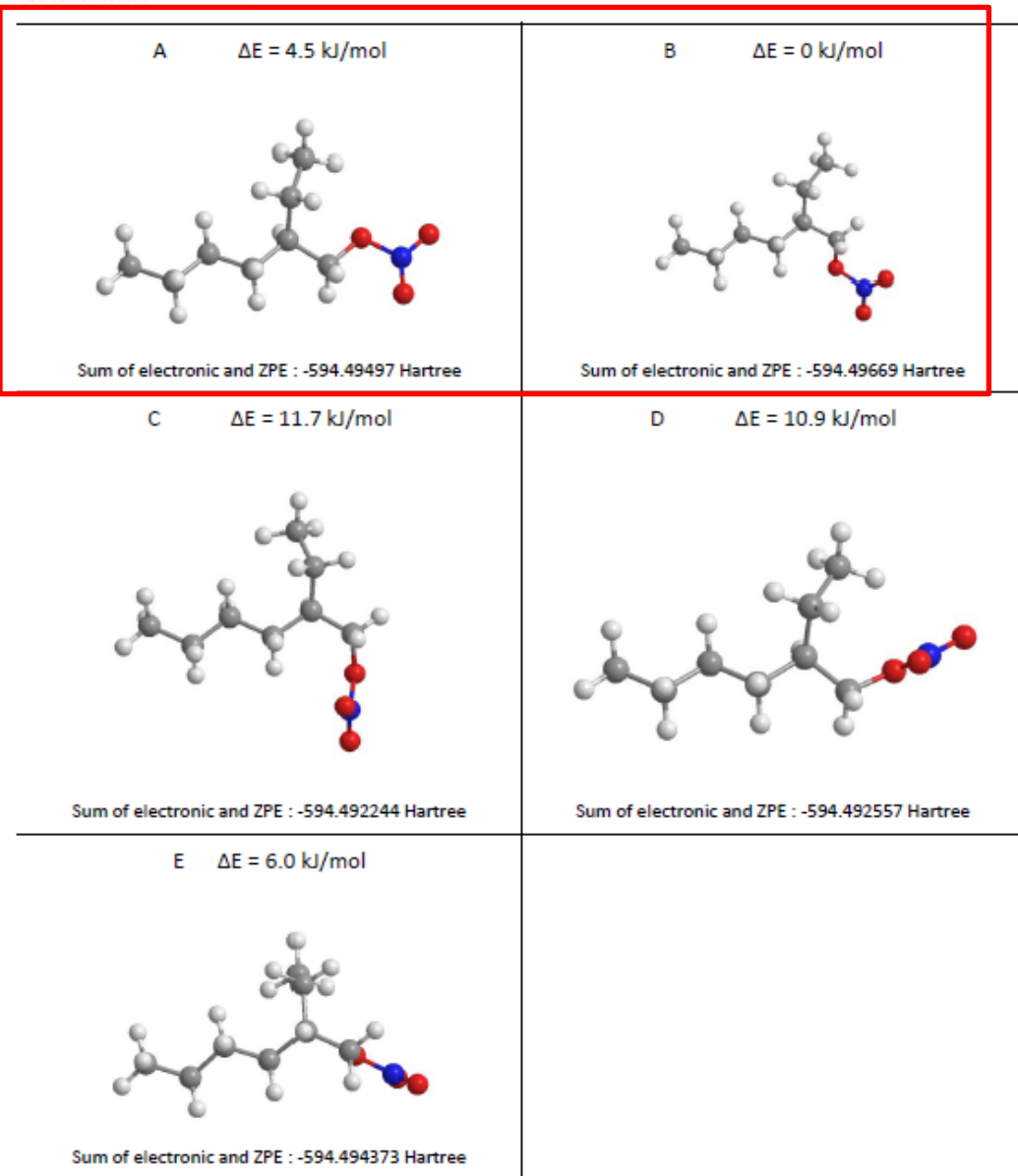


- Passivation layer of 2-EHN
- outgassing rate 0.03/hour (cell)



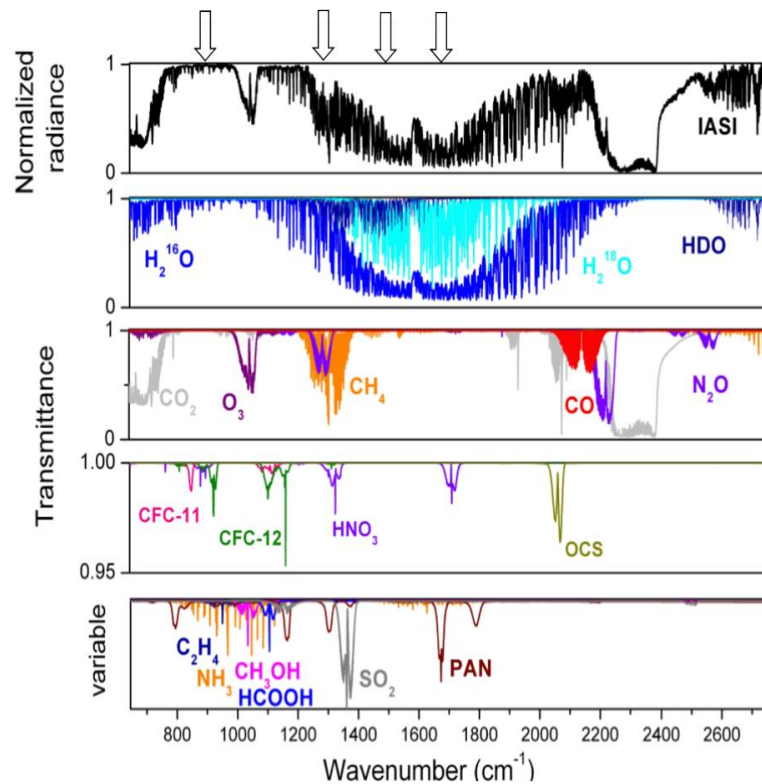
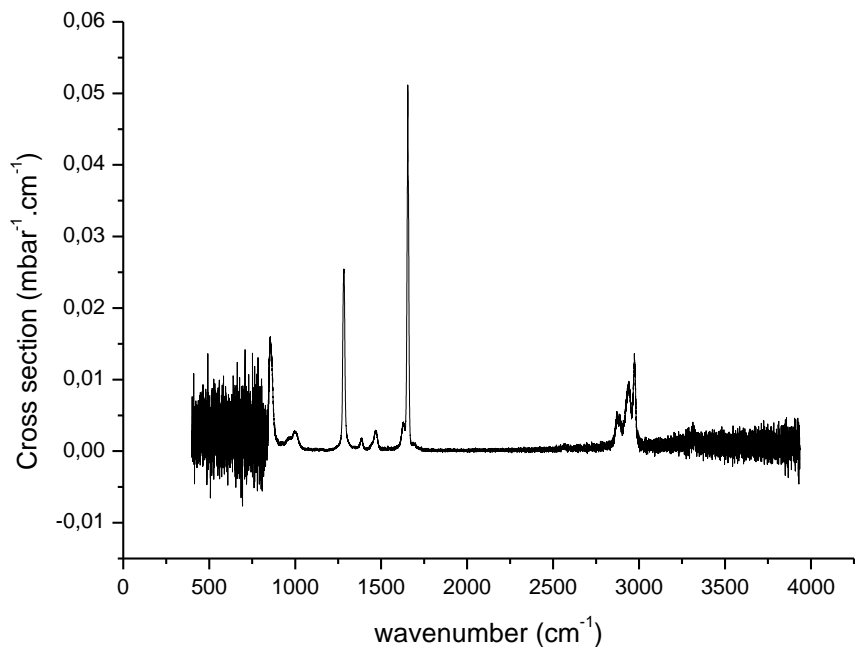
Comparison between a spectrum of pure 2-EHN and the same pressure of 2-EHN<sub>8</sub> with 1013 mbar of air added





Isomer A		Attribution	Isomer B	
(cm <sup>-1</sup> )	Theoretical intensity		(cm <sup>-1</sup> )	Theoretical intensity
1785	428	N-O twisting	1785	429.0552
926	173	N-O stretching linked to the carbon chain		
931	132		934	240
1368	126	H methyl wagging, N-O sym stretching	1366	111
1434	108		1432	110
1385	61		1385	63
1050	13	C-O asymm stretching		
1036	57		1043	58
1068	21	C-O asymm stretching	1061	41
1068	17			
		H methyl wagging, N-O sym stretching	1338	34
792.9368	12	NO <sub>3</sub> umbrella mode	793	12

DFT on Gaussian09




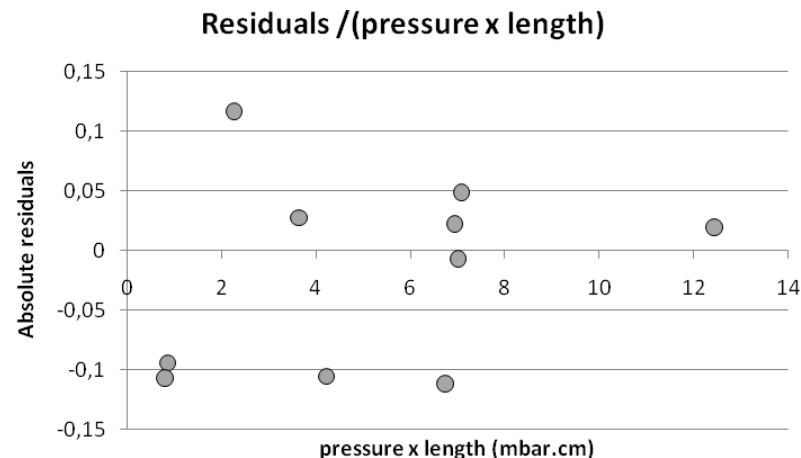
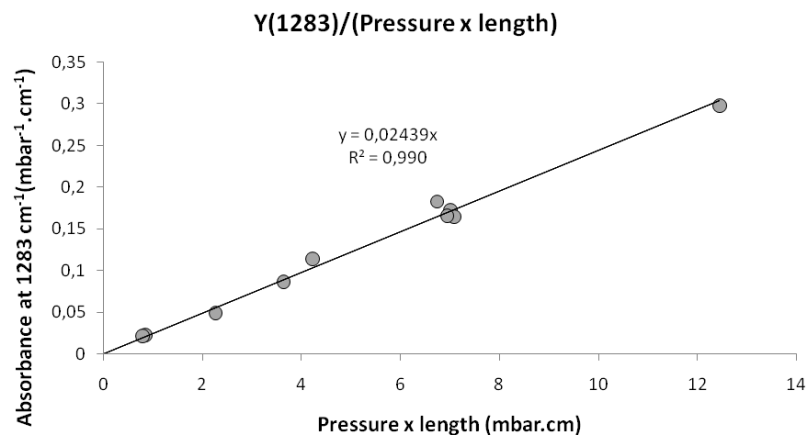
average absorption cross section of 2-EHN (obtained as average of 10 spectra)

Radiance atmospheric spectrum and radiative transfer transmittance simulations of the main absorbing[1]

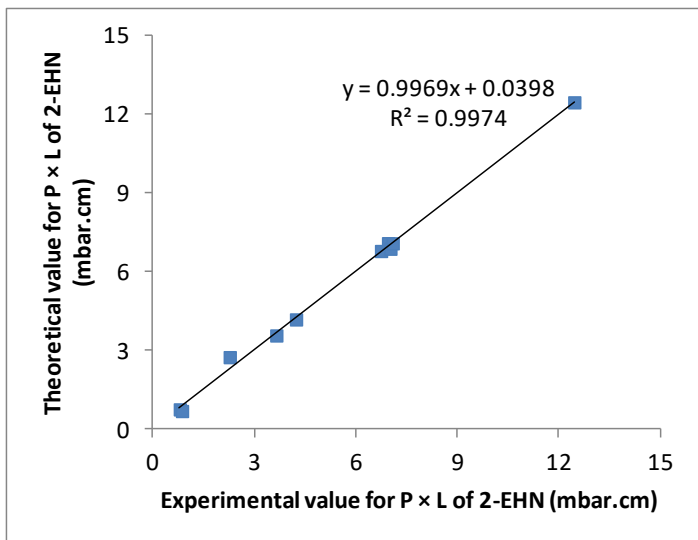
## -Criteria

- Characteristic of the  $\text{NO}_3$  group
- Atmospheric window

 Band at  $1280 \text{ cm}^{-1}$

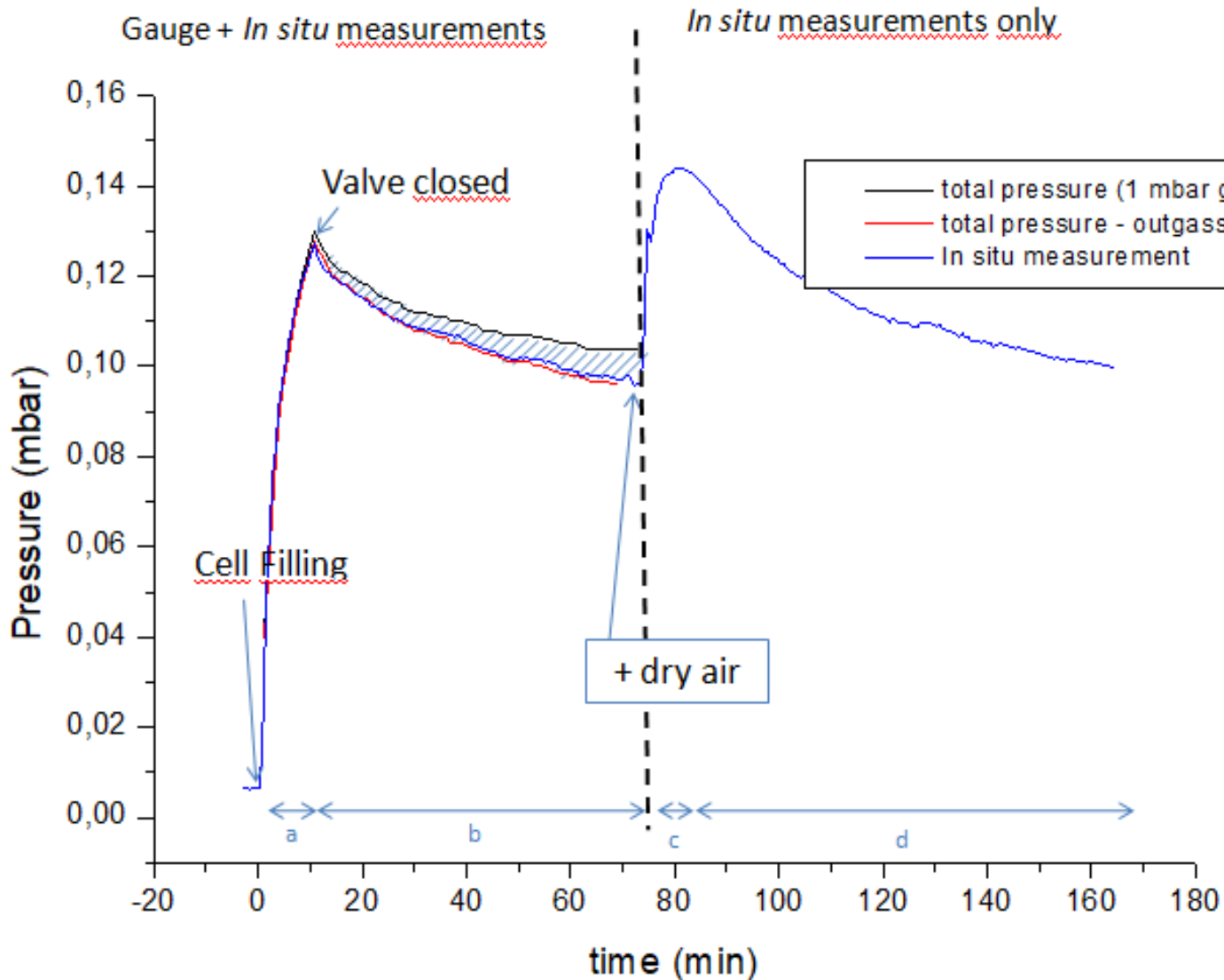
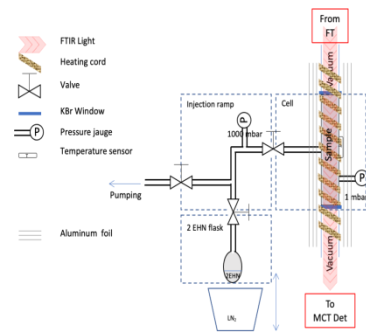


Y(1283.8) as a function of the pressure x length (left) and difference between the affine function and Y(1283) (right)



Experimental value for $P \times L$ of 2-EHN (mbar.cm)	Predicted value for $P \times L$ of 2- EHN(mbar.cm)
0.795	0.763
0.859	0.700
2.27	2.752
3.646	3.577
6.742	6.793
6.949	7.091
7.018	6.879
7.086	7.086
4.229	4.188
12.453	12.453

Determination of the  $R^2$  value associated with the model. Comparison of predicted and measured pressures based on the chemometric analysis of the spectra presented in Table 1.



- measurements absorption cross section of 2-EHN
  - 850 -4000  $\text{cm}^{-1}$
  - 9 % uncertainties
  - results give in a 2 columns file
  - DFT calculations for band attribution
  - Geometry optimizations (conformers)
  - Two approaches
  - Adsorption-desorption study
  - No detection in hyperspectral measurements

## Outlooks

- Filling ramp and cell in glass/ longer cell
  - measurements diesel/biodiesel mixed with 2-EHN
  - Bruker 120 (platform IP2CT)

