

DOAS

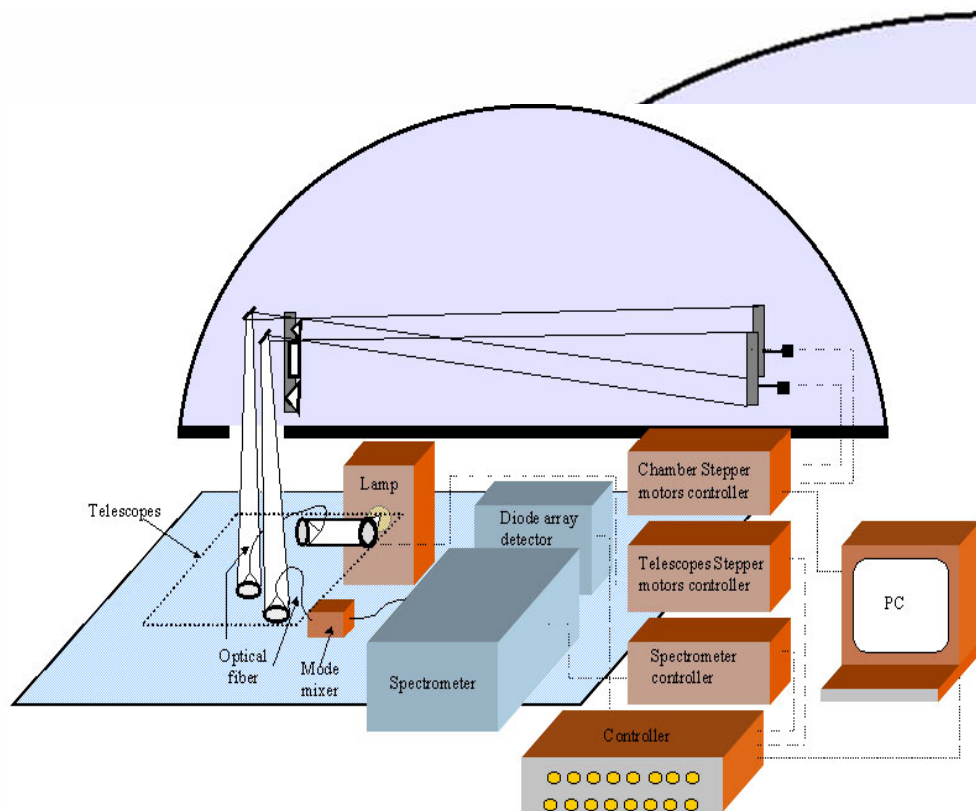
Differential Optical Absorption Spectroscopy

Fundación CEAM

Mila Ródenas. EUPHORE

HONO TECHNICAL WORKSHOP. *Valencia, November 17th-18th, 2008*

DOAS SET-UP AT EUPHORE



Doas scheme

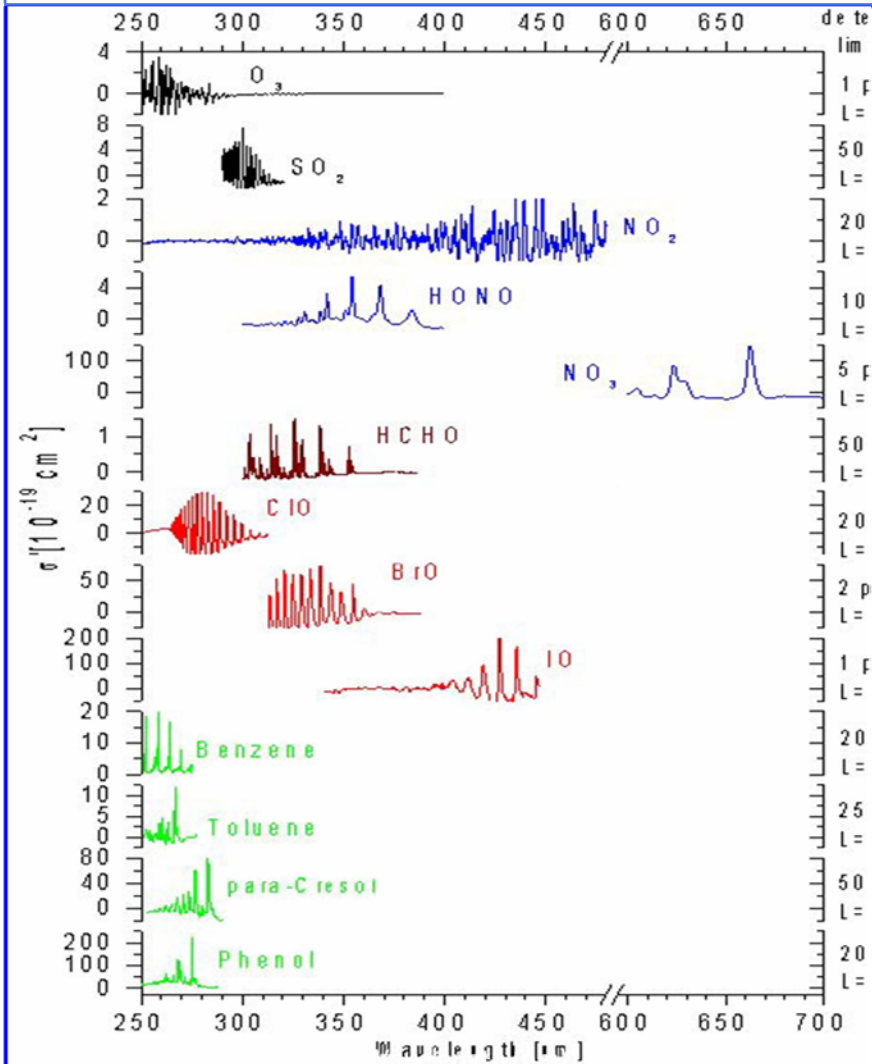
Doas scheme

DOAS Setup

- White-multireflection cell: 8m base-path (EUPHORE)
- Several sets of mirrors for detection of different compounds
- Optical Pathlengths: 128-386-640-896-1154m
- Resolution: 0.04, 0.08, 0.16 nm/pixel (FWHM=0.18, 0.35, 0.72 nm, resp.)
- Range: UV and Visible (200 - 1000 nm)
- Automatic and continuous adjustment of mirrors in the chamber (IUP Heidelberg)
- Automatic positioning of optical fibers
- Spectrometer (Acton-500 Pro) and detector (PDA-3904 Hamamatsu) are thermostated
- Evaluation of spectra by modified minimum squares fitting

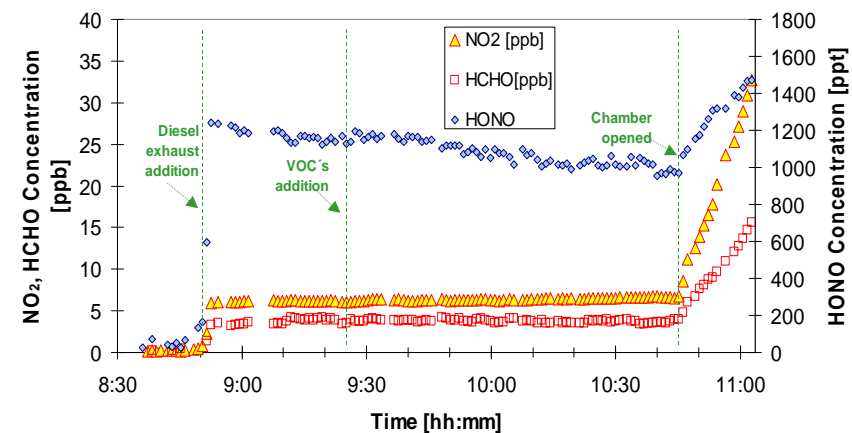
DOAS APPLICATION

Some Measurable Compounds



- Nitrogenated compounds: NO_2 , NO_3 , $HONO$, etc
- Sulfurated comp.: SO_2 , CS_2 , etc
- Halogenated comp.: BrO , ClO , etc
- Aromatics: Benzene, Toluene, Phenol, etc
- PAHs: Naphtalene, etc
- Others: O_3 , $HCHO$, Glyoxal, m-Glyoxal, etc

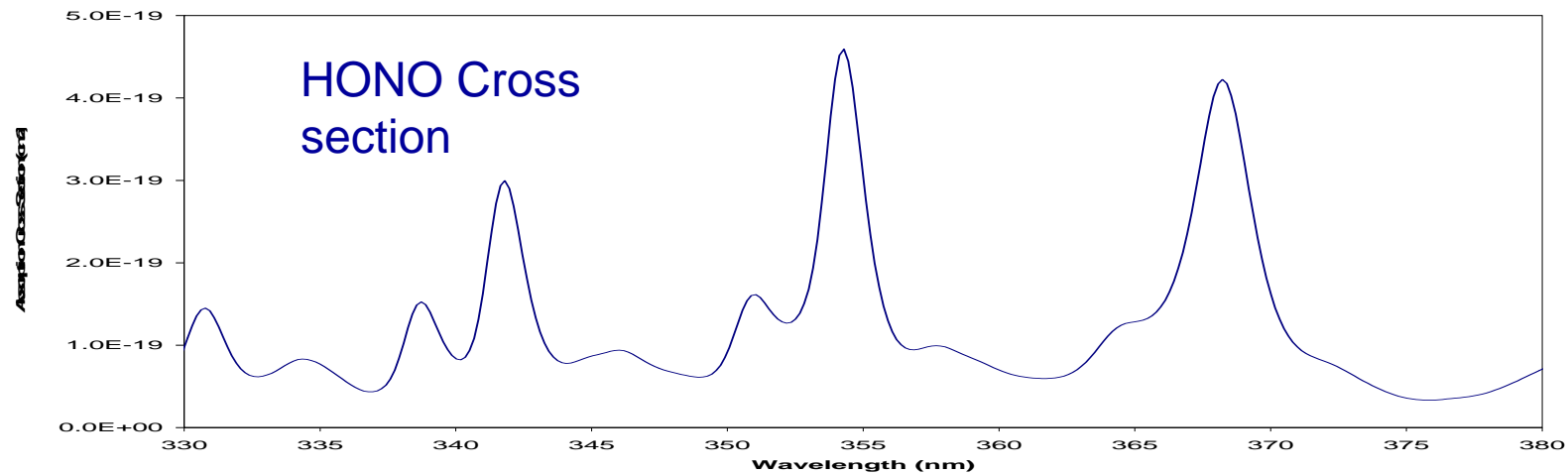
Diesel + VOCs. DIFUSO Project



DOAS ADVANTAGES

- √ High specificity, selectivity and sensitivity needed to measure a variety of compounds
- √ Simultaneous measurement of several species
- √ Low detection limits (ppt to a few ppb)
- √ Well time-resolved measurements (5 sec - 2 min)
- √ Several resolutions (FWHM: 0.18, 0.35 and 0.72 nm)
- √ Inherently calibrated (i.e. absorption cross section)
- √ Optical method
 - ⇒ no wall losses
 - ⇒ non-invasive
 - ⇒ useful to measure highly reactive species and volatile gases

DOAS: HONO Measurements



HONO cross section: Stutz et al., 2000

Resolution time: 1 - 2 min

Dielectric mirrors: R= 99% at 300-390 nm

Path-length: 898 m

Evaluation range: 337-378 nm

Concentration range: <0.4 - 200 ppb

Resolution (FWHM): 0.35 nm

Analysis with modified fitting routine reduces interferences

Access to the chamber not needed for alignment during experiments

FTIR

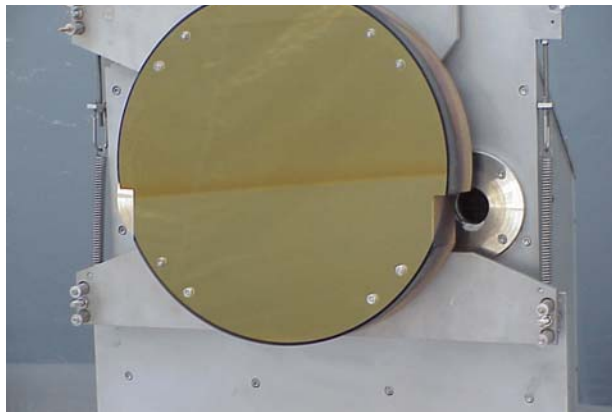
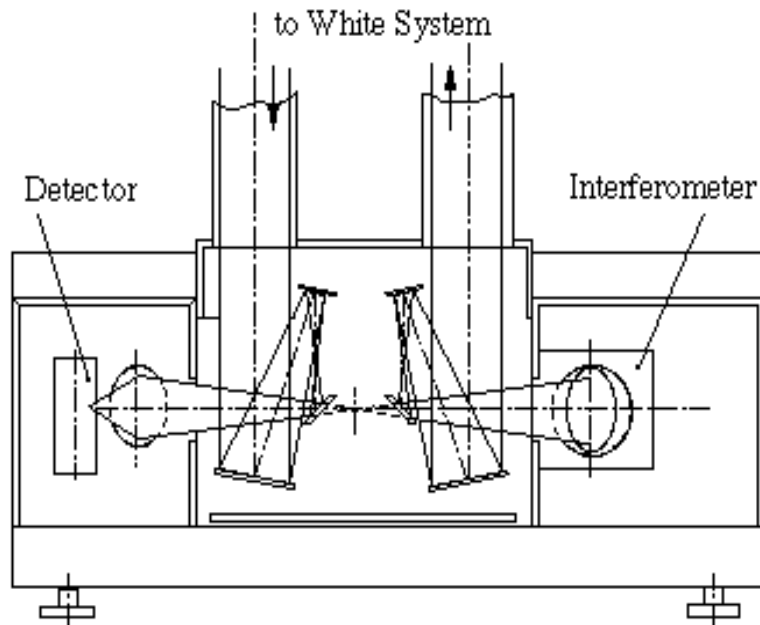
Fourier Transform Infrared

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FTIR: Set-up at EUPHORE



Characteristic Data:

Spectrometer: FTIR NICOLET Magna-550

Detector: MCT

Diam. Mirrors: 0.4 m

Surface Coating: Gold (High Reflectivity
in the IR Spectral Range)

Spectral Range: 4000-400 cm^{-1}

Resolution: 1 cm^{-1}

Base Length: 8.170 m

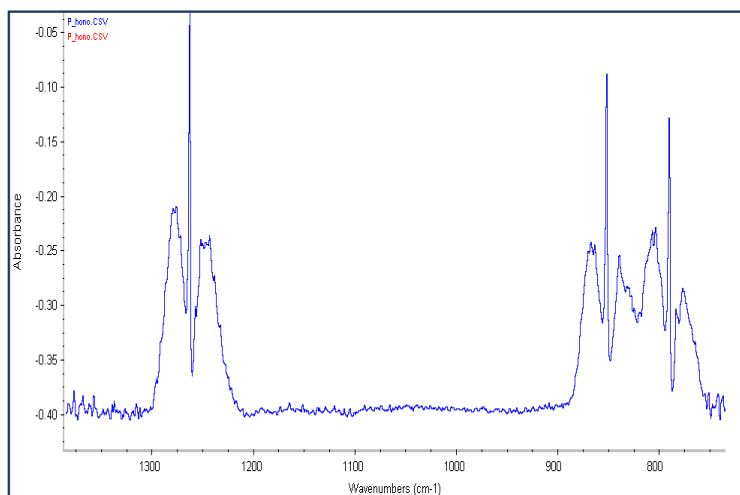
Max. Path-Length of multi-reflection cell:

653.6 m in Chamber A

553.4 m in Chamber B

FTIR APPLICATION

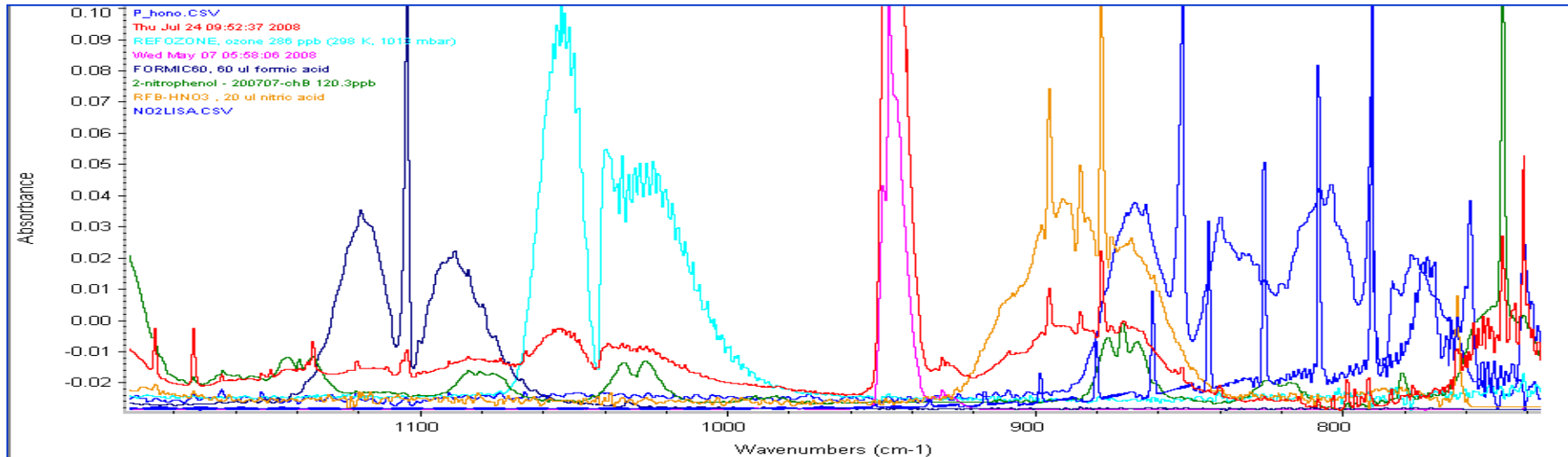
HONO IR ABSORPTION



Bond	Compound Type	Frequency range, cm^{-1}
C-H	Alkanes	2960-2850(s) stretch 1470-1350(v) scissoring and bending
	CH ₃ Umbrella Deformation	1380(m-w) - Doublet - isopropyl, <i>t</i> -butyl
C-H	Alkane	3080-3020(m) stretch 1000-675(s) bend
C-H	Aromatic Rings	3100-3000(m) stretch
	Phenyl Ring Substitution Bands	870-675(s) bend
	Phenyl Ring Substitution Overtones	2000-1600(w) - fingerprint region
C-H	Alkynes	3333-3267(s) stretch 700-610(b) bend
	C=C	Alkenes
C≡C	Alkynes	2260-2100(w,sh) stretch
C=C	Aromatic Rings	1600, 1500(w) stretch
C-O	Alcohols, Ethers, Carboxylic acids, Esters	1260-1000(s) stretch
C=O	Aldehydes, Ketones, Carboxylic acids, Esters	1760-1670(s) stretch
O-H	Monomeric - Alcohols, Phenols	3640-3160(s,br) stretch
	Hydrogen-bonded - Alcohols, Phenols	3600-3200(b) stretch
	Carboxylic acids	3000-2500(b) stretch
N-H	Amines	3500-3300(m) stretch 1650-1580 (m) bend
	C-N	Amines
C≡N	Nitriles	2260-2220(v) stretch
NO ₂	Nitro Compounds	1660-1500(s) asymmetrical stretch
		1390-1260(s) symmetrical stretch

DOAS: HONO Measurements

Experiment of 2-Nitrophenol and NO₂: products formation



HONO reference: EUPHORE (DOAS calibration)

Resolution time: 5 - 10 min

Path-length: 656.5 m (Chamber A)

Concentration range: 1.5 - 200 ppb

Analysis with modified fitting routine reduces interferences but exist

Access to the chamber not needed for alignment during experiments