Nucleation-Particle Formation in Diesel Vehicle Exhaust: Role of Acid-Base interactions

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Diesel-Nucleation-Particles (NUPs)

- NUPs reach large number-concentrations
- NUPs have diameters of about 10 nm
- NUPs have large total surface-area-concentrations
- NUPs have just the perfect size for most efficient intrusion of the lowest and most vulnerable region of human lung (alveolae-region)
- Important aspects of NUP formation are not well understood
  In particular, nucleating gases and condensing gases are not well known
- NUPs are not regulated by legislation!
  Regulation only for particles with D> 20 nm (Europe)

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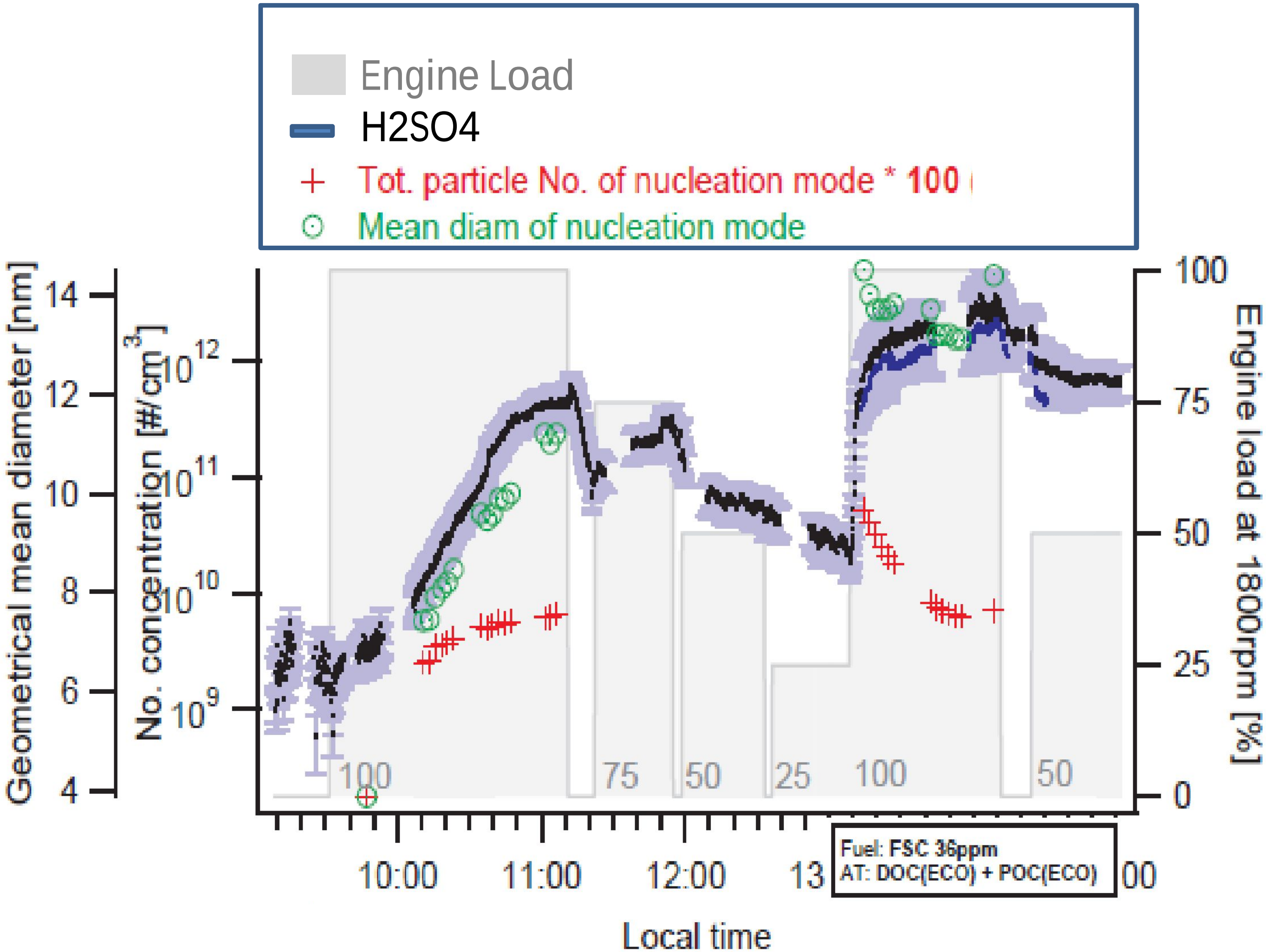
  In particular, nucleating gases and gases involved in early growth of nascent NUOs are not well known
- NUPs are not regulated by legislation!

  Regulation only for particles with D> 20 nm (Europe) and D > 23 nm (USA)

Investigations of Nucleation-Particle (NUP) Formation in Modern Diesel Vehicle Exhaust

- *Lab Experiments*
  - Test bed (with Heavy Duty Diesel Vehicle Engine)
  - different Fuels
  - different Fuel sulfur content (FSC)
  - different engine loads (EL)
  - different exhaust aftertreatment systems (ATS: DOC; DPF)
- *Model Simulations*
  - different nucleation mechanisms
  - different organics
  - different FSC

Time series of gas-phase sulfuric acid in heavy duty vehicle engine test-run
FSC = 36 ppm ; EL = 25, 50, 75, 100 % ; ATS (DOC + POC)



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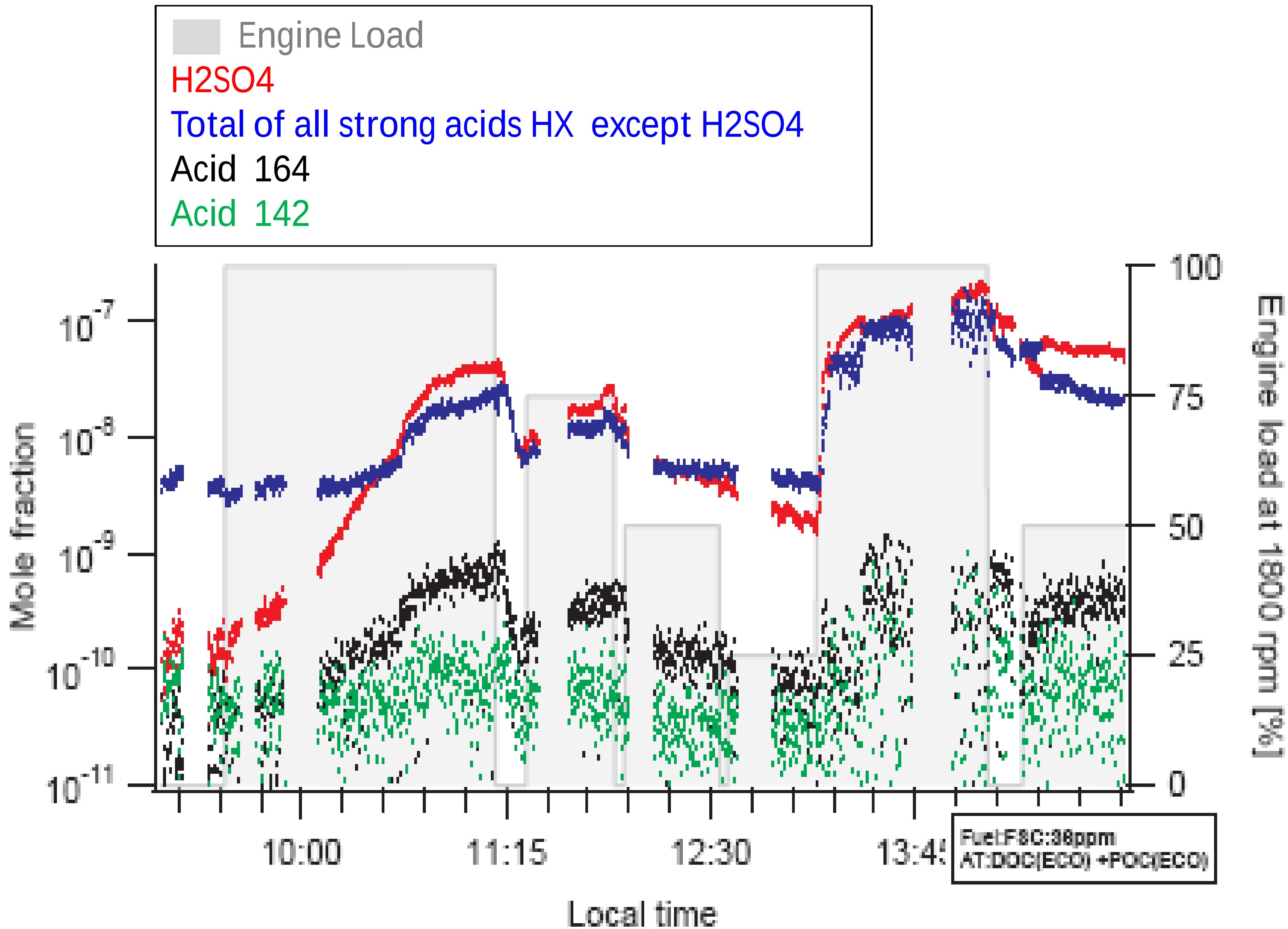
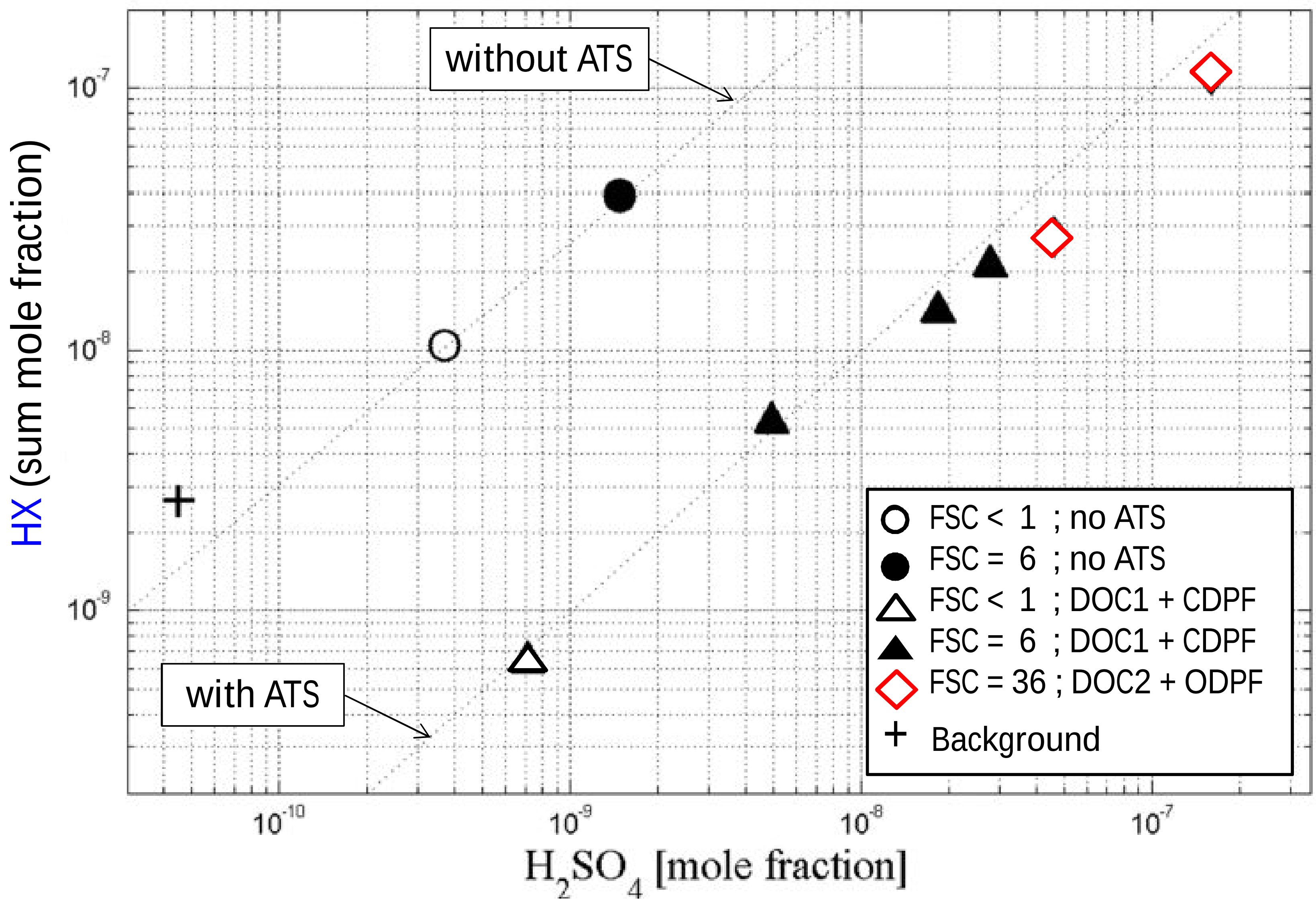
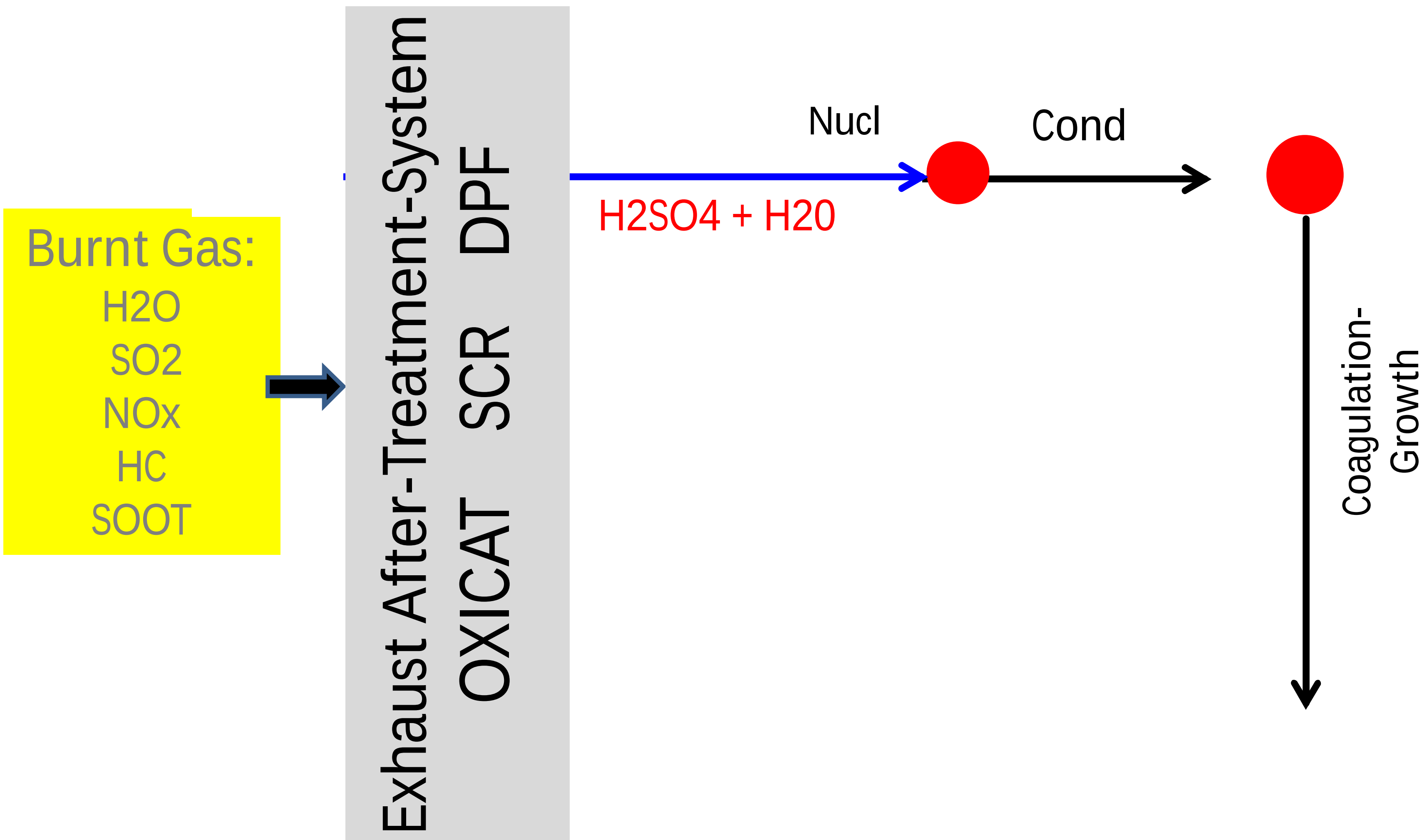




without ATS
with ATS
10^{-7}
10^{-8}
10^{-9}
HX (sum mole fraction)
10^{-10}
10^{-9}
10^{-8}
10^{-7}
H_2SO_4 [mole fraction]
FSC < 1 ; no ATS
FSC = 6 ; no ATS
FSC < 1 ; DOC1 + CDPF
FSC = 6 ; DOC1 + CDPF
FSC = 36 ; DOC2 + ODPF
Background

H2SO4/H2O - Nucleation-Particle Formation in Modern Diesel Vehicle Exhaust (simplified scheme without soot))



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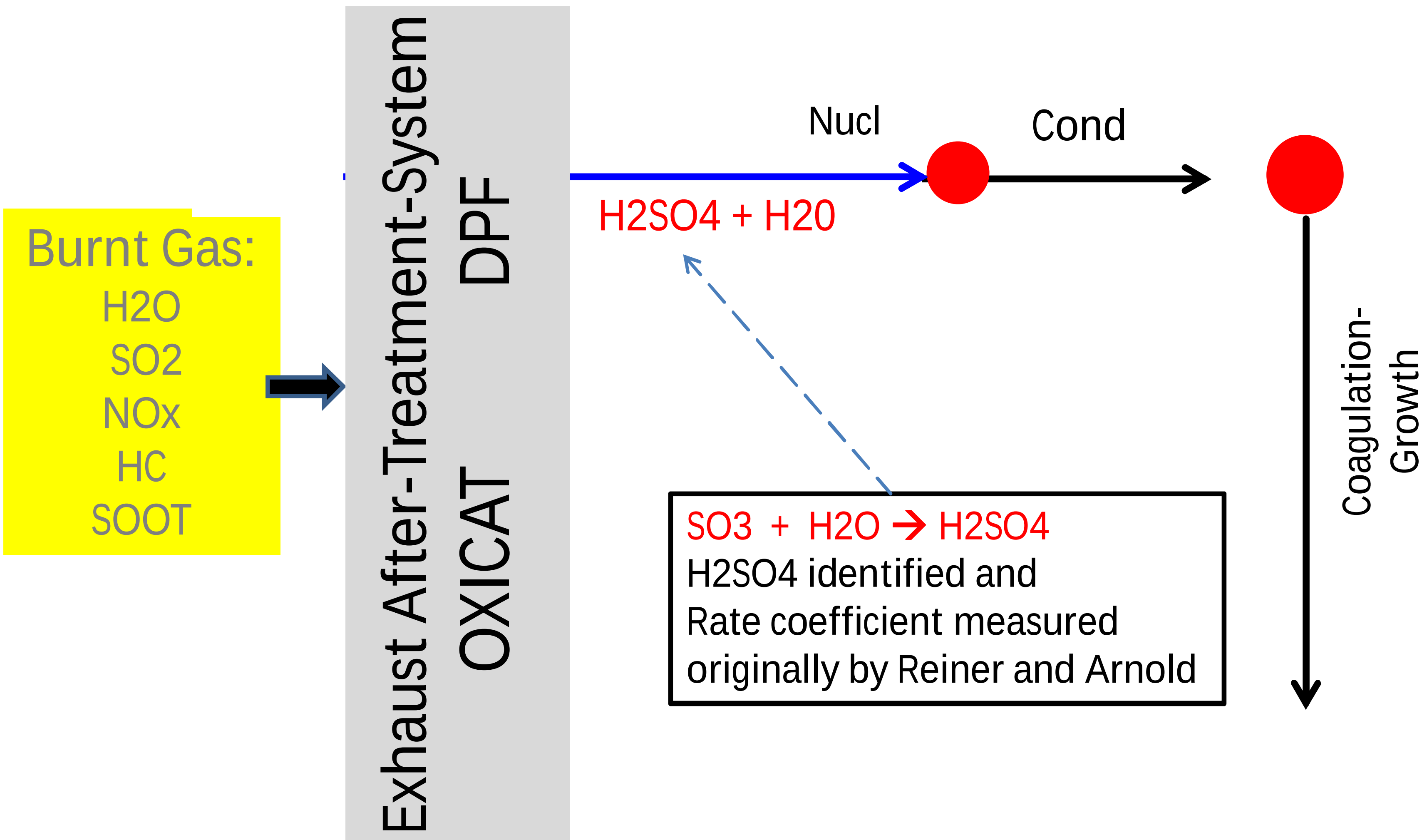
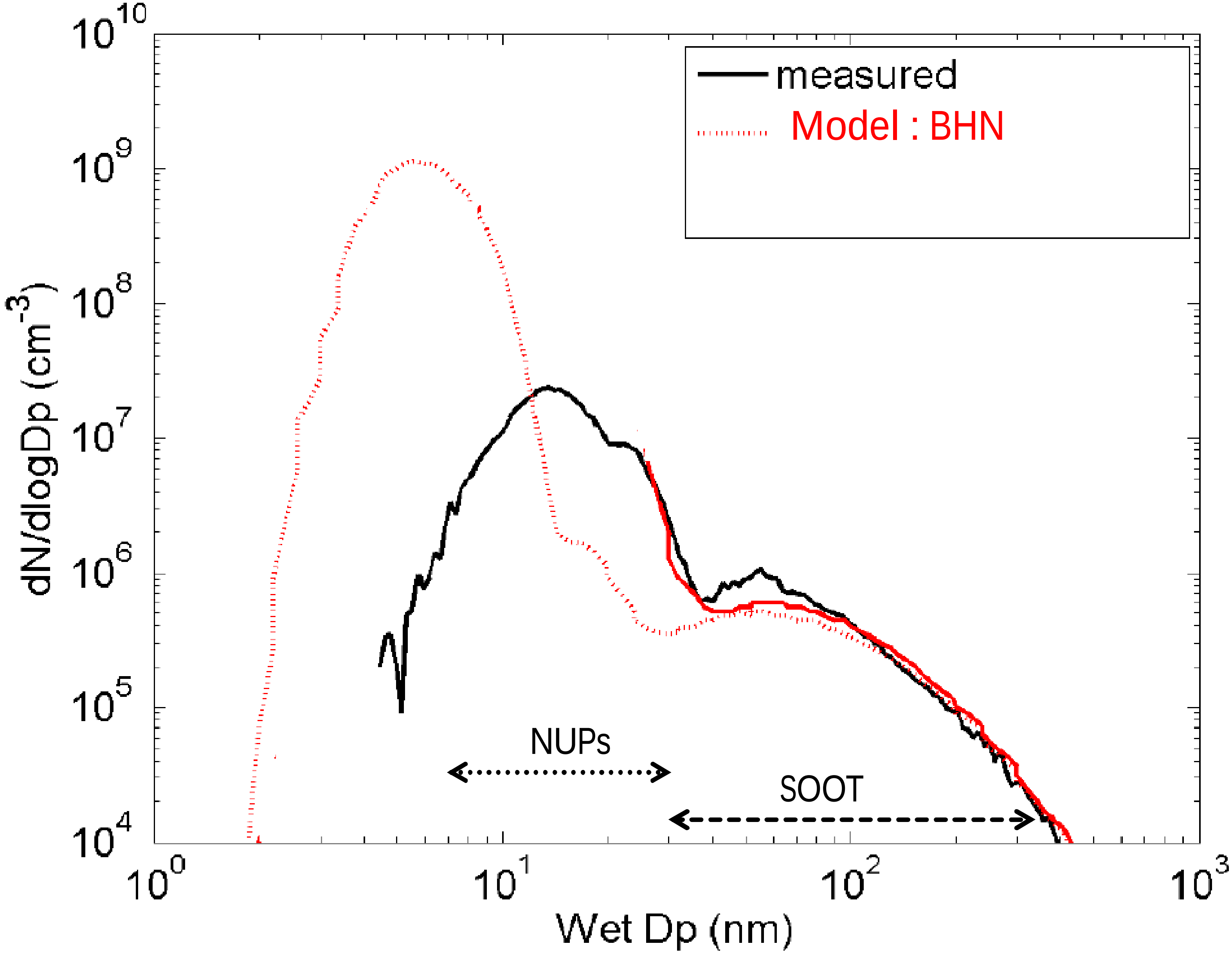


BHN-modelled and measured NUP size-distributions:
FSC = 36 ppm ; ATS (DOC (ECO) + POC (ECO)



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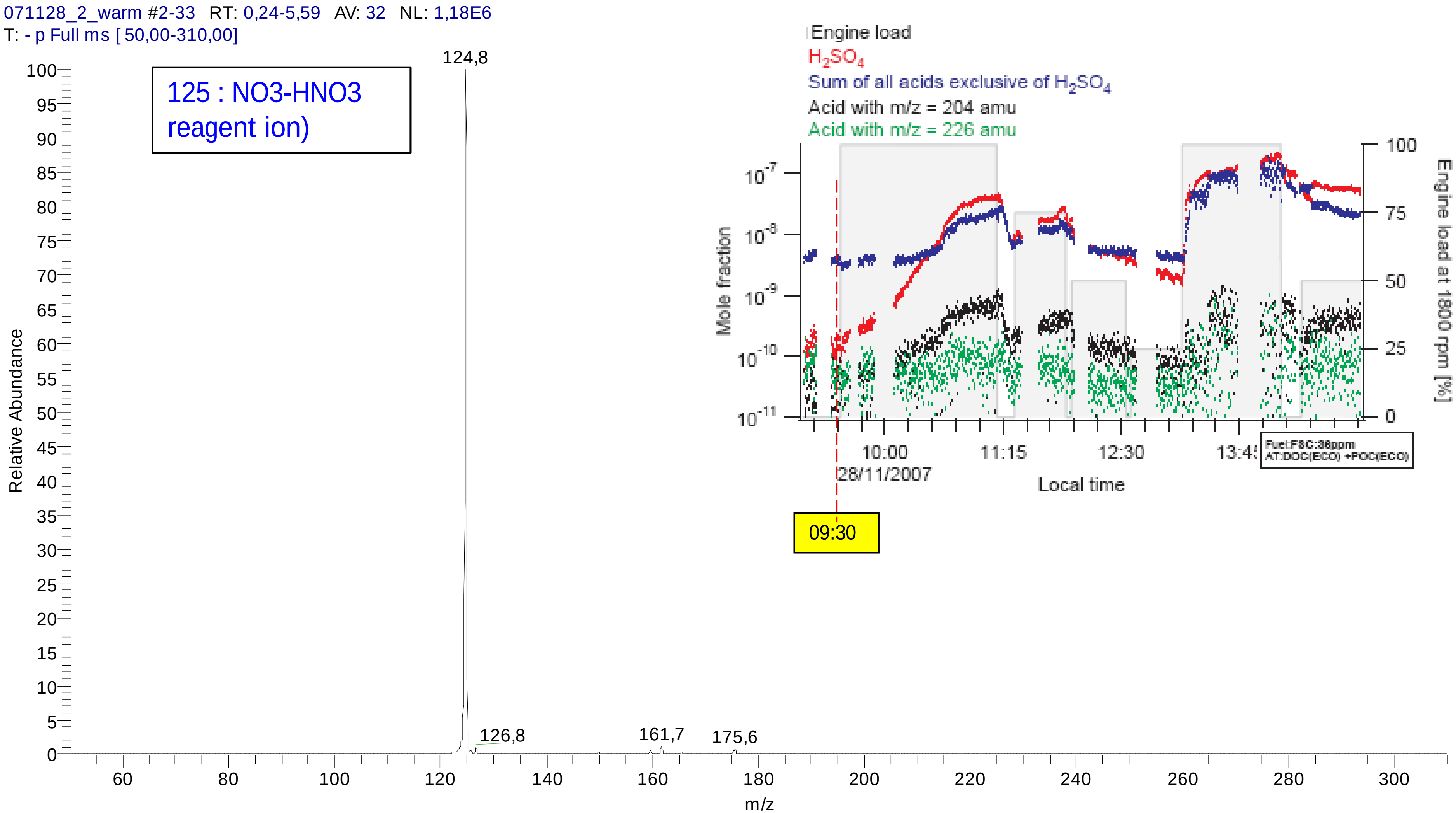
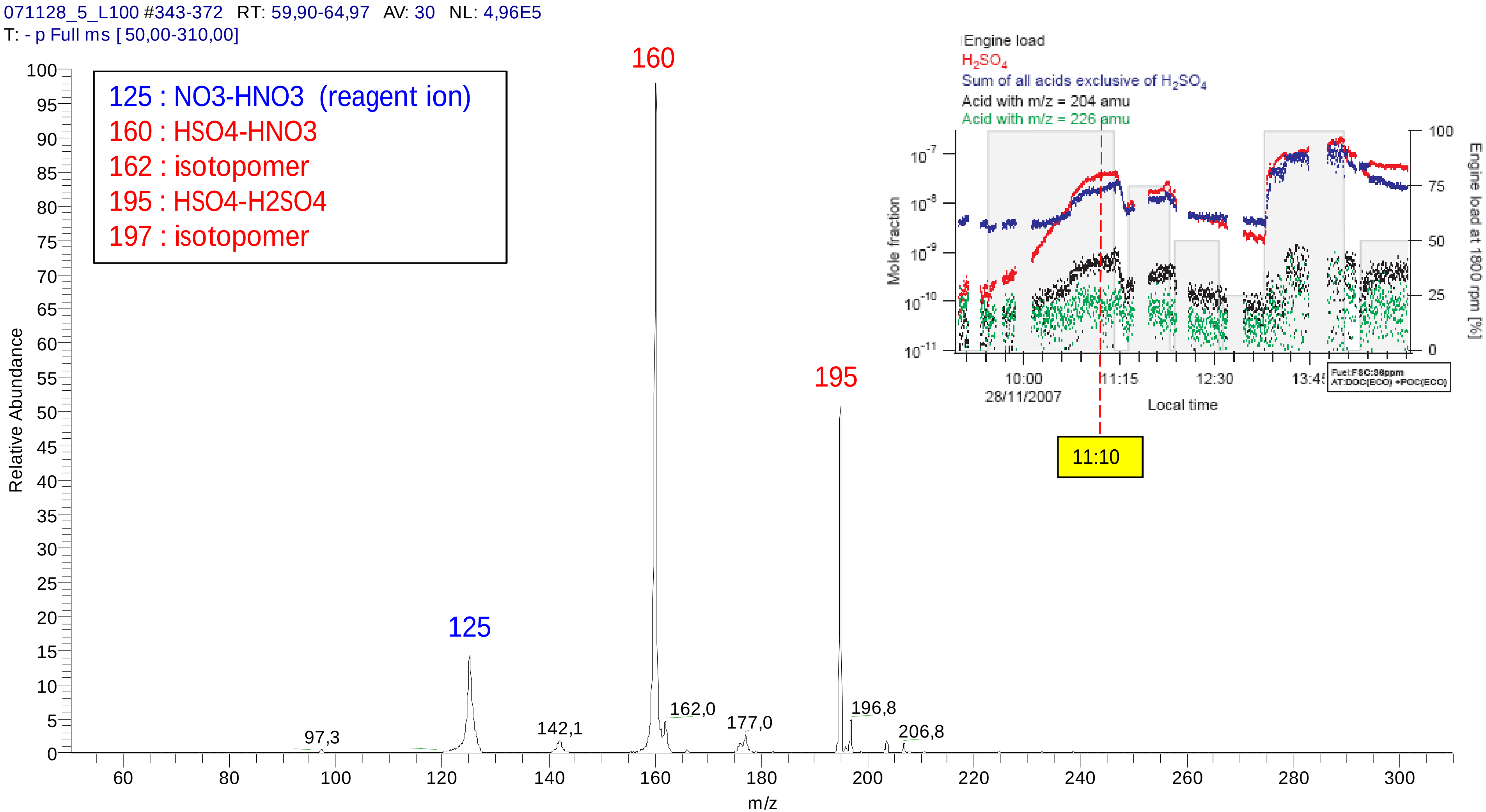


ION-RECTION SCHEME for HX DETECTION:

NO3-HNO3 + HX → X-HNO3 + HNO3 (HX is acid having GA larger than GA (HNO3)

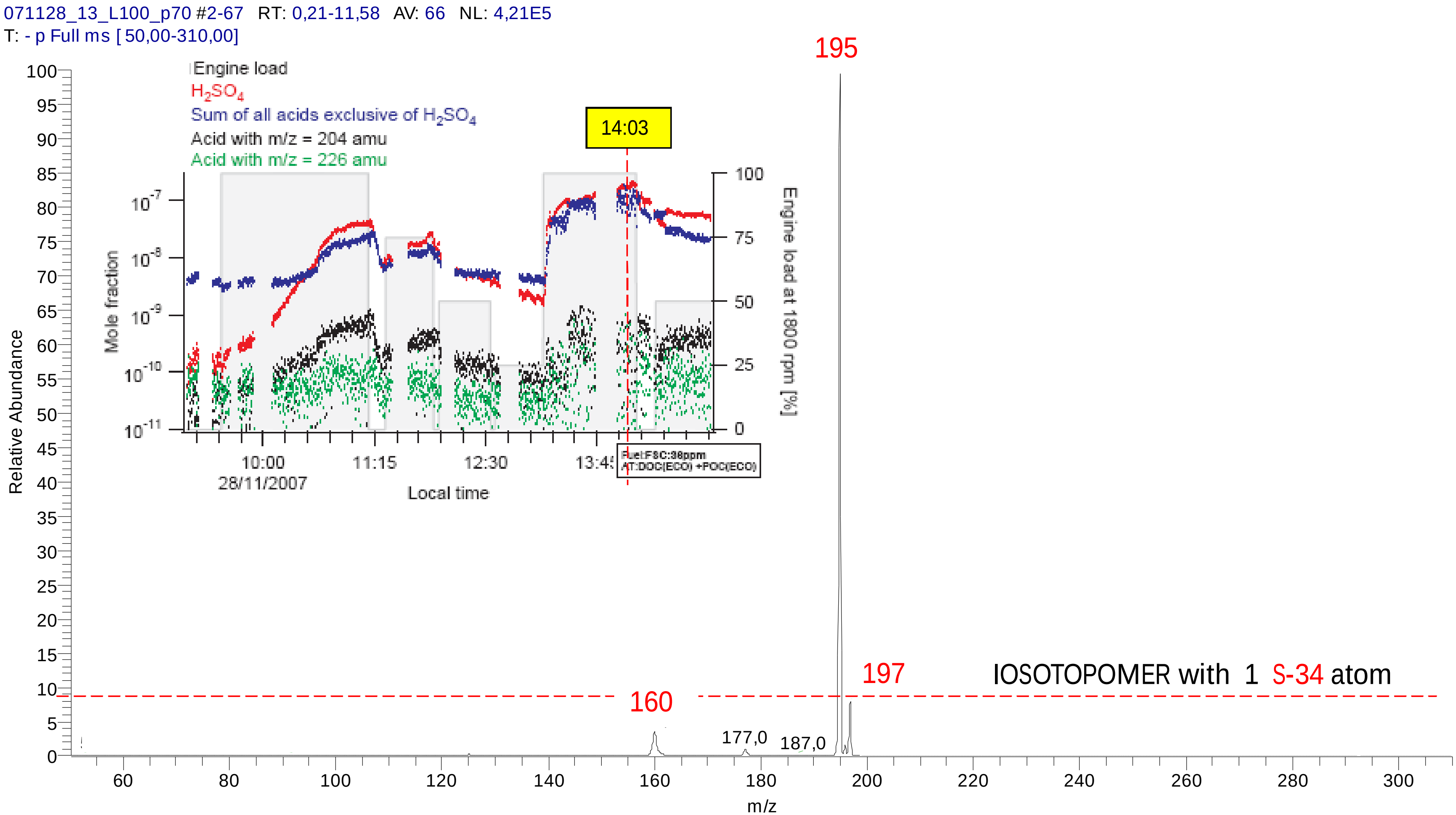


ION-RECTION SCHEME for HX DETECTION: tr = 0.1 s , tc = 0.1 s , tr/tc = 1

NO3-HNO3 + HX → X-HNO3 + HNO3 (HX is acid having GA larger than GA (HNO3)

X-HNO3 + HX → X-HX + HNO3

C:\Users\...\071128\071128_13_L100_p70   28.11.2007 14:03:19



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X-HNO3 + HX → X-HX + HNO3

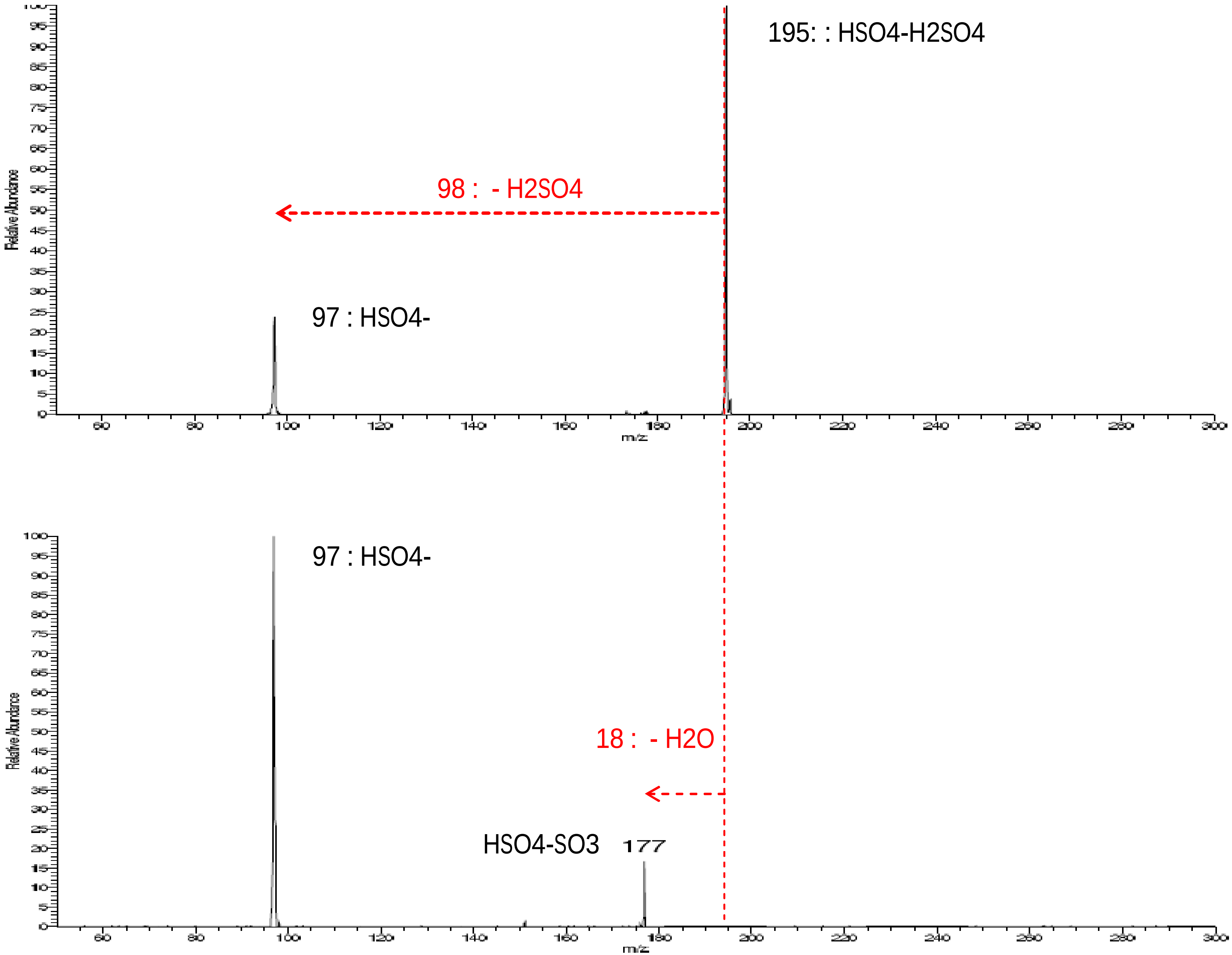
Ion Identification via

- Mass number
- Isotopic signatures
- CID (Collision-Induced-Dissociation). Energetic collisions (with He-Atoms) of mass selected ions stored in a Qudrupole Ion Trap, leading to first-generation fragment ions.

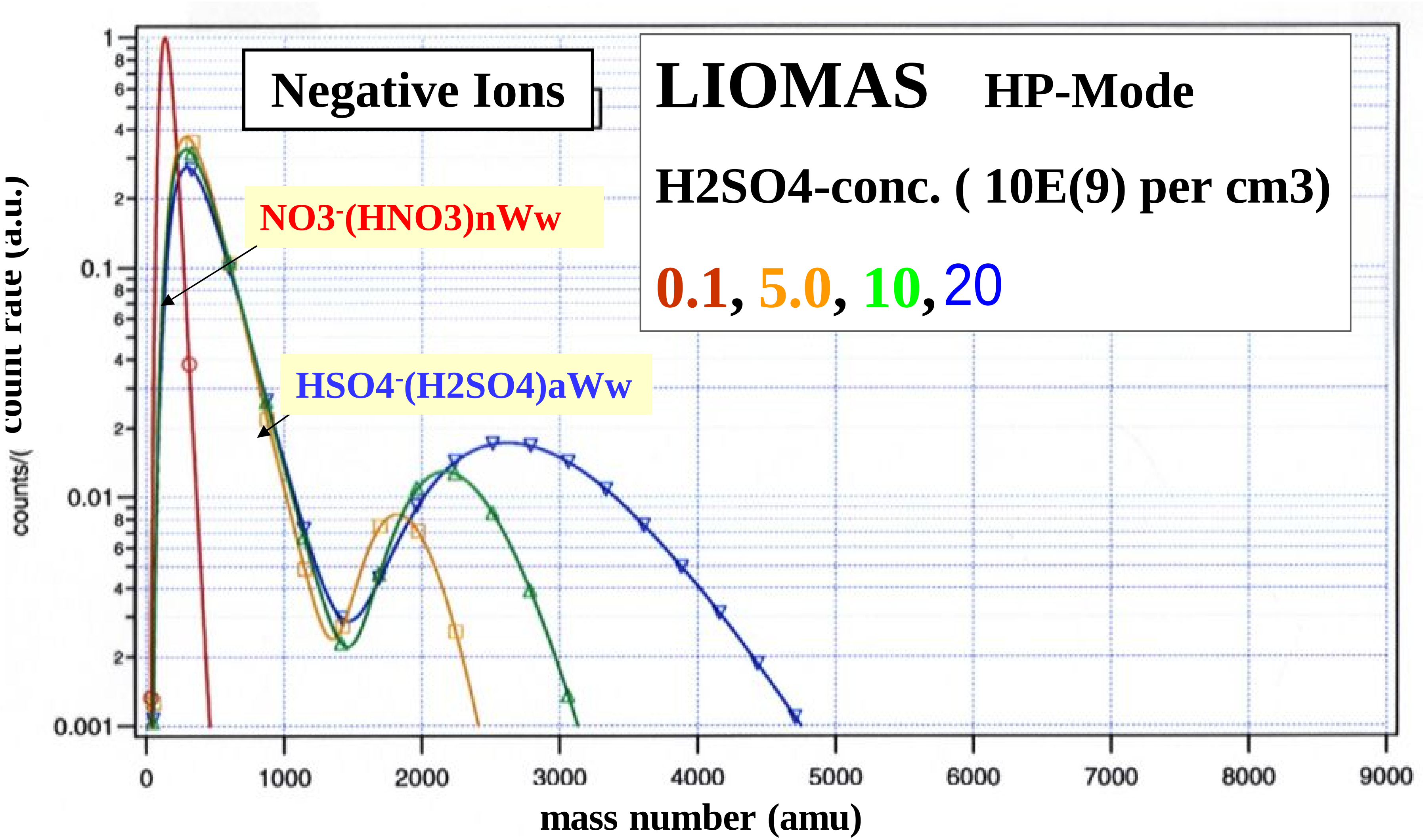
CID-Investigations (negative ions)

- Parent-Ion HSO_4-H_2SO_4 (mass number: 195)
- Fragment ions: HSO_4^- (97) ; $HSO_4SO_3^-$ (177)

Collision-Induced-Dissociation (CID) of mass seleced ion 195 (at two collision-energies)



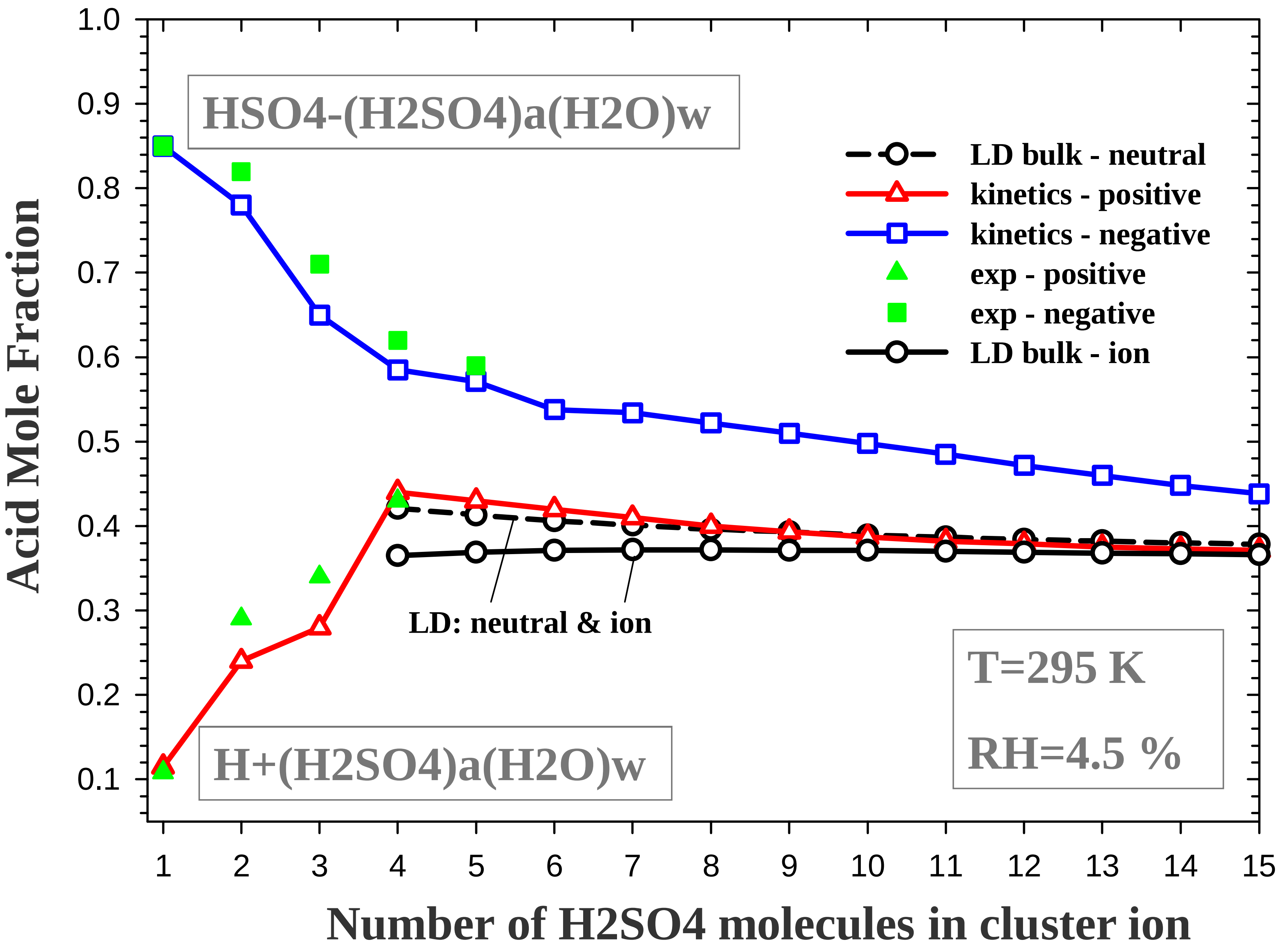
from Arnold (review)



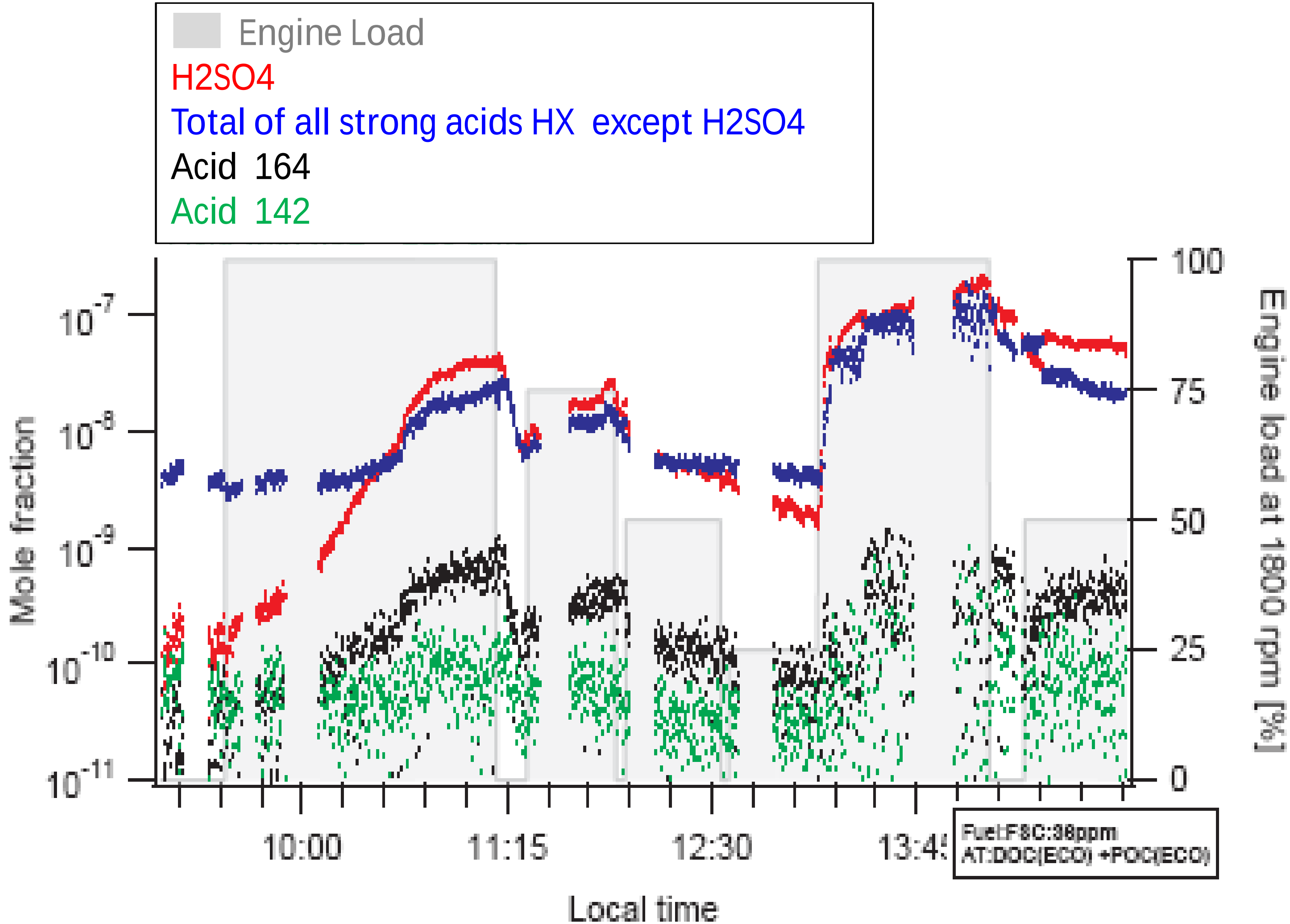
FLOW REACTOR EXPERIMENT: Ion-Nucleation

T=295 K , RH= 4.7 % , RA< 2.0 % → no HONU ! , tres = 0.9 s / tr/tc = 10 , 20 , 40

A. Sorokin, D. Wiedner, and F.Arnold (2006)



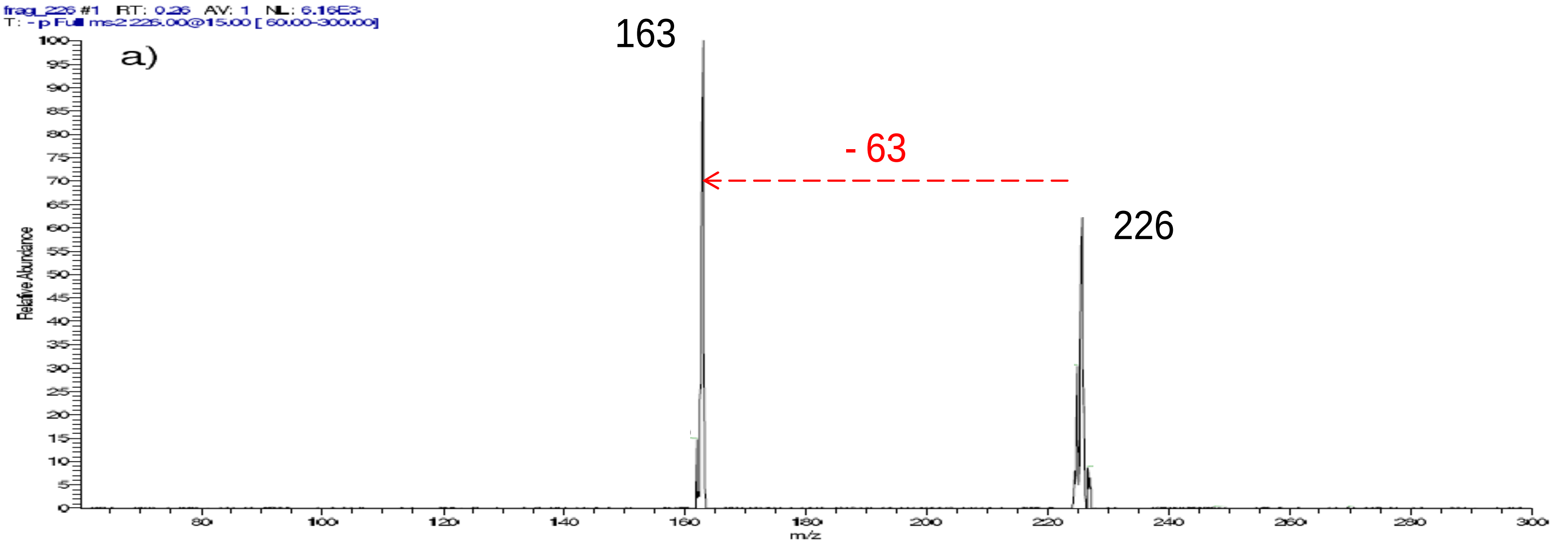
Time series of gas-phase H2SO4 (mole fract. in raw exhaust):
FSC = 36 ppm ; ATS (DOC (ECO) + POC (ECO)

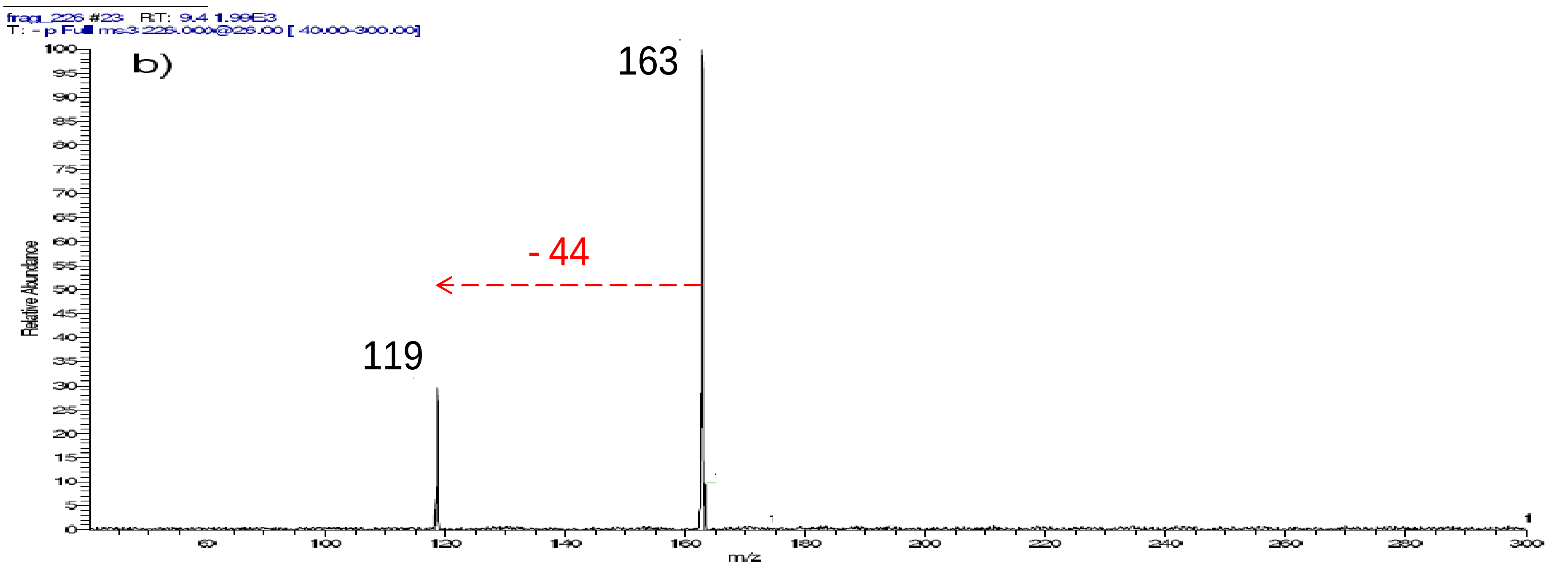


CID-Investigations (negative ions)

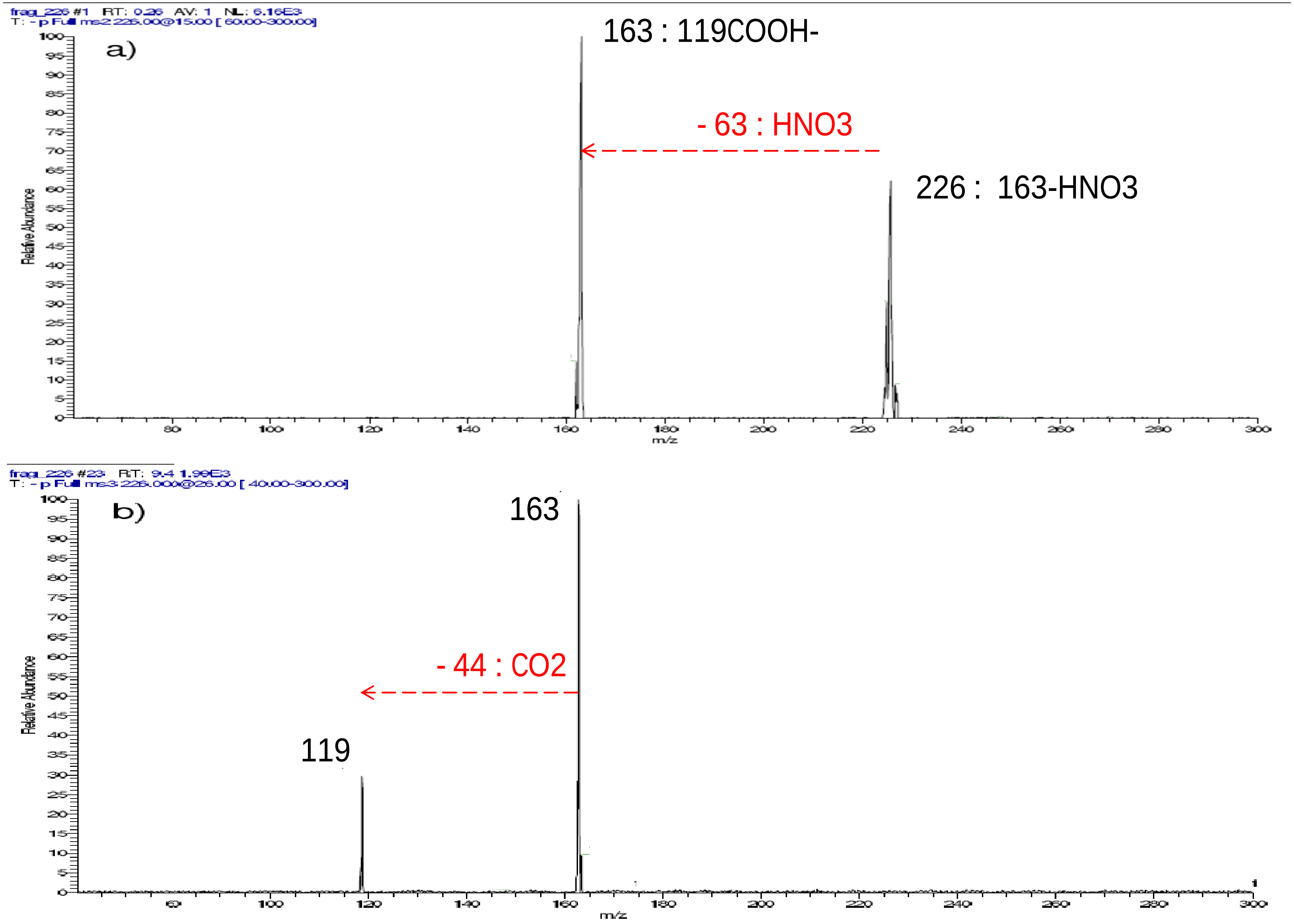
- Parent-Ion (mass number: 226) for 2 collision energies:
- Fragment ions: HSO_4^- (97) ; $HSO_4SO_3^-$ (177)

CID (MS-2) of PARENT-ION 226- (at two collision-energies)





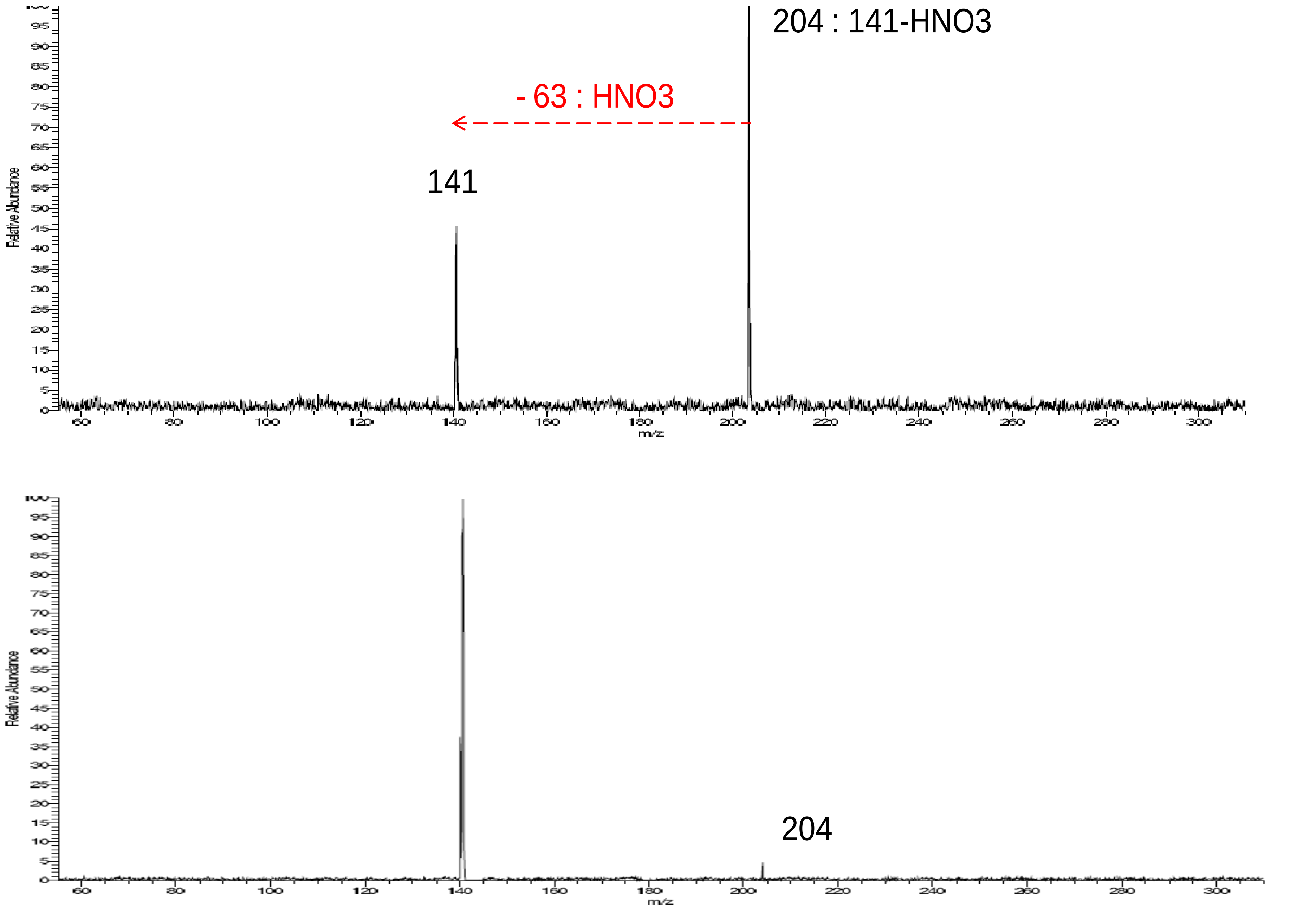
CID (MS-2) of PARENT-ION 226- (at two collision-energies)



CID-Investigations (negative ions)

- Parent-Ion (mass number: 204-) for 2 collision energies:
- Fragment ions: 163- ; 141-
- Neutral fragment 63 (probably HNO3)
- Neutral fragment 44 (probably CO2; if so, indication that ion 163- is de-protonated carboxylic acid)

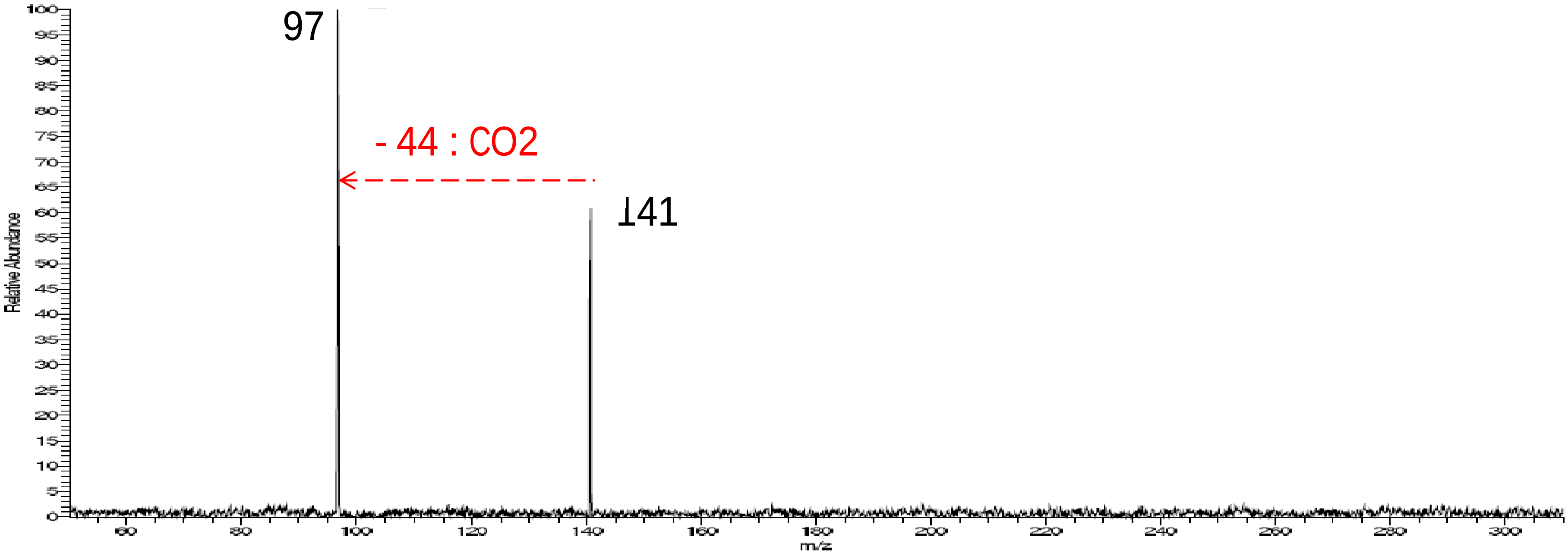
CID (MS-2) of PARENT-ION 204- (at two collision-energies)

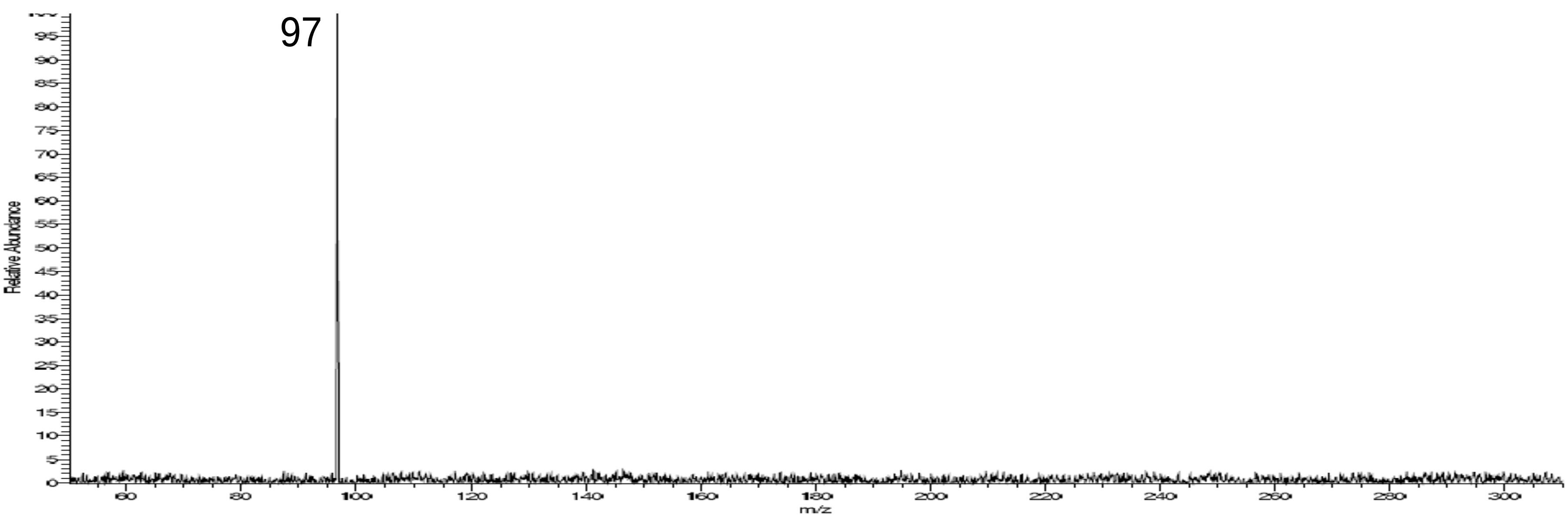


CID-Investigations (negative ions)

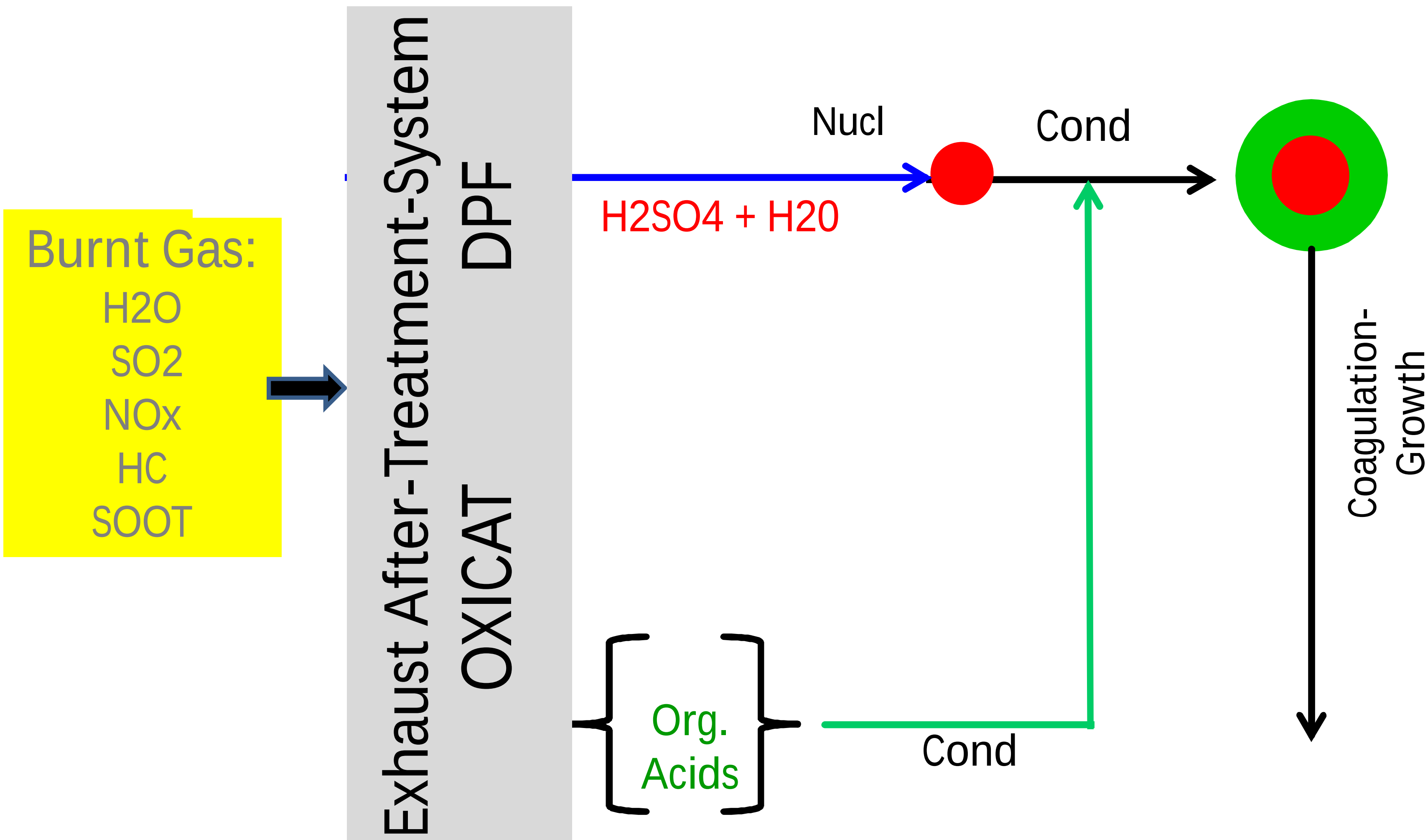
- Mass selected First-Generation Fragment-Ion (mass number: 141) for 2 collision energies:
- Second-generation fragment ion 97
- Neutral fragment: 44 (probably CO_2; if so, indication that ion 141- is de-protonated carboxylic acid)

CID (MS-3) of FRAGMENT-ION 141- (at two collision-energies)





Nucleation-Particle Formation in Diesel Vehicle Exhaust (simplified scheme without soot)



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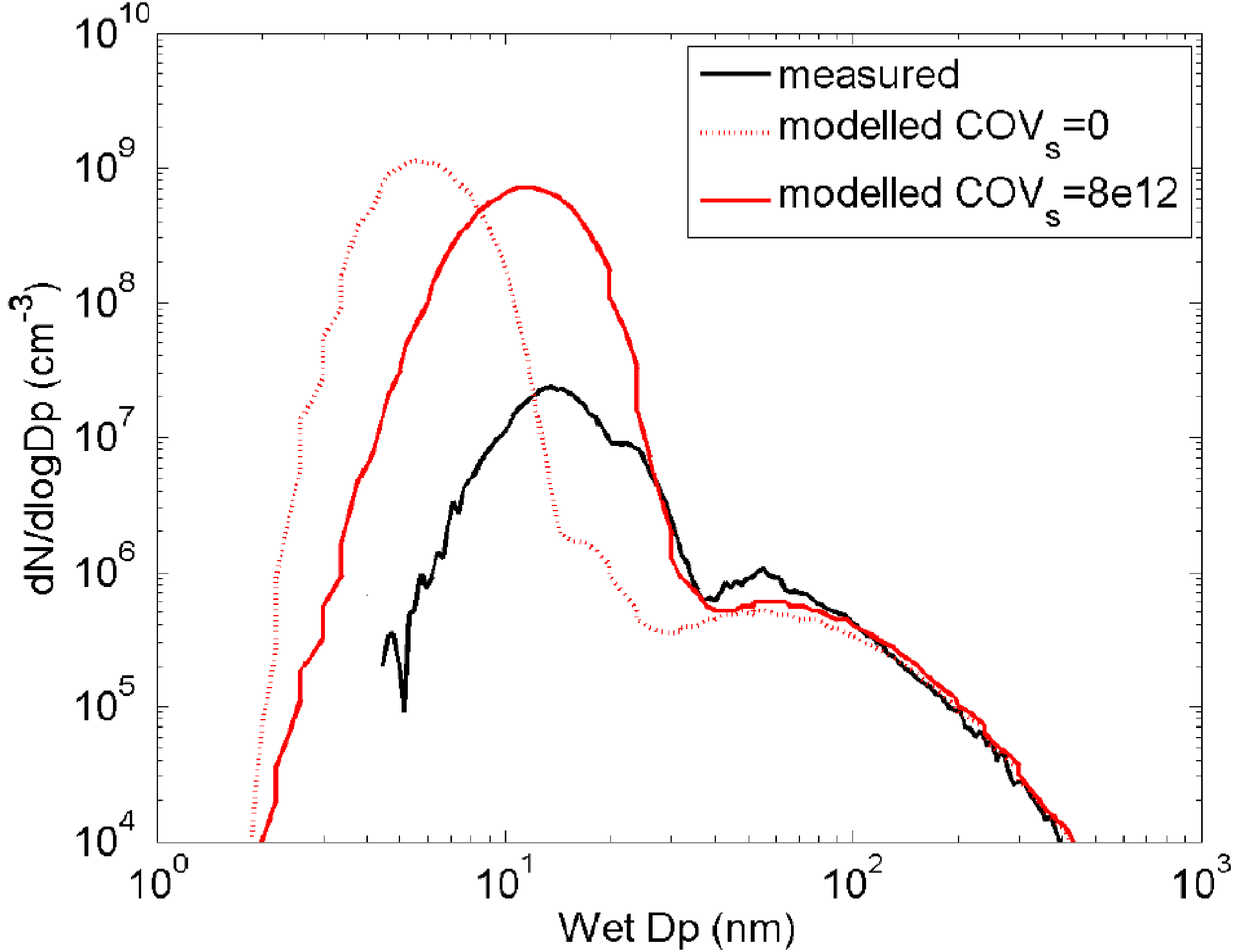
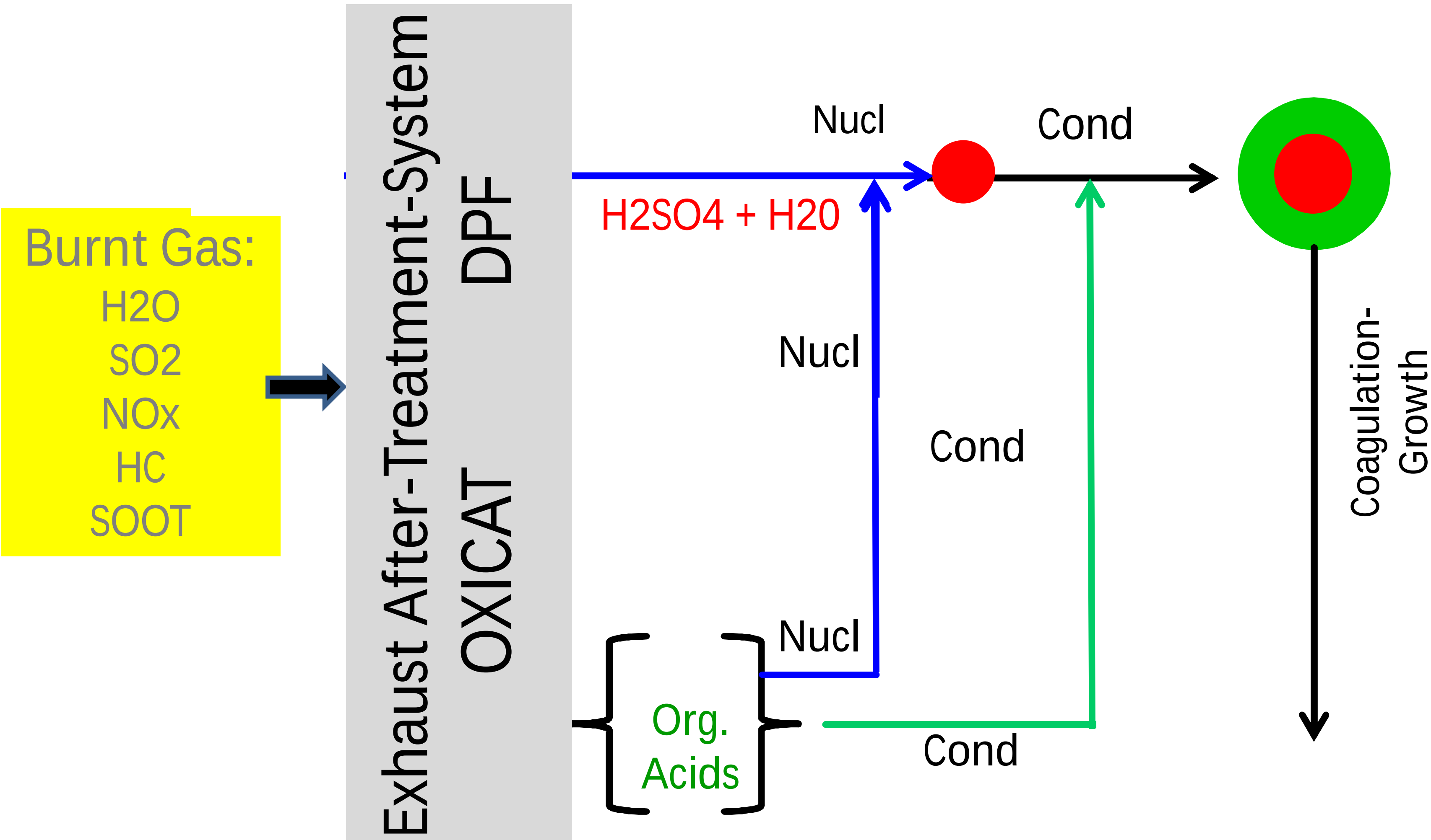
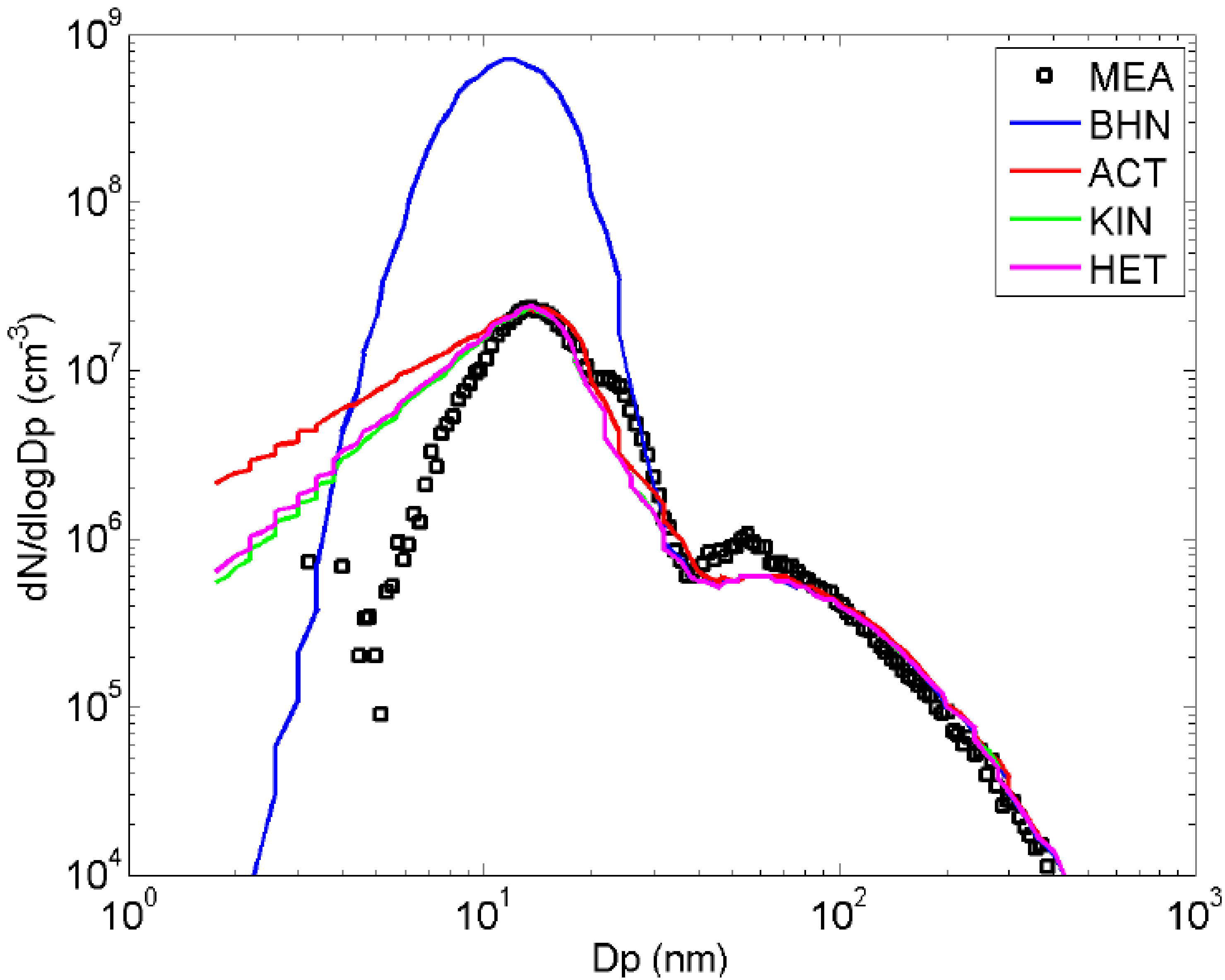


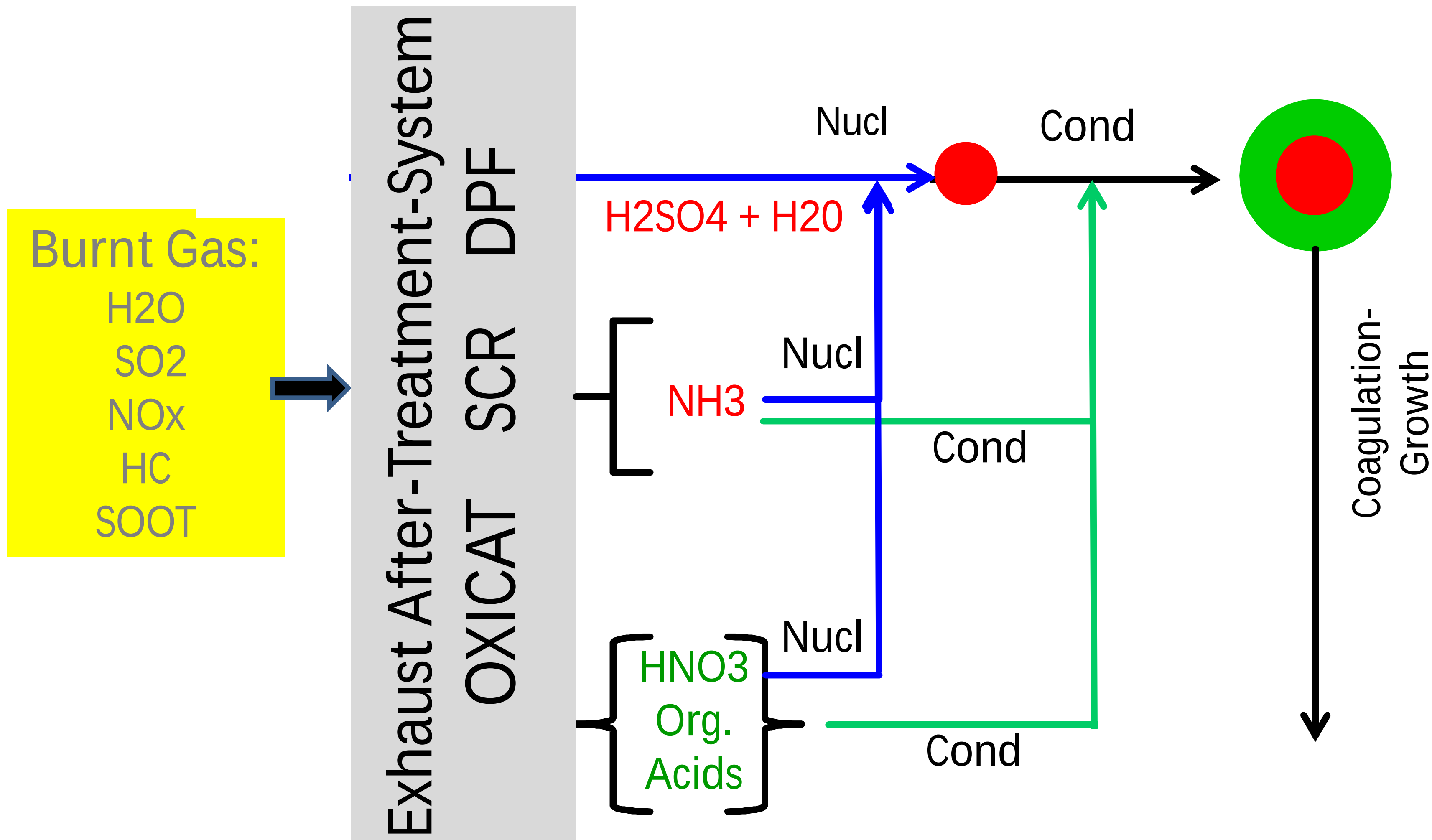
Nucleation-Particle Formation in Diesel Vehicle Exhaust
(simplified scheme without soot)



Particle Number Size Distribution : FSC = 36 ppm ; EL = 100 % ; ATS (DOC + OpenFilter)



Nucleation-Particle Formation in Diesel Vehicle Exhaust (simplified scheme without soot)



For more Information see:
references (following 2 slides)

Environmental Science & Technology

Article

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First Online Measurements of Sulfuric Acid Gas in Modern Heavy-Duty Diesel Engine Exhaust: Implications for Nanoparticle Formation

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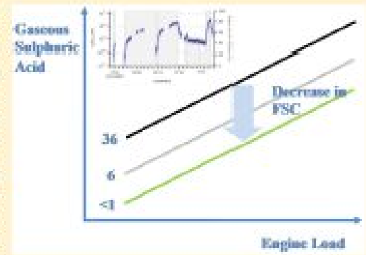
ABSTRACT: To mitigate the diesel particle pollution problem, diesel vehicles are fitted with modern exhaust after-treatment systems (ATS), which efficiently remove engine-generated primary particles (soot and ash) and gaseous hydrocarbons. Unfortunately, ATS can promote formation of low-vapor-pressure gases, which may undergo nucleation and condensation leading to formation of nucleation particles (NUP). The chemical nature and formation mechanism of these particles are only poorly explored. Using a novel mass spectrometric method, online measurements of low-vapor-pressure gases were performed for exhaust of a modern heavy-duty diesel engine operated with modern ATS and combusting low and ultralow sulfur fuels and also biofuel. It was observed that the gaseous sulfuric acid (GSA) concentration varied strongly, although engine operation was stable. However, the exhaust GSA was observed to be affected by fuel sulfur level, exhaust after-treatment, and driving conditions. Significant GSA concentrations were measured also when biofuel was used, indicating that GSA can be originated also from lubricant oil sulfur. Furthermore, accompanying NUP measurements and NUP model simulations were performed. We found that the exhaust GSA promotes NUP formation, but also organic (acidic) precursor gases can have a role. The model results indicate that that the measured GSA concentration alone is not high enough to grow the particles to the detected sizes.



INTRODUCTION

Exhaust aerosol particles emitted by traffic, especially by diesel vehicles, represent major air pollutants in cities and near motorways.[1−3] In order to minimize these emissions, modern diesel vehicles are fitted with exhaust after-treatment systems (ATS) which decreases efficiently the solid soot particle and gaseous emissions. Typically, the ATS with quasi-continuous regeneration involve a combination of a diesel particle filter (DPF) [4] and a diesel oxidation catalyst (DOC).[5] The most efficient DPFs are so-called wall-flow DPFs, which trap more than 95% of the soot particles. However, wall-flow DPFs are subject to relatively rapid clogging by soot; thus, they require active regeneration and, e.g., fuel additives. Nearly continuous soot regeneration is often achieved by NO_2-induced soot burn up. The NO_2, which acts as an oxidant already at typical heavy-duty diesel exhaust temperatures, is generated by catalytic conversion of engine-generated NO using a DOC upstream of the DPF. Unfortunately, the oxidative exhaust after-treatment may also generate undesired oxidation products. A striking example is SO_3, which is formed by oxidation of engine-generated SO_2 and reacts with water vapor, leading to gaseous sulfuric acid (GSA).[6,7] GSA has a very low saturation vapor pressure, and therefore, it may condense and even nucleate in the cooling dilution process of the exhaust. Thus, the existence of GSA can lead to formation and growth of sulfuric acid−water particles, a particular form of nucleation particles (NUP). Due to the small sizes the NUP can intrude the lowest compartment of the human lung.[3,8,9] Other possible oxidation products are partially oxidized hydrocarbons. These may include also condensable gases, particularly organic diacids, some of which possess very low vapor pressures and therefore would be potential condensing and eventually even nucleating gases. In fact, organic diacids have been observed in car exhaust.[10,11] Additionally, oxidation products may include also carcinogenic compounds like oxygenated polycyclic organic compounds, particularly ones bearing a NO_2 group (Nitro-PAHs), whose formation may be promoted by NO_2, and some of which may

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doi:10.5194/acp-15-10435-2015

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Model studies of volatile diesel exhaust particle formation: are organic vapours involved in nucleation and growth?

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Conclusions

- Numerous acidic gases HX with gas-phase acidities GA (HX) >GA (HNO_3) detected in modern Diesel- exhaust
- H_2SO_4 has an important role in NUP formation, but does not seem to be the only relevant nucleating gas
- NUP growth promoted by condensing gases (including also carboxylic di-acids ?)
- As NUP grow, the Kelvin-Effect decreases and more gaseous species may condense on grown NUPs
- We look foreward to greatly improved measurements. We have recently increased (by factor up to 120 !) the sensitivity of our trace gas and gas-phase ion detection instrument

Thank You

for your interest