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V. Boudon, D. Bermejo, J. Vander Auwera, G. Ducros, S. Reymond-Laruinaz,
D. Doizi, L. Manceron

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SENSING RUTHENIUM TETROXIDE EMISSIONS : A SPECTROSCOPIC STUDY

ANR/DECA-PF

GDR HiResMIR 2015 | S, REYMOND-LARUINAZ, D. DOIZI, L. MANCERON, V. BOUDON, D. BERMEJO, J. VANDER AUWERA, G. DUCROS

16 OCTOBER 2015

DE LA RECHERCHE À L'INDUSTRIE

cea den

Feedback from Fukushima

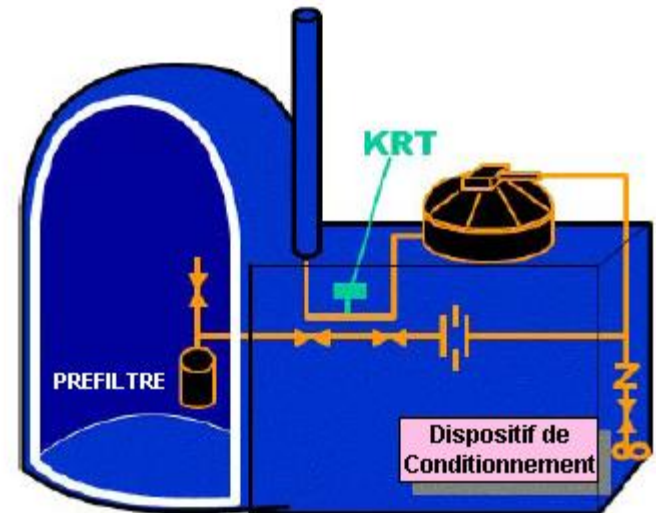
- During the accident information on the nuclear core state was missing
 - No fission products monitoring during the first 12 days, only the dose rates, difficult to use for online diagnosis,
 - First measurements announced with little reliability for low volatile fission products

- Report of the IAEA expert mission in June 2011
 - L13 : « ... improve and refine the existing methods and models to determine the source term involved in a nuclear accident ... »

- Measurement of fission products as a diagnostic tool in support to emergency services ("reliable measurements ", "at the earliest" and "closer" of the emission source)
 - Measure the releases from the nuclear reactor core and not from the spent fuel pools
 - Detect an advanced degradation state with extensive fusion of the nuclear reactor core

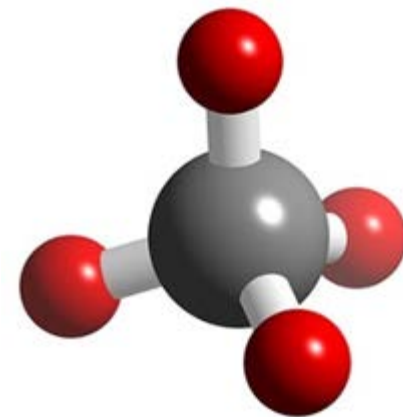
DECA-PF : diagnosis of core degradation from fission products measurements

- Strengthen the existing instrumentation of the PWR plants with additional measurement systems of the fission products (FP) placed downstream the Filtered Containment Venting System
 - Robustness, autonomy in harsh environment
 - Remote operable system
- Diagnostic tool of nuclear core degradation state
 - Online quantification of released fission gas
- Improve the evaluation of environmental releases
 - Discrimination between aerosols and gaseous forms
 - Speciation of potential gaseous species of iodine and ruthenium



The Ruthenium tetroxide

- Ruthenium is a low volatile fission product. But in case of the rupture of the lower head by the molten corium, the air entering into the vessel oxidize Ru into gaseous RuO₄.
- Among gaseous fission products, the tetroxide of ruthenium RuO₄ is of prime importance since it has a significant radiological impact.
- RuO₄ may not be trapped by the Filtered Containment Venting Systems.
 - RuO₄ is a highly dangerous radiological gas
 - RuO₄ is a marker of the vessel rupture by molten corium



=> Necessity to monitor in real time the presence of RuO₄ in case of a severe accident

New sensor based on optical measurement

- RuO₄ has an isolated band in the infrared domain (ν_3 band) with a satisfactory signal intensity.
- Objective: To optically measure RuO₄ by FTIR and quantify it.
 - Optical measurement : Robust
 - Does not require a periodic calibration
 - Simple system in line, remotely operable
- Approach: Acquisition of high resolution IR spectra of RuO₄ and simulation of the signal to have a reference spectrum whatever the environmental conditions.
- RuO₄ is very reactive and easily reduced into contact with a surface:

Requires a synthesis and analytical process fully passivated.

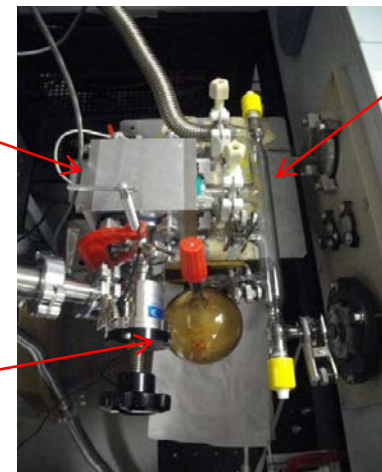
- Measuring cell and specific pressure sensors, fully passivated allowing sufficiently slow degradation of the product to not show too strong compositional changes over time of the analysis.
 - Glass cell (124 mm)
 - ZnSe windows treated AR reflexion
 - Kalrez seals and teflon valves
 - Pressure sensors developed at the French SOLEIL synchrotron facility whose surfaces exposed to the gas were passivated (res: 0.02 mbar)



Measuring cell

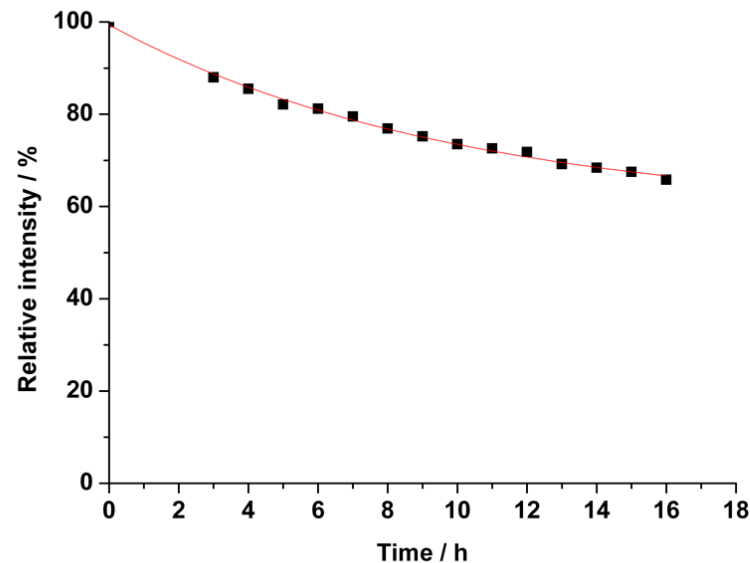
Pressure sensors

RuO₄ bulb

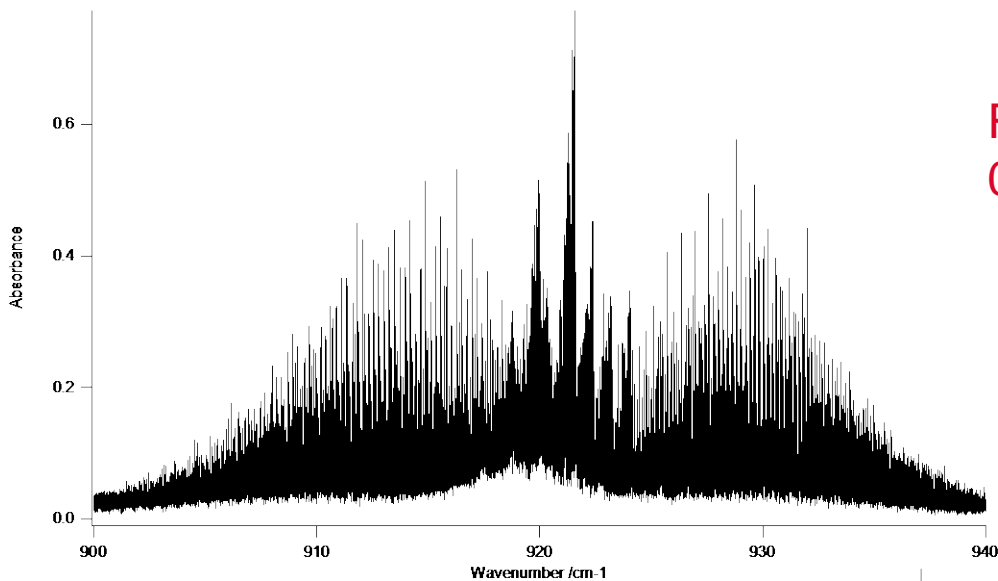


Ramp to the cell

RuO_4 ν_3 intensity decreases over time

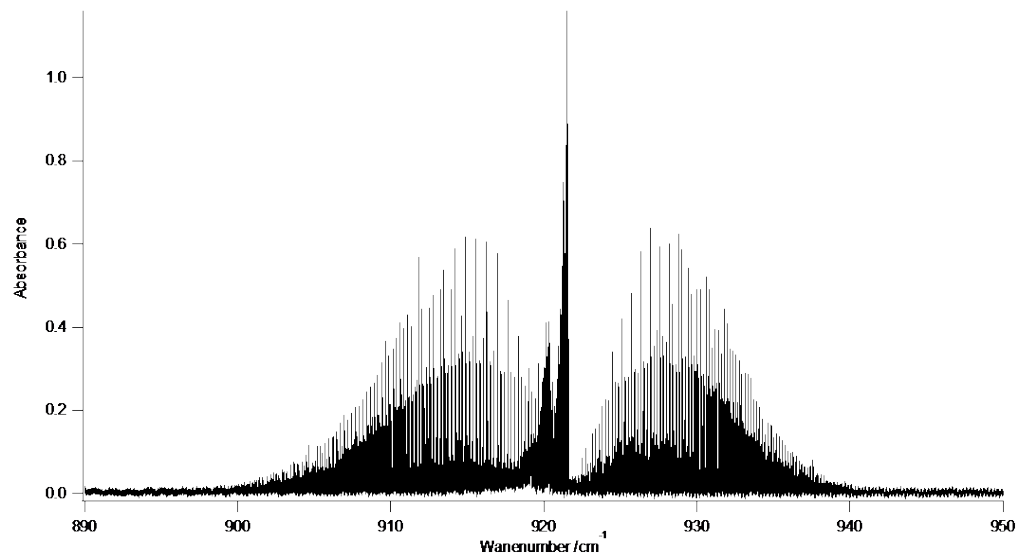


- Major issue of the RuO_4 analysis
=> Necessity to keep the sample in liquid nitrogen and to perform the analyses in a few hours.



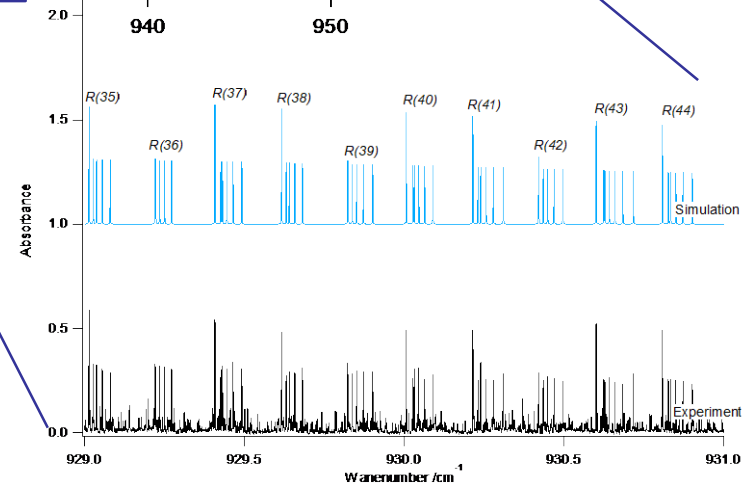
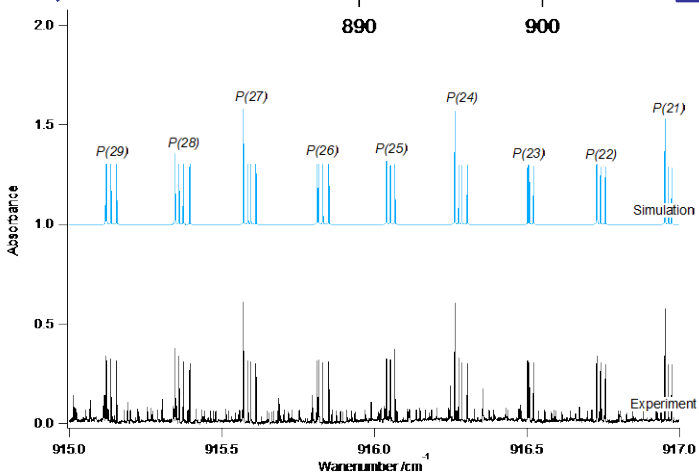
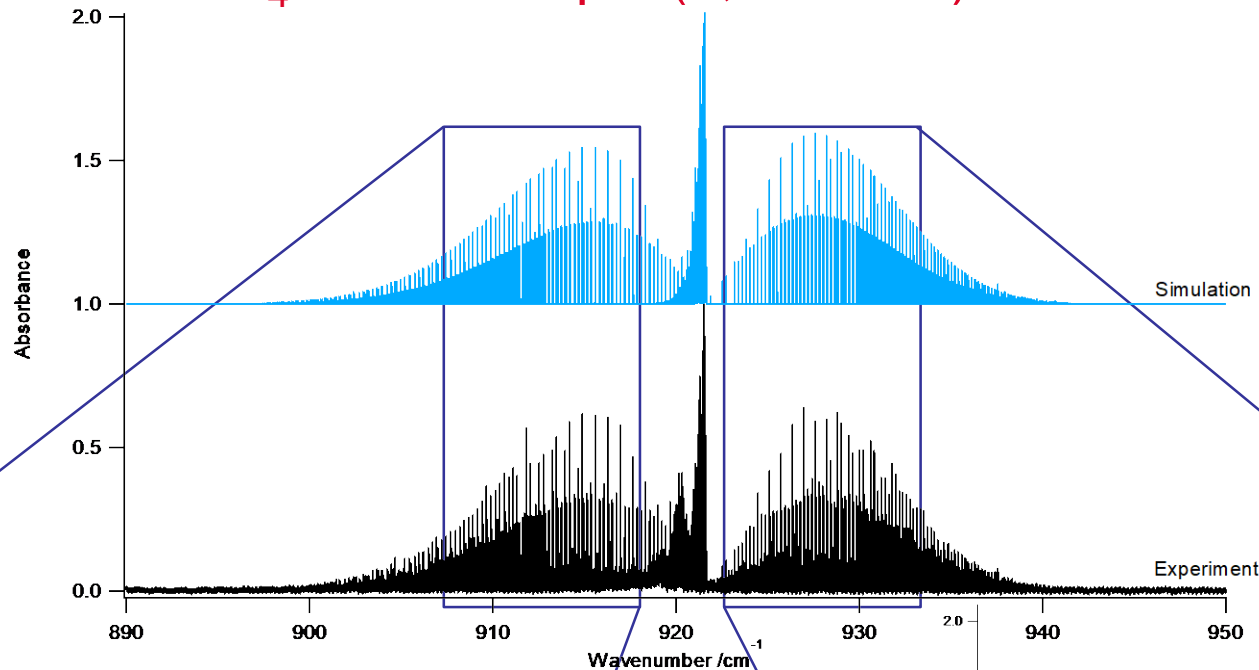
RuO₄ in natural abundance (680 scans ;
0,72 mbar)

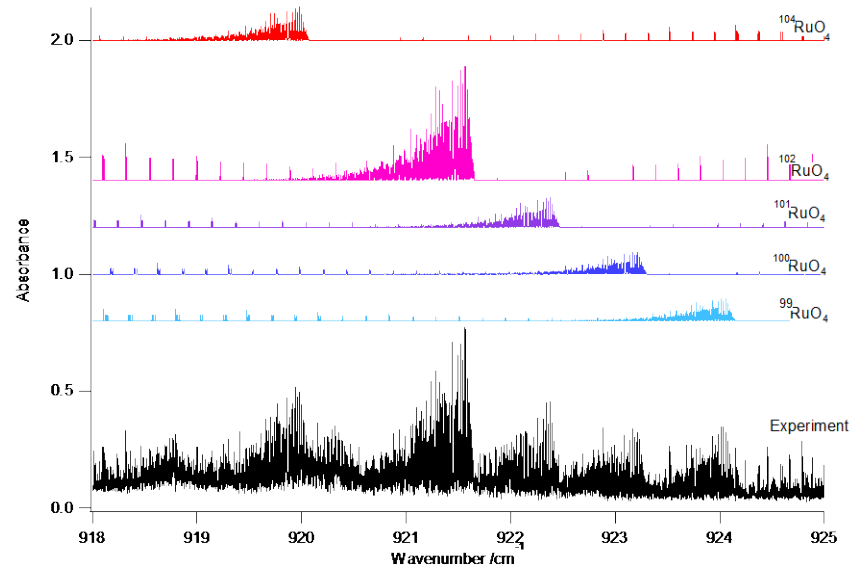
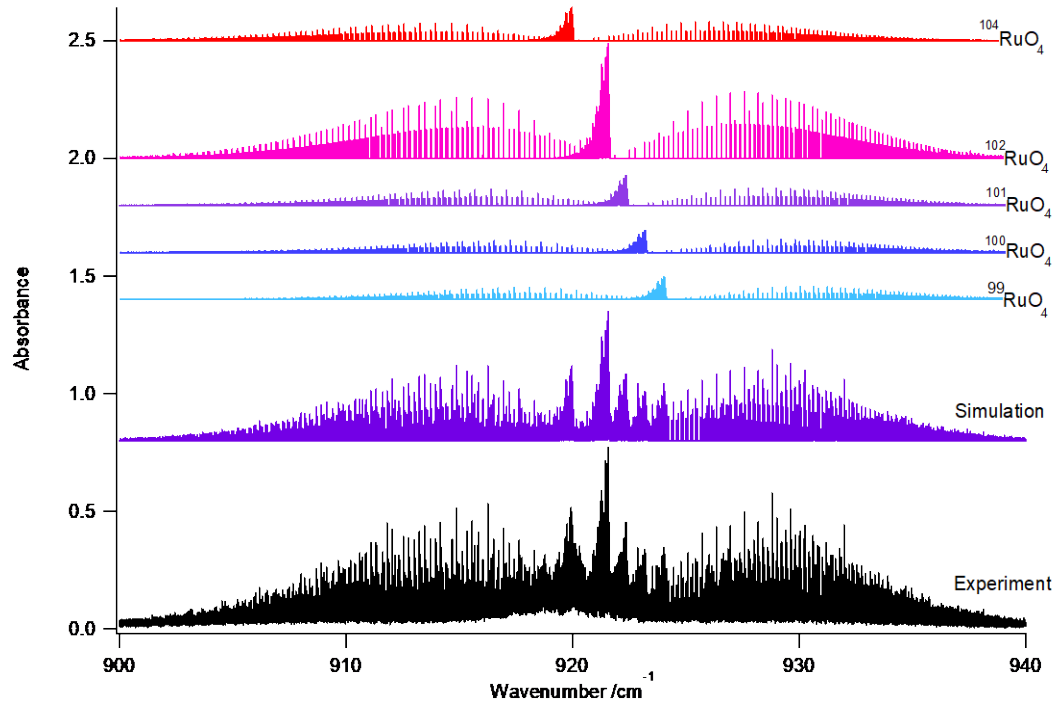
¹⁰²RuO₄ monoisotopic (300 scans ;
0,22 mbar)



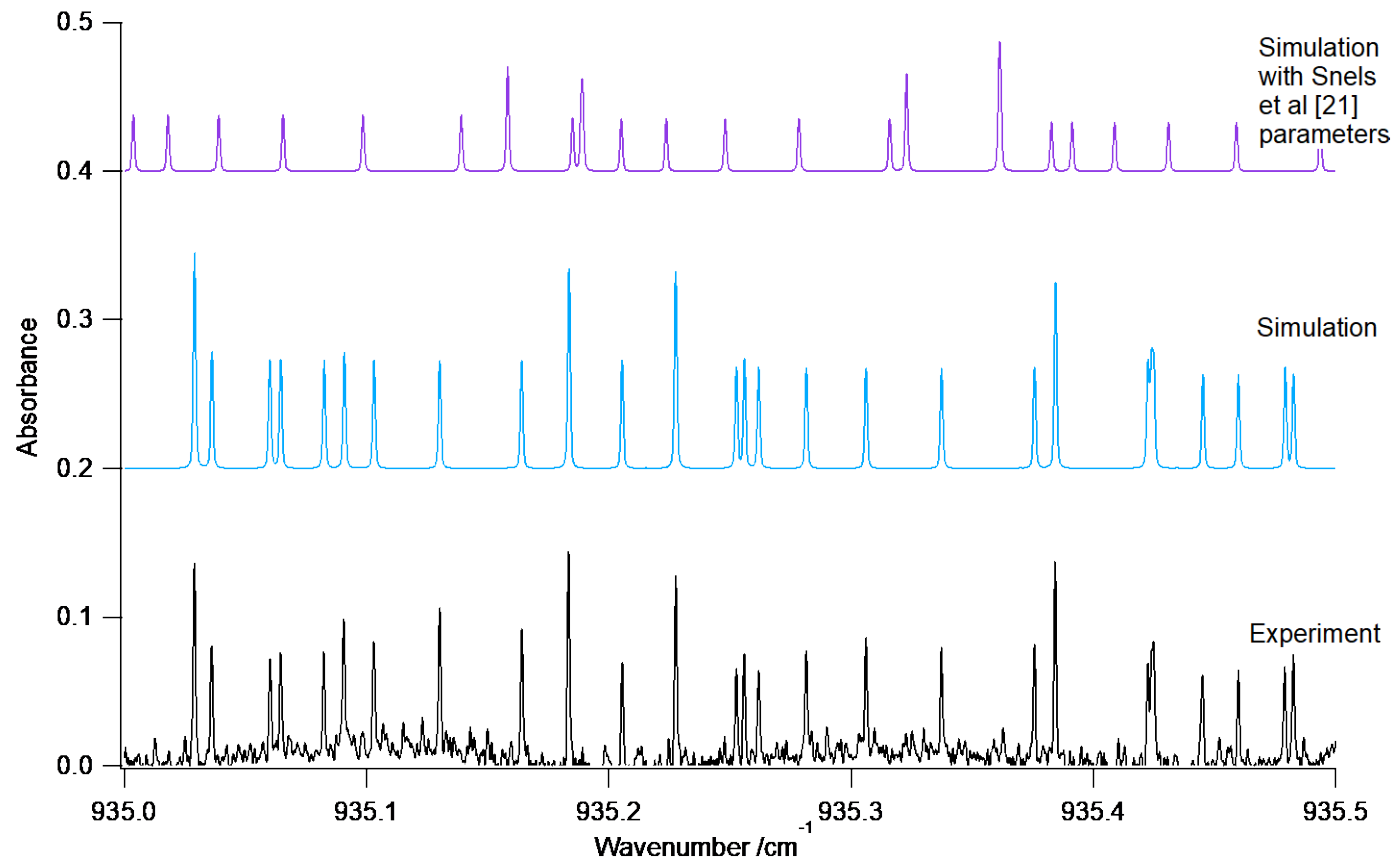
SIMULATIONS (XTDS, SPVIEW)

$^{102}\text{RuO}_4$ monoisotopic (0,22 mbar)

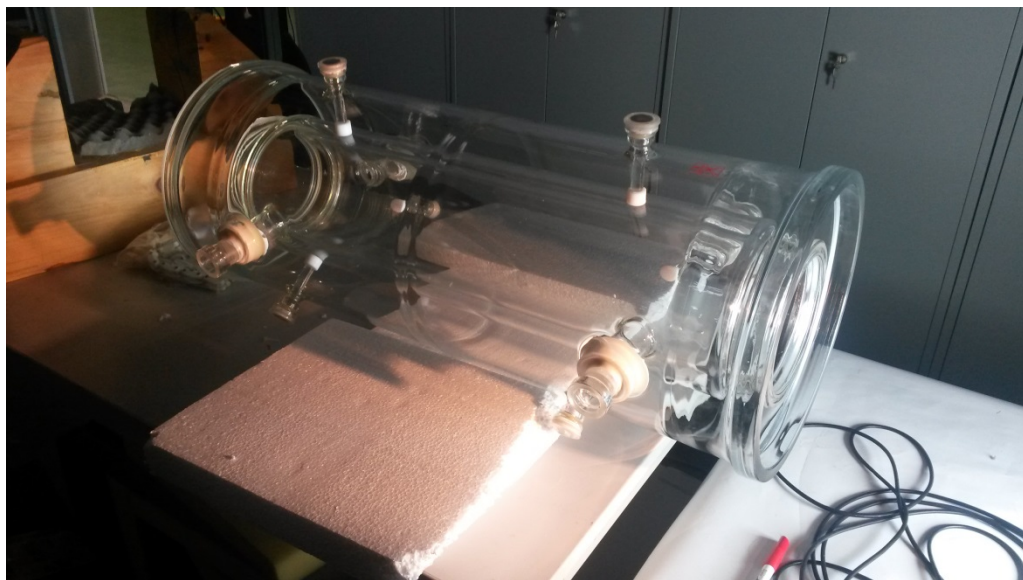
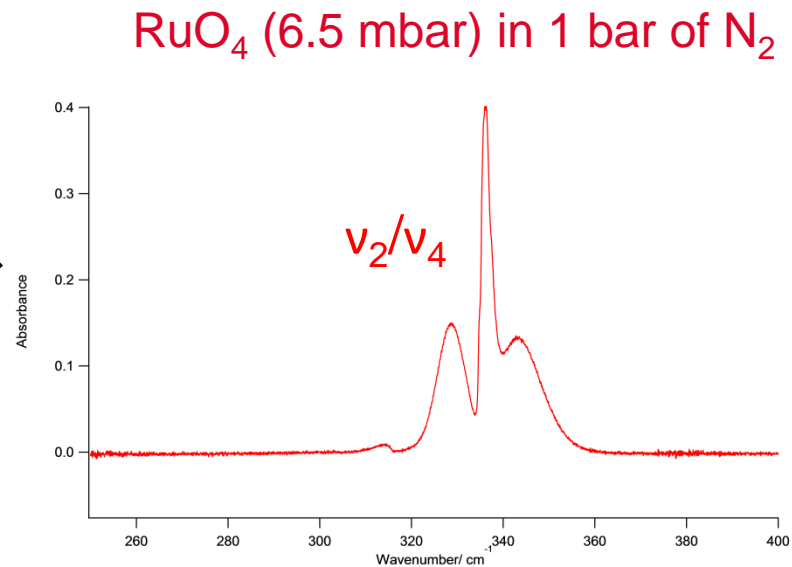
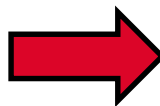
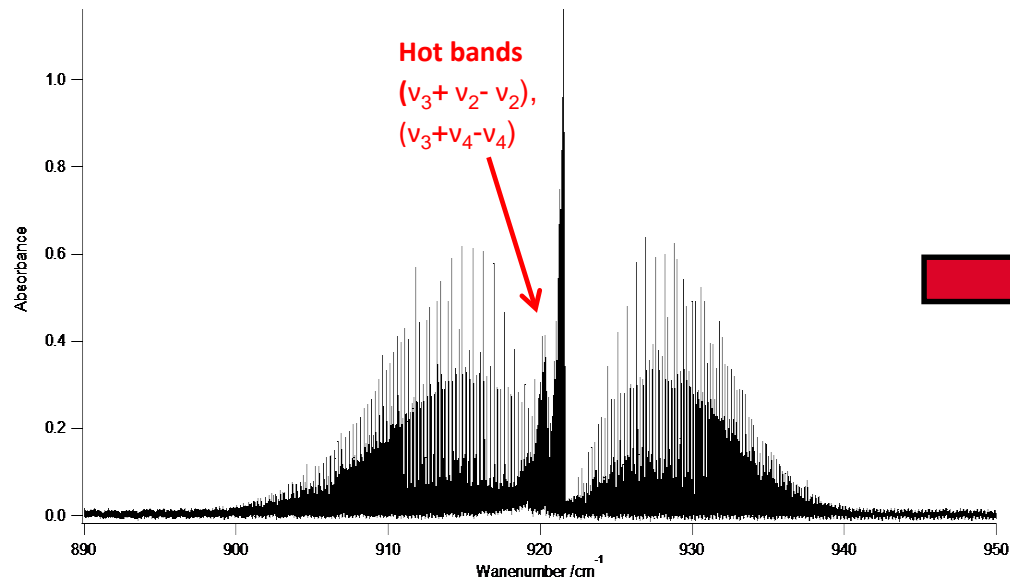


RuO₄ in natural abundance (680 scans ; 0,72 mbar)

Improving data



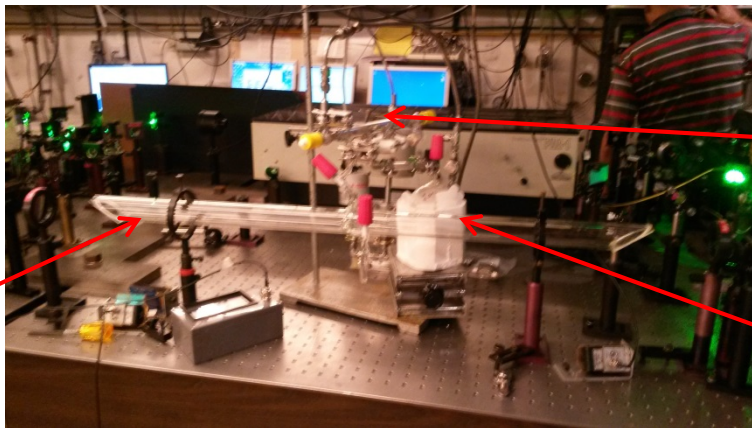
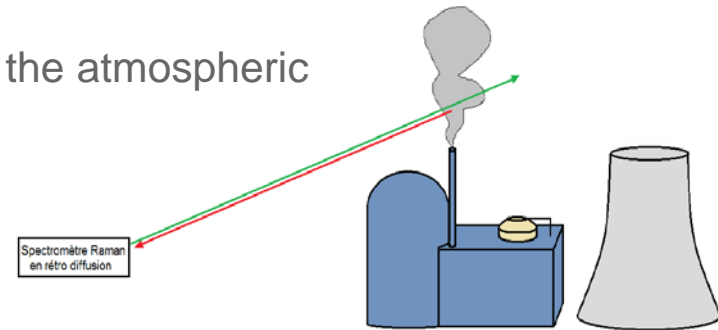
- Determination of the intensity parameters with the assistance of Jean Vander Auwera (Brussels University)



Development of a new cell
 totally passivated (coolable,
 optical path : 4.42 m)

Determination of the ν_1 band parameters by high resolution Raman spectroscopy (CSIC Madrid, D. Bermejo):

- Determination of the four fundamental parameters of RuO_4 ($\nu_1, \nu_2, \nu_3, \nu_4$)
- Possibility to develop a Raman LIDAR to measure the atmospheric emissions at the output of the chimney



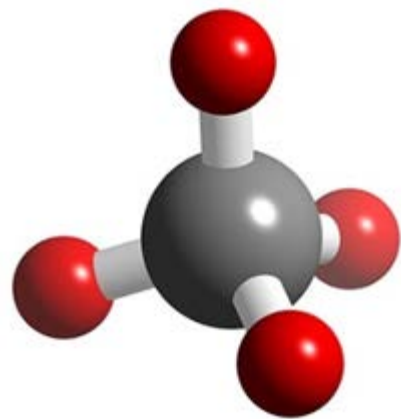
Measuring cell

Ramp to the cell

RuO_4 sample

Failure to record HR Raman spectrum : the Molecule is too photosensitive to withstand a high laser fluence

- Determined the hot bands parameters and make the assignment of intensities for a good match simulation/experiment
- Obtainment of reference spectra of RuO_4 according to the isotopic composition and environmental conditions
- Development of a new sensor based on a FTIR measurement (LIDAR, CES,...)



THANKS



Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Saclay | 91191 Gif-sur-Yvette Cedex
T. +33 (0)1 69 08 74 07

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