



HAL
open science

Sensing ruthenium tetroxide Emissions : a spectroscopic study

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

► **To cite this version:**

V. Boudon, D. Bermejo, J. Vander Auwera, G. Ducros, S. Reymond-Laruinaz, et al.. Sensing ruthenium tetroxide Emissions : a spectroscopic study. Journées du GDRI HiResMIR, Oct 2015, Creteil, France. cea-02509738

HAL Id: cea-02509738

<https://cea.hal.science/cea-02509738v1>

Submitted on 17 Mar 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



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

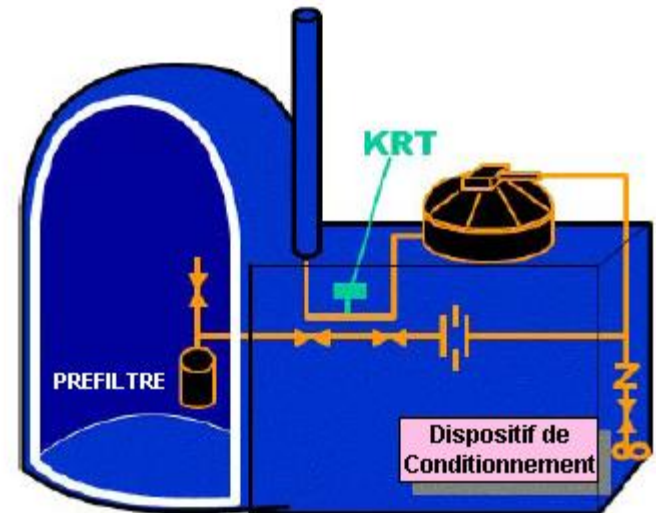
- During the accident information on the nuclear core state was missing
 - No fission products monitoring during the first 12 days, only the dose rates, difficult to use for online diagnosis,
 - First measurements announced with little reliability for low volatile fission products

- 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

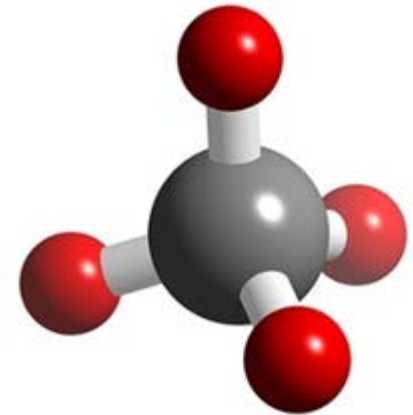
DECA-PF : diagnosis of core degradation from fission products measurements

- 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.

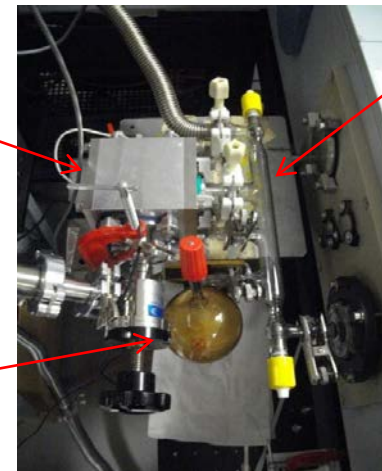
- Measuring cell and specific pressure sensors, fully passivated allowing sufficiently slow degradation of the product to not show too strong compositional changes over time of the analysis.
 - Glass cell (124 mm)
 - ZnSe windows treated AR reflexion
 - Kalrez seals and teflon valves
 - Pressure sensors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



Measuring cell

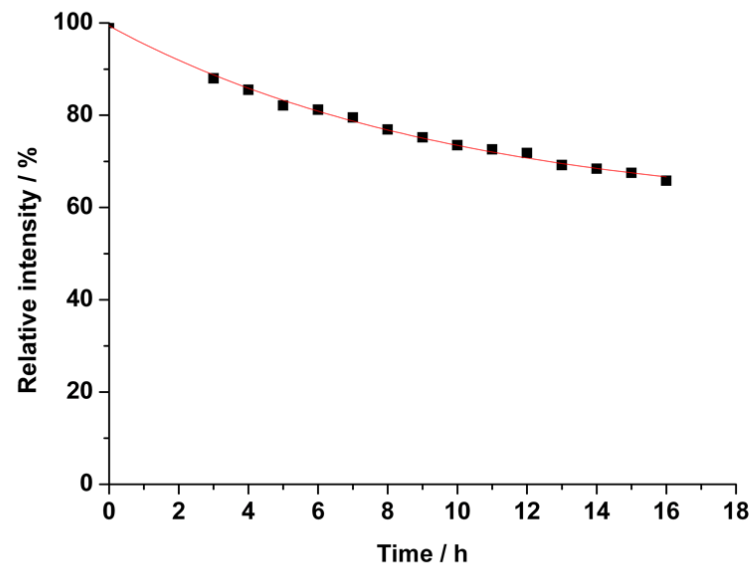
Pressure
sensors

RuO₄
bulb

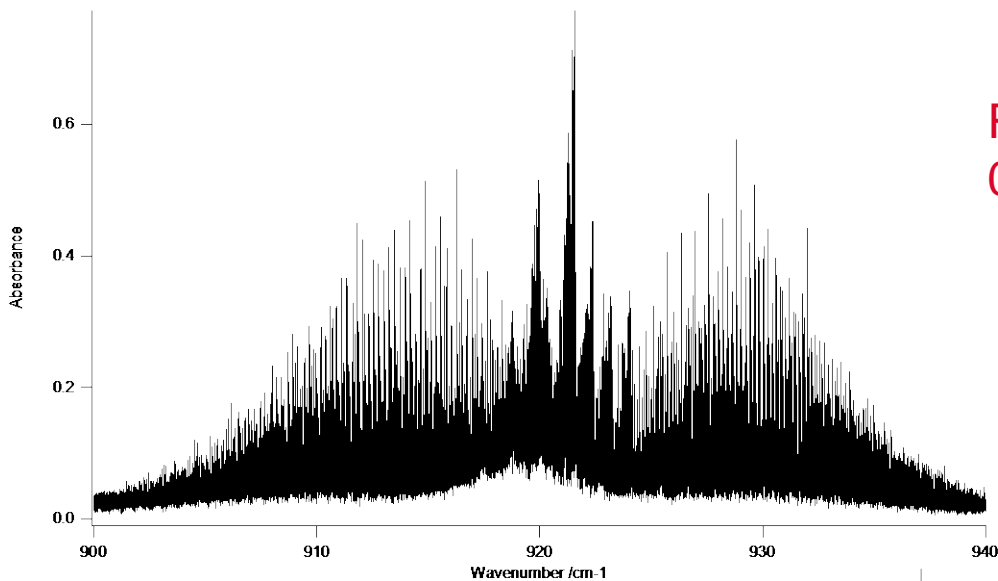


Ramp to
the cell

RuO_4 ν_3 intensity decreases over time

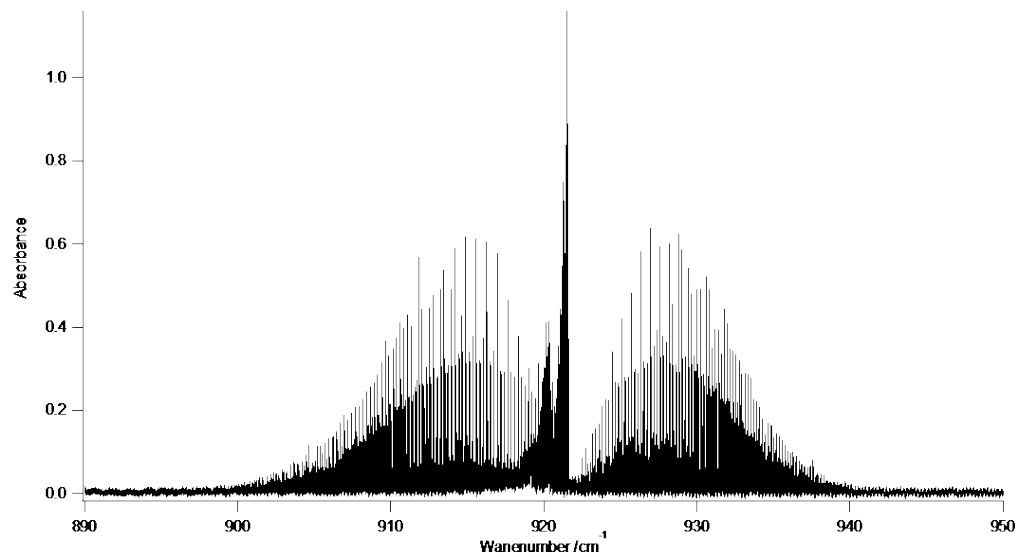


- Major issue of the RuO_4 analysis
=> Necessity to keep the sample in liquid nitrogen and to perform the analyses in a few hours.

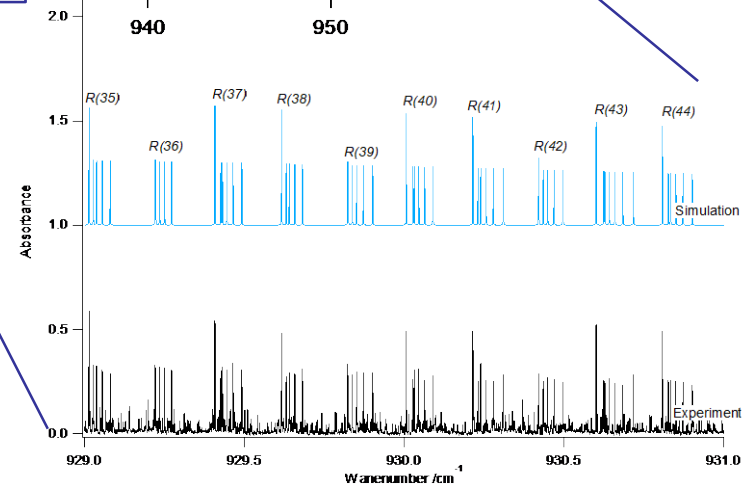
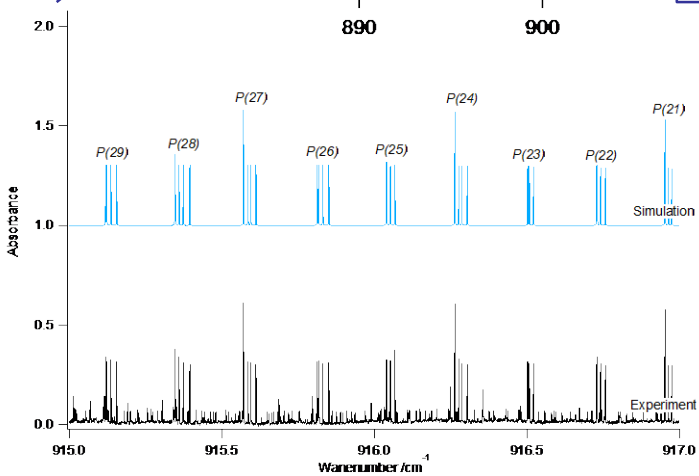
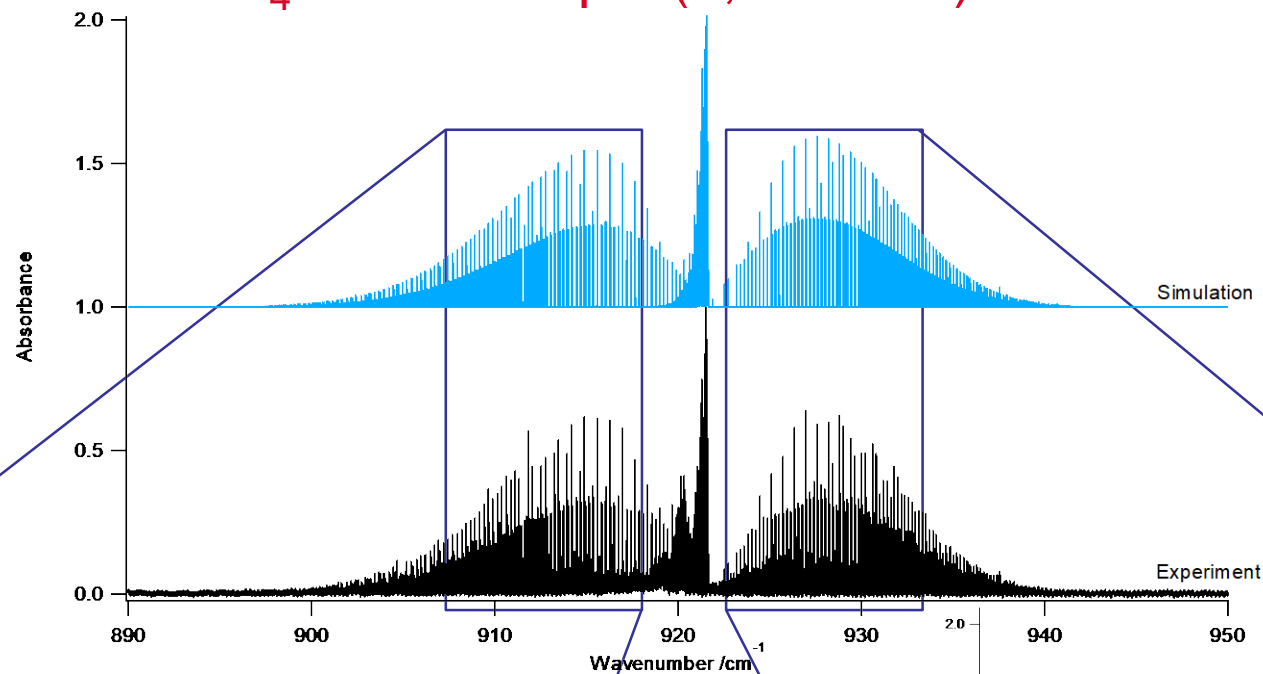


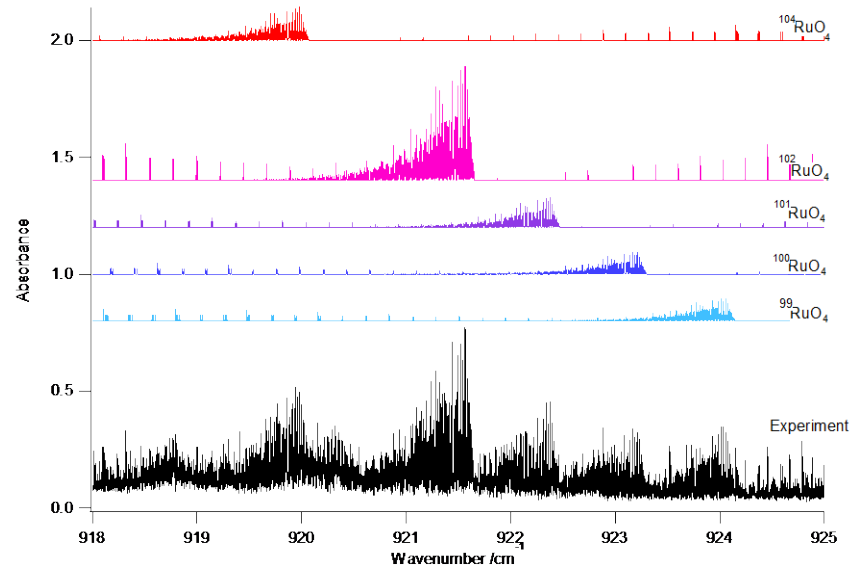
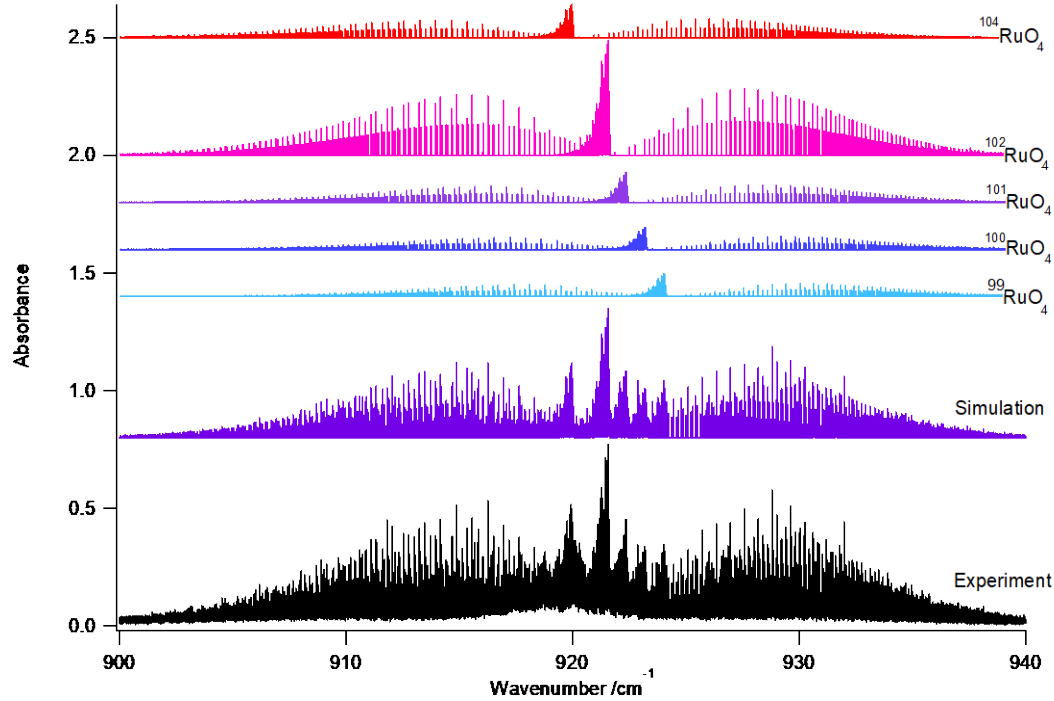
RuO₄ in natural abundance (680 scans ;
0,72 mbar)

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

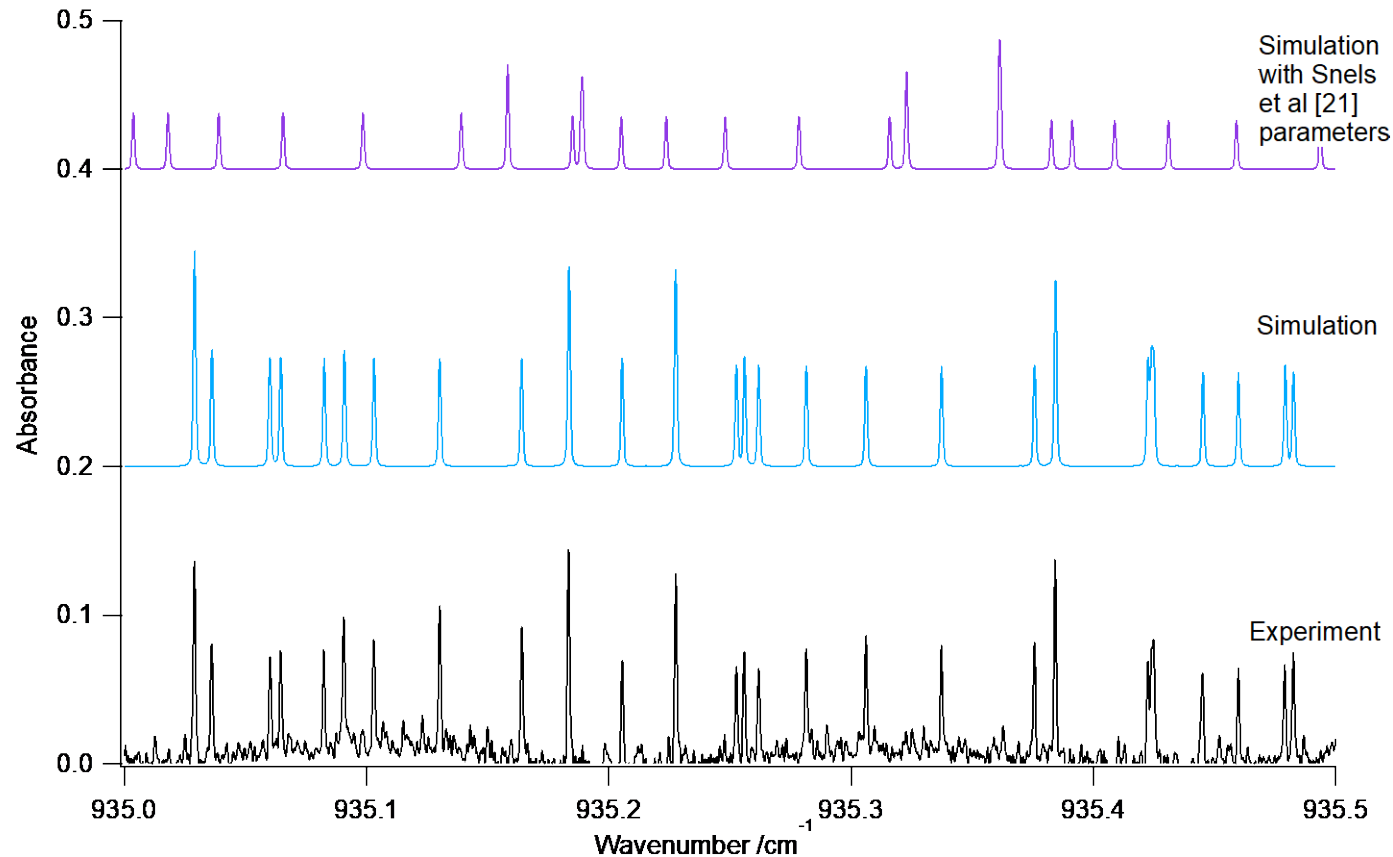


SIMULATIONS (XTDS, SPVIEW)

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

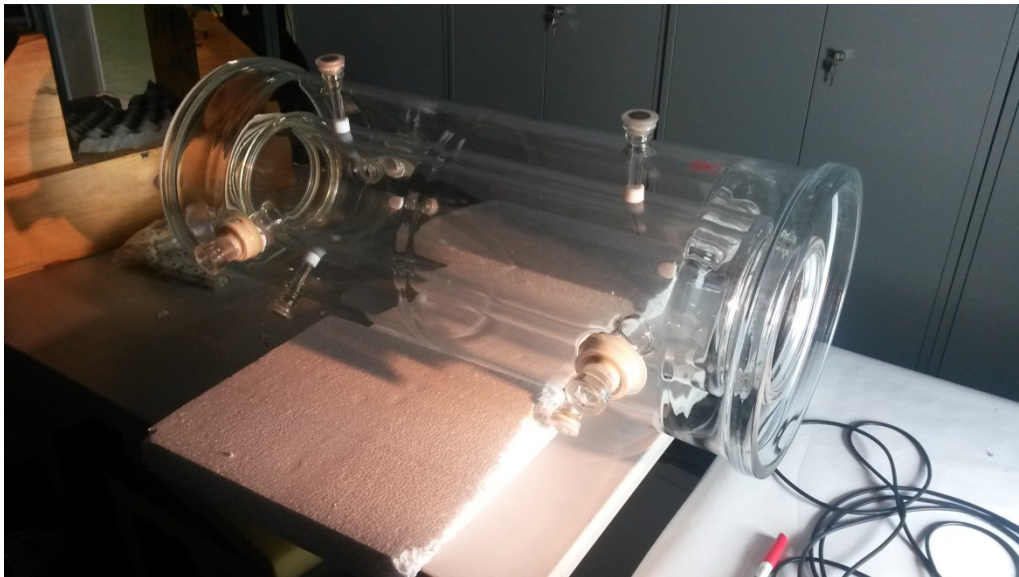
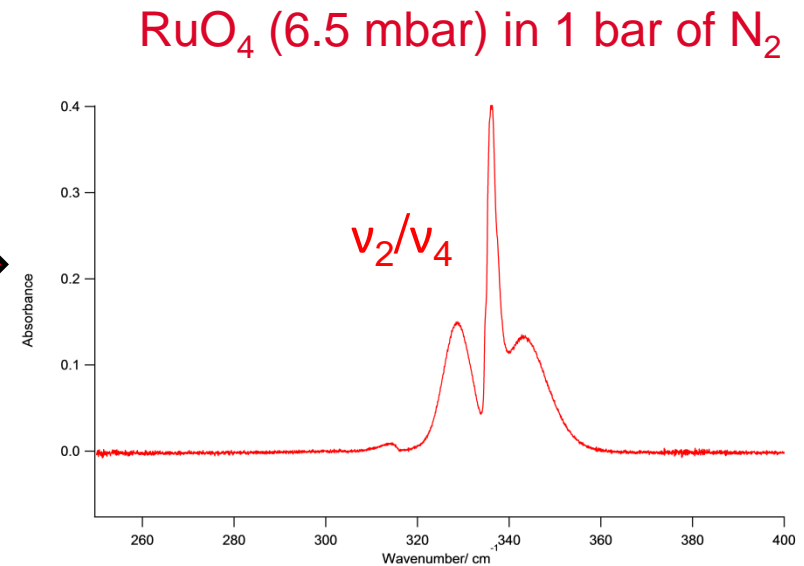
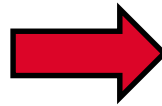
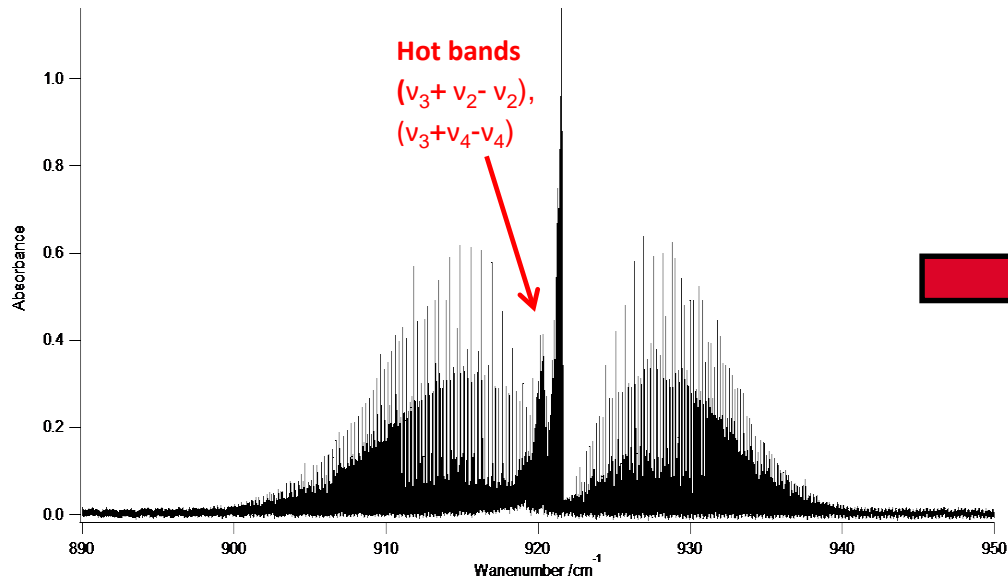
RuO₄ in natural abundance (680 scans ; 0,72 mbar)

Improving data



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

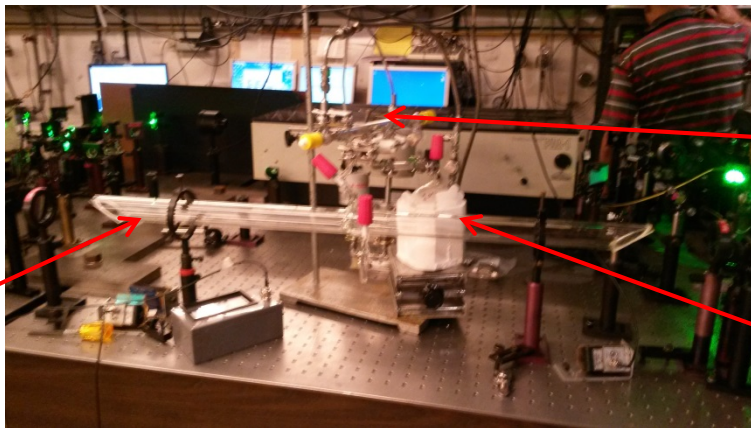
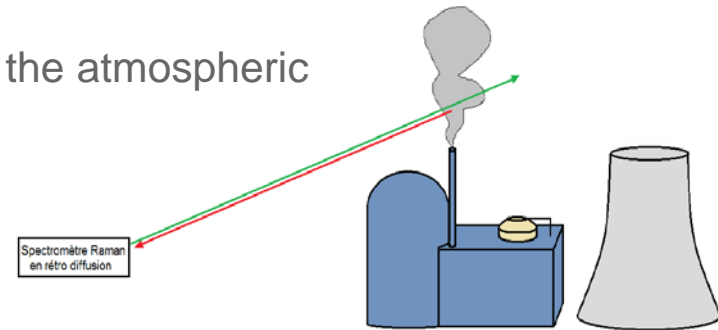
EXPERIMENTAL SPECTRA



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



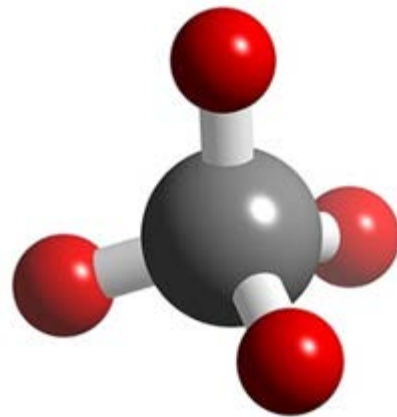
Measuring cell

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

Etablissement public à caractère industriel et commercial | R.C.S Paris B 775
685 019

DEN/DANS/DPC/SECR/LRMO