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On-line measurements of RuO_4 during a PWR severe accident

S. Reymond-Laruinaz[1]; D. Doizi[1]; L. Manceron[2,3]; V. Boudon[4]; G. Ducros[5]

***Abstract*– After the Fukushima accident, it became essential to have a way to monitor in real time the evolution of a nuclear reactor during a severe accident, in order to react efficiently and minimize the industrial, ecological and health consequences of the accident. Among gaseous fission products, the tetroxide of ruthenium RuO_4 is of prime importance since it has a significant radiological impact. Ruthenium is a low volatile fission product but in case of the rupture of the vessel lower head by the molten corium, the air entering into the vessel oxidizes Ru into gaseous RuO_4, which is not trapped by the Filtered Containment Venting Systems. To monitor the presence of RuO_4 allows making a diagnosis of the core degradation and quantifying the release into the atmosphere.**

To determine the presence of RuO_4, FTIR spectrometry was selected. To study the feasibility of the monitoring, high-resolution IR measurements were realized at the French synchrotron facility SOLEIL on the infrared beam line AILES. Thereafter, theoretical calculations were done to simulate the FTIR spectrum to describe the specific IR fingerprint of the molecule for each isotope and based on its partial pressure in the air.

I. Introduction

THE Fukushima accident showed a lack to monitor in real time the evolution of a nuclear reactor during a severe accident. In particular no fission products measurements were available during the first twelve days, only dose rates were registered, which is not sufficient to perform a reliable online diagnosis of the event. In addition, the first measures relative to low volatile fission products were often not consistent. In order to improve the safety of nuclear plants and minimize the industrial, ecological and health consequences of a severe accident, it is necessary to develop new reliable measurement systems [1]. Through the French program ANR « projet d'investissement d'avenir », the aim of the DECA-PF project (diagnosis of core degradation from fission products measurements) is to monitor in real time the release of the major fission products (krypton, xenon, gaseous forms of iodine and ruthenium, aerosols) outside the nuclear reactor containment. These products are released at different time during a nuclear accident and at different states of the nuclear core degradation. Thus, monitoring these fission products gives information on the situation inside the containment and helps to assess the radiological impact into the environment. This paper focuses on RuO_4 measurement by optical IR absorption spectroscopy**.**

II. Severe accident

A severe accident could occur if these events happen:

- the loss of the primary cooling due to an initiating event,
- the partial or total failure of backup systems.

The consequences could be the fusion of the core (resulting in the formation of a mixture of molten materials called corium) and the release of radioactive materials into the primary circuit, and then into the containment. So the severity of the accident depends on the degree of damage of the fuel and the degree of confinement loss. During a severe accident, various physical phenomena may occur and lead to the release of fission products from the fuel to the containment [2]:

- emptying of the core ("uncovering" or "dewatering"),
- heating of the fuel rods, and then oxidation of the cladding by the water steam (very exothermic reaction),
- degradation of the fuel rods and rupture of the claddings,
- fusion of materials (claddings, fuels, structural materials),
- volatilization and release of fission products, which are transported in gaseous or aerosol forms, in the primary circuit, by the hot gases from the core (steam and hydrogen), and then deposited inside the primary circuit and / or transferred in the containment,
- breakthrough of the vessel and erosion of the basemat, due to the corium-concrete interaction,
- transfer of certain fission products, in gaseous or aerosol forms outside of the containment, causing radioactive contamination of the environment (source term). Filtered containment venting systems are implemented in order to avoid a large containment failure and to minimize the release of radioactive materials into the environment.

Another phenomenon can play a key role in the development of a severe accident: an air inlet into the reactor vessel. It is highly unexpected but can be due to a breakthrough of the vessel bottom by the corium. From this

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phenomenon, a gas flow occurs between the vessel well and the breach via the vessel and the primary circuit. Studies [4] [5] showed that, just after the breaking of the vessel bottom, air is expelled from the cavity to the surrounding areas due to high flows of gas from the corium-concrete interaction (H_2, CO_2, CO). A few minutes later, a quasi-steady state is established with gas flow rates generated by the erosion of the basemat.

This quasi-stationary state then balances the pressures between the reactor pit and the surrounding areas, and due to the strong thermal gradients existing between these areas, a loop of convection induces an air inlet into the vessel.

III. Ruthenium tetroxide

Ruthenium metal is a fission product with a low volatility; indeed the fraction emitted during a severe accident from a pellet of UO_2 heated to 2300°C is generally assessed between 1% and 10% [6]. However, in the presence of oxidizing conditions and in particular under air ingress, the Ru is oxidized in much more volatile forms. Therefore, accidents with air inlet (the most oxidizing accident conditions) are particularly associated with ruthenium problematic.

The ruthenium content is more important in a MOX fuel than in a conventional UO_2 fuel. It is therefore very likely that in the future, the amount of ruthenium formed during the life of the fuel will continue to increase, given the constant fuel performance optimization research by the operators.

The ruthenium has, besides its already well known chemical toxicity in toxicological studies [7], a high radiotoxicity through the isotopes ^{106}Ru ($T_{1/2}$=373 j) and ^{103}Ru ($T_{1/2}$=39.3 days). That makes it an important radiologic contaminant at short and medium term. In radioprotection, four groups were defined [7]. The isotope ^{106}Ru was ranked in the group 2 "high radiotoxicity," the same as ^{131}I, and the isotope ^{103}Ru in the group 3 "radiotoxicity moderate ", the same as ^{137}Cs.

However the ruthenium has a low risk of contamination because of its low volatility, and suspended ruthenium particles settle down strongly into the containment of a nuclear reactor. But, the risk is much higher with ruthenium tetroxide that is in gaseous form.

For severe accidents ruthenium release is low before the rupture of the vessel. But in case of the rupture of the lower head by the molten corium, the air entering into the vessel oxidize Ru into gaseous RuO_4, which can persist in gaseous forms in the containment, and, as a consequence, is not trapped by the Filtered Containment Venting Systems [2].

So monitoring the presence of RuO_4 is of prime importance in case of a severe accident, because it allows making a diagnosis of the core degradation and quantifying the potential release into the atmosphere.

IV. FTIR measurement

The Fourier transform infrared spectroscopy (FTIR) was chosen due to its intrinsic qualities for an optical measurement. It is robust, does not require a periodic calibration and can be used in a simple system on line, remotely operable. These properties are essential for an efficient monitoring system and for operability by a crisis intervention team.

RuO_4 has not been much studied by FTIR measurements until now. But it presents a vibration mode around 921 cm^{-1} (ν_3) which is isolated in the atmospheric window [8] and can be used as the molecule fingerprint for the development of a new sensor which could be placed at the outlet of the filtered containment venting system on a nuclear reactor**.** To study the feasibility of monitoring this product in air by an infrared measurement, high-resolution IR measurements were carried out at the French synchrotron facility SOLEIL on the infrared beam line AILES. Thereafter, theoretical calculations were done to simulate the FTIR spectrum to describe the specific IR fingerprint of the molecule for each isotope and based on its partial pressure in the air. By this way a really precise spectrum is determined for each natural isotopologue of the ruthenium and can be expected for minor and radiological isotopologues (^{103}Ru and ^{106}Ru). This allows describing the spectrum of any isotopic ratio of ruthenium in fission product and diluting in the air. These simulations implemented in a new specific sensor can thus allow to detect and quantify quickly and precisely the amount of ruthenium tetroxide which could be released outside of the containment of a nuclear reactor.

V. Experimental and theoretical works

The exhaustive details of these works were published in 2015, February. [9]. Pure RuO_4 and monoisotopic $^{102}RuO_4$ samples have been prepared using the method of Ruff and Vidic [10], starting from Ru powder.

The main difficulty with the ruthenium tetroxide is its high reactivity with surfaces (especially the metallic surfaces). So the synthesis and analysis of this compound requires using specific passivated equipment. This equipment was developed and tested at SOLEIL, the French synchrotron facility.

The measurements were carried out on the AILES Beamline of the synchrotron Soleil, with the IFS 125 Bruker interferometer coupled to the synchrotron radiation source. Around 900 cm^{-1}, the light flux for HR measurements is about nine times greater, resulting in a recording time shorter than using the internal globar source, an important advantage when studying reactive molecules.

Thanks to the measurements carried out, the simulation of the RuO_4 spectrum with a model software developed in the ICB Institute of Dijon was possible. Due to the overlap of the different isotopologue spectra, it is not possible to reliably assign lines with a natural abundance spectrum. Thus, an isotopically pure sample of $^{102}RuO_4$ was first studied, allowing much easier assignments. As a consequence, a first set of line assignments was possible, using the SPVIEW software [11], followed by a least-square fit for effective Hamiltonian parameters for the ν_3 stretching dyad, using the XTDS software [11]. A simulation using the parameters

refined in this way allowed to assign new lines and thus to fit again effective Hamiltonian parameters. Then, this first calculated spectrum was shifted in order to perform initial simulations for $^{104}RuO_4$, $^{101}RuO_4$, $^{100}RuO_4$ and $^{99}RuO_4$. The shifts were approximately determined from the position of the different Q branches. This allowed to perform rough simulations and to begin assignments and fits for those most abundant isotopologues (Fig. 1).

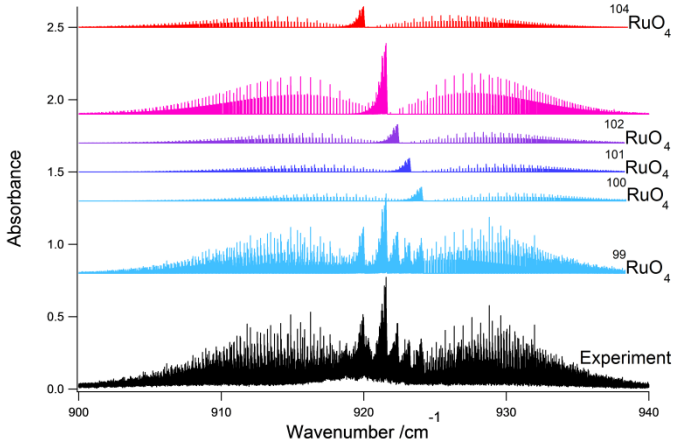


Fig. 1. Overview of the ν_3 region of natural abundance RuO_4, compared to the simulation. The five upper curves are simulations for individual isotopologues.

The spectra of $^{98}RuO_4$ and $^{97}RuO_4$ appear too weak due to natural abundance to allow line assignments. But the previous results allowed us to estimate the spectrum of these isotopic species as well as the spectrum for the two radioactive isotopologues ($^{103}RuO_4$ and $^{106}RuO_4$). The band center and ν_3 Coriolis parameters were extrapolated from $^{102}RuO_4$, $^{104}RuO_4$, $^{101}RuO_4$, $^{100}RuO_4$ and $^{99}RuO_4$ values through linear regression as a function of the atomic mass number A (Fig. 2).

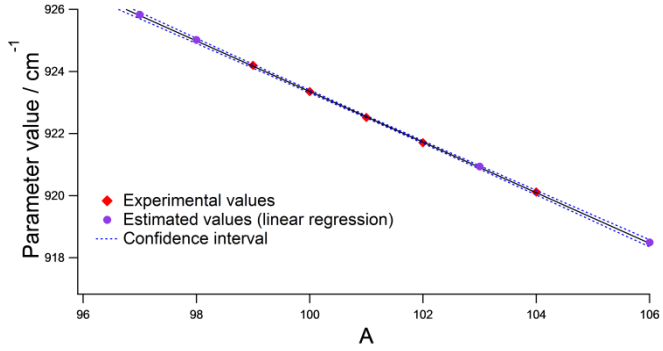


Fig. 2. Estimate of the ν_3 band center parameter for minor isotopologues through linear regression.

VI. Conclusion

This work shows the first detailed FTIR high resolution spectroscopic study of the 921 cm^{-1} region of RuO_4 as a ν_3 stretching mode. The five major isotopologues were analyzed in detail; the two minor ones have been extrapolated. The analysis also extends the range of line assignments to higher J values from previous work [8].

The effective Hamiltonian parameters determined in this work allow to generate reliable simulated spectra in frequency of all RuO_4 isotopologues, including the radioactive isotopologues $^{103}RuO_4$ and $^{106}RuO_4$. The parameters and simulations can be obtained thanks to the XTDS software [11].

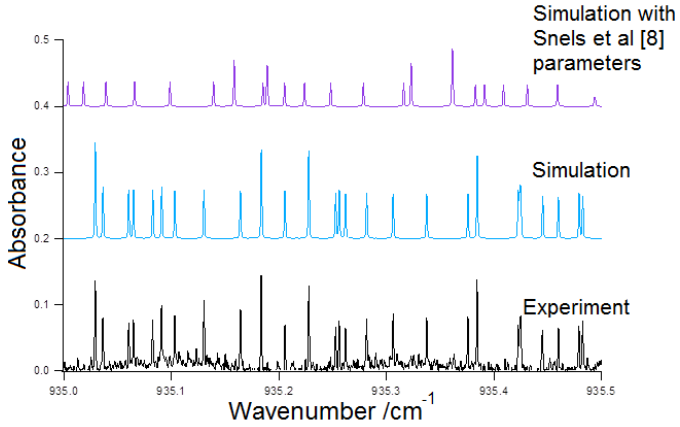


Fig. 3. Comparison between this work and precedent work of simulation for high J values (65 < J < 68).

It is clear that this study leads to a more precise determination of the spectroscopic molecular parameters for the ν_3 vibration mode of RuO_4, especially for high J values (J < 65) (Fig. 3). It is a first step on the way to develop a new specific sensor of this molecule which could be included in a new set of monitoring systems of the fission products (DECA-PF project) which aim to improve the safety of the nuclear plants.

Further analysis and simulations works will be essential to determine the parameters to fit accurately the intensity of the rotational modes of the $^{102}RuO_4$ spectrum and then the RuO_4 in natural abundance spectrum. Then by simulating the broadening of the RuO_4 spectrum diluted in the air (Fig. 4), it will be easy to analyze the signal of RuO_4 at the output of the containment venting systems regardless of the environment (temperature, pressure, composition of the atmosphere).

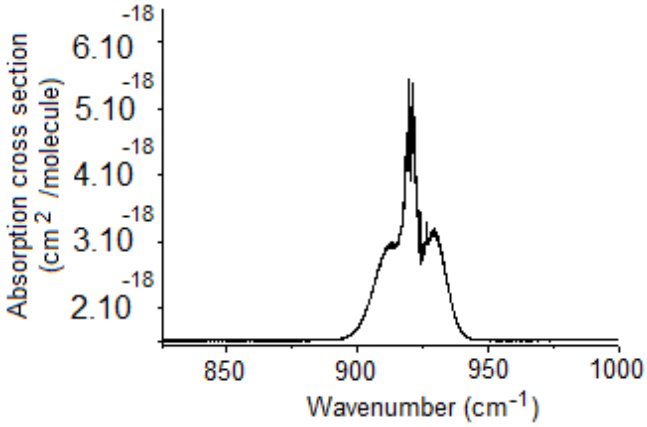


Fig. 4. Approximate absorption cross section for RuO_4 in the 10^{-12} µm atmospheric window. Approximately 10 mbar of ruthenium tetroxyde in 1012mbar nitrogen at 298K.

ACKNOWLEDGMENT

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