PhD hour:
Ruthenium speciation along its purification process

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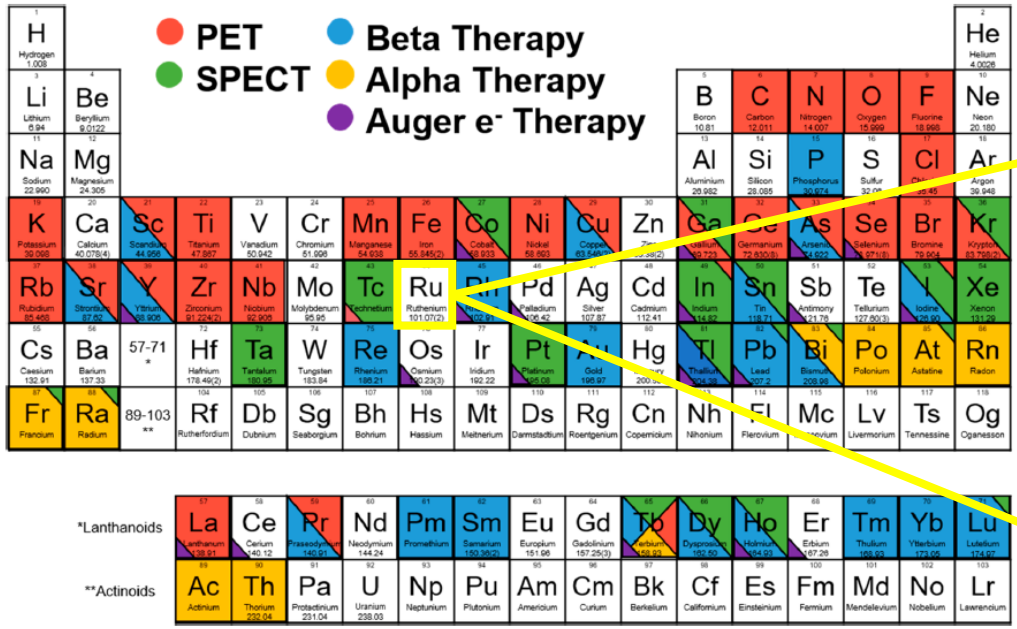
Subatech

ARRONAX

Context of the thesis and overview of the objectives



T. I. Kostelnik et al. , *Nucl Med Biol*, 2023, **122–123**, 108352.

$^{nat}Mo(\alpha,xn)^{97+103}Ru$

- Diameter : 20mm / Thickness : 75 µm (250 mg)
- Alpha beam of 28 MeV
- Average current : 15 µA
- 10h of irradiation
- Produced activity : 200- 250 MBq

^{97}Ru production at Arronax :

- Produce from ^{nat}**Mo** target
- Eγ = **216 keV** (85%)
- Interesting properties for SPECT imaging
- **Decay by electronic capture**
- $t_{½}$ = **2.9 days**

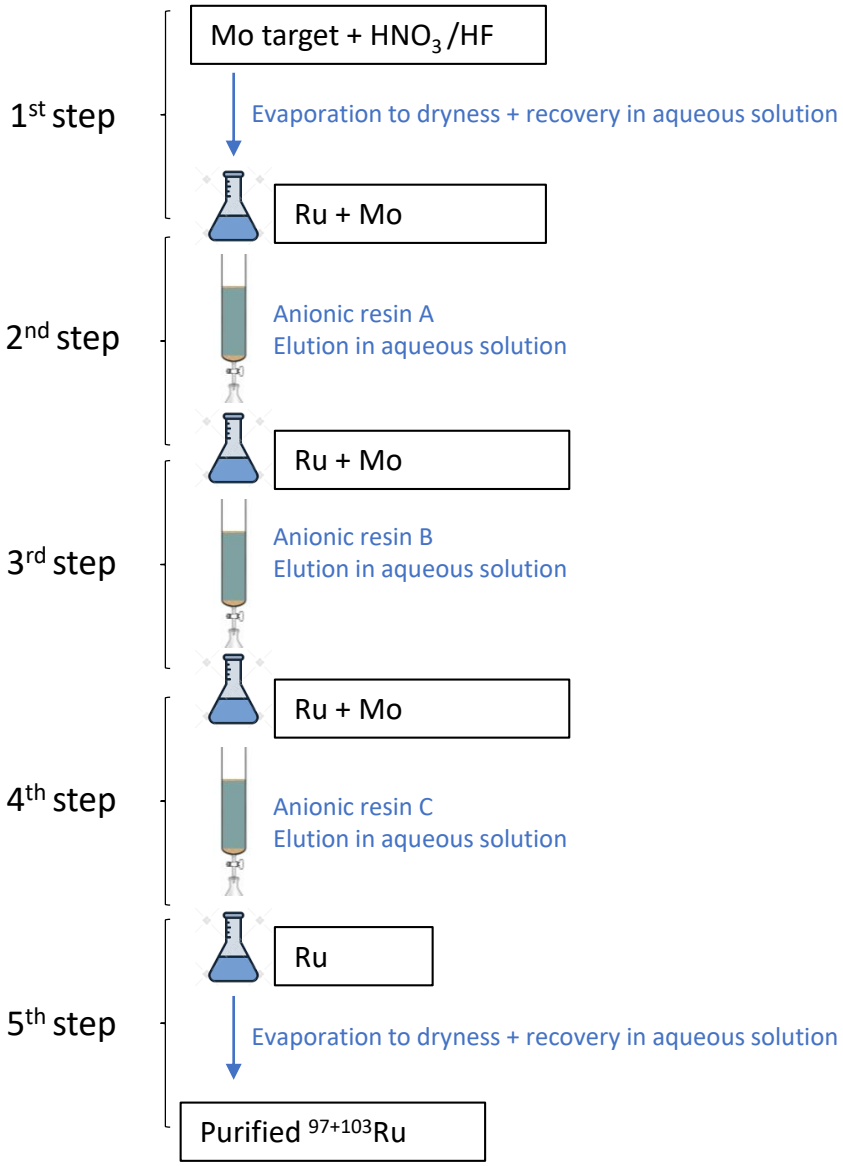
^{103}Ru production at Arronax :

- Also produced from ^{nat}**Mo** target
- $t_{½}$ = **39.2 days**
- Activity ratio of $^{103}Ru/^{97}Ru$ = **0.3%**
- Decay in ^{103m}**Rh** ($t_{½}$ = 56.1min) which have interesting properties for Auger therapy

Context of the thesis and overview of the goals

Main objective : Optimization of the purification process to remove traces of metal contaminants (Fe, Cu, Ni, Zn, Cr)

- Need to understand ruthenium speciation in the current process



Knowledge from the work of M.Théry (2024)

From Ru_{met} powder + basic oxidizing conditions (NaOCl)

From $RuCl_3.xH_2O$

7M HCl: $[Ru_2^{IV}OCl_{10}]^{4-}$ and $[Ru^{IV}Cl_6]^{2-}$

2M HCl: $[Ru^{IV}(OH)_2Cl_4]^{2-}$

Fully controlled speciation in 2M and 7M HCl medium

Marie Théry's thesis work has led to a **better understanding** of the **ruthenium chemistry** in **HCl** and has enabled the development of experimental methodologies for speciation studies

Context of the thesis and overview of the objectives

Ruthenium speciation was studied in HCl medium during the different step of the purification process based on M.Théry's work

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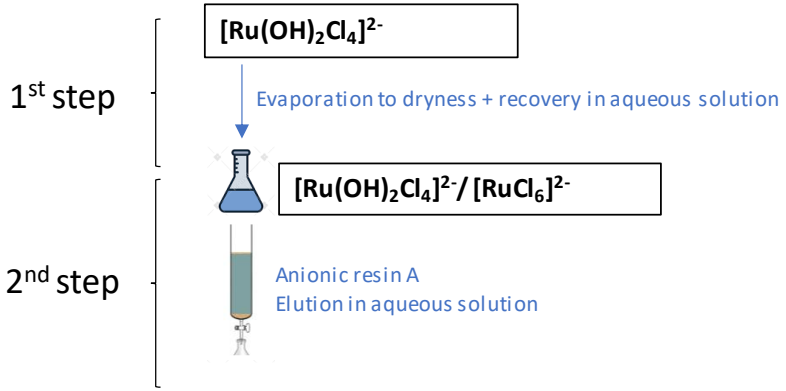

----------> $[Ru^{IV}(OH)_2Cl_4]^{2-}$ after evaporation and recovery

----------> **Ruthenium IV retention (either $[Ru^{IV}Cl_6]^{2-}$ or $[Ru^{IV}(OH)_2Cl_4]^{2-}$)**

--> To be checked with Ru(III) and with nitrate complexes

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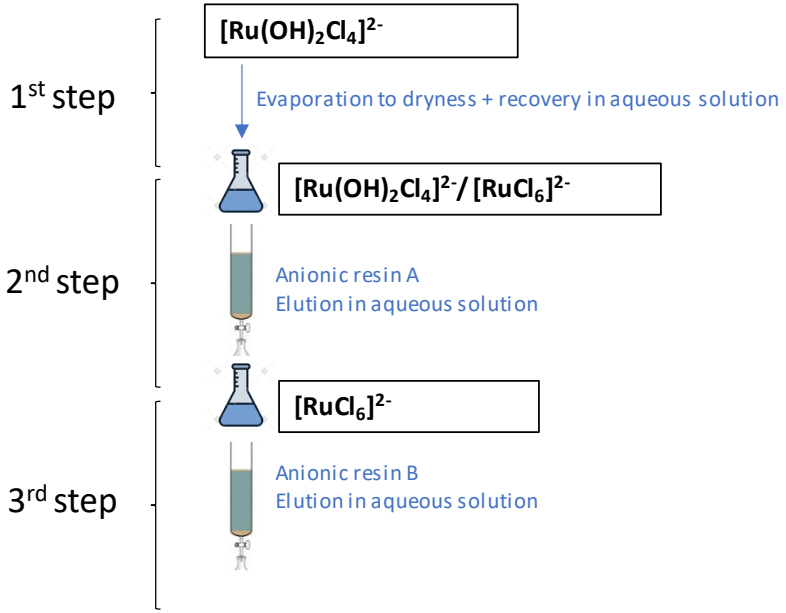

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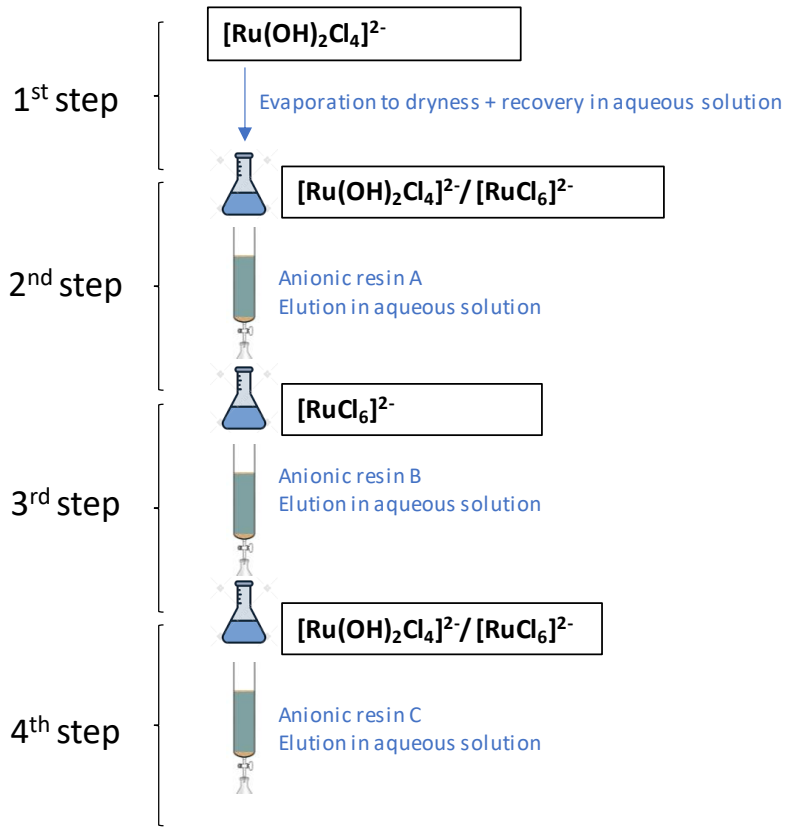

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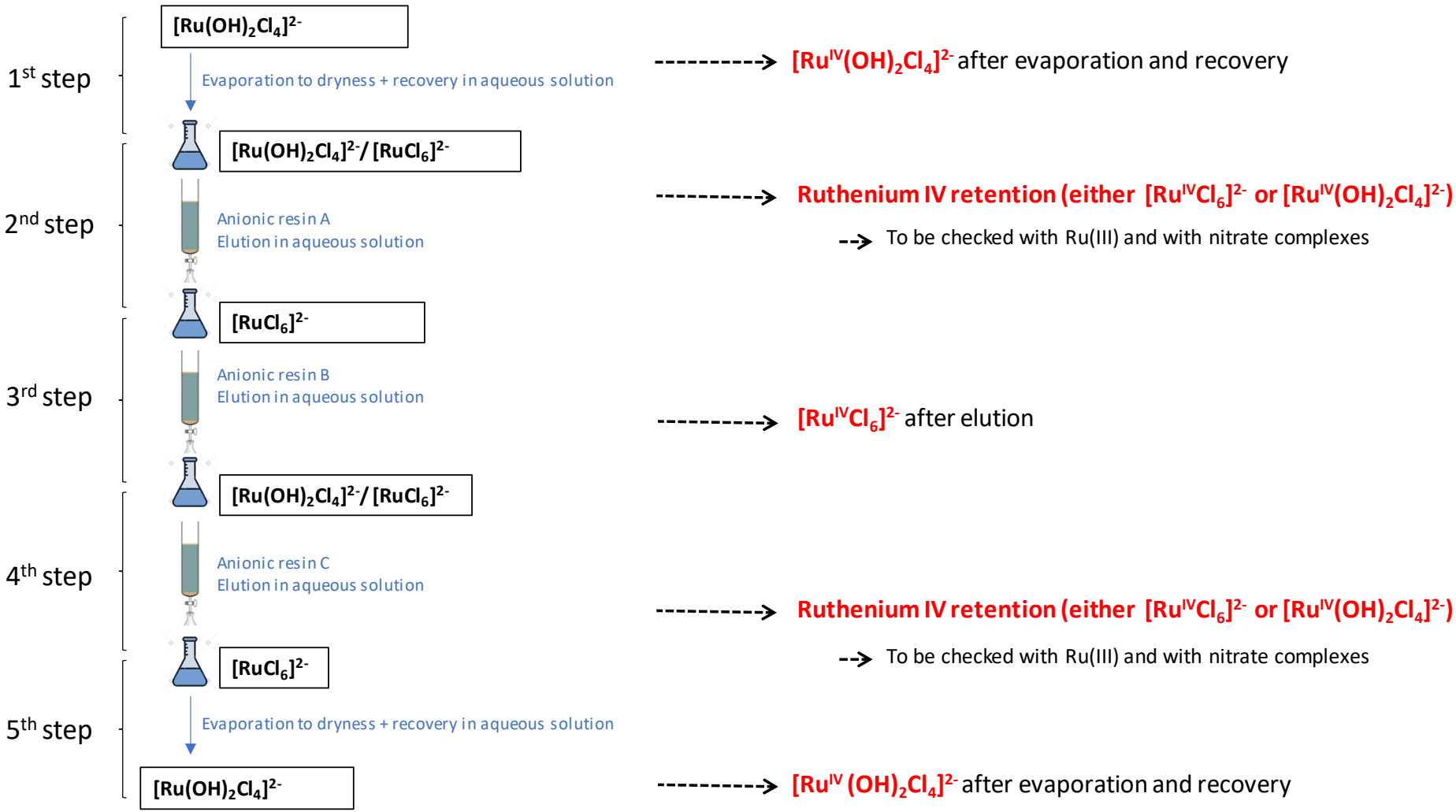


The assumption is that the purification process for $^{97+103}$Ru is carried out in HNO_3/HF solutions and would **generate** more **Ru(III)**. However, the literature indicates that **HNO_3** has an **oxidizing effect** and would tend to **keep Ru in its +IV form**. However, **anionic resin A and C** resin **selectively retains Ru(IV)**. This is not consistent with experimental observations regarding the production of ^{97}Ru since 95 - 100% of Ru is eluted.

Two assumptions are then proposed:

1) **Ru(III)** species are formed during the production of $^{97+103}Ru$ (due to HNO_3 radiolysis). Radiolysis produces **radicals** ($NO^{\bullet}$) as well as **HNO_2,** which are reducing **species** that would **maintain ruthenium at the +III oxidation state**.

$NO_3^- + e_s^- \xrightarrow{k_{II.26} = 9{,}7 \times 10^9\ L\,mol^{-1}\,s^{-1}} NO_3^{2-\bullet}$ Réaction II.8. 26[126]

$NO_3^- + H^\bullet \xrightarrow{k_{II.27} = 1 \times 10^7\ L\,mol^{-1}\,s^{-1}} HNO_3^{-\bullet}$ Réaction II.8. 27[126]

$NO_3^{2-\bullet} \underset{}{\overset{pK_1 = 4{,}8}{\rightleftharpoons}} HNO_3^{-\bullet} \overset{pK_2 = 7{,}5}{\rightleftharpoons} H_2NO_3^\bullet$ Réaction II.8. 28[126]

$NO_3^{2-\bullet} + H_2O \xrightarrow{k_{II.29} = 1 \times 10^3\ L\,mol^{-1}\,s^{-1}} NO_2^\bullet + 2OH^-$ Réaction II.8. 29[126]

$HNO_3^{-\bullet} \xrightarrow{k_{II.30} = 2 \times 10^5\ L\,mol^{-1}\,s^{-1}} NO_2^\bullet + HO^-$ Réaction II.8. 30[126]

$H_2NO_3^\bullet \xrightarrow{k_{II.31} = 7 \times 10^5\ L\,mol^{-1}\,s^{-1}} NO_2^\bullet + H_2O$ Réaction II.8. 31[126]

Le radical $NO_2^\bullet$ issu de la radiolyse des solutions diluées d'acide nitrique se recombine avec d'autres radicaux pour donner l'espèce N_2O_4 puis, à partir du déclin lent (disparition) de cette dernière molécule, les espèces HNO_2 et HNO_3 se forment par réaction d'hydrolyse.

$NO_2^\bullet + NO_2^\bullet \underset{k_{-II.32} = 6 \times 10^3\ L\,mol^{-1}\,s^{-1}}{\overset{k_{II.32} = 4{,}5 \times 10^8\ L\,mol^{-1}\,s^{-1}}{\rightleftharpoons}} N_2O_4$ Réaction II.8. 32[126]

$N_2O_4 + H_2O \xrightarrow{k_{II.33} = 18\ L\,mol^{-1}\,s^{-1}} HNO_2 + HNO_3$ Réaction II.8. 33[126]

Thèse A.K El Omar; **Études des réactions primaires en solutions par la radiolyse pulsée picoseconde; Université Paris-Sud; 2014**

Context of the thesis and overview of the objectives

2) Ruthenium nitrate complexes are produced during the dissolution of the molybdenum target in an HNO_3 + HF medium, which may have a different behavior on the anionic resin A and C. It's also possible that ruthenium fluoride complexes are formed at room temperature but most of them are formed under more extreme temperature and pressure conditions than those used at Arronax. At first, we decided not to take them into account.

Objective

Characterization of Ru nitrate species in $^{97+103}$Ru purification process conditions

Methodology

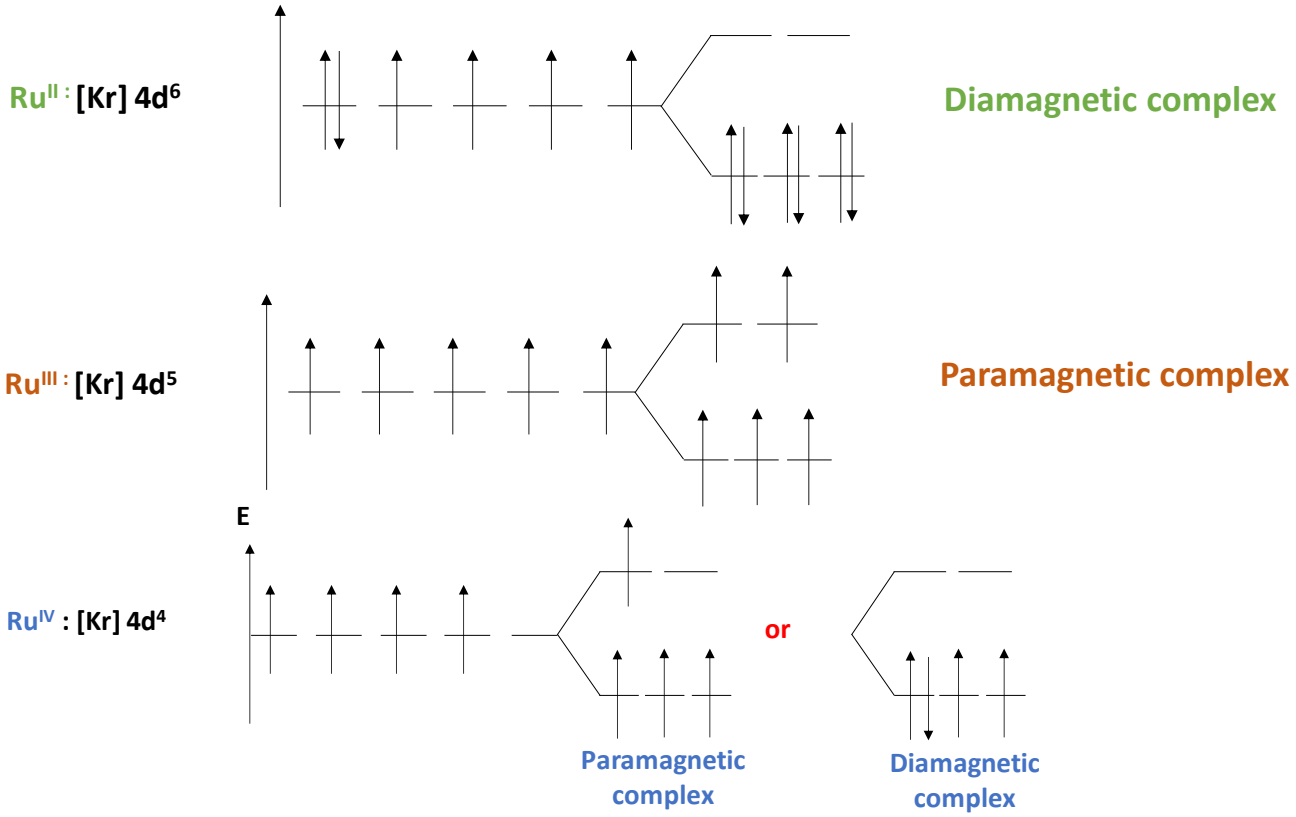
- NMR
- EPR
- Raman spectroscopy
- Infrared spectroscopy

Oxidation states + 1st coordination sphere

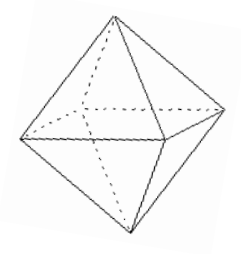
Summary :

Characterization of the oxidation state of Ru – NMR and EPR

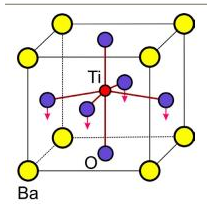
Depending on the oxidation state of ruthenium, the electronic configuration is different and depends on the ligands and on the geometry. The degenerated energy levels are then lifted depending upon the geometry considered.



Octahedral symmetry



Orthorhombic symmetry



However, according to ligand field theory, the following information can also be derived:

- A colorless complex is always diamagnetic
- A colored complex is always paramagnetic

But the electron transfer from the ligand to the metal cation is the second explanation for the color of transition-metal compounds

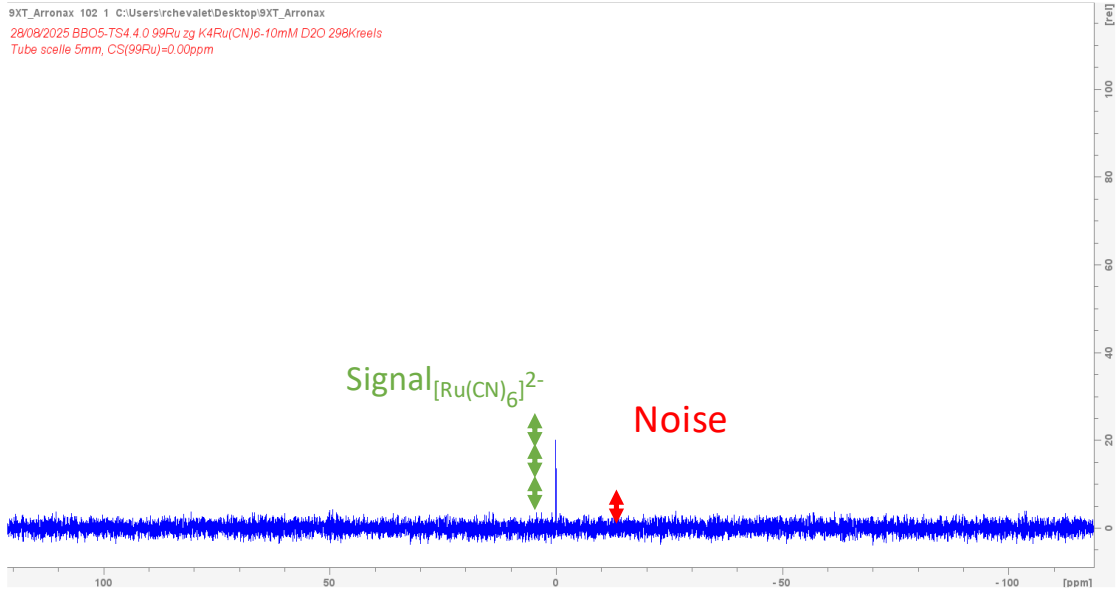
Characterization of the oxidation state of Ru – NMR and EPR

Results obtained by NMR (Nuclear Magnetic Resonance)

NMR spectroscopy of transition metals can be used to investigate the structure, electronic properties, and catalytic activity of diamagnetic transition metal complexes (those with a non-bonding doublet) such as Ru(II) and Ru(IV)

Goal n°1: Determine the minimum ruthenium concentration required to perform ^{99}Ru NMR analysis

Analyzed sample: $K_4[Ru^{II}(CN)_6]$ at 100/10/1 mM (^{99}Ru NMR standard)

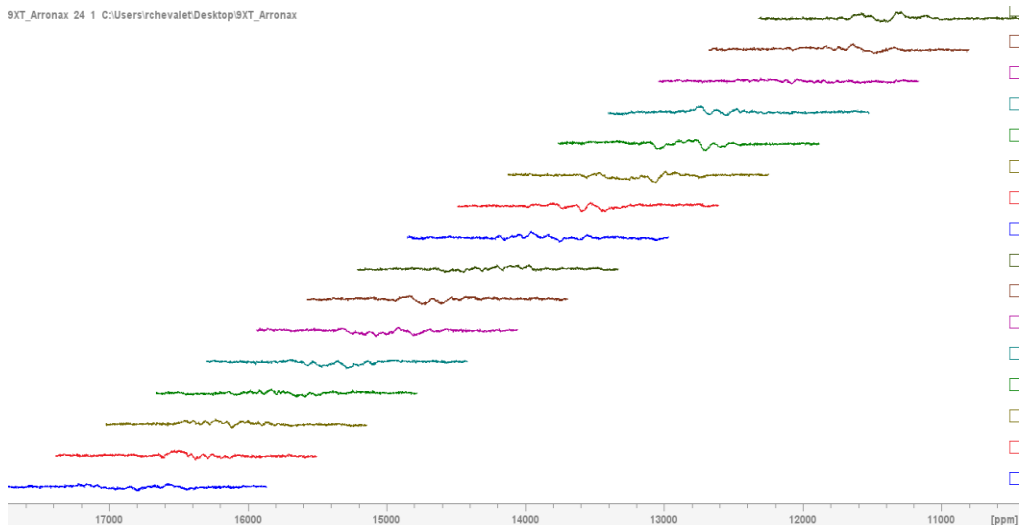


Conclusion

- Limite of detection → [Ru] ≈ 10 mM

Goal n°2 : Determine the first coordination sphere of various ruthenium complexes

Analyzed sample: $[Ru^{IV}Cl_6]^{2-}$ 1 mM



Conclusion

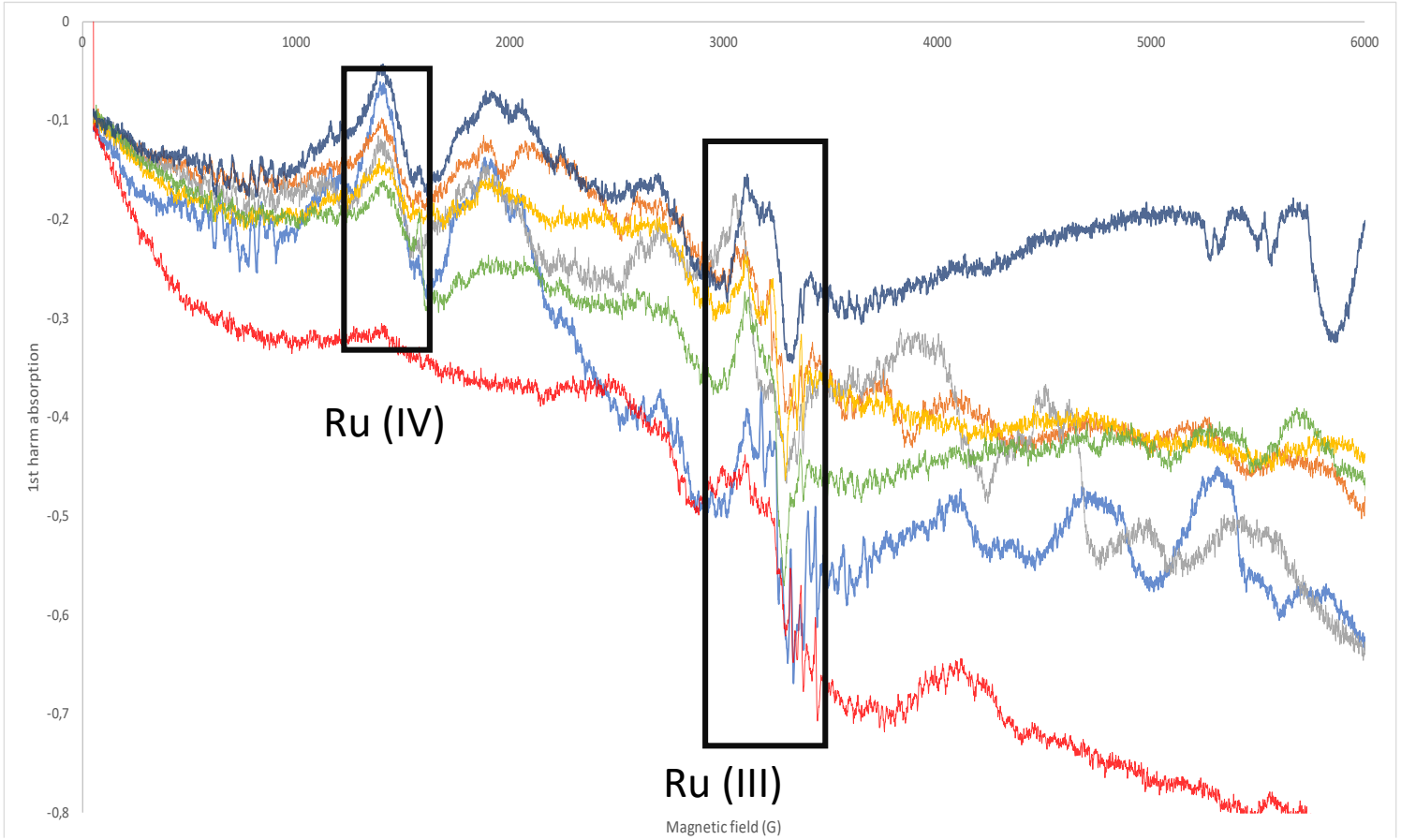
- The sample was not enough concentrated?
- Analysis performed in the wrong spectral range?

- **Paramagnetic behavior of Ru =>** We are not sure to have diamagnetic Ru(IV). There may be paramagnetic Ru(III) that is not visible by ^{99}Ru NMR but is visible by EPR

Characterization of the oxidation state of Ru – NMR and EPR

Results obtained by EPR (Electron Paramagnetic Resonance)

EPR is a complementary technique to NMR, as it allows for the characterization of the chemical environment and the degree of oxidation of **paramagnetic elements** (those with a lone electron). It complements NMR, which is sensitive to diamagnetic nuclei



- Old solution of $[Ru^{IV}Cl_6]^{2-}$ in 5M HCl : Orange solution
- Freshly prepared solution of $[Ru^{IV}Cl_6]^{2-}$ in 5M HCl Orange solution
- $Ru^{IV}OH)_2Cl_4]^{2-}$ in 2M HCl : Red – orange solution
- Ru_{met} in 16M HNO_3 : Light yellow solution
- $RuCl_3$ in 16M HNO_3 : Red solution
- $Ru(NO)(NO_3)_3$ in 16M HNO_3 : Light pink solution
- Stock solution of $Ru(NO)(NO_3)_3$: Brown solution

Colored solutions
⇒ paramagnetic Ru(III) and Ru(IV) complexes
⇒ Corroborates the NMR observations

Conclusion

- Initial analyses appear to provide informations on the oxidation states of the complexes, which are likely paramagnetic.
- Further analyses will be conducted to improve the signal-to-noise ratio and to obtain informations on the first coordination sphere

Summary :

Characterization of the 1st coordination sphere of Ru – Raman, infrared and UV-visible spectroscopy

Raman spectroscopy is an analytical technique that involves hitting a material with a laser and observing the scattered light to characterize the vibrational bands of molecules, providing informations about the metal-ligand bonds in a complex.

Goal : Characterize freshly prepared solutions under the same conditions than those described in the literature

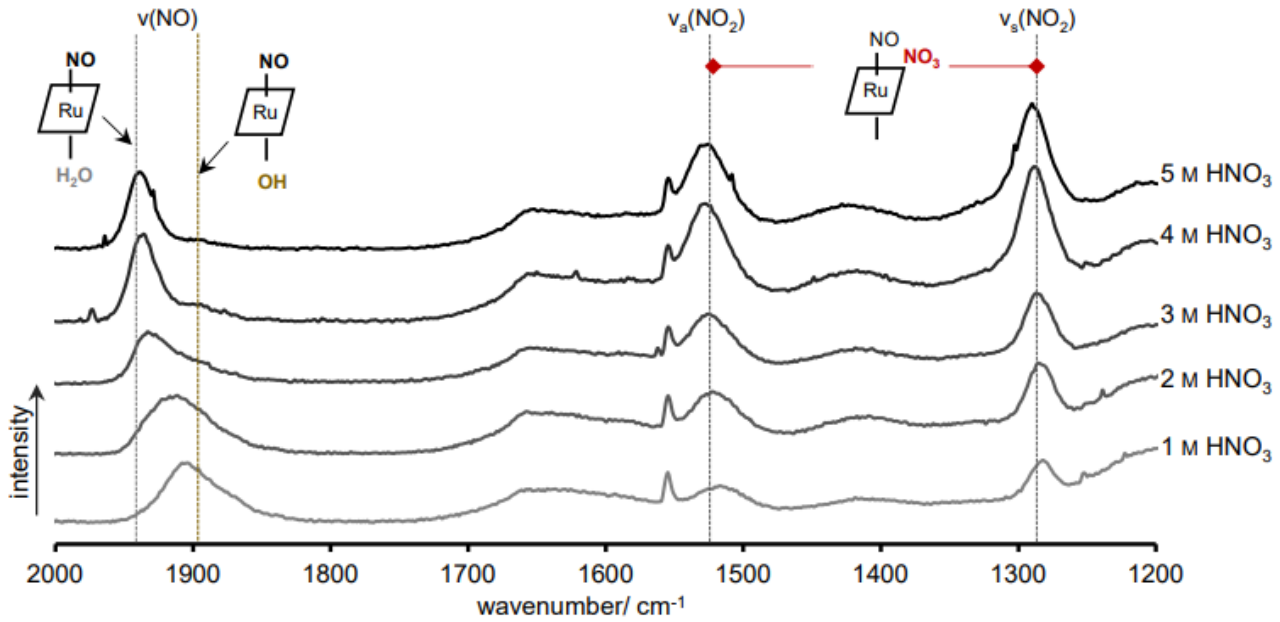


Figure 46 – Raman spectra of 0.6 M ruthenium(III) nitrosyl nitrate in 1 to 5 M nitric acid; The solutions were heated for 3 h at 70°C and stored 3 months before the measurement.

T. Dirks. Spéciation du ruthénium dans les solutions d'extraction des procédés de recyclage du combustible nucléaire. Thèse de doctorat. Université de Montpellier, 2020

Analysed samples

- Stock solution $[Ru^{II}(NO)(NO_3)_3]$
- 2M HNO_3
- 2M $NaNO_2$

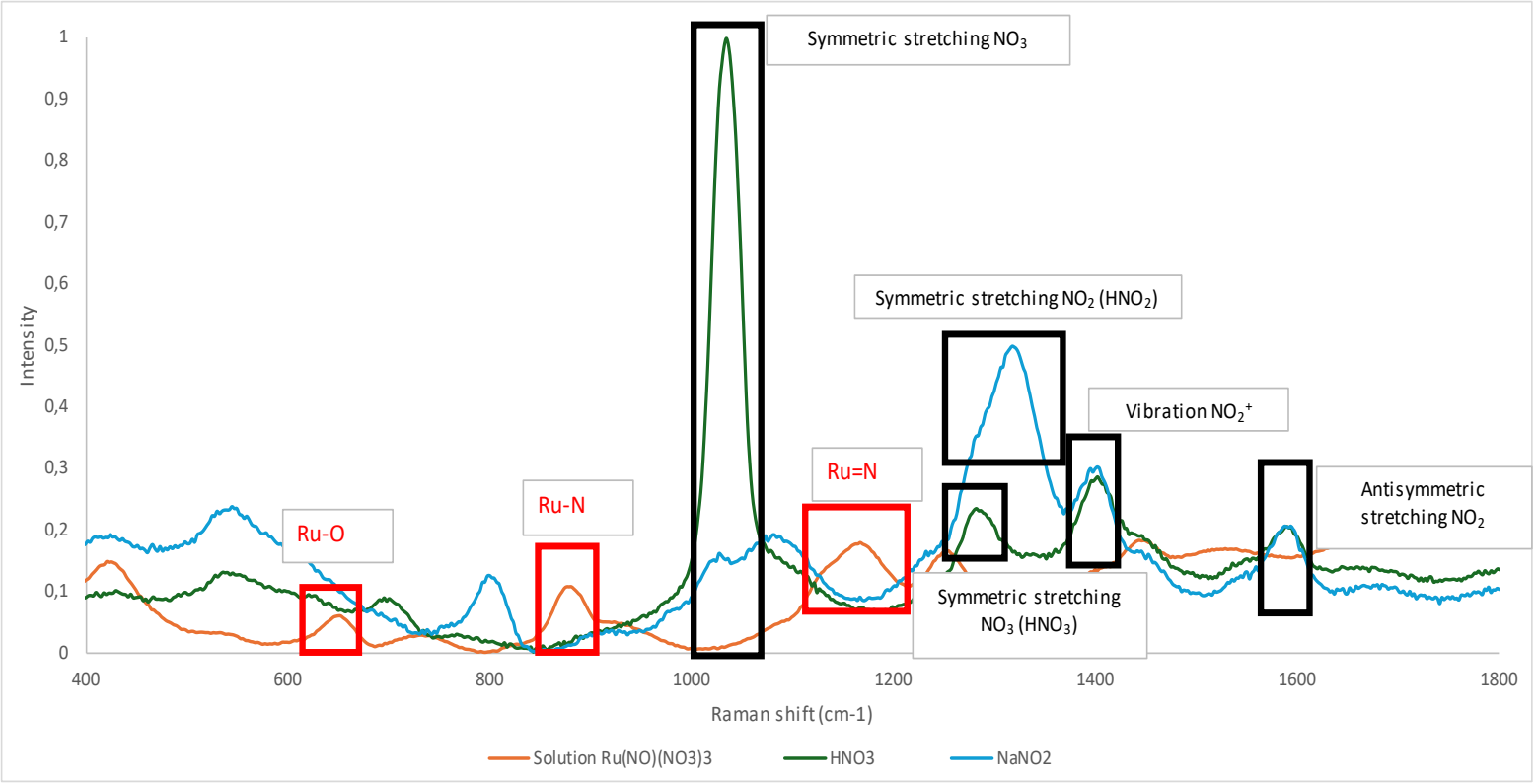
Characterization of the 1st coordination sphere of Ru – Raman, infrared and UV-visible spectroscopy

Results obtained by Raman spectroscopy

Experimental conditions

Temperature = 25°C
Side entrance : 100 µm
Front exit: 100 µm
Grating : 1200

Acquisition : 60 secondes
Number of repetition: 20
[Ru] starting product = 0.2M
[Ru] inHNO3 medium = 2.10^{-3}M



Raman spectrum of : orange curve) Old stock solution of $Ru(NO)(NO_3)_3$, green curve) 2M HNO_3, blue curve) 2M $NaNO_2$

Lucas, H.; Petitet, J.-P. High Pressure Raman Spectroscopy of Nitric Acid. J. Phys. Chem. A ***1999****, 103 (45), 8952–8958.*
Leblanc, M.; Baghdadi, S.; Martin, P. M.; Prieur, D.; Quemet, A.; Aupiais, J. Ruthenium Speciation during Acidification of Alkaline Solution. *ACS Omega* **2026**, *11* (18), 27438–27448.
Ianoul, A.; Coleman, T.; Asher, S. A. UV Resonance Raman Spectroscopic Detection of Nitrate and Nitrite in Wastewater Treatment Processes. *Anal. Chem.* **2002**, *74* (6), 1458–1461.

Conclusion

- Result consistant with the bibliography (Lucas, 1999 / Ianoul, 2002 /Leblanc, 2026)
  - Complexes with H_2O et NO_2 ligands
- Caracteristic bands of nitric acid at 1080, 1280, 1600 cm^{-1}
- Caracteristic band of $NaNO_2$ at 1320 cm^{-1}

Continue the analyses with these complexes :

- $[Ru^{IV}Cl_6]^{2-}$
- $Ru^{IV}(OH)_2Cl_4]^{2-}$
- $Ru^{III}(NH_3)_6$
- $Ru^{II}(NO)(NO_3)_3$ in 1, 5, 10, 16M HNO_3

Characterization of the 1st coordination sphere of Ru – Raman, infrared and UV-visible spectroscopy

Infrared spectroscopy (IR) is a technique similar to Raman spectroscopy. It involves passing a beam of infrared light through a sample and observing which wavelengths are absorbed, which provides information about the vibrations of chemical bonds within the molecule.

Goal: Identify the vibration bands associated with ruthenium

Type de vibration	1	2	3	4
ν(NO)	1830	1932 (+ 1847 faible)	1906	1917
δ(H₂O)-δ(OH)	(très large) 1650 - 1520	(très large) 1620	(très large) 1560	
$\delta_d(NH_3)$				1583
$\nu_{asym}(ONO)$ NO_3				1515
$\delta_s(NH_3)$ et $\delta_d(NH_3)$	1320 + 1290	(très large) 1380 - 1200	1321 + 1305	(large) 1330
$\nu_{sym}(ONO)$ NO_3				1260
$\delta_d(NH_3)$			1305	
$\nu(N\text{-}O)$ NO_3		1040		1045 + 990
$\rho(NH_3)$	848 - 837	846 - 821	850	846 - 827

Thèse C. Lefebvre, 2018

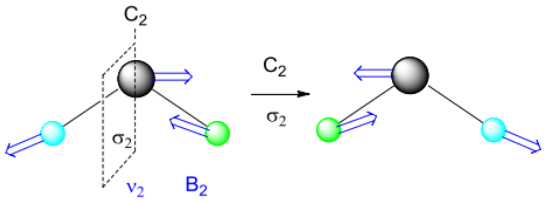
Attribution		NO_3 covalent	NO_3 ionique	HNO_3
		Fréquence (en cm^{-1})		
Elongation O=N=O	Asymétrique	1530 - 1480	1390 - 1350	1700 - 1620
	Symétrique	1300 - 1250		1330 - 1280
Elongation N-O		1030 - 970	1050	900 - 850
Déformation hors du plan		820 - 780	830 - 820	790 - 750
Torsion O=N=O dans le plan	Symétrique	750 - 710	720 - 700	700 - 680
	Asymétrique	720 - 680		580

Thèse C. Lefebvre, 2018

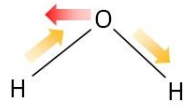
Analyzed samples

- Commercial solution $[Ru^{II}(NO)(NO_3)_3]$
- $[Ru^{II}(NO)(NO_3)_3]$ in 1M HNO_3
- $[Ru^{II}(NO)(NO_3)_3]$ in 5M HNO_3
- $[Ru^{II}(NO)(NO_3)_3]$ in 10M HNO_3
- $[Ru^{II}(NO)(NO_3)_3]$ in 16M HNO_3

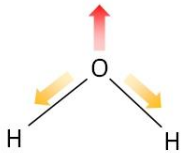
Reminder



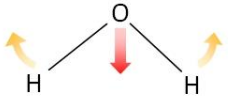
Vibrational



Antisymmetric stretching



Symmetric stretching

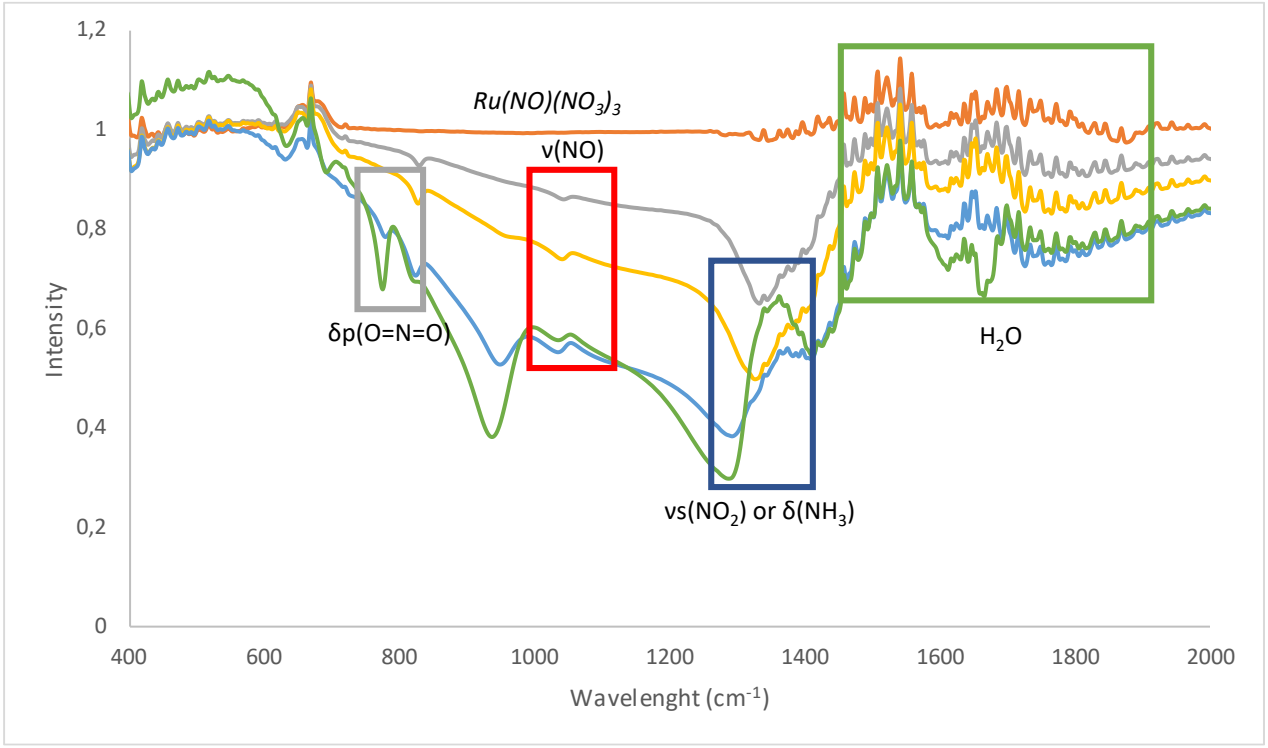


Angular deformation

Characterization of the 1st coordination sphere of Ru – Raman, infrared and UV-visible spectroscopy

Results obtained by infrared spectroscopy

Goal: Identify the vibration bands associated with ruthenium



Stock solution of $Ru^{II}(NO)(NO_3)_3$

$Ru^{II}(NO)(NO_3)_3$ in 1M HNO_3

$Ru^{II}(NO)(NO_3)_3$ in 5M HNO_3

$Ru^{II}(NO)(NO_3)_3$ in 10M HNO_3

$Ru^{II}(NO)(NO_3)_3$ in 16M HNO_3

Experimental conditions

Temperature = 25°C
Analyse range: 400 – 2000 cm^{-1}
Acquisition : 60 secondes
Number of repetition: 5

Interpretations :

Bands at **710 – 750** cm^{-1} → In-plane symmetrical torsion $\delta_p(N=O=N)$ of NO_3 ligand

Bands at **1040** cm^{-1} → $\nu(N=O)$ stretching of NO_3 ligand

Bands at **1250 – 1300** cm^{-1} →Symmetrical stretching $\nu_s(N=O=N)$ of NO_2 ligand

Bands at **1520 -1650** cm^{-1} → Vibrational band of $\nu(H_2O)$

Conclusion

- The first analyses provide important informations, particularly regarding the presence of NO_2, NO_3 and H_2O ligands
- Further analyses will be conducted to improve the signal-to-noise ratio. These analyses will be compared with the new results obtained by raman spectroscopy

Conclusions about NMR / EPR / Raman / Infrared/ UV-visible

Characterization of the oxydation states

NMR

Paramagnetic behaviour of our complexes

EPR

Mixture of Ru(III)/Ru(IV) in our complexes

Characterization of the chemical environment

Raman

Presence of NO_3 and NO_2 ligands in our ruthenium complexes

Infrared

Presence of NO_2, NO_3, H_2O ligands

Conduct more in-depth analyses to confirm the redox state of the complexes

Gather more detailed information on the first coordination sphere

Further analyses will be conducted to improve the signal-to-noise ratio. The new Raman and infrared analyses will be compared with each other to obtain more detailed information

Ruthenium speciation along the purification process

Thank you for your attention

Infrared VS Raman

If a molecule has a center of symmetry and the vibration itself is symmetric

→ No permanent dipole moment

→ Changes in molecular polarizability

✗ IR inactive

✓ Raman active

If the molecular vibrational states are asymmetric

→ Permanent dipole moment

→ No changes in molecular polarizability

✓ IR active

✗ Raman inactive