

Studying the effectiveness of V-incorporation in the Al-metal-organic framework MIL-53 with electron-nuclear double resonance spectroscopy

Irena Nevjestic⁽¹⁾, Hannes Depauw⁽²⁾, Karen Leus⁽²⁾, Freddy Callens⁽¹⁾, Pascal Van Der Voort⁽²⁾, Henk Vrielinck⁽¹⁾

(1) Ghent University, Dept. of Solid State Sciences, Krijgslaan 281-S1, B-9000 Gent, Belgium
(2) Ghent University, Dept. of Inorganic and Physical Chemistry, COMOC, Krijgslaan 281-S3, B-9000 Gent, Belgium

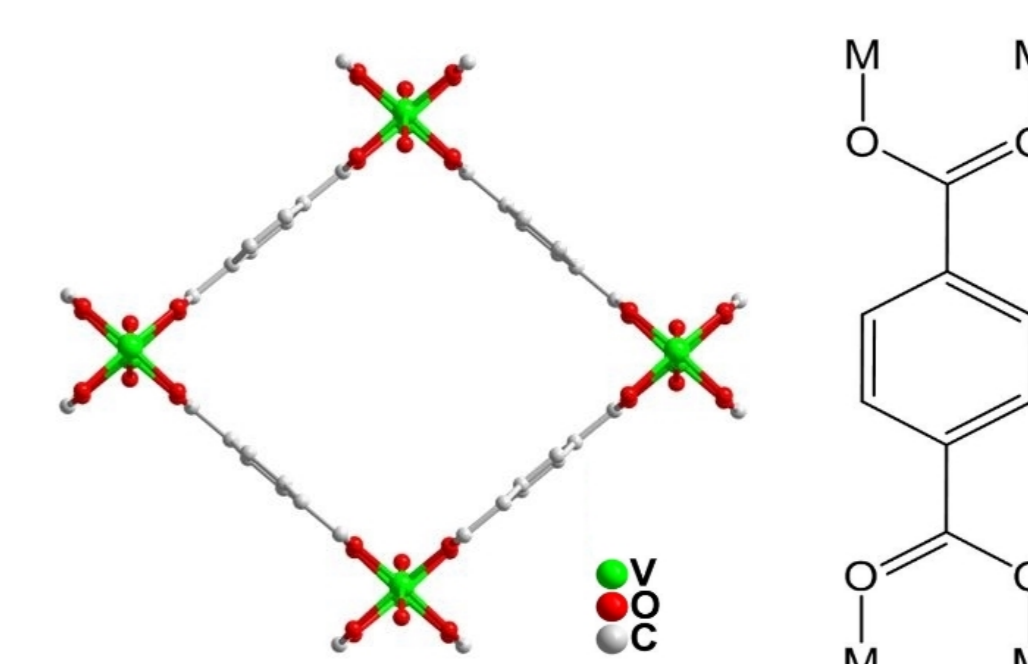
Introduction

- ▶ Metal Organic Frameworks (MOFs) → 'superzeolites' or 'the next generation of porous materials'
- ▶ 3D structures are self-assembled by coordination of suitable metal ions/clusters with organic ligands
- ▶ Combining different 'metal nodes' and organic linkers → tuning the structure, functionality
- ▶ Wide range of applications in catalysis, hydrogen storage, optics, ...
- ▶ MIL-47 [VO(BDC)] and MIL-53 [Al(OH)(BDC)]
- ▶ BDC = terephthalate or 1,4-benzenedicarboxylate
- ▶ MIL = Matériaux de l'Institut Lavoisier

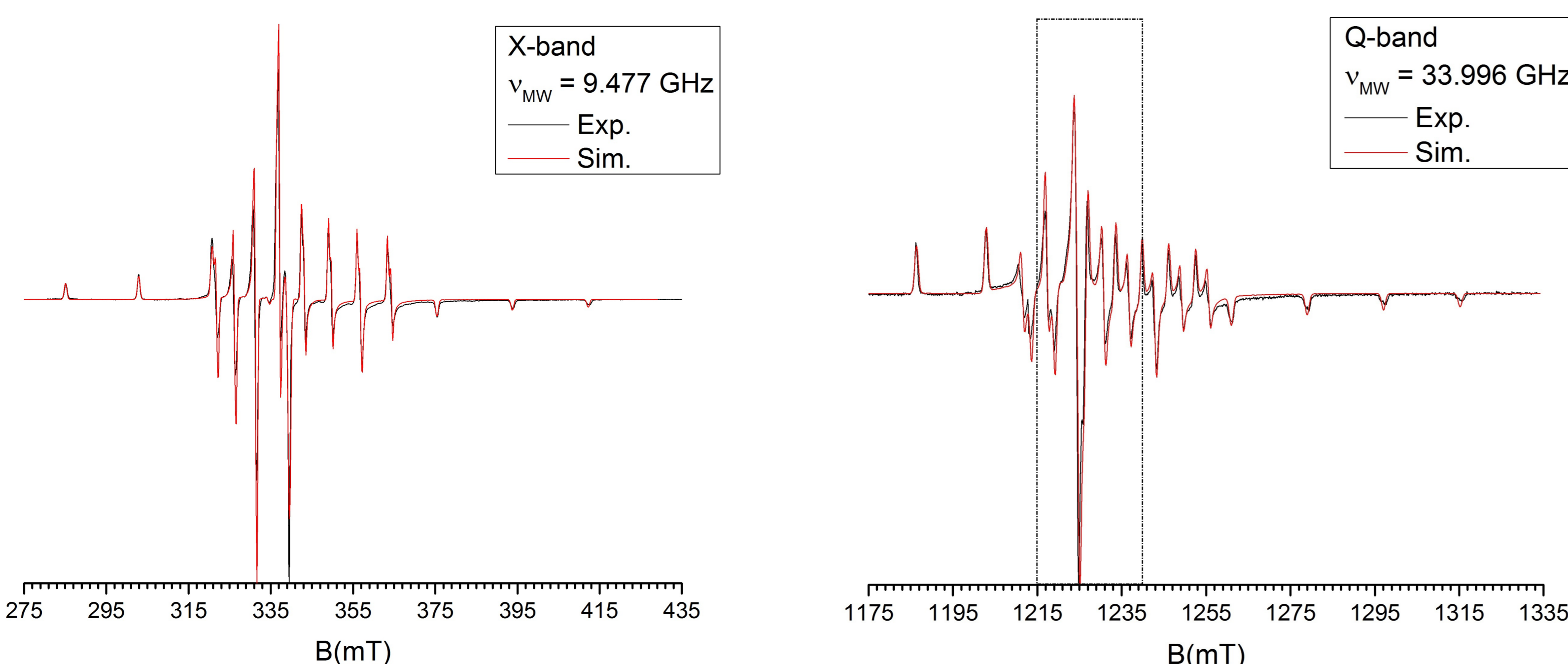
MIL-47 vs. doped MIL-53

- ▶ Recently, we have demonstrated that MIL-47 is an efficient catalyst in the liquid phase oxidation of cyclohexene^[1]
- ▶ Problem: MIL-47 exhibits limited stability in aqueous environments
- ▶ Solution: Doping the highly stable MIL-53 with catalytically active V^{IV} ions

- ▶ Question: Is vanadium really incorporated in the framework?
- ▶ V^{IV} (3d¹) → a paramagnetic ion
- ▶ Electron paramagnetic resonance (EPR) and ENDOR spectroscopy may provide the answer



EPR spectra



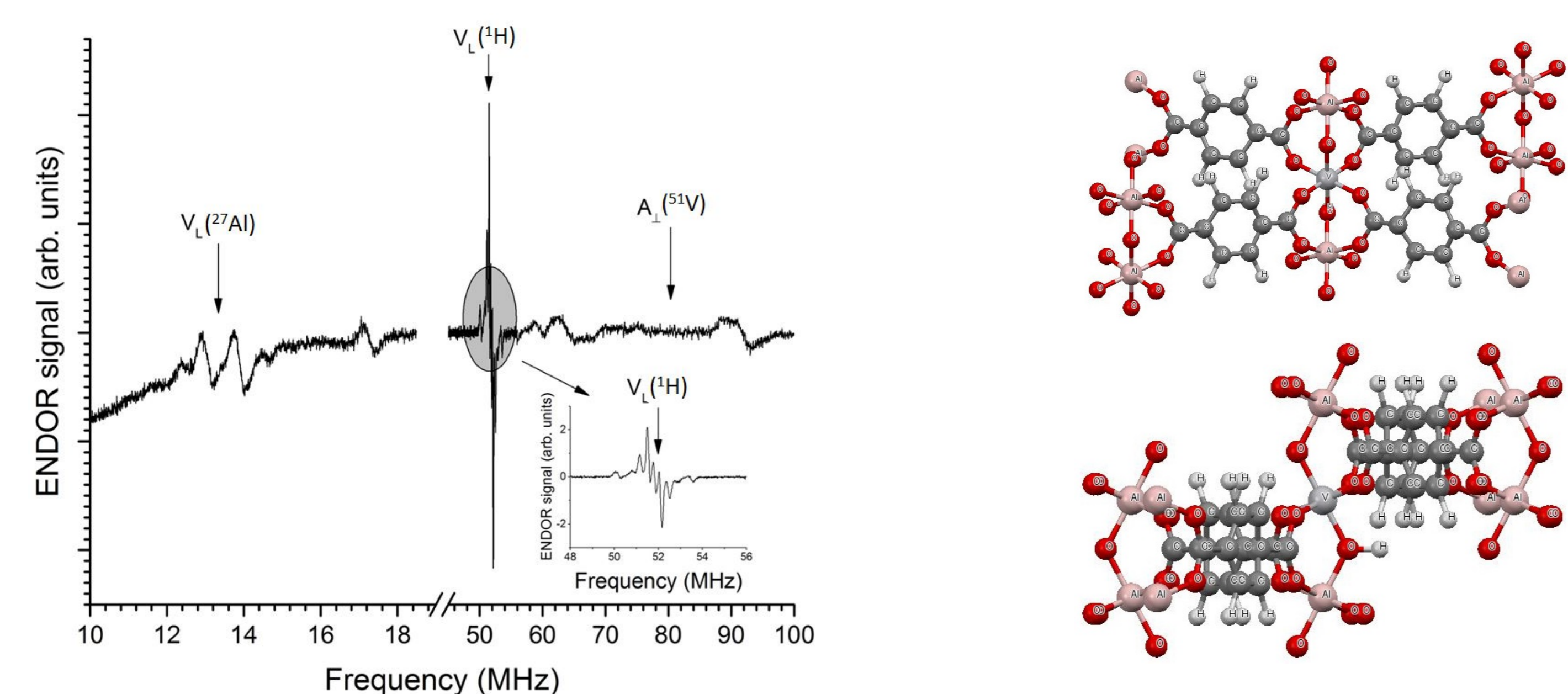
Analysis

- ▶ In two figures (left) the powder EPR spectrum in X and Q-band for as-synthesized V-doped MIL-53 at RT is shown
- ▶ The spectra are dominated by just one V^{IV} center with rhombic g and ⁵¹V hyperfine (HF) tensors whose principal axes do not coincide

g	x	y	z
1.9725	1	0	0
1.9669	0	1	0
1.9396	0	0	1

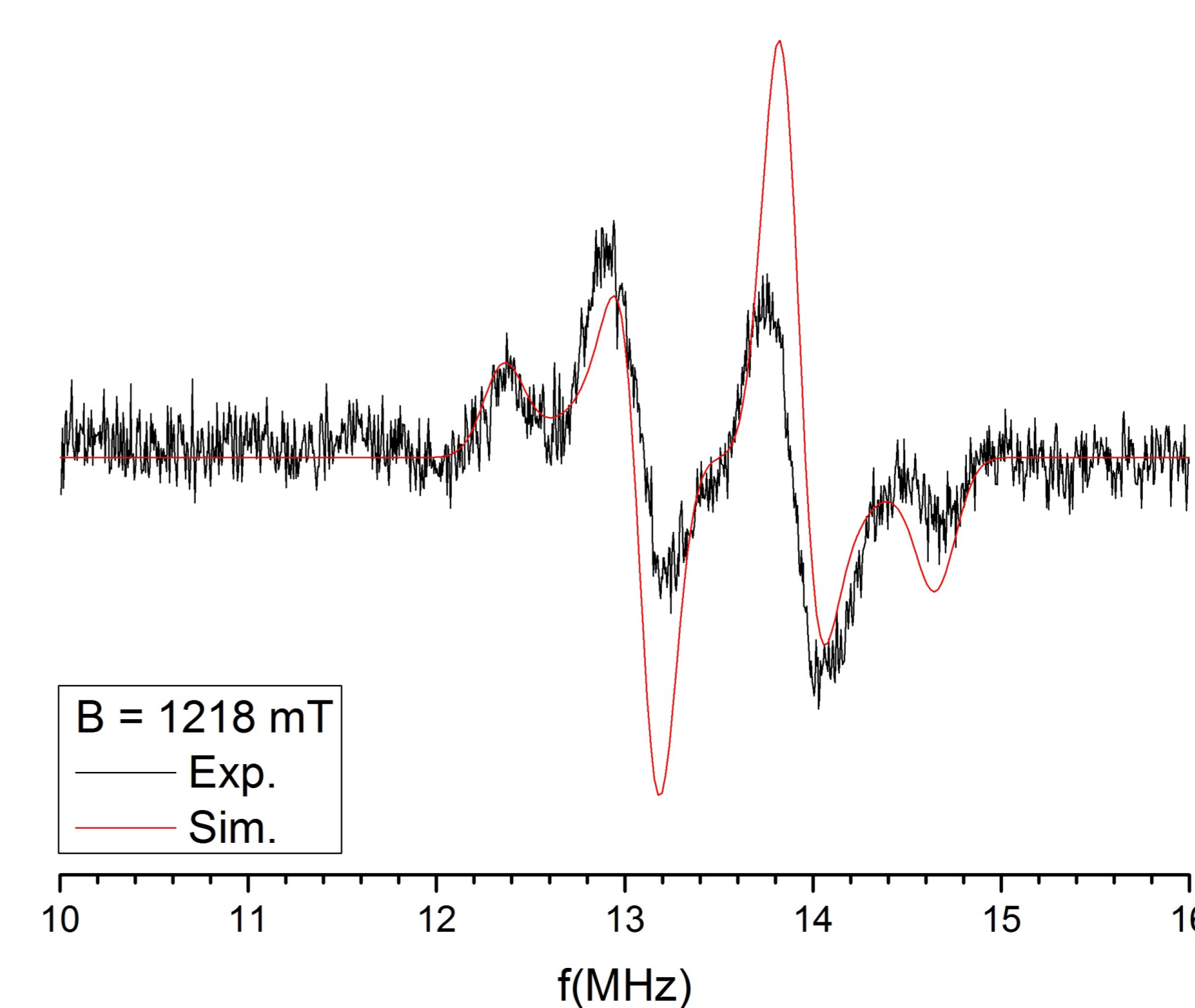
A [MHz]	x	y	z
163	0.9686	-0.1361	0.2079
165	0.1392	0.9903	0
493	-0.2059	0.0289	0.9781

MIL-53 ¹H, ²⁷Al and ⁵¹V range



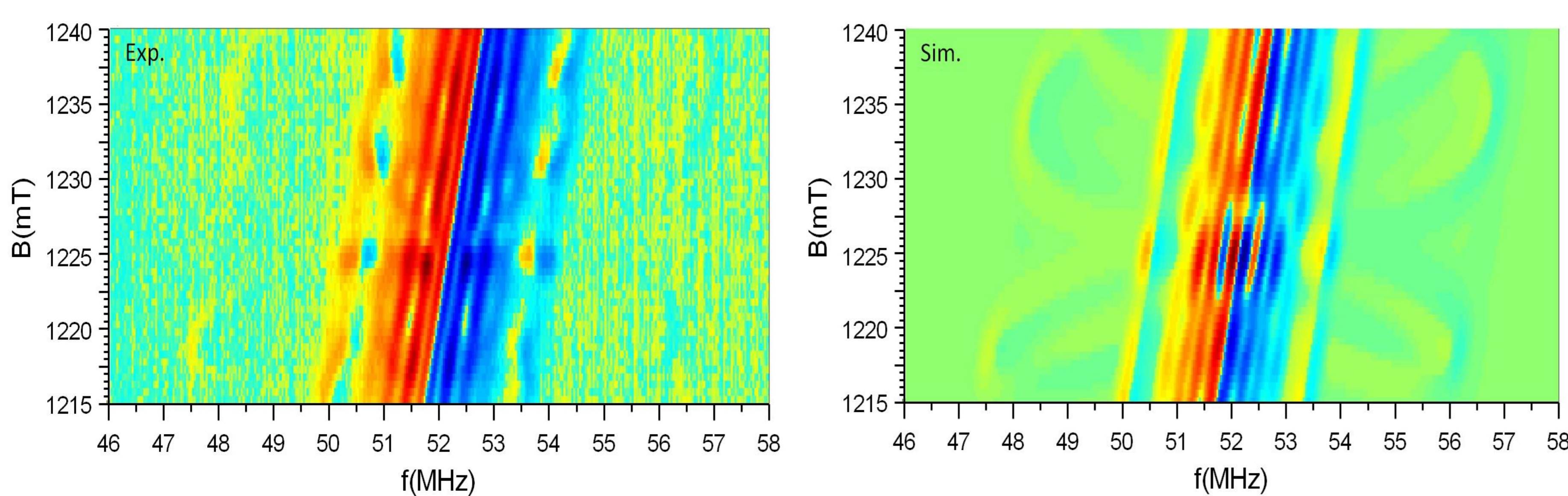
- ▶ The ENDOR spectra of V^{IV} in MIL-53 reveal HF interactions with the central ⁵¹V, ¹H and ²⁷Al nuclei

MIL-53 ENDOR spectrum in ²⁷Al range



- ▶ Interaction with two nearest ²⁷Al nuclei →
A_⊥ = 0.75 MHz and
A_∥ = 2.3 MHz →
d_{exp} = 3.4 Å, d_c = 3.31 Å
- ▶ Suggesting that the V^{IV} ions are incorporated in the framework

MIL-53 field dependence ENDOR spectra in ¹H range



	OH	H ₁₁	H ₁₂	H ₁₃	H ₁₄	H ₂₁	H ₂₂	H ₂₃	H ₂₄
A _⊥ [MHz]	-3.3	-1.3	-1.3	-1.3	-1.3	-0.8	-0.8	-0.8	-0.8
A _∥ [MHz]	8.6	2.0	2.0	2.0	2.0	0.9	0.9	0.9	0.9
φ [deg]	0	-37	37	217	143	-37	37	217	143
θ [deg]	45	100	100	80	80	95	95	85	85

	H ₃₁	H ₃₂	H ₃₃	H ₃₄	Distances				
A _⊥ [MHz]	-0.1	-0.1	-0.1	-0.1	OH	d _{exp} = 2.7 Å	d _c = 2.47 Å		
A _∥ [MHz]	0.3	0.3	0.3	0.3	H ₁	d _{exp} = 4.14 Å	d _c = 3.49 Å		
φ [deg]	-37	37	217	143	H ₂	d _{exp} = 5.16 Å	d _c = 5.59 Å		
θ [deg]	95	95	85	85	H ₃	d _{exp} = 8.42 Å	d _c = 6.65 Å		

References :

- [1] K. Leus et al., J. Catal. 2012, 285, 196-207.
[2] O. Kosachuk et al., Eur. J. Inorg. Chem. 2013, 4546-4557.

Acknowledgments :



Contact :

Henk Vrielinck
Ghent University, Dept. of Solid State Sciences
Krijgslaan 281-S1, B-9000 Gent, Belgium
E-mail: Henk.Vrielinck@UGent.be