

Studying the environment of vanadyl complexes in the Al-Metal-Organic framework MIL-53 by a multifrequency EPR and ENDOR approach

Irena Nevjestic⁽¹⁾, Hannes Depauw⁽²⁾, Karen Leus⁽²⁾, Vidmantas Kalendra⁽³⁾, Ignacio Caretti⁽⁴⁾, Gunnar Jeschke⁽³⁾, Sabine Van Doorslaer⁽⁴⁾, 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
 (3) ETH Zürich, Wolfgang-Pauli-Str. 10, CH-8093 Zürich, Switzerland
 (4) University of Antwerp, Campus Drie Eiken, Universiteitsplein 1, 2610 Wilrijk, Belgium

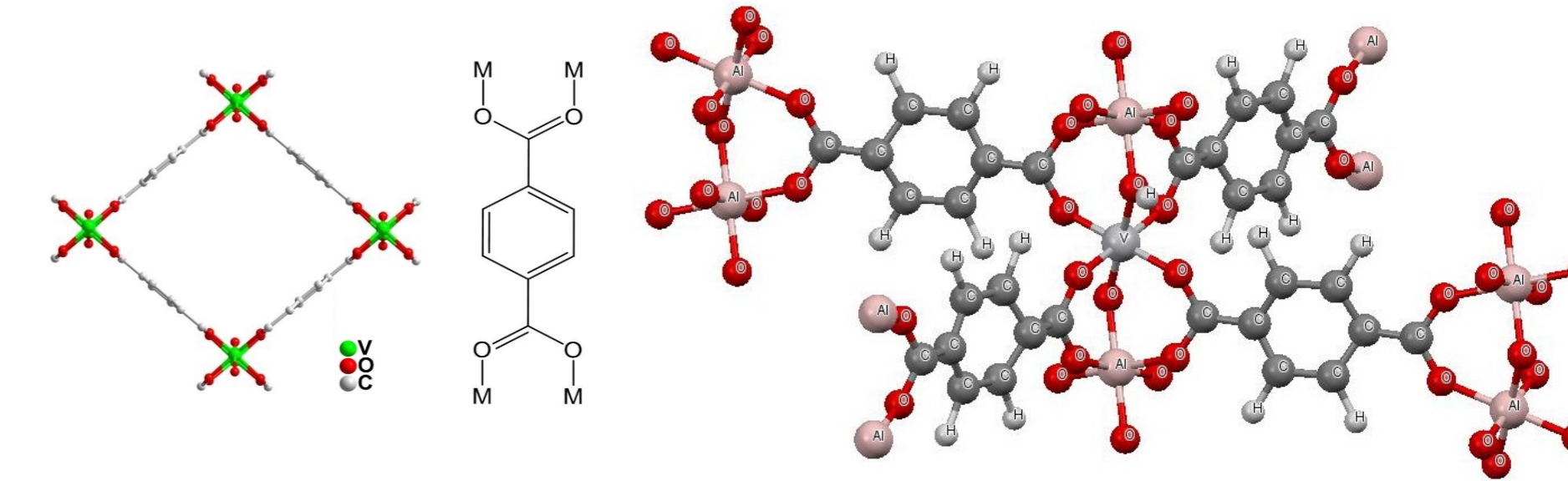
Introduction

MIL-47 vs. doped MIL-53

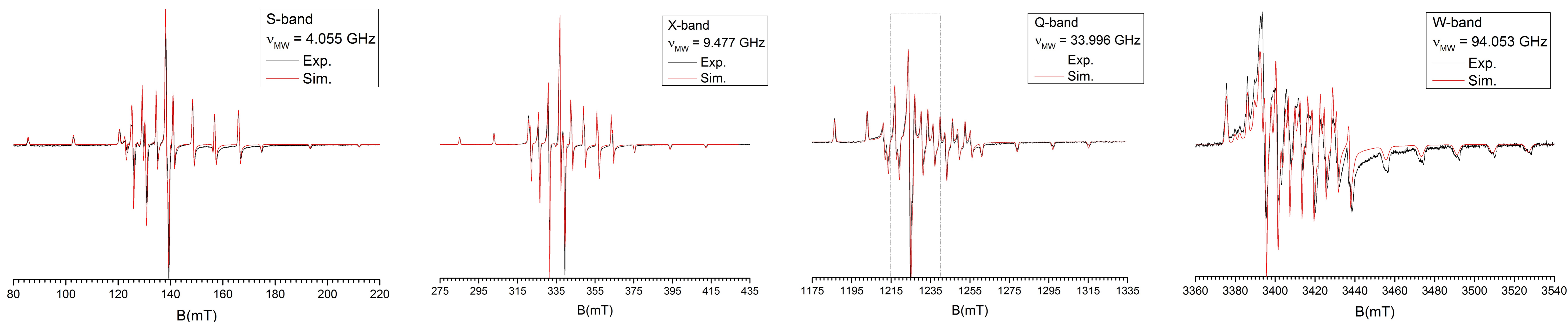
- ▶ Metal Organic Frameworks (MOFs) → ordered porous materials constructed of metal ions connected by organic linkers
- ▶ Possess many attractive features → possibility of tuning the structure by varying the organic linkers or metal atoms
- ▶ Promising materials for use in catalysis, gas storage and gas separation
- ▶ MIL-47 [VO(BDC)] and MIL-53 [Al(OH)(BDC)]
- ▶ BDC = terephthalate or 1,4-benzenedicarboxylate
- ▶ MIL = Matériaux de l'Institut Lavoisier

- ▶ Recently we reported that V-MIL-47 can be a highly selective 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? → here checked for as-synthesized structures

- ▶ V^{IV} (3d¹) → a paramagnetic ion
- ▶ Electron Paramagnetic Resonance (EPR) and ENDOR spectroscopy can reveal the nearest environment of the dopant ions



EPR spectra at 295 K



Analysis

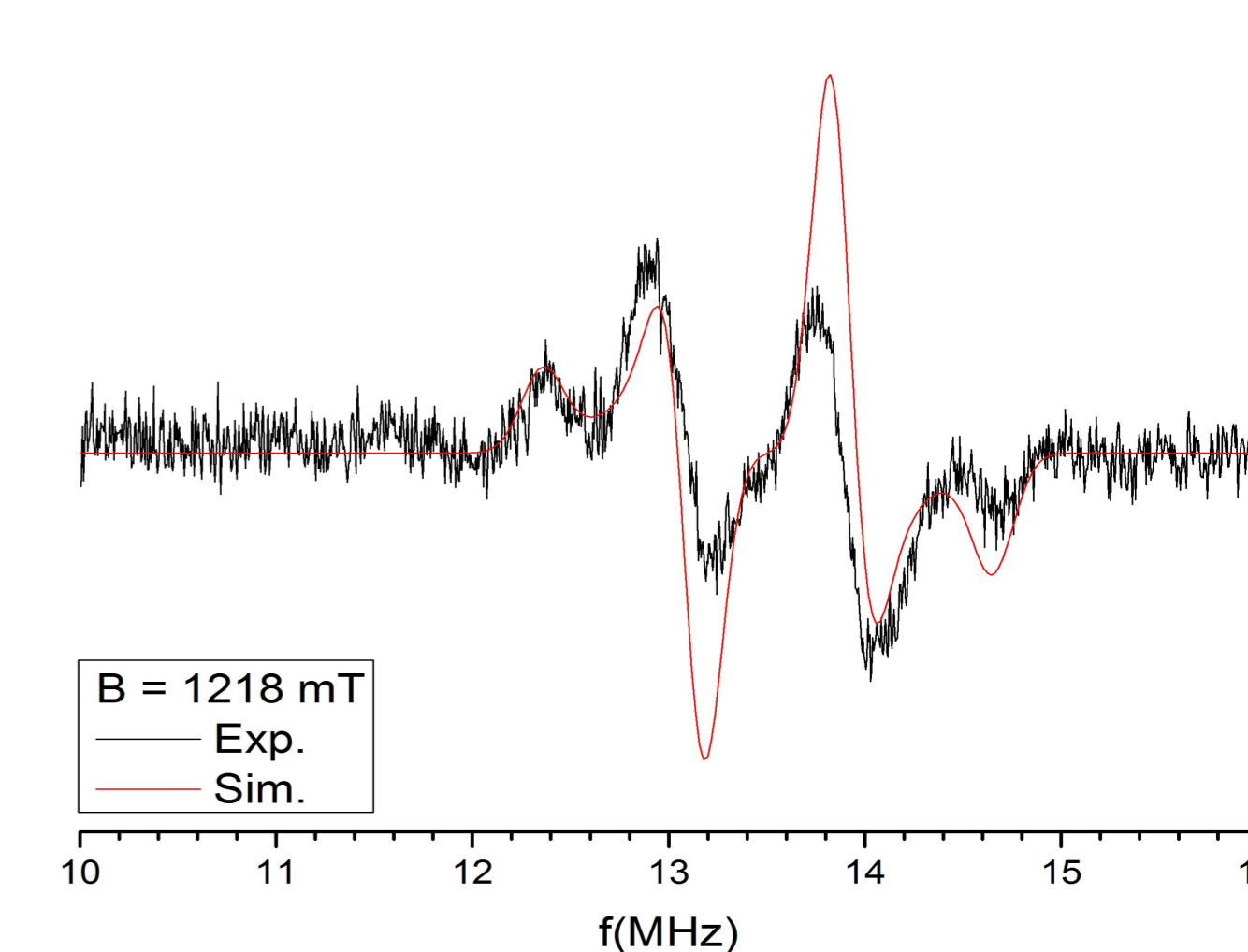
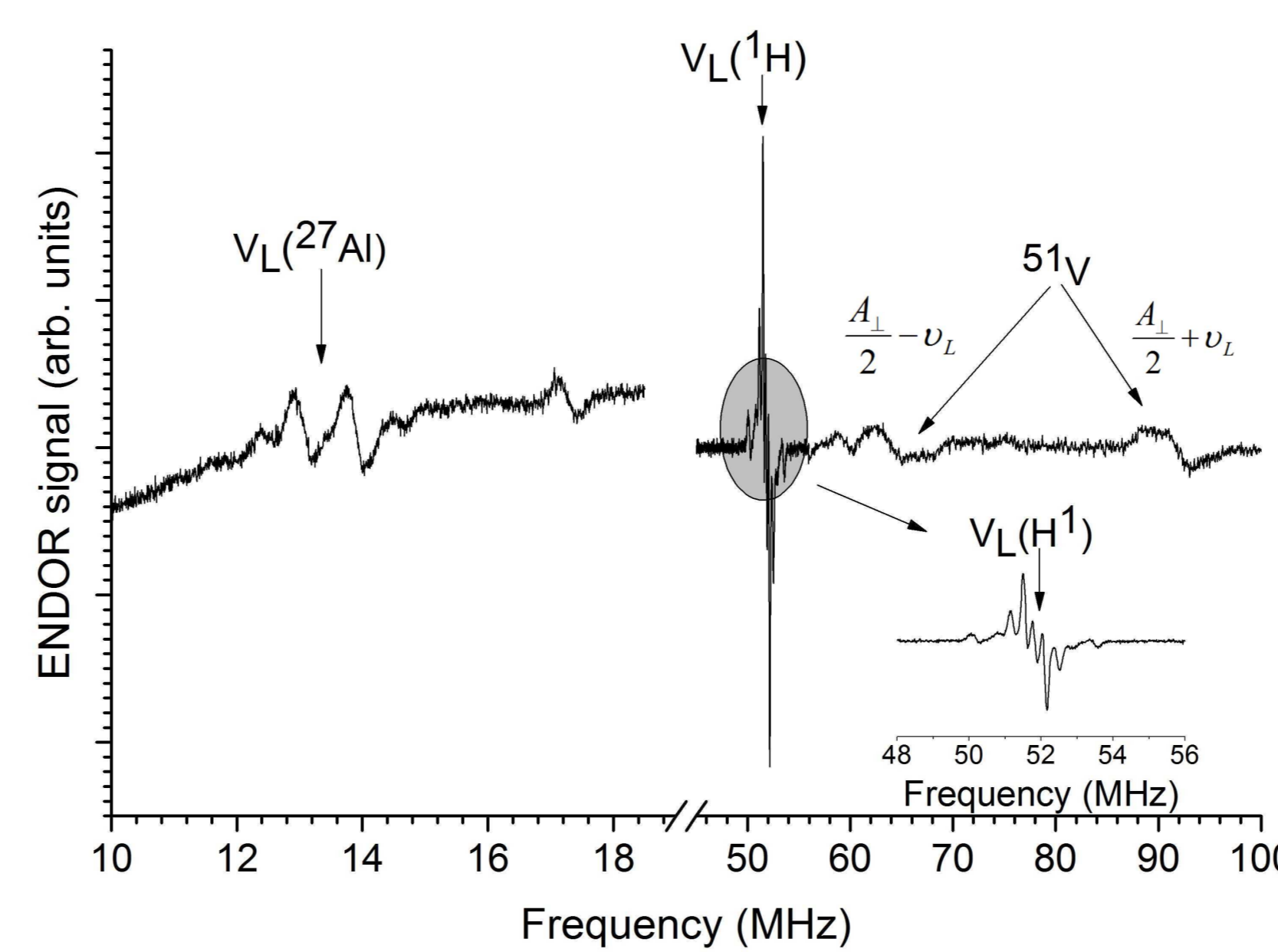
CW-ENDOR at Q-band at 10 K

CW-ENDOR in ²⁷Al range

- ▶ In four figures (up) the evolution of the powder EPR spectrum with microwave frequency 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

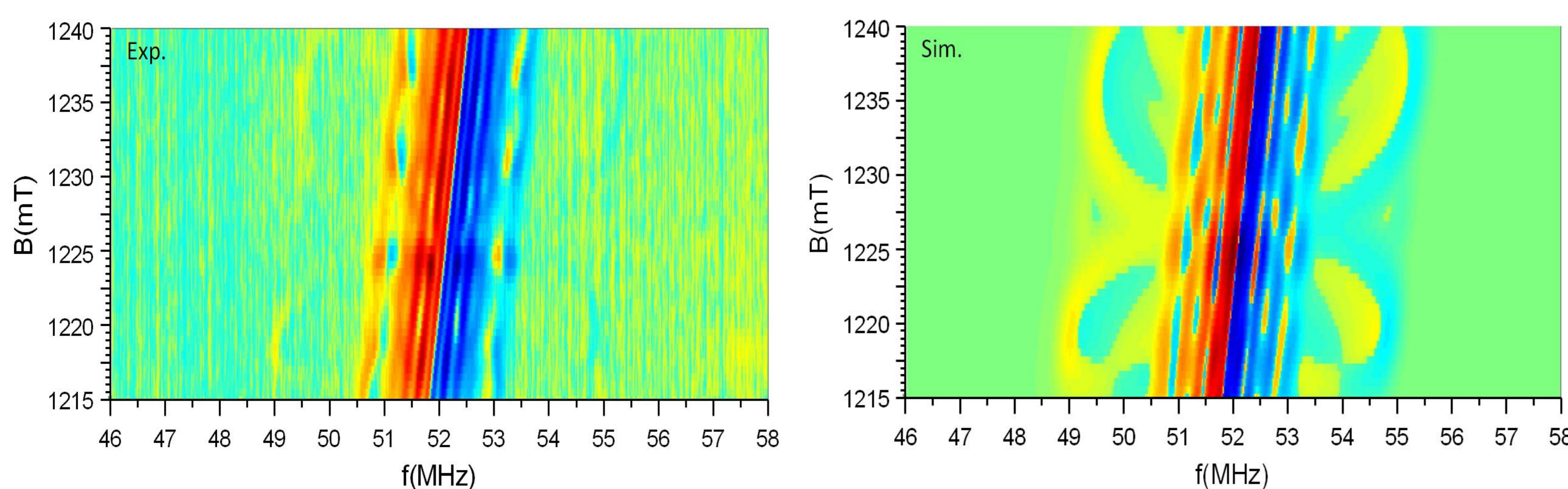


- ▶ The ENDOR spectra of V^{IV} in as-synthesized MIL-53 reveal HF interactions with the central ⁵¹V, ¹H and ²⁷Al nuclei

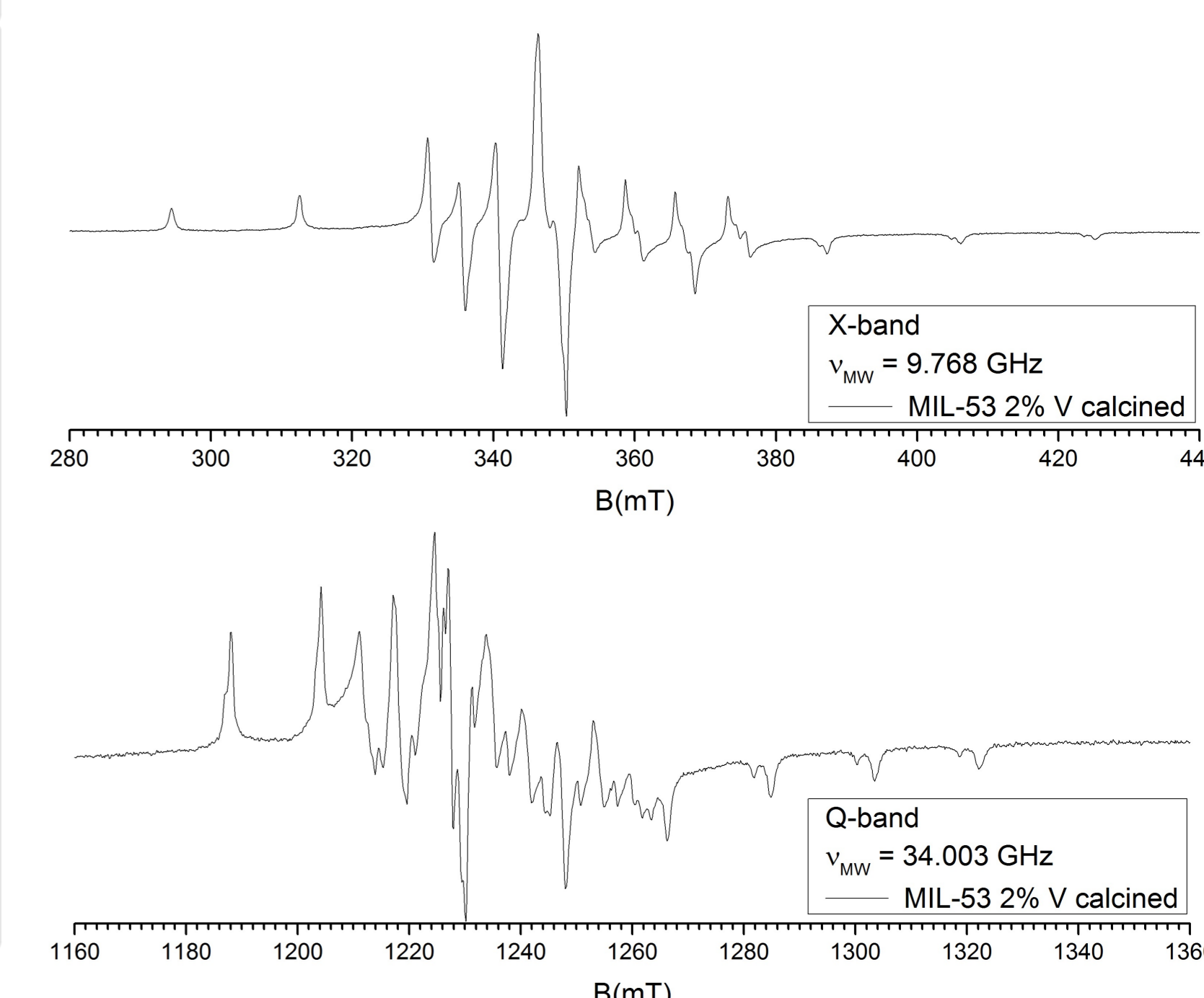
- ▶ Interaction with two nearest ²⁷Al nuclei → A_⊥ = 0.75 MHz and A_∥ = 2.3 MHz → d_{exp} = 3.4 Å, d_c = 3.31 Å
- ▶ Suggesting that the V^{IV} ions substitute Al in the framework

Field dependence ENDOR spectra in ¹H range

To do: Calcined structures



	MHz
OH	A _x = -3.1 A _y = -3.4 A _z = 8.6
H ₁	A _⊥ = -1.3 A _∥ = 2.4
H ₂	A _⊥ = -0.6 A _∥ = 0.7
H ₃	A _⊥ = -0.2 A _∥ = 0.6
H ₄	A _⊥ = -0.1 A _∥ = 0.4



References :

[1] K. Leus et al., J. Catal. 2012, 285, 196-207.

Acknowledgments :



Contact :

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