Resolving the relative tilting of hyperfine and g tensors for vanadyl complexes in the Al-metal-organic framework MIL-53 by a multifrequency (S, X, Q and W-band) EPR approach

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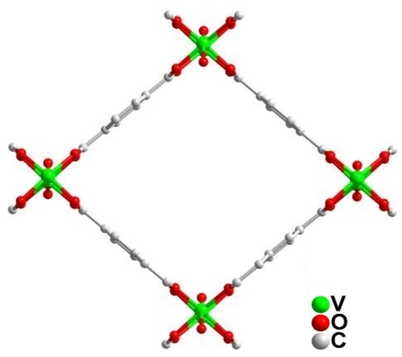
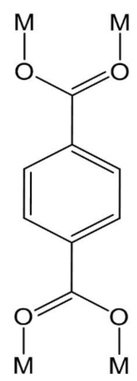
Introduction

- Metal Organic Frameworks (MOFs) → ordered porous materials
- Built of metal ions or clusters connected by organic linkers
- Interesting for many applications because they provide possibilities of designing structure, pore size or shape to desired functionality
- Potential use in catalysis, gas storage and gas separation
- MIL-47[1] [VO(BDC)] and MIL-53[2] [Al(OH)(BDC)]
- BDC = terephthalate or 1,4-benzenedicarboxylate
- MIL = Matériaux de l'Institut Lavoisier

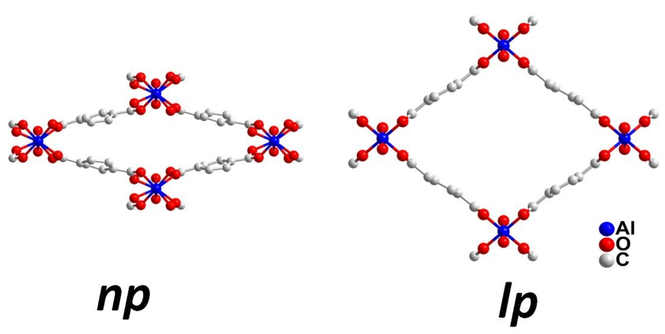
MIL-47





- Recently we reported that V-MIL-47 can be a highly selective catalyst in the liquid phase oxidation of cyclohexene[3]
- Problem: Exhibits limited stability in aqueous environments
- Solution: Doping the highly stable MIL-53 with catalytically active V^{IV} ions

MIL-53



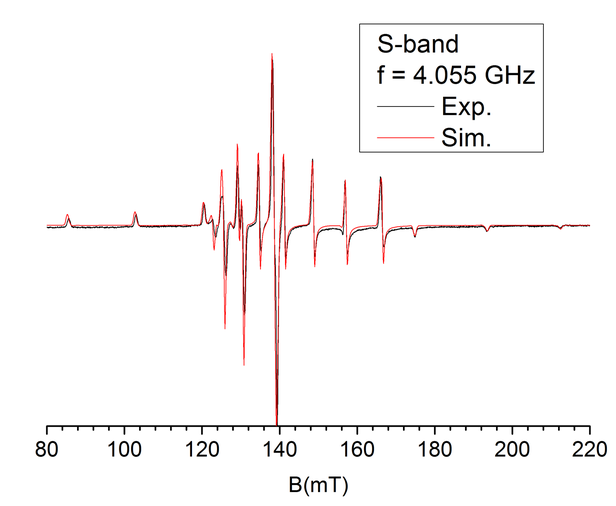
- After calcination → breathing
- To understand the catalytic activity of such doped framework → verify where dopant ions actually are
- V^{IV} ($3d^1$) → a paramagnetic ion

Multifrequency EPR spectrum and principal values

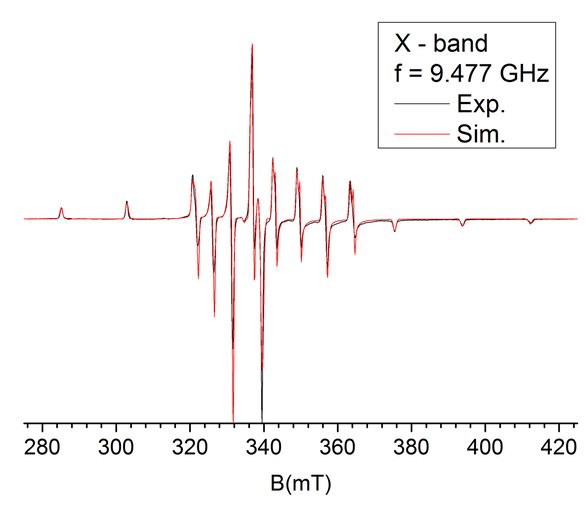
- In four figures (down) the evolution of the powder EPR spectrum with microwave frequency for V-doped MIL-53 is shown
- The spectra are dominated by just one V^{IV} center with rhombic g and V^{51} hyperfine (HF) tensors whose principal axes do not coincide

g	x	y	z
1.9667	1	0	0
1.9730	0	1	0
1.9394	0	0	1
A [MHz]	**x**	**y**	**z**
163	-0.1699	-0.9633	0.2079
165	0.9848	-0.1736	0
493	0.0361	0.2048	0.9781

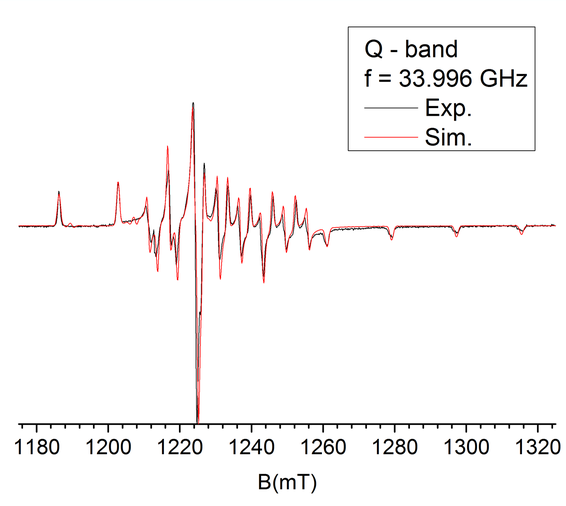
S-band



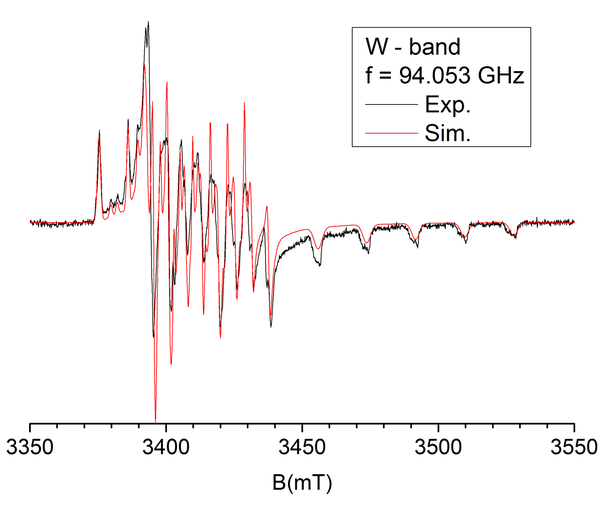
X-band



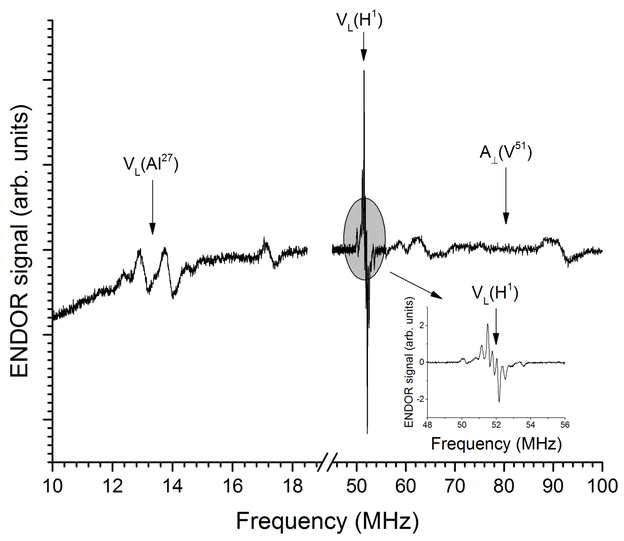
Q-band



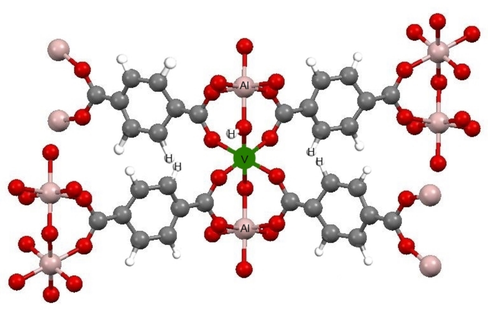
W-band



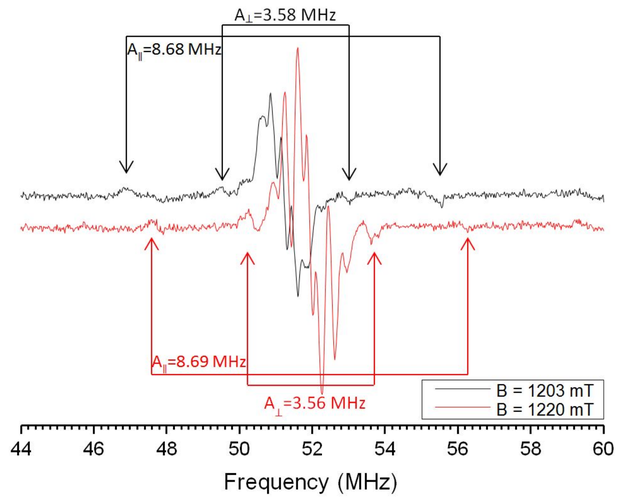
MIL-53 H^1, Al^{27} and V^{51} range

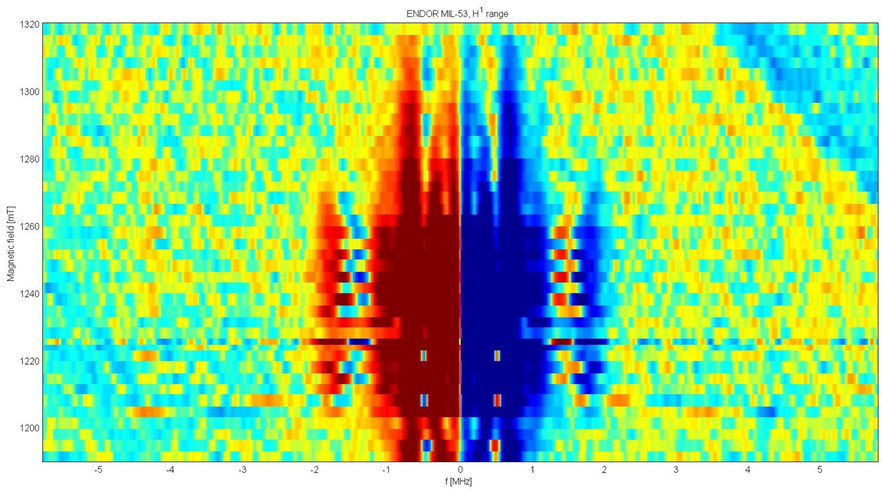


- The ENDOR spectra of V^{IV} in MIL-53 reveal HF interactions with H^1 and Al^{27} nuclei



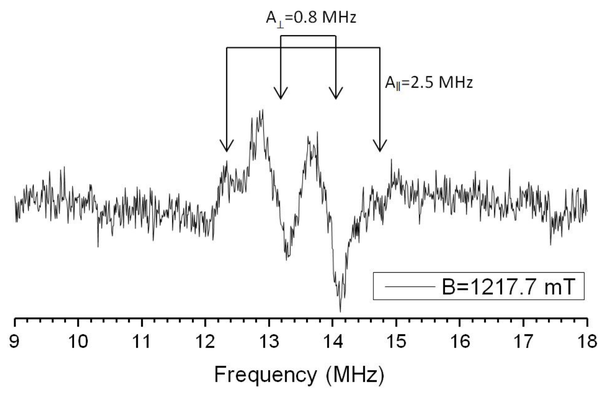
MIL-53 field dependence ENDOR spectra in H^1 range





- In central position → several weaker interactions with few distant protons
- Large interaction with nearest proton →
  $|A_\perp| = 3.57$ MHz, $|A_\parallel| = 8.69$ MHz
  → $d_{exp} = 1.72$ Å, $d_{calc} = 1.87$ Å

MIL-53 ENDOR spectrum in Al^{27} range



- Interaction with two nearest Al^{27} nuclei →
  $A_\perp = 0.8$ MHz and $A_\parallel = 2.5$ MHz →
  $d_{exp} = 3.32$ Å, $d_{calc} = 3.31$ Å
- Suggesting that the V^{IV} ions are incorporated in the framework

References :

[1] K. Barthelet et al., Angew. Chem. Int. Ed. 2002, 41, 281-284
[2] C. Serre et al., J. Am. Chem. Soc. 2002, 124, 13519-13526
[3] K. Leus et al., J. Catal. 2012, 285, 196-207

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FWO VLAANDEREN for  !

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