Characterizing vanadium dopant sites in an Al-Metal-Organic Framework by Electron Magnetic Resonance spectroscopy

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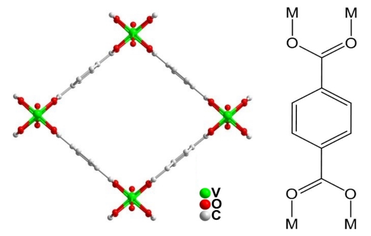
Introduction

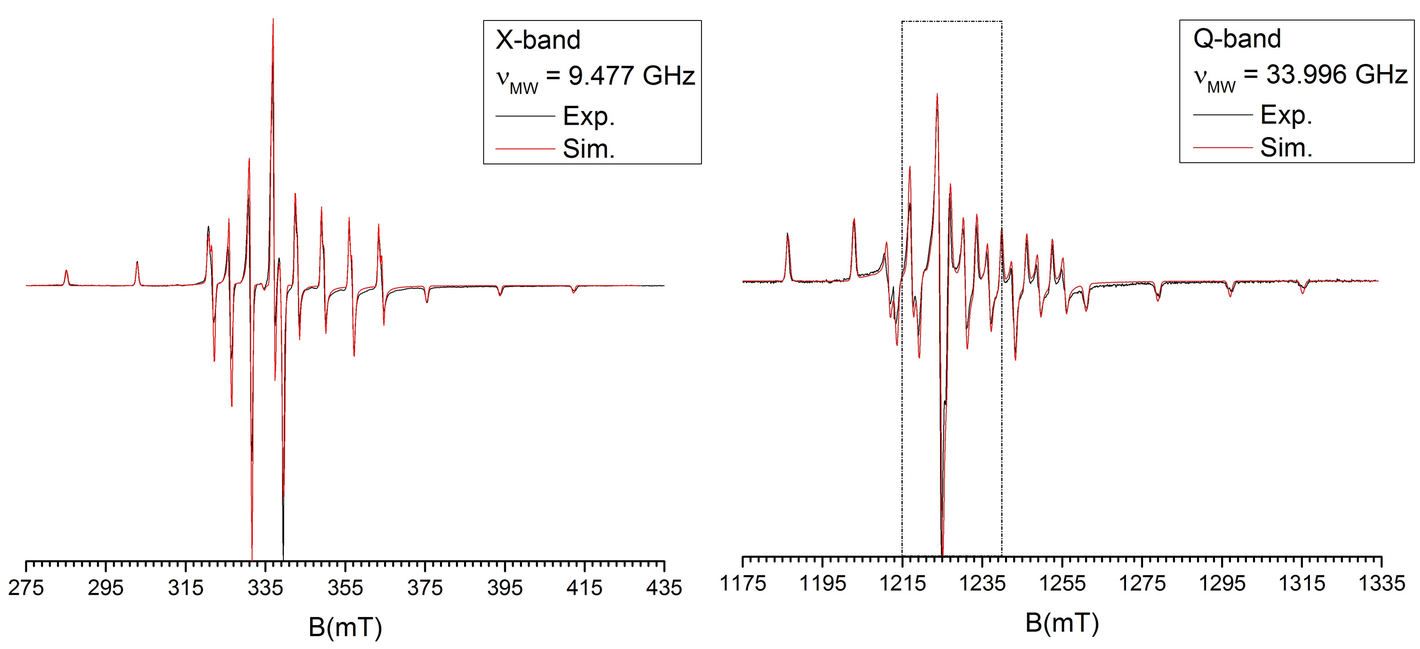
- Metal Organic Frameworks (MOFs) are crystalline porous solids constructed of metal ions or clusters linked by organic ligands to form an infinite network
- Interesting for many applications, structure can easily be tuned to specific chemical functionalities
- Potential use in catalysis, gas storage and purification
- 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 vs. doped MIL-53

- Recently we reported that V-MIL-47 can be a highly selective catalyst in the epoxidation of cyclohexene[3]
- 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 lattice? $\rightarrow$ here checked for as-synthesized structures
- V^{IV} ($3d^1$) $\rightarrow$ a paramagnetic ion
- Electron Paramagnetic Resonance (EPR) and Electron Nuclear DOuble Resonance spectroscopy can reveal the nearest environment of the dopant ions



EPR spectra at 295 K

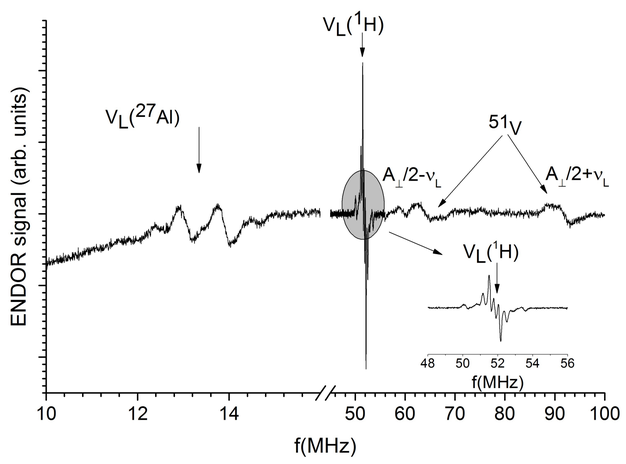


Analysis

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

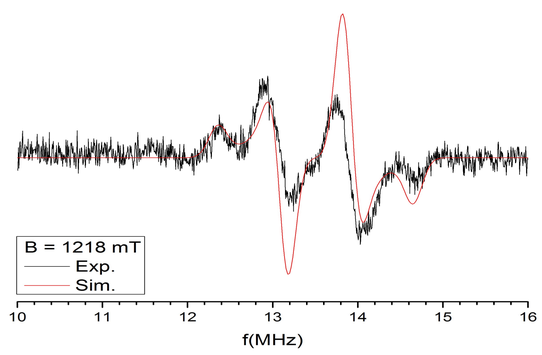
g	x	y	z
1.9725	1	0	0
1.9669	0	1	0
1.9396	0	0	1
A [MHz]	**x**	**y**	**z**
163	0.9686	-0.1361	0.2079
165	0.1392	0.9903	0
493	-0.2059	0.0289	0.9781

CW-ENDOR at Q-band at 10 K



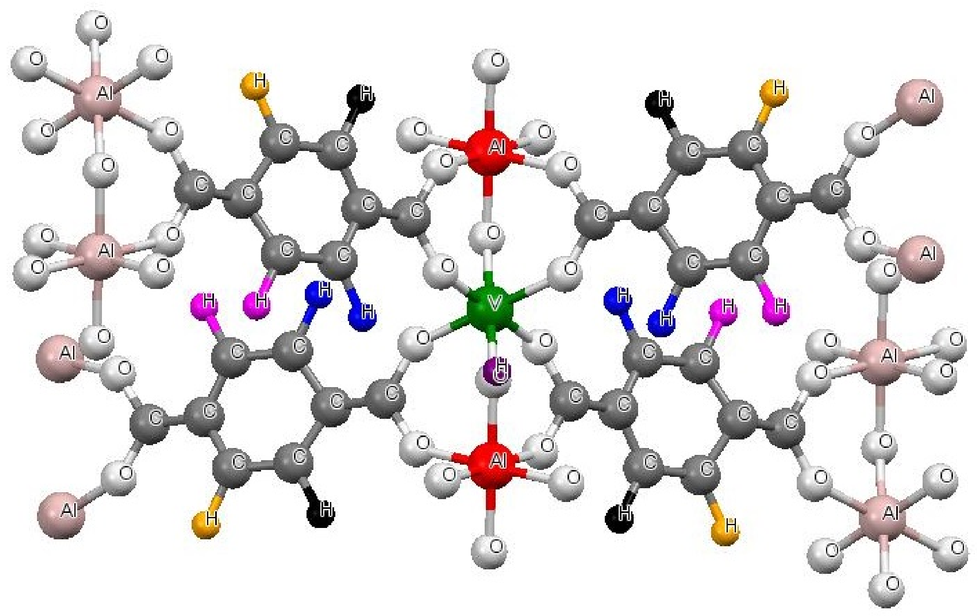
- The ENDOR spectra of V^{IV} in as-synthesized MIL-53 reveal HF interactions with the central ^{51}V, ^1H and ^{27}Al nuclei

CW-ENDOR in ^{27}Al range

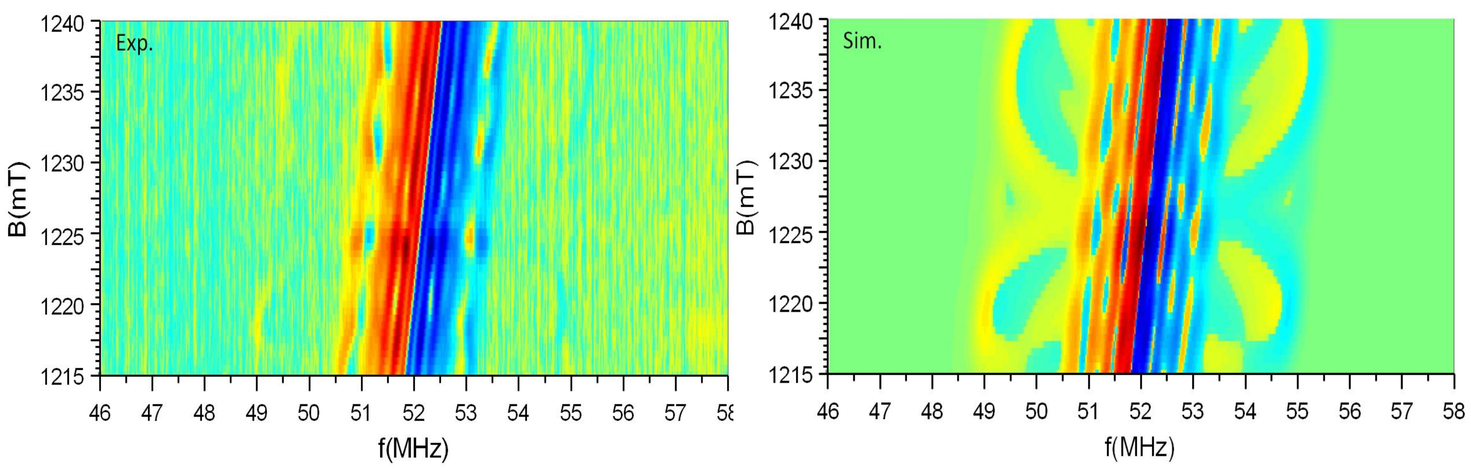


- Interaction with two nearest ^{27}Al nuclei $\rightarrow$ $A_\perp = 0.75$ MHz and $A_\parallel = 2.3$ MHz $\rightarrow$ $d_{th} = 3.31$ Å, $d_{exp} = 3.4$ Å
- Suggesting that the V^{IV} ions substitute Al in the MIL-53 lattice

Doped MIL-53 structure



Field dependence of ENDOR spectra in ^1H range



	H_{11}	H_{12}	H_{13}	H_{14}	H_{21}	H_{22}	H_{23}	H_{24}
$A_\perp$ [MHz]	-1.3	-1.3	-1.3	-1.3	-0.6	-0.6	-0.6	-0.6
$A_\parallel$ [MHz]	2.4	2.4	2.4	2.4	0.7	0.7	0.7	0.7
ϕ [deg]	53	127	233	-53	53	127	233	-53
θ [deg]	100	80	80	100	45	135	135	45
	H_{31}	H_{32}	H_{33}	H_{34}	H_{41}	H_{42}	H_{43}	H_{44}
$A_\perp$ [MHz]	-0.2	-0.2	-0.2	-0.2	-0.1	-0.1	-0.1	-0.1
$A_\parallel$ [MHz]	0.6	0.6	0.6	0.6	0.4	0.4	0.4	0.4
ϕ [deg]	53	127	233	53	53	127	233	-53
θ [deg]	95	85	85	95	60	120	120	60

	MHz
OH	$A_x = -3.1$
	$A_y = -3.4$
	$A_z = 8.6$
	Distances
OH	$d_{th} = 2.47$ Å
	$d_{exp} = 2.49$ Å
H_1	$d_{th} = 3.99$ Å
	$d_{exp} = 3.98$ Å
H_2	$d_{th} = 5.59$ Å
	$d_{exp} = 5.64$ Å
H_3	$d_{th} = 6.65$ Å
	$d_{exp} = 6.63$ Å
H_4	$d_{th} = 7.71$ Å
	$d_{exp} = 7.76$ Å

References :

[1] K. Barthelet et al., Angew. Chem. Int. Ed. 2002, 41, 281-284
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[3] K. Leus et al., J. Catal. 2012, 285, 196-207

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FWO VLAANDEREN for  !

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