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# ELECTRON PARAMAGNETIC RESONANCE CHARACTERIZATION OF VANADIUM DOPANT SITES IN DUT-5(Al)

## Introduction

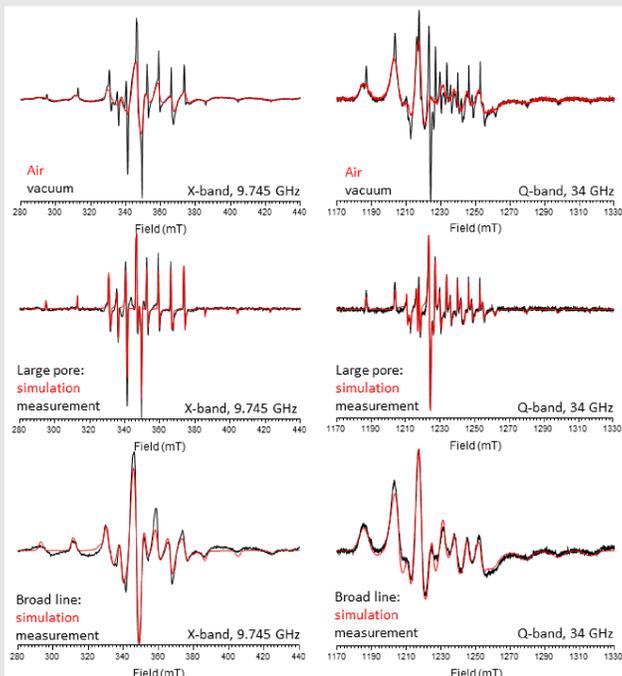
Metal-Organic Frameworks (MOFs) are ordered porous crystalline materials constructed of metal ions connected by organic linkers. Because of their many interesting properties, a diverse scale of applications are being explored (e.g. catalysis, gas adsorption, separation and storage). Some MOFs exhibit the breathing phenomenon: the framework can reversibly change from an open (large pore) to a closed (narrow pore) structure. In general breathing can be induced by various external triggers like temperature, mechanical pressure or exposure to (and the presence of) certain gasses. Recent work showed that EPR spectroscopy using  $V^{IV}$  as a paramagnetic probe is able to distinguish between the large pore and the narrow pore state of such a breathing MOF: V-doped MIL-53(Al) ( $[Al^{III}OH]BDC$ , BDC: 1,4-benzenedicarboxylate) [1-3]. For the research presented here we study a closely related MOF: DUT-5(Al) ( $[Al^{III}OH]BPDC$ , BPDC: biphenyl-4,4'-dicarboxylate), which is a rigid structure that does not exhibit breathing [4]. However, in  $(V^{IV}=O)BPDC$ , i.e. COMOC-2(V), part of the framework does breathe [5]. In mixed  $[Al^{III}OH]_x(V^{IV}=O)_{1-x}BPDC$  MOFs, an EPR spectral component was observed that showed similar characteristics as  $V^{IV}=O$  in large pore MIL-53(Al), but also other components were found [6]. In the present study we further explore the EPR spectrum of this mixed-metal MOF.

## Sample: DUT-5(Al)

DUT-5(Al) consists of  $Al^{III}$  ions that are coordinated to six oxygen atoms forming a distorted octahedral geometry, with at the axial positions hydroxyl groups forming large chains. These chains are linked together by biphenyl-4,4'-dicarboxylate (BPDC) molecules. This creates a porous rigid structure with a large internal volume.

## Measurement procedure

Eight DUT-5(Al) samples, doped with increasing  $V^{IV}$  concentration, and COMOC-2(V) were measured in two different frequency bands: X-band (9,745 GHz) and Q-band (34 GHz). First in ambient air conditions, then the sample was evacuated ( $p \approx 0,3$  mbar). Simulations of the EPR spectra were performed using the Easyspin toolbox (version 5.2.11) for Matlab.

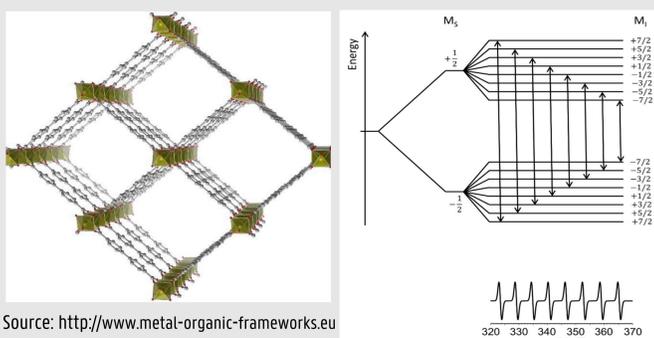


## Conclusions

- Doping DUT-5(Al) with low (1% - 7%) concentrations of  $V^{IV}$  reveals two vanadyl components in the EPR spectrum:
  - A component with spin-Hamiltonian parameters similar to the large pore state of MIL-53(Al) and equally sensitive to oxygen pressure.
  - A component with unique characteristics that cannot be linked to currently known vanadyl centers in MOFs. Therefore additional research will be necessary to identify this component.
- Increasing the concentration of  $V^{IV}$  in the framework of DUT-5(Al) reveals two additional spectral components.
  - An additional component linked to the narrow pore state of MIL-53(Al).
  - A broad single line that steadily grows with increasing  $V^{IV}$  concentration.

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Source: <http://www.metal-organic-frameworks.eu>

## Low (1% - 7%) $V^{IV}$ concentration

### Large pore

This component becomes visible by subtracting the spectrum measured at ambient air pressure from the spectrum at low pressure. It has spin-Hamiltonian parameters nearly identical to the parameters of the large pore state of V-doped MIL-53(Al).

### Broad line

This component is dominant at ambient air pressure. Its spin-Hamiltonian parameters cannot be associated with those of other known vanadyl centers in MOFs. Additional research will be needed to identify this component.

	g			A (MHz)			$\beta$ (°)
	X	Y	Z	X	Y	Z	
MIL-53 (np)*	1,9719	1,9634	1,9292	165,9	173,0	505,7	-14
MIL-53 (lp)*	1,9724	1,9675	1,9387	165,6	164,3	495,5	-11
DUT-5 (lp)	1,9729	1,9685	1,9391	167,3	165,7	495,5	-10
DUT-5 (BL)	1,9760	1,9701	1,9408	184,8	154,7	509,3	0

\*reproduced from ref [3]

## Higher (9%+) $V^{IV}$ concentration

### Narrow pore

As indicated by the arrows, the z-component hyperfine pattern of an additional isolated vanadyl center is observed. Its spin-Hamiltonian parameters are comparable to those of V-doped MIL-53(Al) in the narrow pore state.

### COMOC signal

With increasing  $V^{IV}$  concentration, a broad single line without hyperfine structure, similar to the spectrum of COMOC-2(V), steadily grows until the structure from other components is no longer visible.

## References

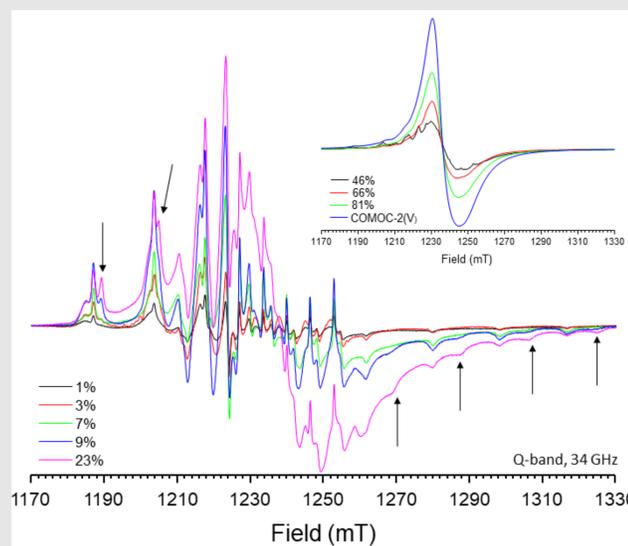
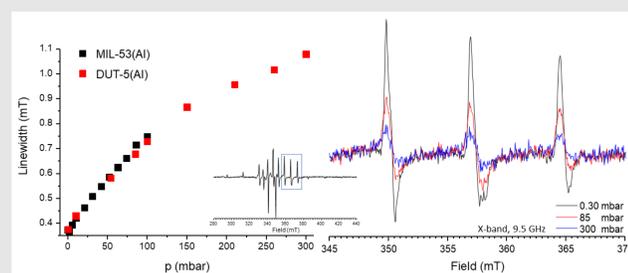
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## Technique: Electron Paramagnetic Resonance

EPR is a spectroscopic technique that studies the interaction of an unpaired electron in a sample with an applied magnetic field, i.e. the Zeeman effect. Additionally, there is also the interaction between the nuclei in the molecule and the unpaired electron, called nuclear hyperfine interaction. The Al-MOFs form a diamagnetic environment and the  $V^{IV}$  ions act as paramagnetic probes.  $V^{IV}$  has a  $1/2$  electron spin and a  $7/2$  nuclear spin. The electron Zeeman energy levels are split into eight levels each, resulting in a typical eight lines pattern.

## Oxygen sensing

The EPR spectrum of the large pore component exhibits the same EPR linewidth broadening with oxygen pressure as found for the large pore state of V-doped MIL-53(Al). The EPR linewidth increases monotonously with oxygen pressure.



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