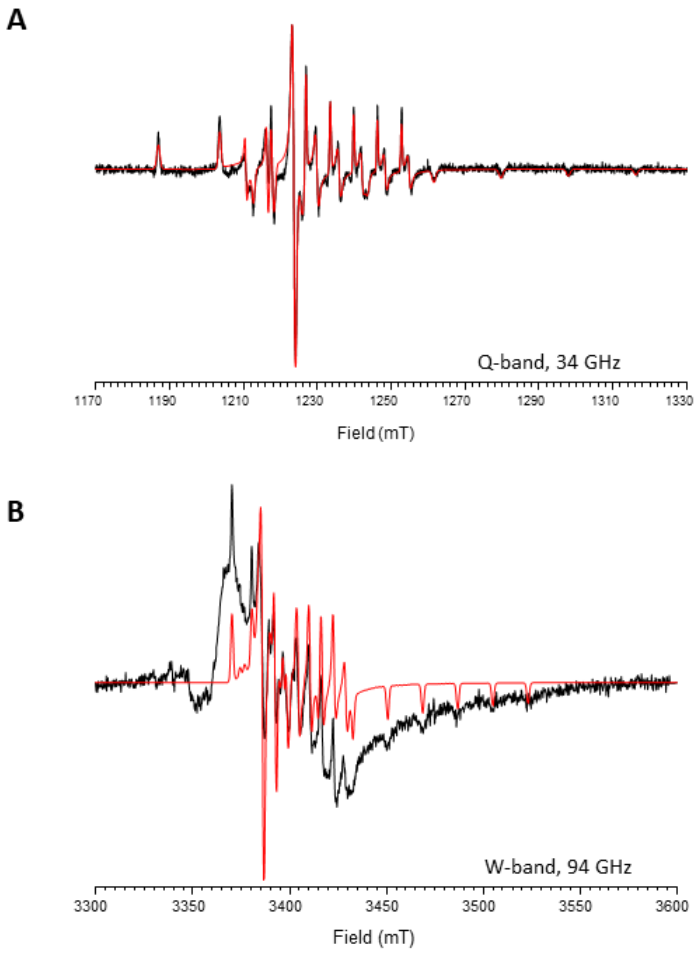
Multi-Frequency EPR characterization of vanadium dopant sites in DUT-5(Al)

Kwinten Maes[a], Karen Leus[b], Pascal Van Der Voort[b], Etienne Goovaerts[c], Henk Vrielinck[a] and Freddy Callens[a]

[a]Department of Solid State Sciences, Ghent University, Krijgslaan 281-S1, B-9000 Gent, Belgium
[b]Department of Chemistry, Ghent University, Krijgslaan 281-S3, B-9000 Gent, Belgium
[c]Department of Physics, University of Antwerp, Universiteitsplein 1, B-2610 Antwerp, Belgium
Kwinten.Maes@ugent.be

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). For the research presented here we use DUT-5(Al), which consists of Al(OH) chains linked together by biphenyl-4,4'-dicarboxylate (BPDC), creating a rigid lattice with large one-dimensional pores. In (V^{IV}=O)BPDC, i.e. COMOC-2(V), part of the framework exhibits the breathing phenomenon: the framework can reversibly change from an open (large pore) to a closed (narrow pore) structure [1]. Recently EPR spectroscopy using V(IV) as a paramagnetic probe was able to distinguish between the large pore and the narrow pore state of V-doped MIL-53(Al) ((Al^{III}OH)BDC, BDC: 1,4-benzenedicarboxylate) [2-4]. 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 [5].



In the present study we further explore the EPR spectrum of mixed $(Al^{III}OH)_x(V^{IV}=O)_{1-x}$BPDC MOFs. Spin-Hamiltonian parameters were derived from X- (9.5 GHz) and Q-band (34 GHz) spectra and resulting simulations were compared to W-band (94 GHz) spectra. Doping DUT-5(Al) with low (1% - 7%) concentrations of V^{IV} reveals two components in the EPR spectrum measured in vacuum: a narrow-line and a broad-line component. Going to higher (9%+) concentrations of V^{IV} reveals two additional spectral components: a narrow-line component of isolated vanadyl centers, and a broad structureless line of the V-concentrated phase (V^{IV}=O) BPDC.

Figure 1: Room temperature powder EPR spectra of DUT-5(Al), doped with 3% V^{IV}. A: Q-band (34 GHz) large pore spectrum, obtained by elimination of the broad-line component from the spectrum measured in vacuum ($p \approx 0.3$ mbar). B: W-band (94 GHz) spectrum measured in vacuum ($p \approx 2$ mbar). Black - experiment, red – simulation large pore component.

[1] Liu, Y.-Y., et al., Inorganic Chemistry, 2013. **52**(1): p. 113-120.
[2] Nevjestic, I., et al., Chemphyschem, 2015. **16**(14): p. 2968-73.
[3] Nevjestić, I., et al., The Journal of Physical Chemistry C, 2016. **120**(31): p. 17400-17407.
[4] Nevjestic, I., et al., Phys Chem Chem Phys, 2017. **19**(36): p. 24545-24554.
[5] Depauw, H., et al., Journal of Materials Chemistry A, 2017. **5**(47): p. 24580-24584.