Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Sensing the framework state and guest molecules in MIL-53(Al) via the electron paramagnetic resonance spectrum of V^{IV} dopant ions

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Powder X-Ray Diffraction

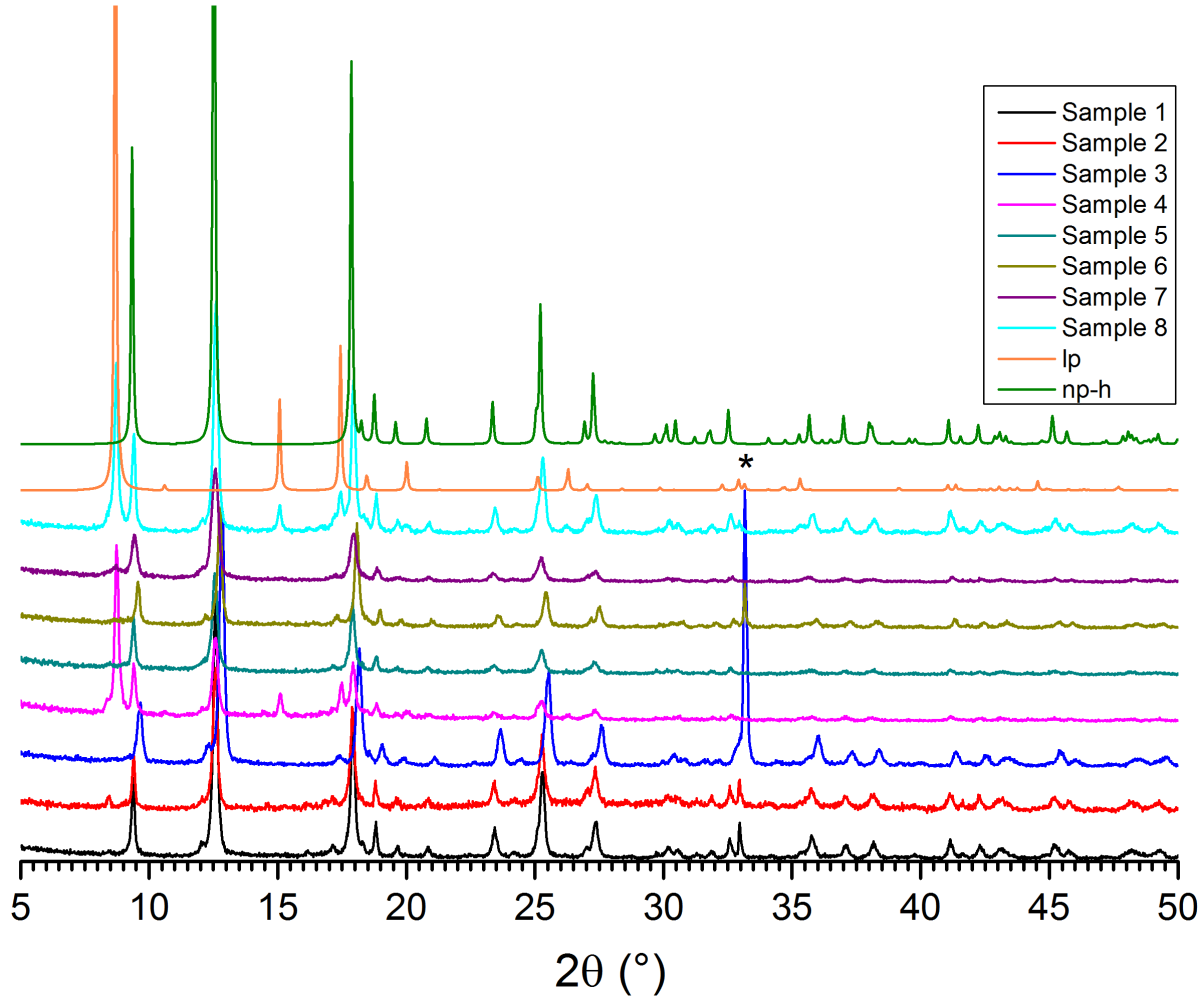
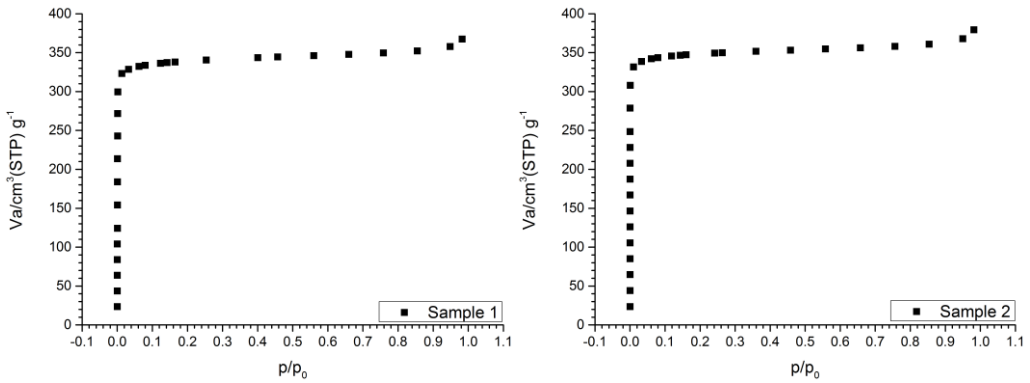


*Figure S1 – X-Ray powder diffraction patterns of activated V-doped MIL-53(Al) samples no. 1-8 together with theoretical XRD patterns of activated MIL-53(Al) in **lp** and **np-h** states. The asterisk shows the XRD peak due to the silicon wafer.*

N_2 adsorption



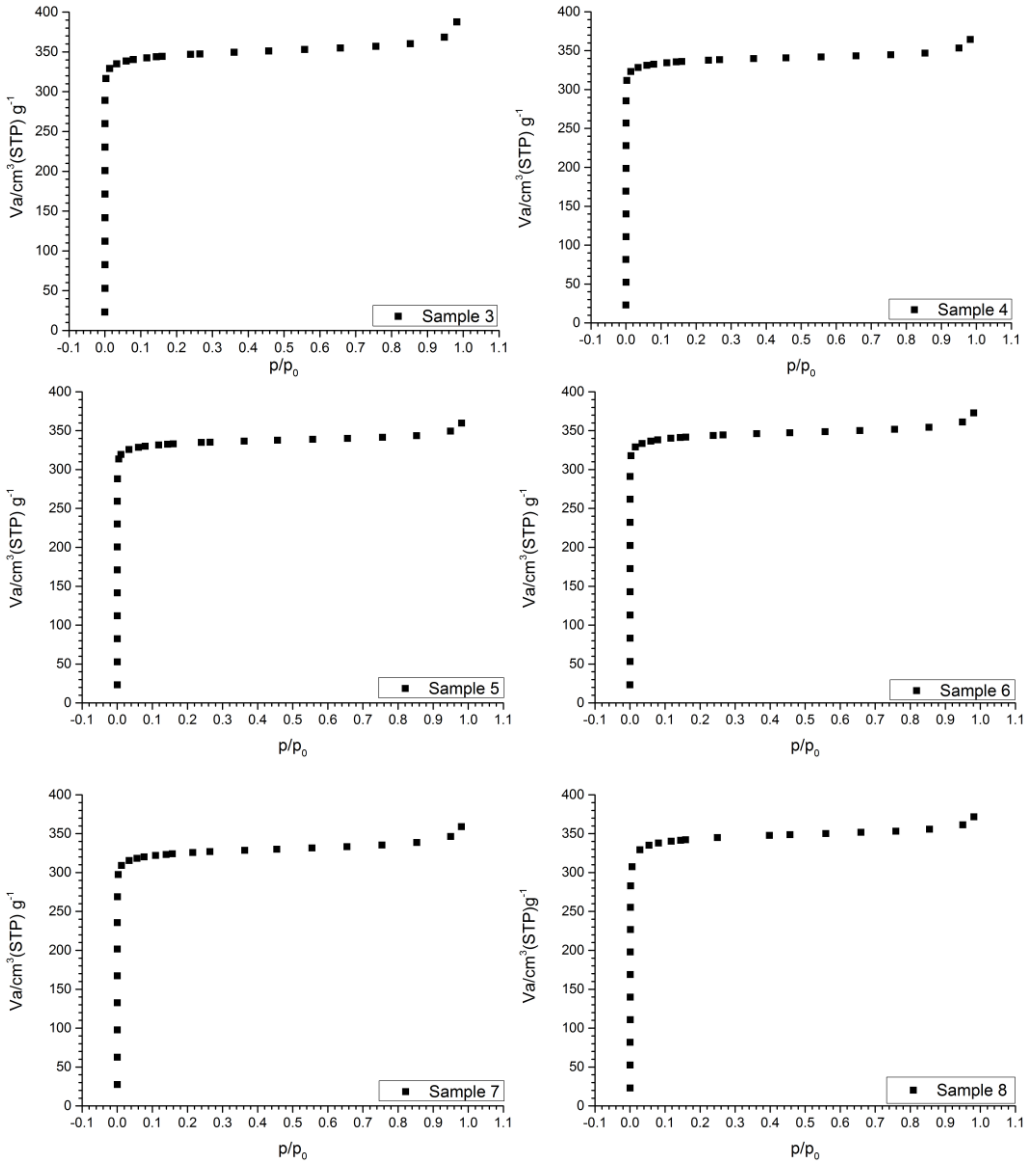


Figure S2 – N_2 adsorption isotherms of reported samples no. 1-8 at 77 K. P_0 represents the saturation pressure.

Lattice parameters for three states in MIL-53(Al) and MIL-53(Ga)

*Table S1 – Available lattice parameters for the **np-h**, **np-d** and **lp** states in MIL-53(Al) and MIL-53(Ga). LT and HT refer to **np** and **lp** respectively. Crystallographic data of **lp** state of V-doped MIL-53(Al) reported here at 455 K is determined from Lebail refinements of synchrotron powder diffraction data in vacuum[1]. The space groups and lattice parameters have been converted[2] in such way that for each structure a corresponds to the longest lattice parameter and c to the shortest. In this way for all three structures the c axis lies along the Al–OH chains in the framework and indicates the direction of the channel-like pores.*

	***a* (Å)**	***b* (Å)**	***c* (Å)**	***β* (°)**	***Space group***	***Ref.***
MIL-53(Al/V) **np-h** (298 K)	19.5392(6)	7.61970(11)	6.57475(17)	104.2890(4)	*Monoclinic Cc*	1
MIL-53(Al/V) **np-d** (419 K)	19.8889(14)	7.3982(7)	6.6033(4)	106.002(6)	*Monoclinic Cc*	1
MIL-53(Al/V) **lp** (455 K)	16.6609(3)	12.9607(3)	6.63362(15)	90	*Orthorhombic Imcm*	*This work*
MIL-53(Al) **np-d** (295 K)	20.756(1)	7.055(2)	6.6087(5)	113.580(6)	*Monoclinic C2/c*	3

MIL-53(Al) **lp** (450 K)	16.744(2)	12.847(2)	6.6361(5)	90	*Orthorhombic Imcm*	3
MIL-53(Al) **np-h** (295 K)	19.513(2)	7.612(1)	6.576(1)	104.24(1)	*Monoclinic Cc*	4
MIL-53(Al) **lp** (550 K)	16.675(3)	12.813(2)	6.608(1)	90	*Orthorhombic Imcm*	4
MIL-53(Ga) **np-d** (293 K)	19.8331(2)	6.8556(4)	6.7143(2)	103.8752(9)	*Monoclinic C2/c*	5

Hydration of np-d followed *in situ* with EPR spectroscopy

Since simulating the EPR spectra of the **np-h** state with only one set of parameters in all four bands (X, Q, W and J-band) was not possible, a two-component approach was tried. In order to deconvolute the EPR spectra into two components an additional experiment was performed. Hydration of the **np-d** state was followed *in situ* with Q-band EPR by recording EPR spectra as a function of time (Figure S3). The sample was originally in the **np-d** state in a sealed sample tube (spectrum 1). After recording spectrum 1 the seal was broken and EPR spectra were recorded over a period of 45 h, during which water from the air started occupying the pores (gradually) leading to the **np-h** state (spectrum 7). To obtain additional information how hydration of the framework influences the EPR spectrum, spectra 1-6 were analyzed and results are presented in Table S2. Spectrum 6 was taken as the first component of the **np-h** EPR spectrum since a one-component fitting was (nearly) possible with only a small contribution of a second component. The second component was obtained by subtracting the first component from the **np-h** EPR spectrum. In order to obtain reliable parameters, a fitting of the spectra in all bands simultaneously for the **np-h** state was performed.

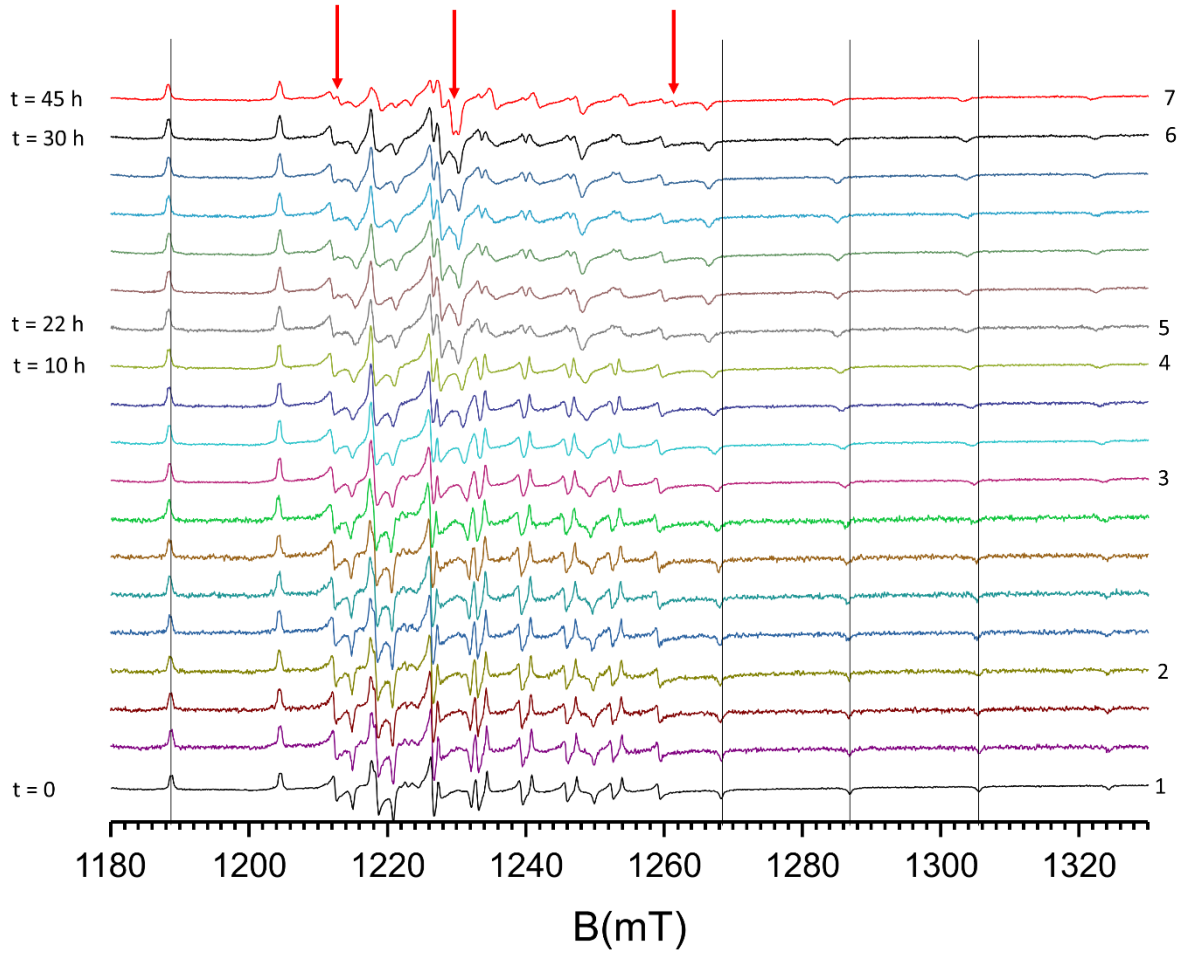


*Figure S3 – The hydration process of V-doped MIL-53(Al) was followed with in situ Q-band EPR at RT (sample 4). At t = 0 the sample was in the **np-d** (spectrum 1) state and still sealed with Parafilm. After this measurement the seal was broken and the sample started to hydrate. The spectrum recorded after 45 h (spectrum 7) is considered to correspond to the **np-h** state. The red arrows indicate three peaks in the **np-h** spectrum that were not reproduced by simulations with only one component.*

*Table S2 – Simulation parameters extracted from EPR spectra 1-6 presented in Figure S3. **g**, **A**(^{51}V) tensor principal values and the Euler angles (see Experimental Section) of the **A** tensor with respect to the **g** tensor (tilting angles) are given. The errors are estimated as Δ**g** = ±0.00010, Δ**A** = ±1.0 MHz and Δα, Δβ, Δγ = ±2°*

Spectrum	g_x	g_y	g_z	A_x	A_y	A_z	α	β	γ
1	1.97193	1.96342	1.92922	165.9	173.0	505.7	0	13.7	8.0
2	1.97212	1.96348	1.92923	166.6	174.0	506.7	0	13.5	8.0
3	1.97220	1.96341	1.93007	166.2	174.3	506.1	0	13.2	8.0
4	1.97244	1.96322	1.93120	165.5	174.7	506.0	0	12.7	8.0
5	1.97200	1.96230	1.93164	165.7	174.8	507.4	0	12.0	8.0
6	1.97194	1.96221	1.93167	165.6	174.8	507.1	0	12.1	8.0

Simulation of activated V-doped MIL-53(Al) in np-h state with two components

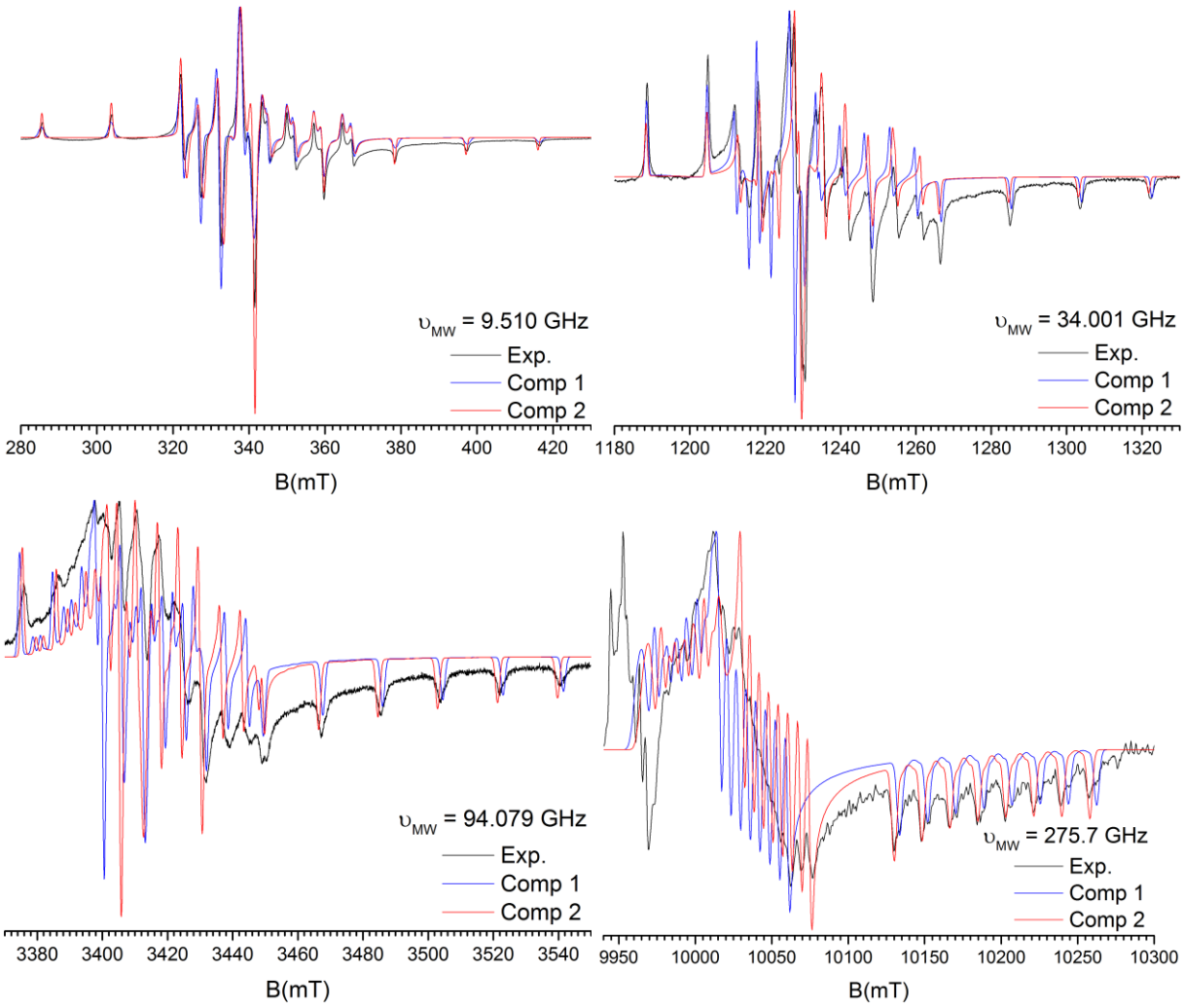


*Figure S4 – Multi-frequency (X, Q, W and J-band) powder EPR spectra of activated V-doped MIL-53(Al) in **np-h** state at RT in air, J-band in N_2 atmosphere. The experimental spectra are shown in black and the simulation of the two components separately with the parameters from Table 5 are shown in blue and red.*

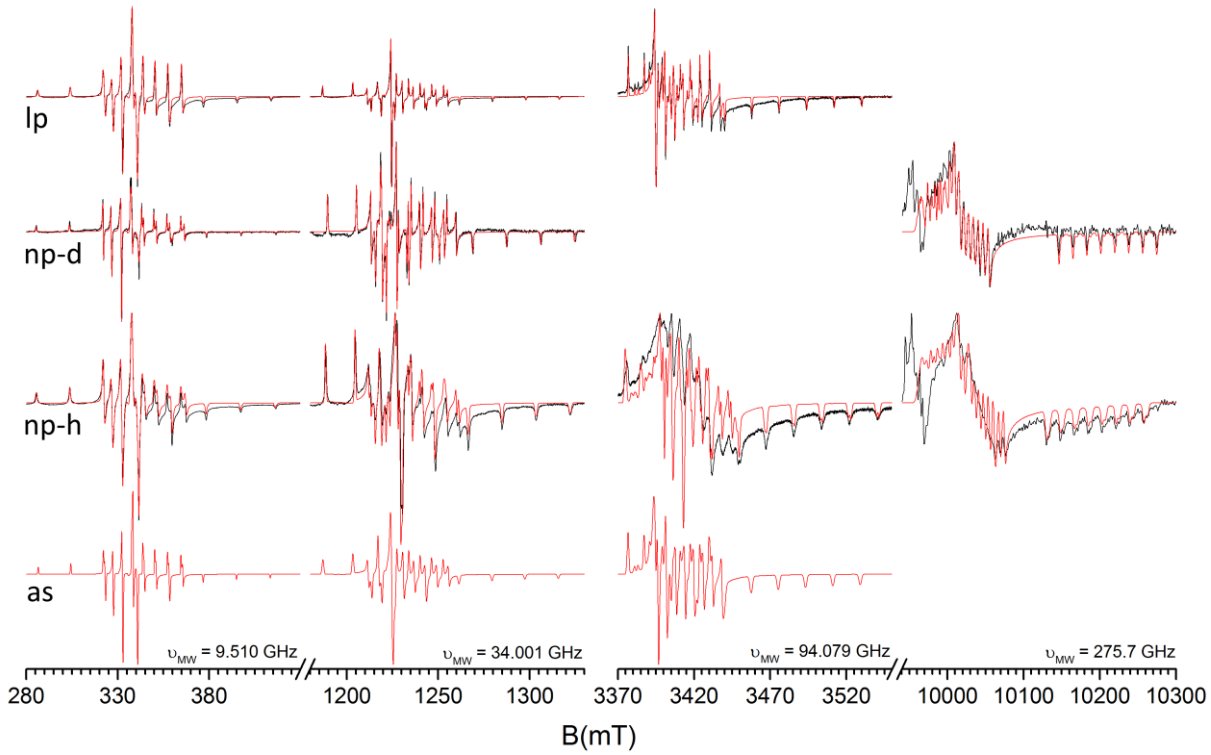


*Figure S5 – Powder EPR spectra of V-doped MIL-53(Al) in the **lp**, **np-d**, **np-h** and **as** state. Experimental spectra are shown in black and simulated spectra in red. Simulations were done with parameters from Table 3 for the **lp** state, Table 4 for the **np-d** and Table 5 for the **np-h** state. Parameters for the **as** state were taken from Nevjestić et al.[6] for comparison. Spectra are intensity normalized. EPR spectra of activated V-doped MIL-53(Al) in **lp** state were recorded at RT in N_2 atmosphere. EPR spectra of activated V-doped MIL-53(Al) in the **np-d** state were recorded in vacuum. X and Q-band spectra were recorded at RT while the J-band spectrum is recorded at 325 K. EPR spectra of activated V-doped MIL-53(Al) in the **np-h** state were recorded at RT in air, J-band in N_2 atmosphere.*

Superhyperfine interaction

In the EPR spectra of activated V-doped MIL-53(Al) in the **lp** and **np-d** state superhyperfine splitting is observed in the first two peaks (Figure S6). These spectra were simulated with parameters for the **lp** and **np-d** states reported in Table 3 and Table 4 and including HF interaction with the nearest hydroxyl proton from V-doped MIL-53(Al) in the **as** state (A_x = -3.1 MHz, A_y = -3.4 MHz, A_z = 8.6 MHz, θ = 37°, Φ

= 0°).[6] Experimental and simulated spectra are in good agreement leading to the conclusion that the hydroxyl proton in the activated V-doped MIL-53(Al) matrix is in a similar position as in the **as** state.

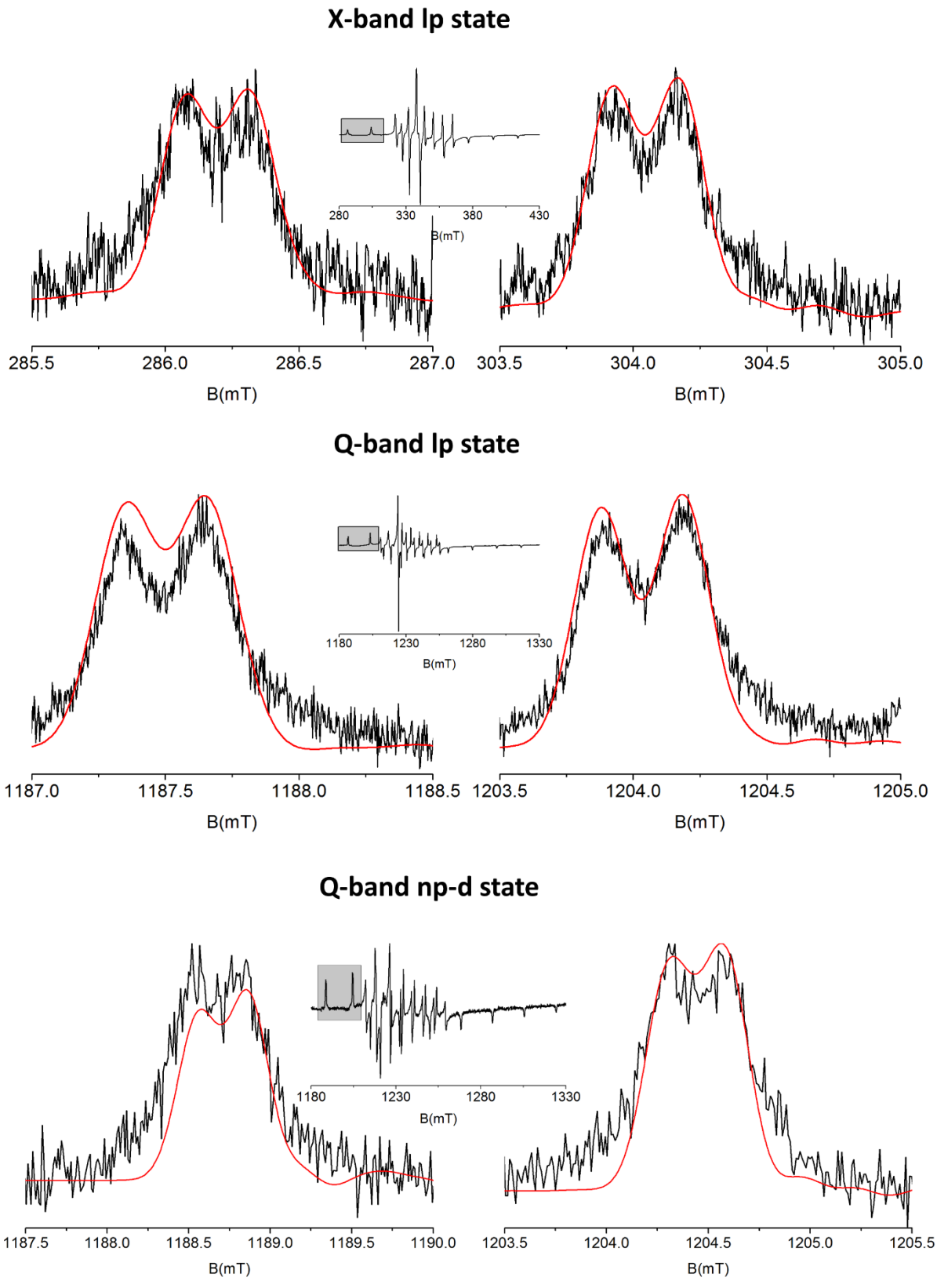


*Figure S6 – RT EPR spectra (zoomed regions, first and second peak of the EPR spectrum) of V-doped MIL53(Al) sample 5 in the **lp** state in X (top) and Q-band (middle) and **np-d** state in Q-band (bottom) in vacuum. Insets show the complete EPR spectrum in X and Q-band indicating the zoomed region. Experimental (black) and simulated (red) spectra are shown. Simulations were*

*made with the parameters for the **lp** state (Table 3) and **np-d** state (Table 4) including interaction with the nearest hydroxyl proton in the V-doped MIL-53(Al) framework from Nevjestić et al.[6]. Spectra are recorded with 0.05 mT modulation amplitude.*

ENDOR of V-doped MIL-53(Al) in the np-h state

Figure S7 shows ENDOR spectra of V^{IV}=O in the **np-h** state of V-doped MIL-53(Al). At 10K ENDOR transitions are observed close to the Larmor frequencies of ^{27}Al (I=5/2) and ^{1}H (I=1/2) at 10 K. In the ^{1}H region (Figure S7a) a very rich structure is observed that is explored in detail by recording the field dependence of the ENDOR spectrum in the range indicated in the inset. The 2D spectrum shows similarity with already reported ENDOR results on V-doped MIL-53(Al) in the **as** state.[6] In that study ENDOR spectra were convincingly simulated including an interaction with the nearest hydroxyl proton and further with 4 sets of 4 equivalent protons on the 4 BDC linkers surrounding the V^{IV} ion. In the case of the **np-h** state, interaction with the nearest hydroxyl proton is not visible from the ENDOR spectra but it is visible in the EPR spectra (Figure S6). The spectrum in the ^{27}Al range was also recorded for several magnetic field positions, as shown in the Figure S7b. These spectra can be explained assuming an axial HF tensor similar to the one reported in the above mentioned study. Due to the low signal-to-noise ratio a more detailed analysis of the ENDOR spectra was not attempted.

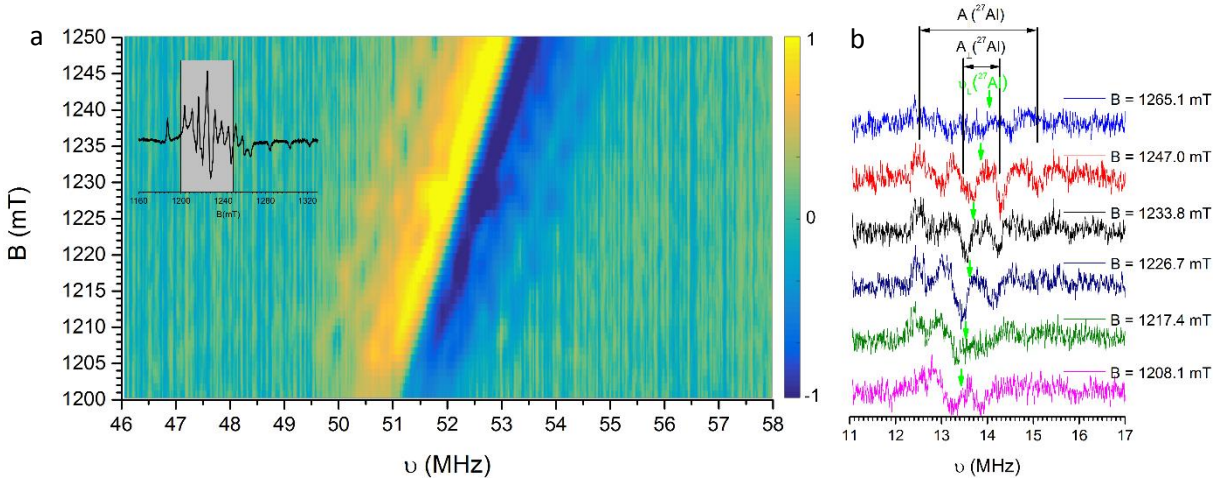


Figure S7 – a: Experimental field dependence of ENDOR spectra (normalized signal heights in color scale) near the ^{1}H Larmor frequency of activated V-doped MIL-53(Al) sample 1 at 10 K (ENDOR ν_{MW} = 34.007 GHz, EPR ν_{MW} = 34.000 GHz). Inset shows the EPR spectrum at 10K and the grey region where the field dependent ENDOR spectra were recorded. b: ENDOR spectra near the ^{27}Al Larmor frequency at 10 K. The green arrows indicate the ^{27}Al Larmor frequency for every field, $A_{\parallel}$ and $A_{\perp}$ are also shown.

References

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