

# V<sup>IV</sup> Ions As Paramagnetic Probes For Monitoring the Structural Flexibility of V-Doped MIL-53(Al)

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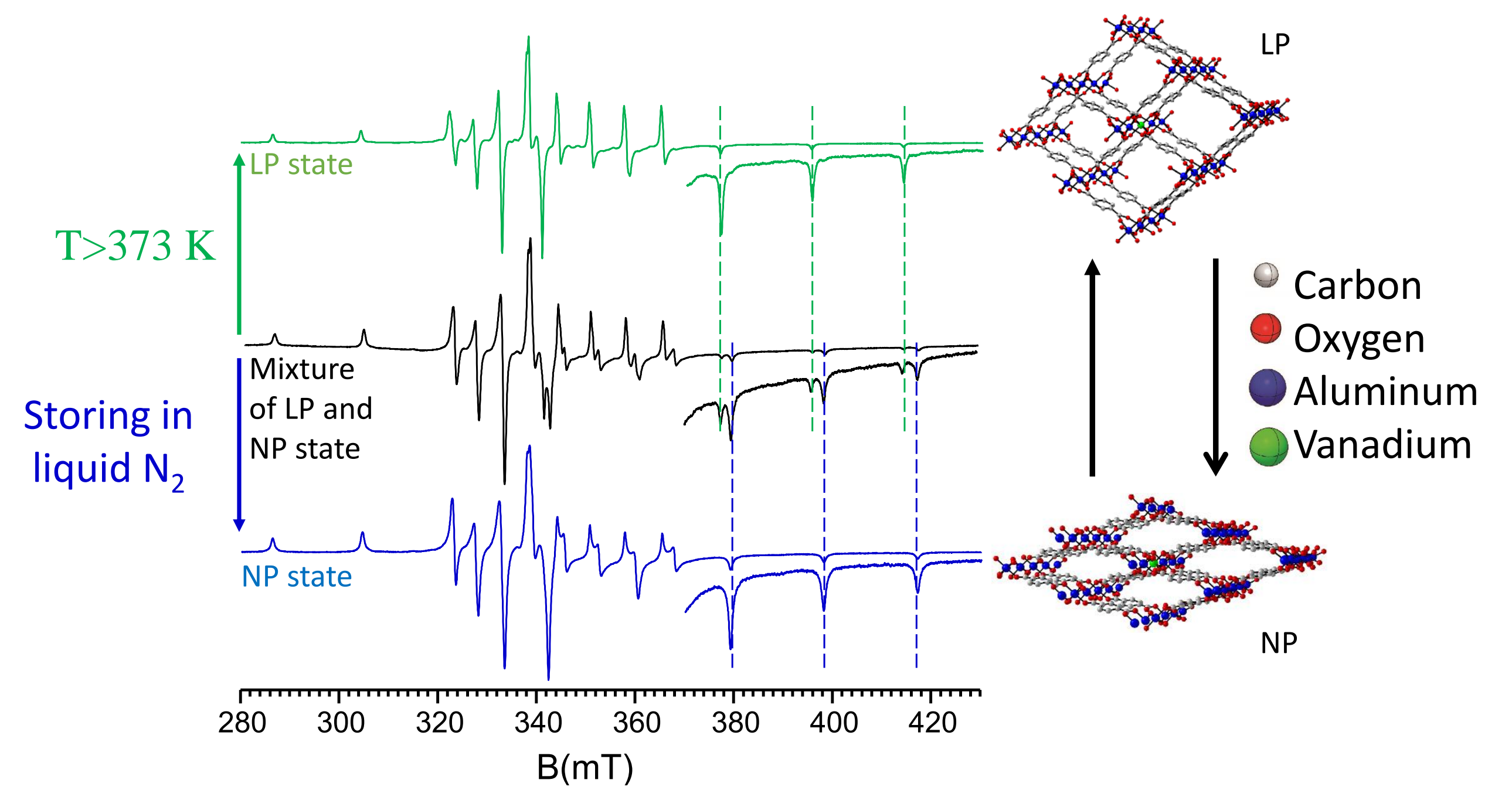
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## Introduction

- ▶ Metal-organic frameworks (MOFs) are crystalline porous materials constructed from metal moieties connected by organic ligands
- ▶ Many interesting features: well-defined pore size, pore shape, ultra-high porosity, ...
- ▶ Their tunability in porosity and in functionalization of the internal surface makes MOFs an important class of materials with potential major impact in catalysis, gas sensing and gas storage
- ▶ MIL-53(Al) [Al(OH)(BDC)] [1]  
BDC = terephthalate or 1,4-benzenedicarboxylate  
MIL = Matériaux de l'Institut Lavoisier
- ▶ After synthesis, in the MIL-53(Al)AS the channels are filled with uncoordinated BDC molecules
- ▶ These can be removed by calcination or solvent extraction, which is referred to as activation of the MOF
- ▶ Activated MIL-53(Al) exhibits a structural flexibility, referred to as breathing: the structure can reversibly change from a large open pore (LP) to a narrow pore (NP) form without any loss of crystallinity

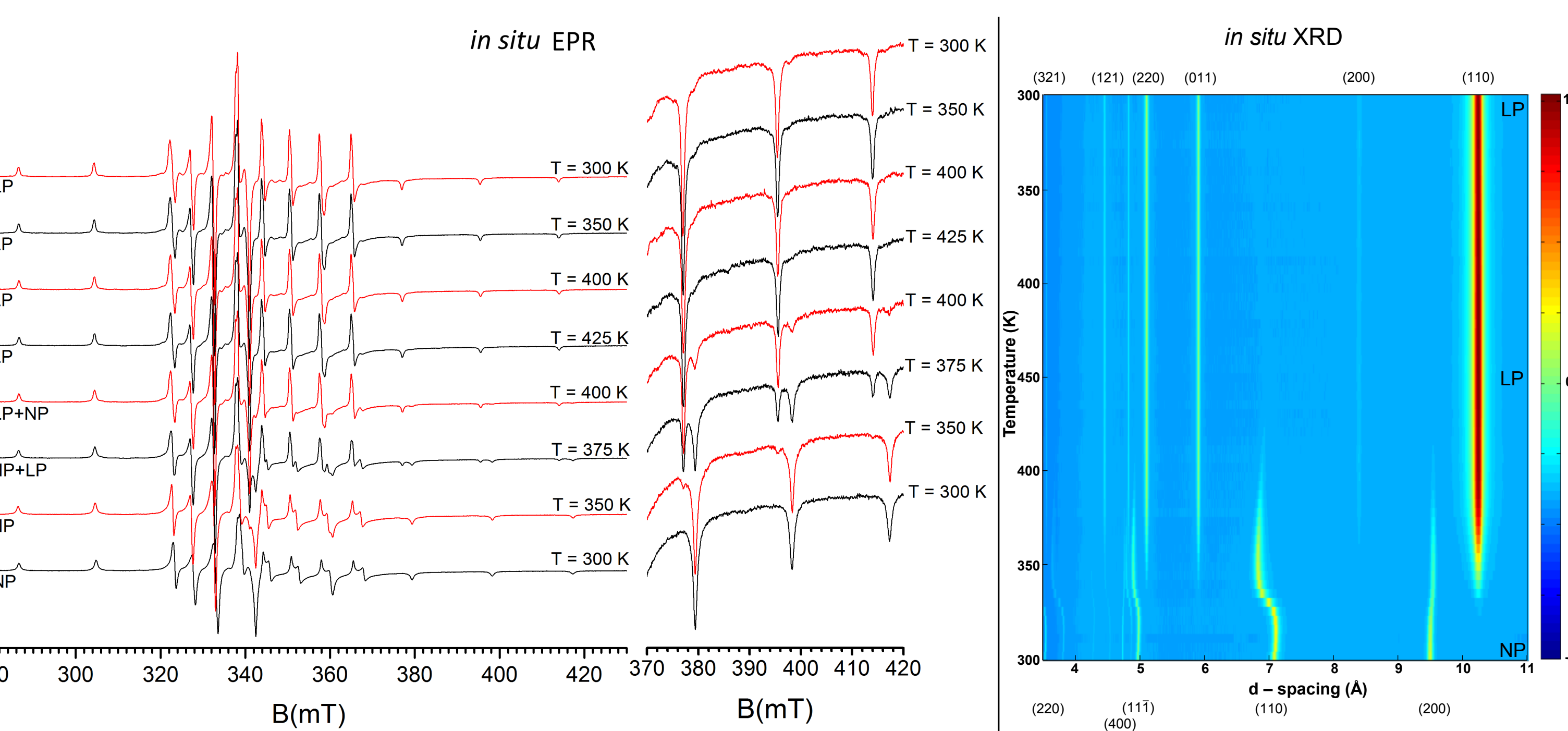
## Two V<sup>IV</sup> states in activated V-doped MIL-53(Al)

- ▶ Temperature-triggered breathing was investigated in MIL-53(Al) doped with V<sup>IV</sup> ions (3d<sup>1</sup>, S = 1/2) ions
- ▶ Powder EPR spectra of activated 1.5% V-doped MIL-53(Al) in vacuum at room temperature (RT) are shown in NP and LP states



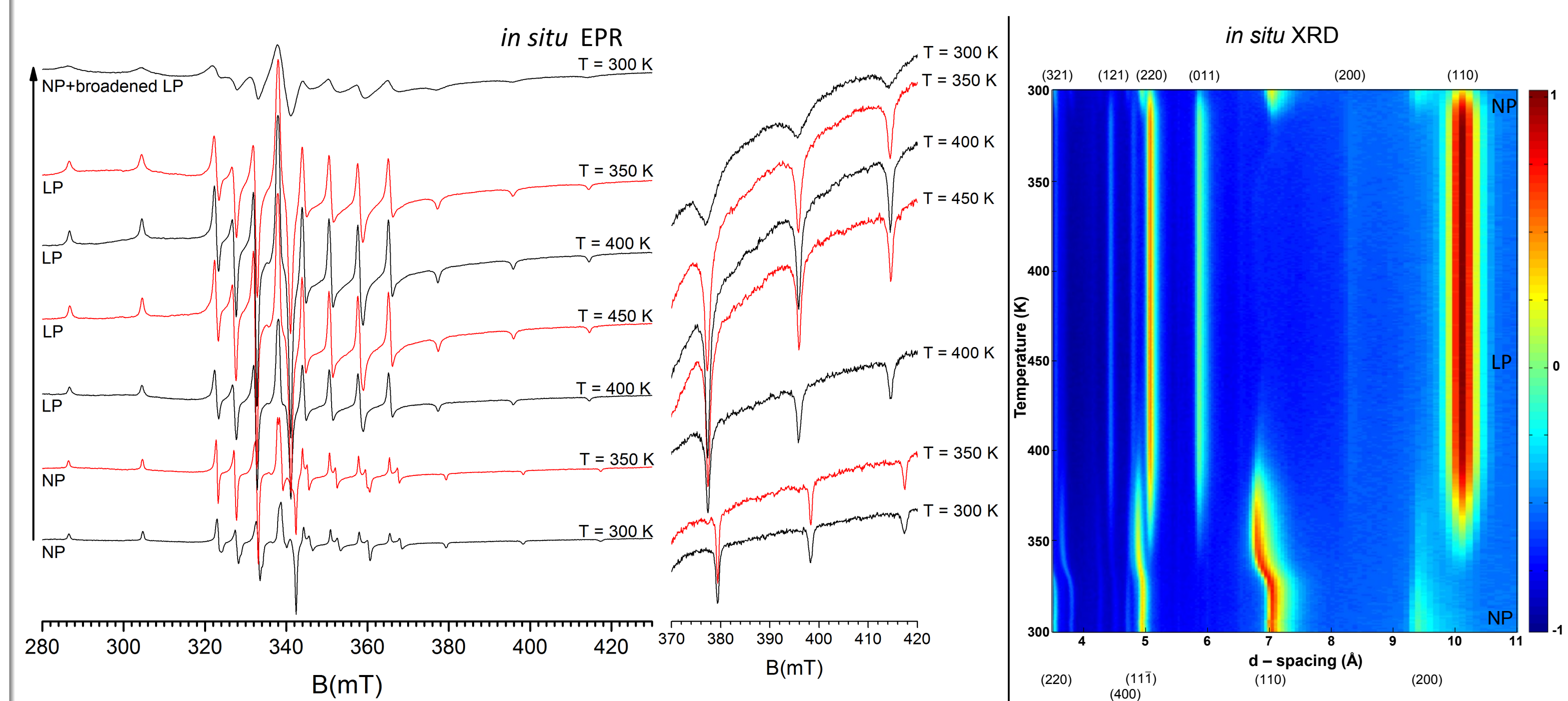
- ▶ EPR spectra of V<sup>IV</sup> in NP and LP MIL-53(Al) are clearly different
  - ▶ V<sup>IV</sup> is paramagnetic probe for detecting the phase transition in the framework
- EPR insets show a magnification of the high-field part of the spectra

## Breathing effect monitored *in situ* in vacuum



EPR insets show a magnification of the high-field part of the spectra  
XRD  $\lambda = 0.825086 \text{ \AA}$ ,  $2\theta$  is converted to d-spacing in  $\text{\AA}$  via Bragg's law. Miller indices are indicated for both the NP (below) and LP (above) state. The sample was at RT in the NP state, after the heating cycle the XRD pattern of the LP state is observed. [2]

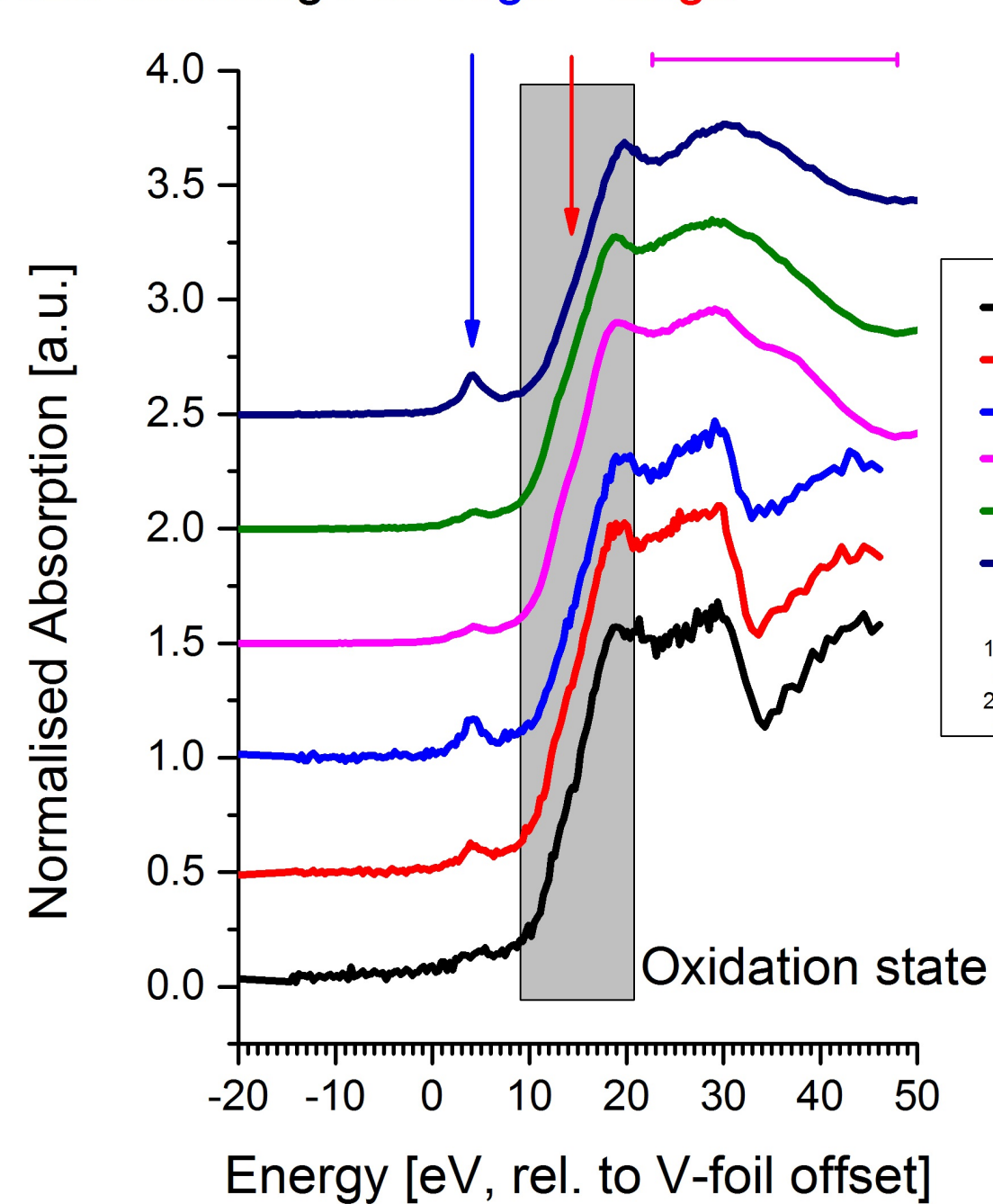
## Breathing effect monitored *in situ* in air



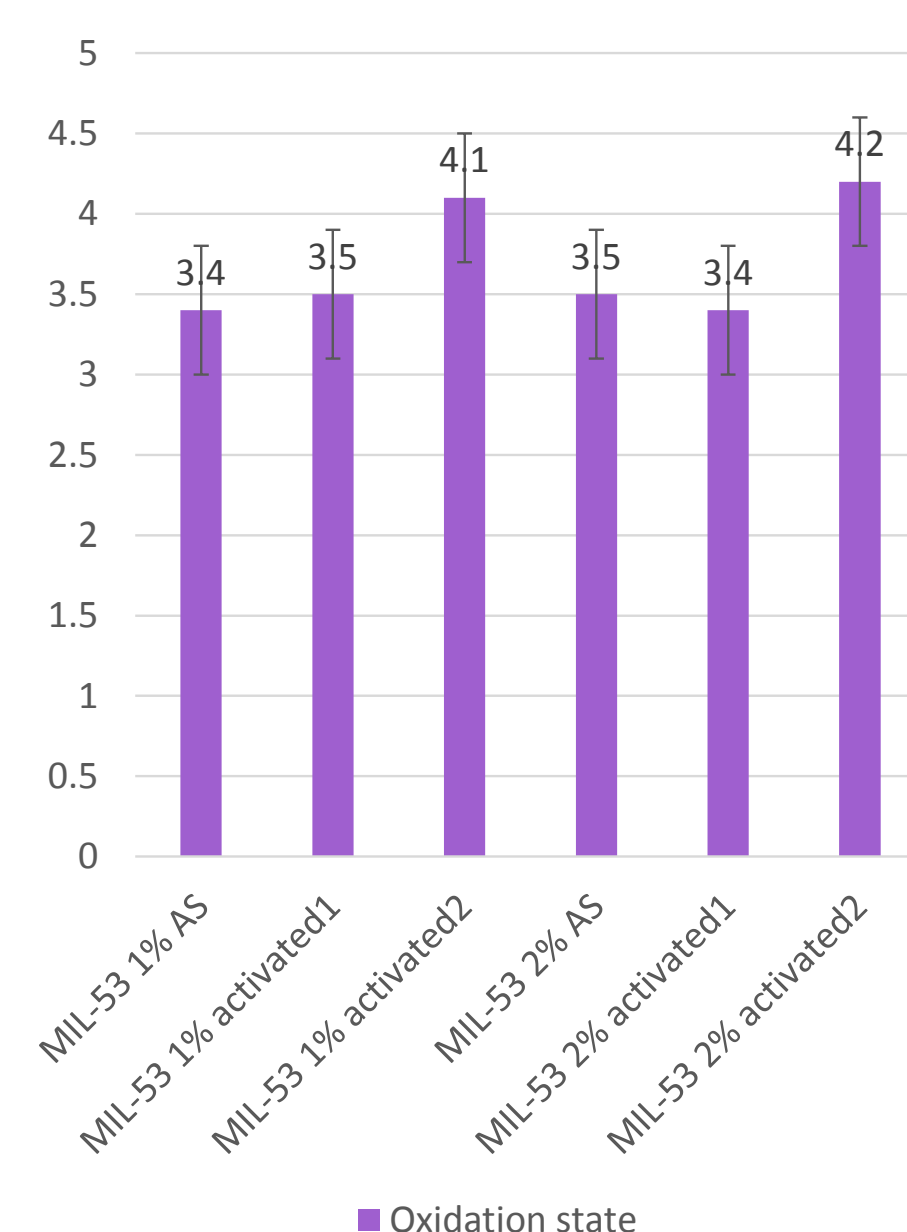
EPR insets show a magnification of the high-field part of the spectra  
XRD  $\lambda = 1.54056 \text{ \AA}$ ,  $2\theta$  is converted to d-spacing in  $\text{\AA}$  via Bragg's law. Miller indices are indicated for both the NP (below) and LP (above) state. The sample was at RT in the NP state, at approximately 425 K full transition to the LP state occurred. Cooling down the sample to RT, the XRD pattern of the NP state starts appearing again. [2]

## X-ray absorption near edge structure (XANES) and EPR

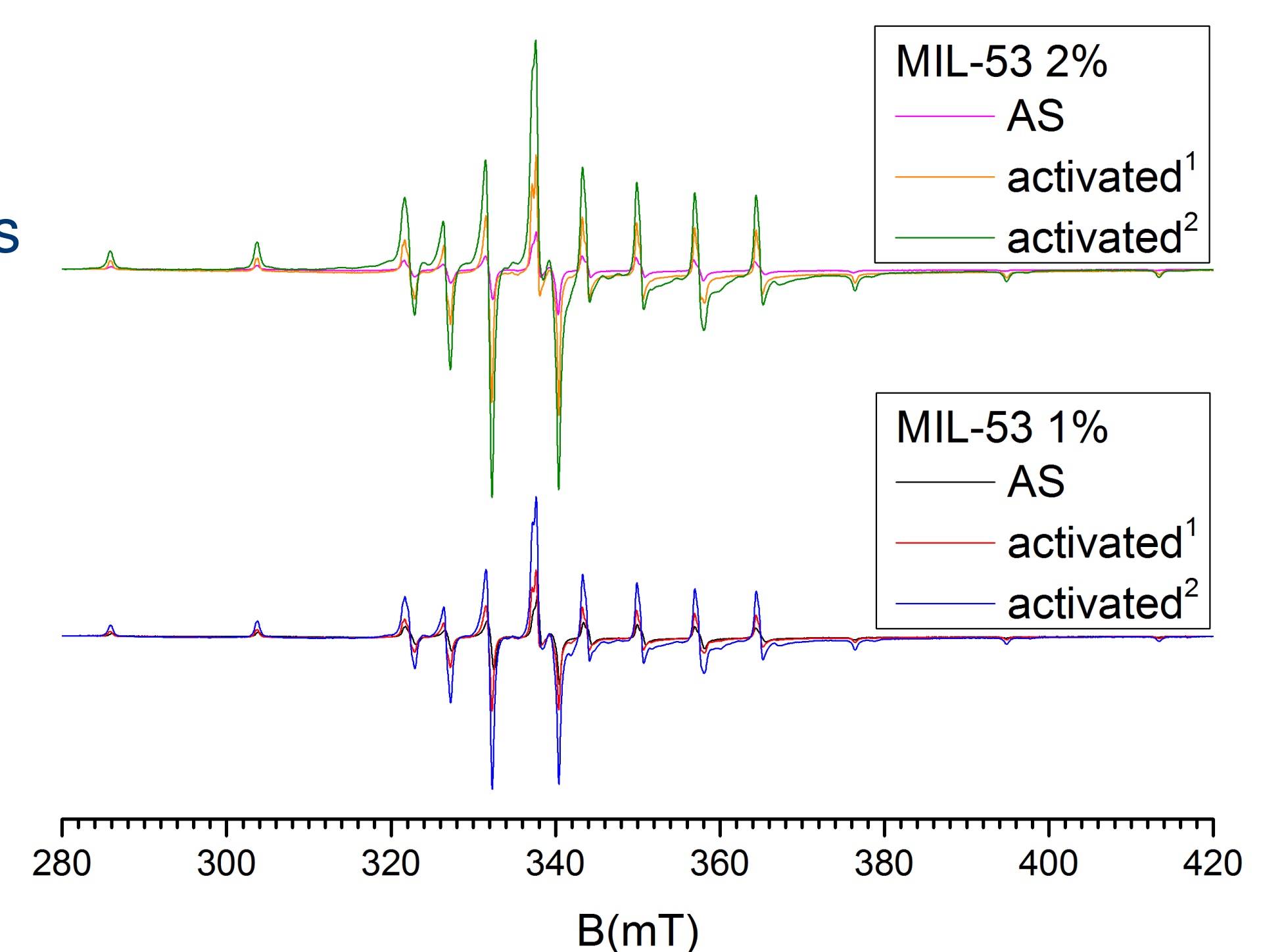
XANES including Pre-edge + Edge



Oxidation state of V-doped MIL-53 determined from XANES



- ▶ Position of main edge peak defines ionization threshold to continuum states
- ▶ Main edge peak shifts to higher energy with increased oxidation state



- ▶ After activation increase in concentration of V<sup>IV</sup> ions is observed in EPR spectrum

## Conclusions

- ▶ The EPR spectra of V<sup>IV</sup> in the NP and LP MIL-53(Al) states are clearly distinguishable
- ▶ The EPR active V<sup>IV</sup> ions (3d<sup>1</sup>, S = 1/2) can be used as a local probe to detect the phase transitions in the framework
- ▶ Oxidation states of V-doped MIL-53 determined with XANES is in agreement (within error) with EPR quantitative measurements

## References :

- [1] T. Loiseau et al., Chem.-Eur. J., 2004, 10 (6), 1373-1382.  
[2] I. Nevjestic et al., J. Phys. Chem. C, 2016, 120 (31), 17400-17407.

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