

Breathing effect in the V-doped Metal Organic Framework MIL-53(Al) monitored in situ by Electron Paramagnetic Resonance (EPR) and X-Ray Diffraction (XRD)

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Introduction

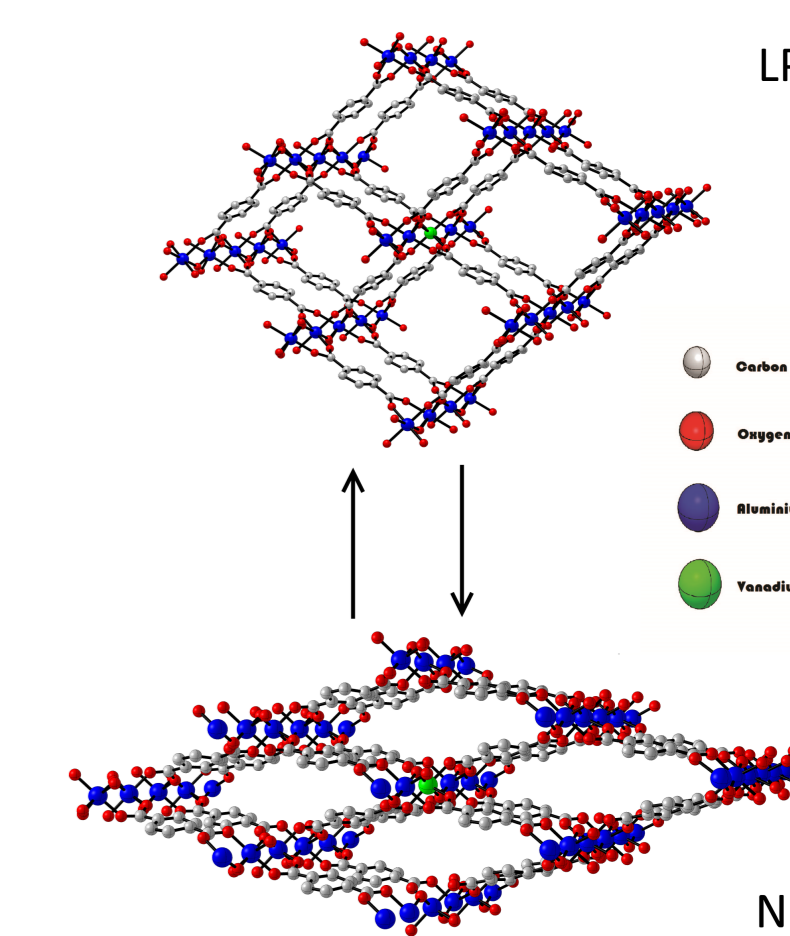
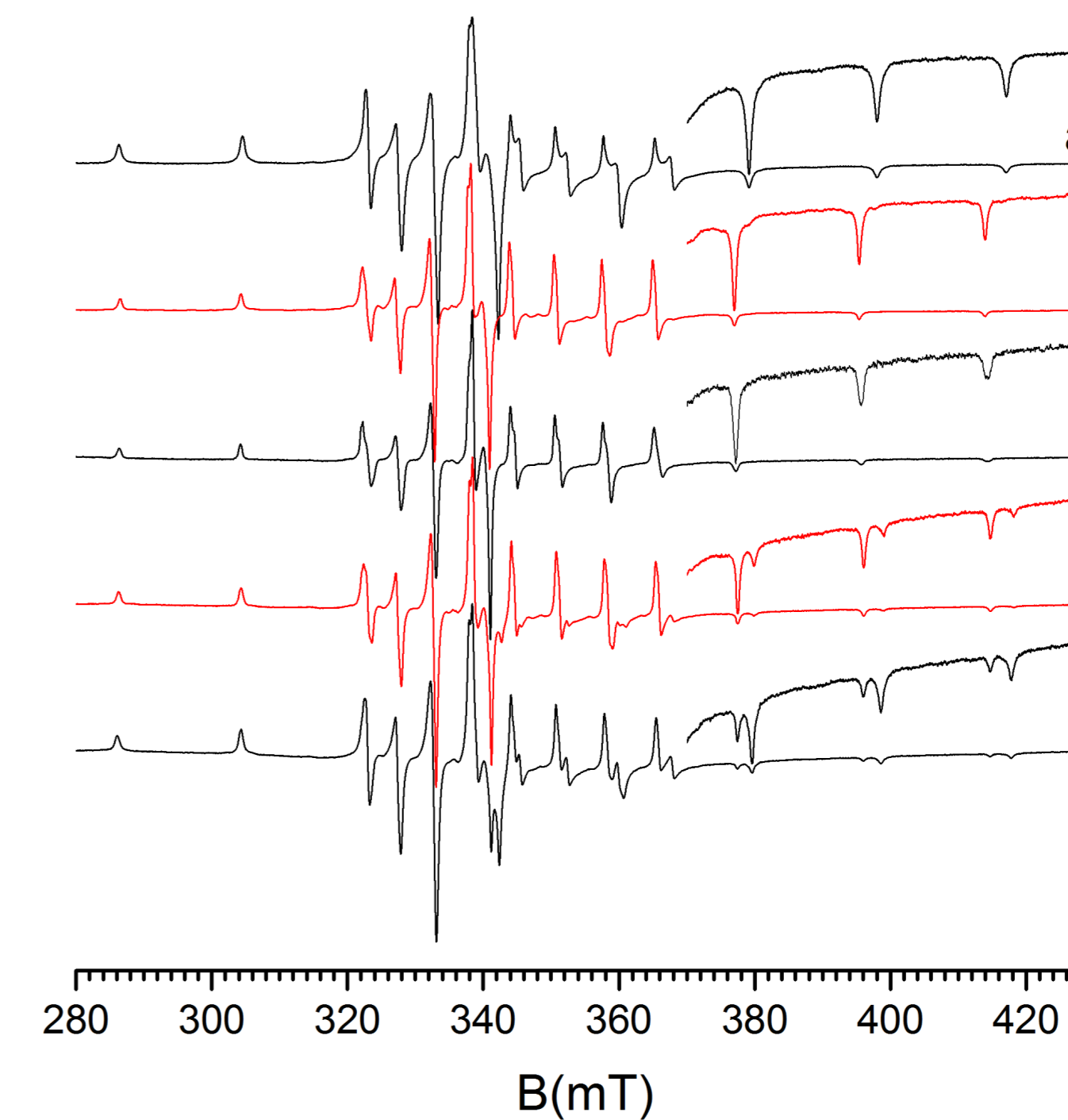
- ▶ Metal Organic Frameworks (MOFs) → crystalline porous materials constructed of metal ions connected by organic linkers
- ▶ Many interesting features: well-defined pore size, pore shape, ultra-high porosity, ...
- ▶ Wide range of potential applications: catalysis, hydrogen storage, gas sensing, gas storage, optics, ...
- ▶ 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 breathing: the structure can reversibly change from a large open pore (LP) to a narrow closed pore state (NP) by changing the temperature and/or pressure conditions

Two V^{IV} states in activated V-doped MIL-53(Al)

- ▶ Temperature-triggered breathing was investigated in MIL-53(Al) doped with V^{IV} ions (3d¹, S = 1/2) ions
- ▶ Powder EPR spectra of activated 1.5% V-doped MIL-53(Al) in vacuum at room temperature (RT) are shown

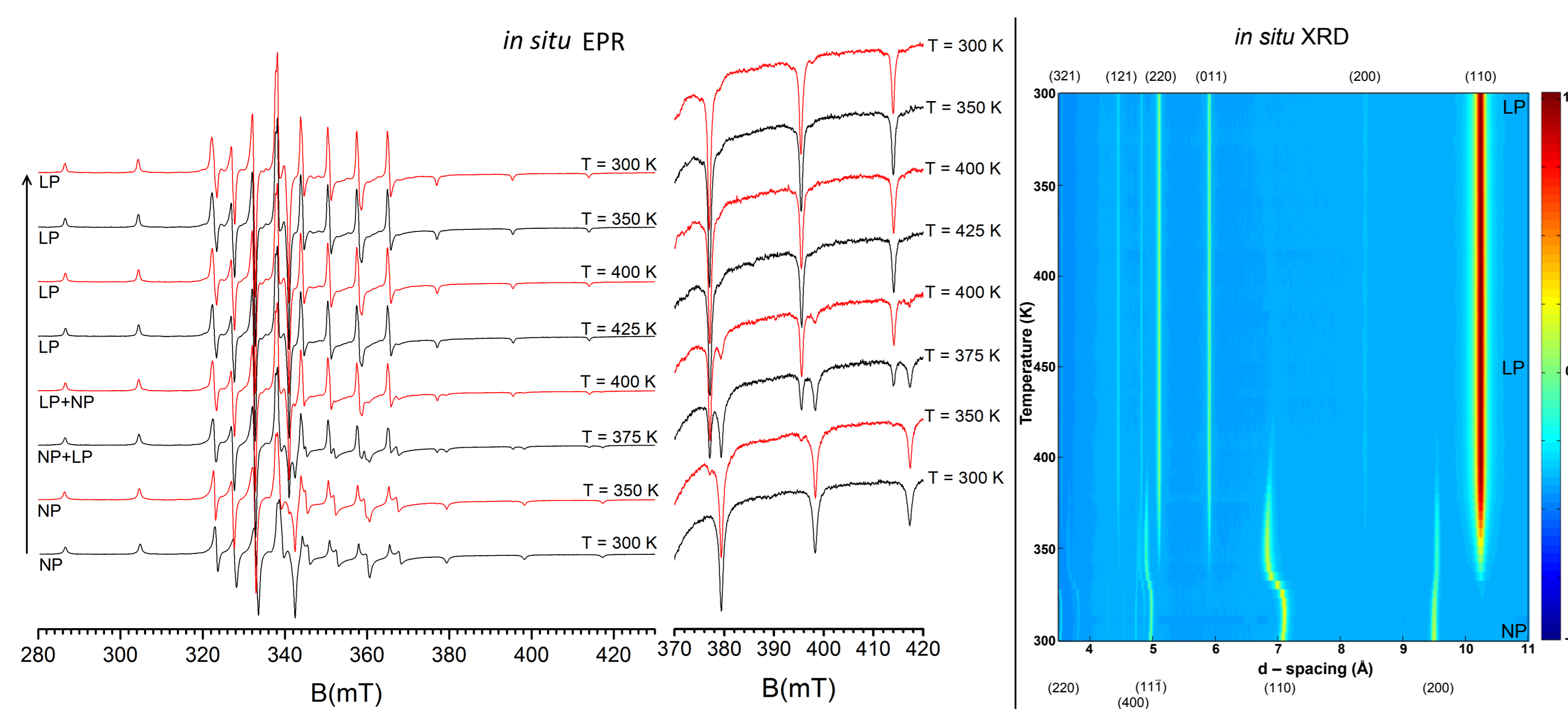
- ▶ a—NP state
- ▶ b—LP state
- ▶ c—AS state
- ▶ d and e—mixture of LP and NP state

- ▶ EPR spectra of V^{IV} in NP and LP MIL-53(Al) are clearly different
- ▶ V^{IV} is paramagnetic probe



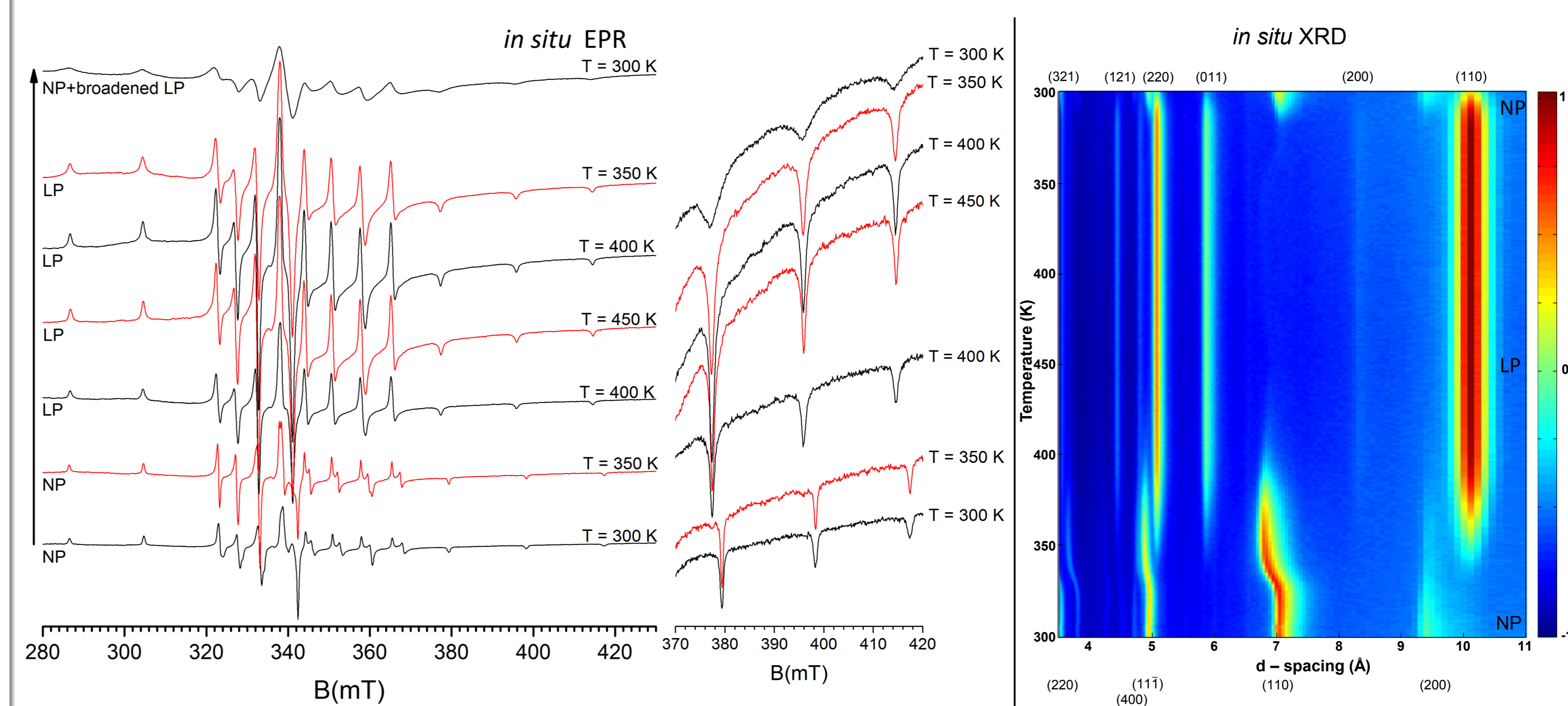
*EPR insets show a magnification of the high-field part of the spectra

Breathing effect monitored *in situ* in vacuum



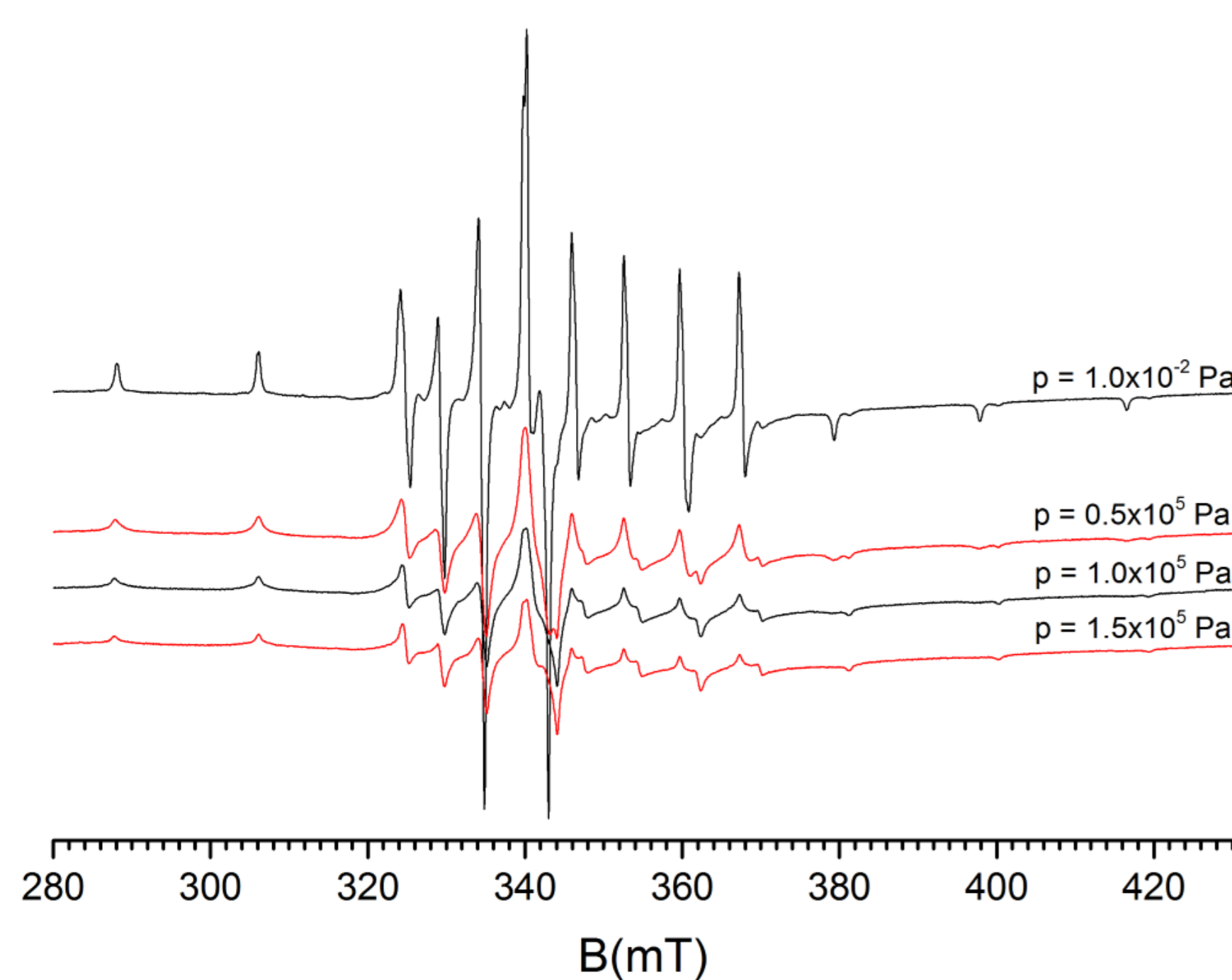
*EPR insets show a magnification of the high-field part of the spectra
*XRD $\lambda = 0.825086 \text{ \AA}$, 2θ is converted to d-spacing in \AA via Bragg's law. Miller indices are indicated for both the NP (below) and LP (above) state. The sample was at RT in the NP state, after the heating cycle the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

Breathing effect monitored *in situ* in air

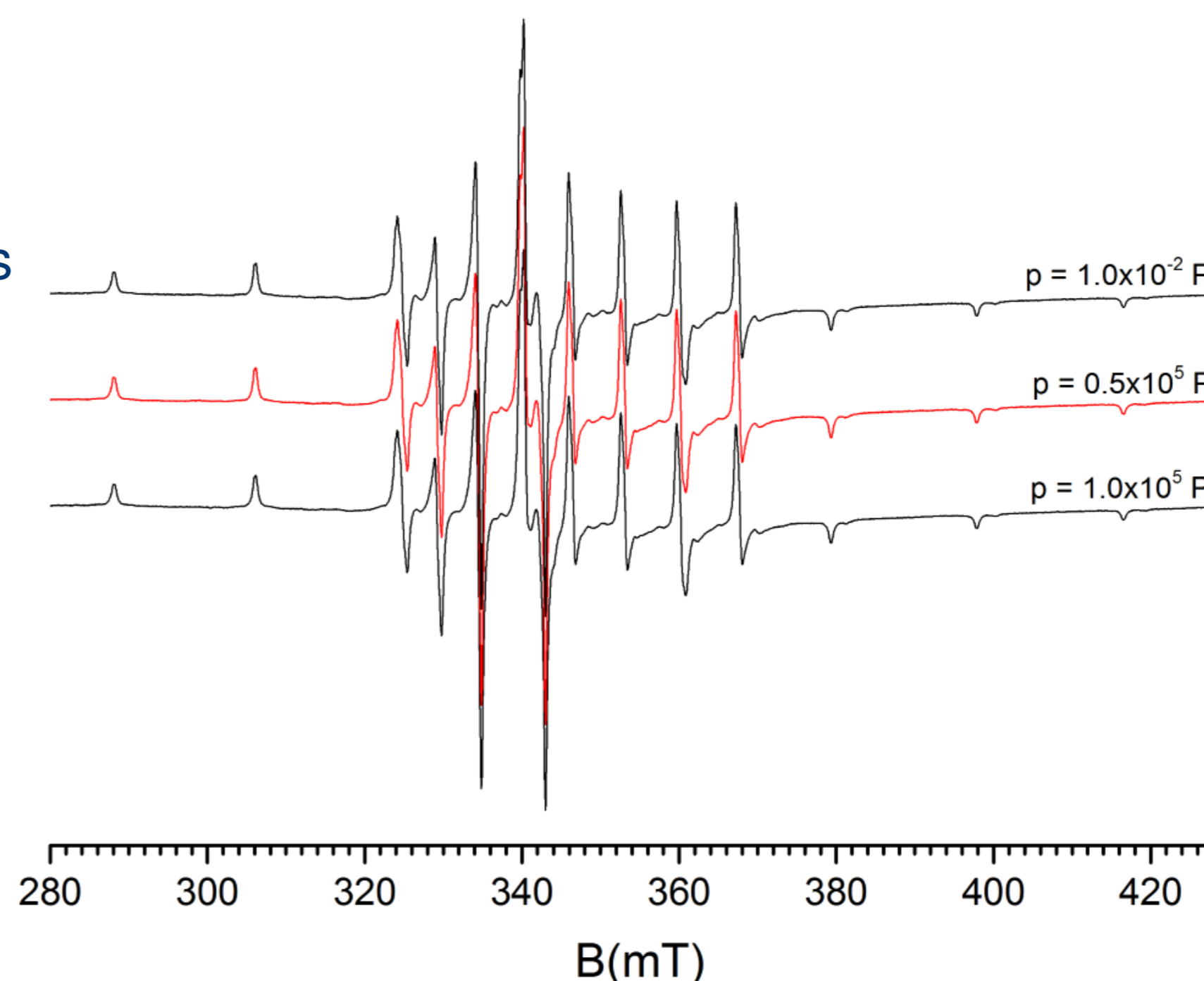


*EPR insets show a magnification of the high-field part of the spectra
*XRD $\lambda = 1.54056 \text{ \AA}$, 2θ is converted to d-spacing in \AA via Bragg's law. Miller indices are indicated for both the NP (below) and LP (above) state. The sample was at RT in the NP state, at approximately 425 K full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

Interaction between paramagnetic V^{IV} centers and O₂ molecules



- ▶ RT EPR spectra of MIL-53(Al), predominantly in the LP state, as a function of air pressure are shown on the left
- ▶ Increasing the air pressure clearly increases the line width of V^{IV} in LP MIL-53(Al)
- ▶ Meanwhile the NP component, present as a trace, hardly experiences any broadening



- ▶ The EPR spectra as a function of N₂ pressure are shown
- ▶ The spectra for both LP and NP states experience virtually no broadening by exposure to N₂
- ▶ The line broadening should thus be associated with the exchange interaction between the V^{IV} centers and paramagnetic O₂ molecules.

Conclusions

- ▶ The EPR spectra of V^{IV} in the NP and LP MIL-53(Al) states are clearly distinguishable
- ▶ The EPR active V^{IV} ions (3d¹, S = 1/2) can be used as a local probe to detect the phase transitions in the framework
- ▶ EPR showed that exchange interaction between paramagnetic V^{IV} centers and O₂ molecules causes broadening, only of the LP EPR spectrum
- ▶ This indicates that only in the LP state O₂ molecules can come close enough to V^{IV} to produce a measurable broadening

References :

[1] T. Loiseau et al., Chem.-Eur. J. 2004, 10 (6), 1373-1382.

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