

Breathing effect in V-doped Metal Organic Framework MIL-53(Al) studied by Electron Paramagnetic Resonance (EPR)

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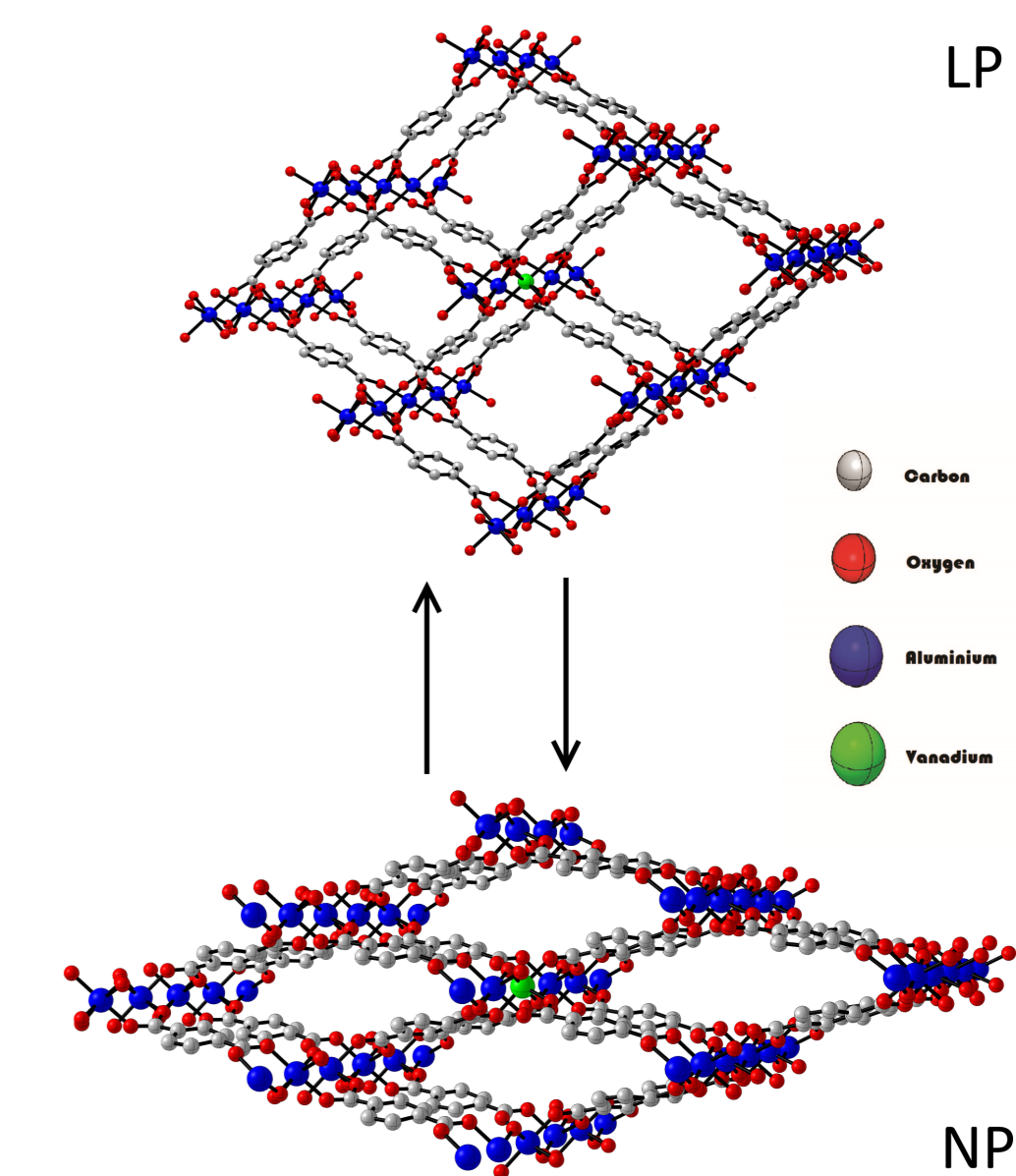
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Introduction

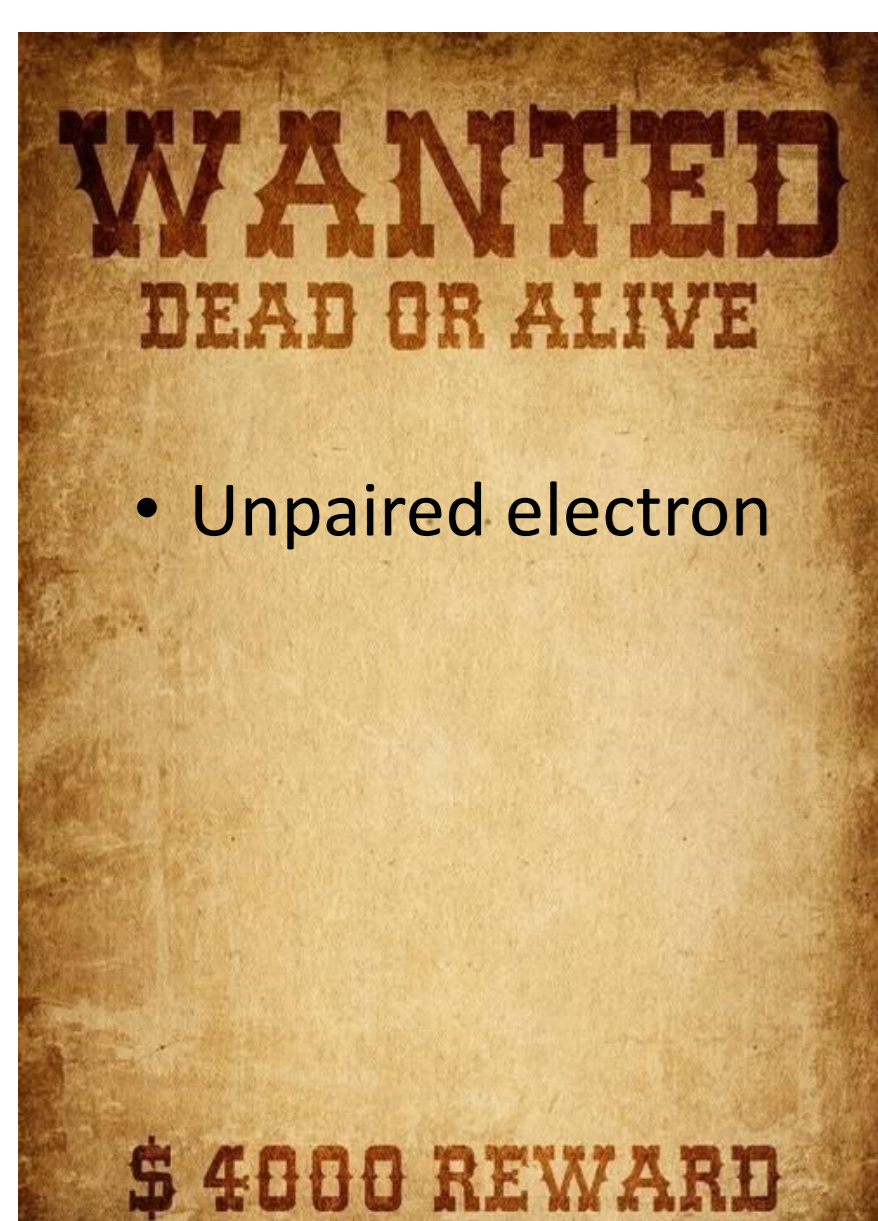
- ▶ Metal Organic Frameworks (MOFs) → crystalline porous materials constructed of metal ions connected by organic linkers
- ▶ Many interesting features: well-defined pore size, pore shape, ultra-high porosity, ...
- ▶ Wide range of potential applications: catalysis, hydrogen storage, gas sensing, gas separation ...
- ▶ MIL-53(Al) [Al(OH)(BDC)] (Loiseau, Serre et al. 2004)
BDC = terephthalate or 1,4-benzenedicarboxylate
MIL = Matériaux de l'Institut Lavoisier

Breathing effect

- ▶ 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
- ▶ The activated MIL-53(Al) structure 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
- ▶ The breathing effect triggered by temperature was investigated in MIL-53(Al) doped with V^{IV} ions (3d¹, S = 1/2) ions

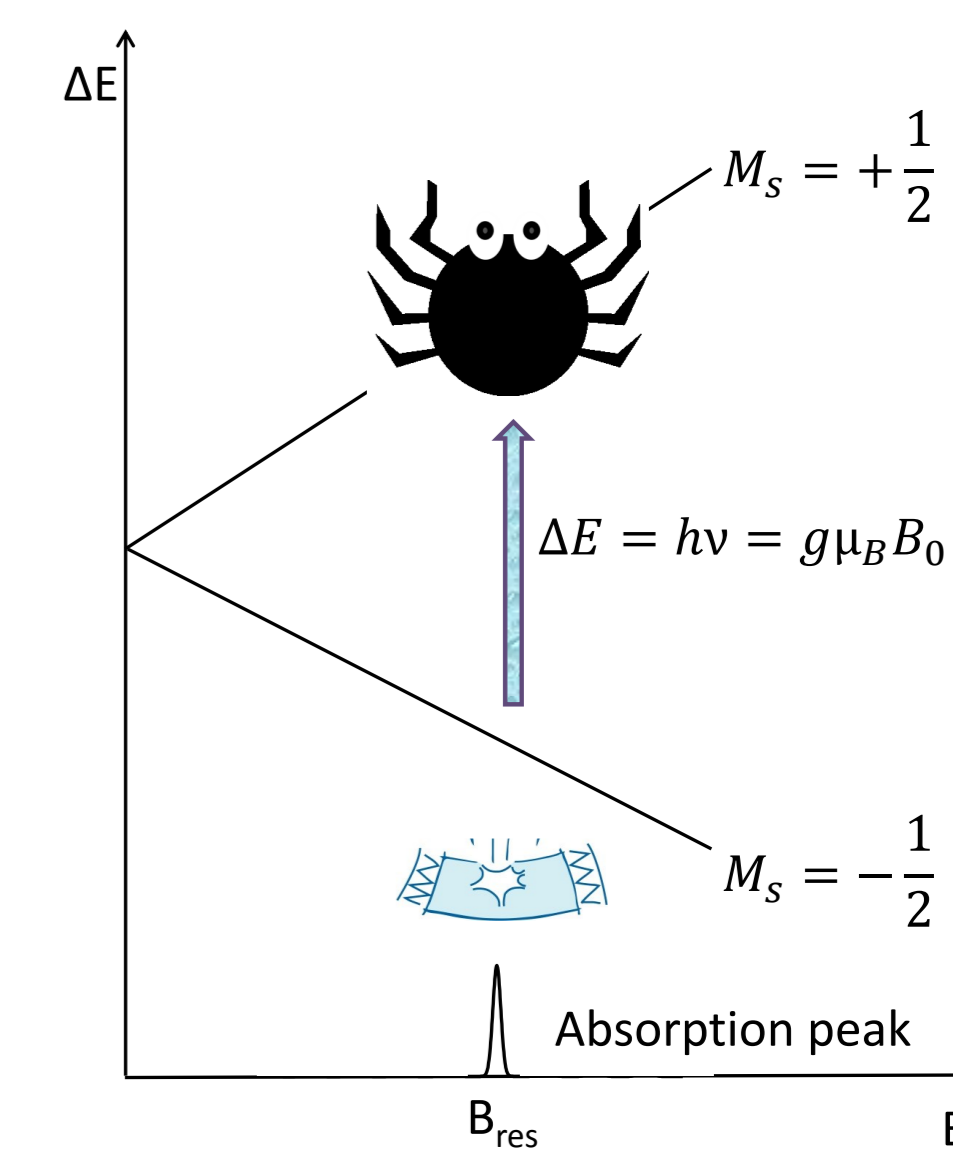
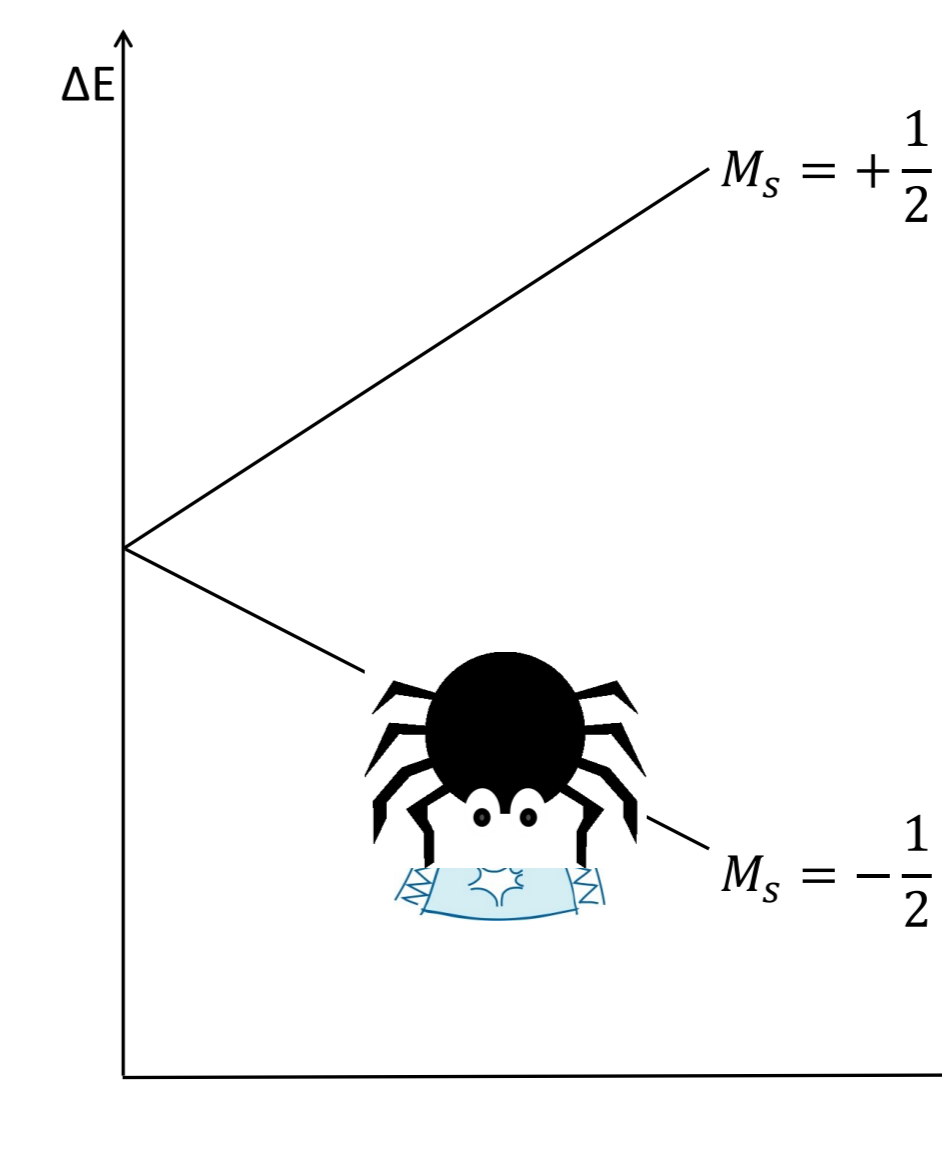
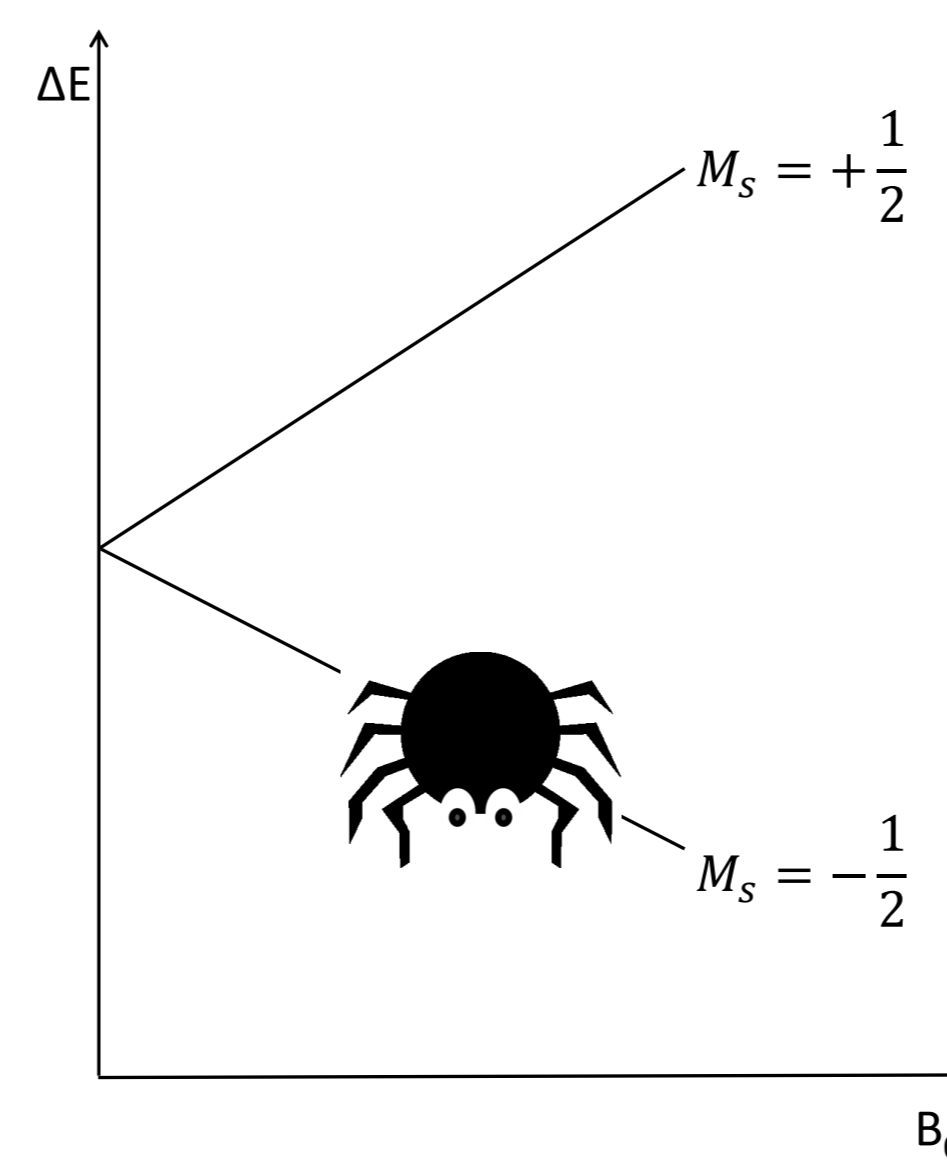


Electron Paramagnetic Resonance (EPR)



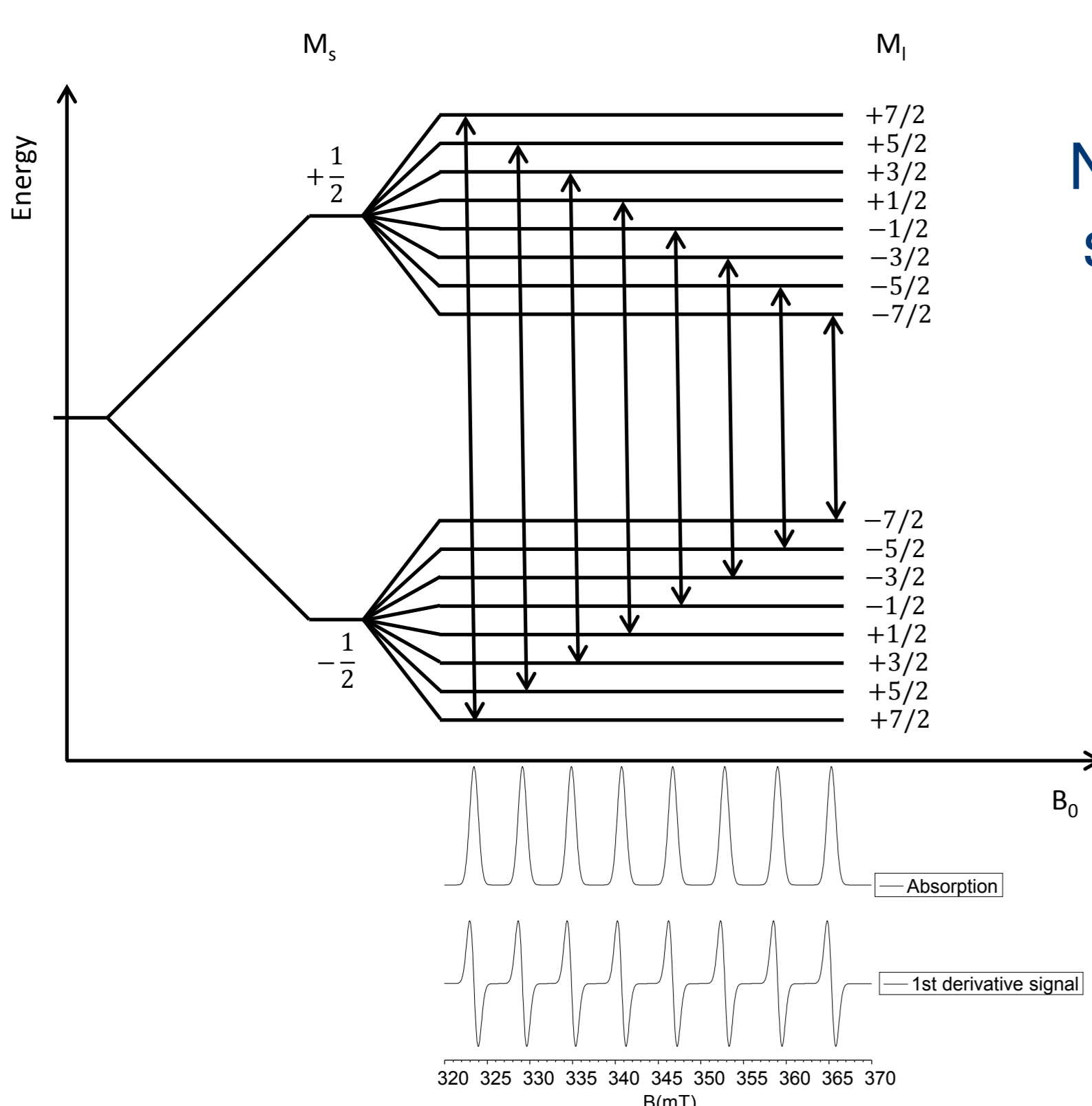
What can we do for you?

- ▶ Identify paramagnetic centers
- ▶ Local environment near the unpaired electron
- ▶ Molecular structure
- ▶ Molecular motions
- ▶ Elucidate the role of free radicals
- ▶ ...
- ▶ 4 K - 1000 K
- ▶ Different gases

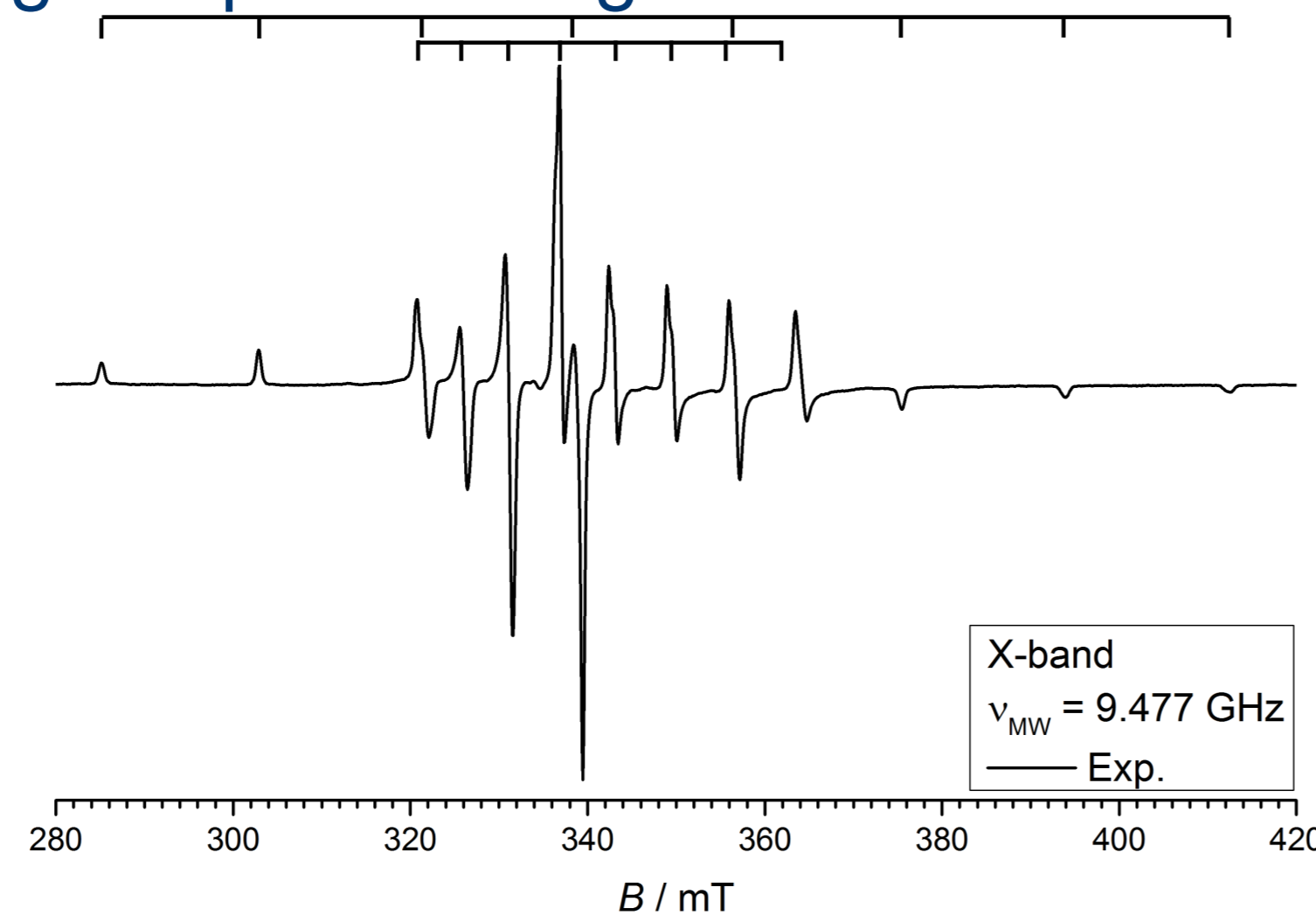


Hyperfine interaction (⁵¹V, 3d¹, S = 1/2)

Hyperfine interaction is interaction between the unpaired electron spin and a nuclear spin, in our case it is vanadium nucleus

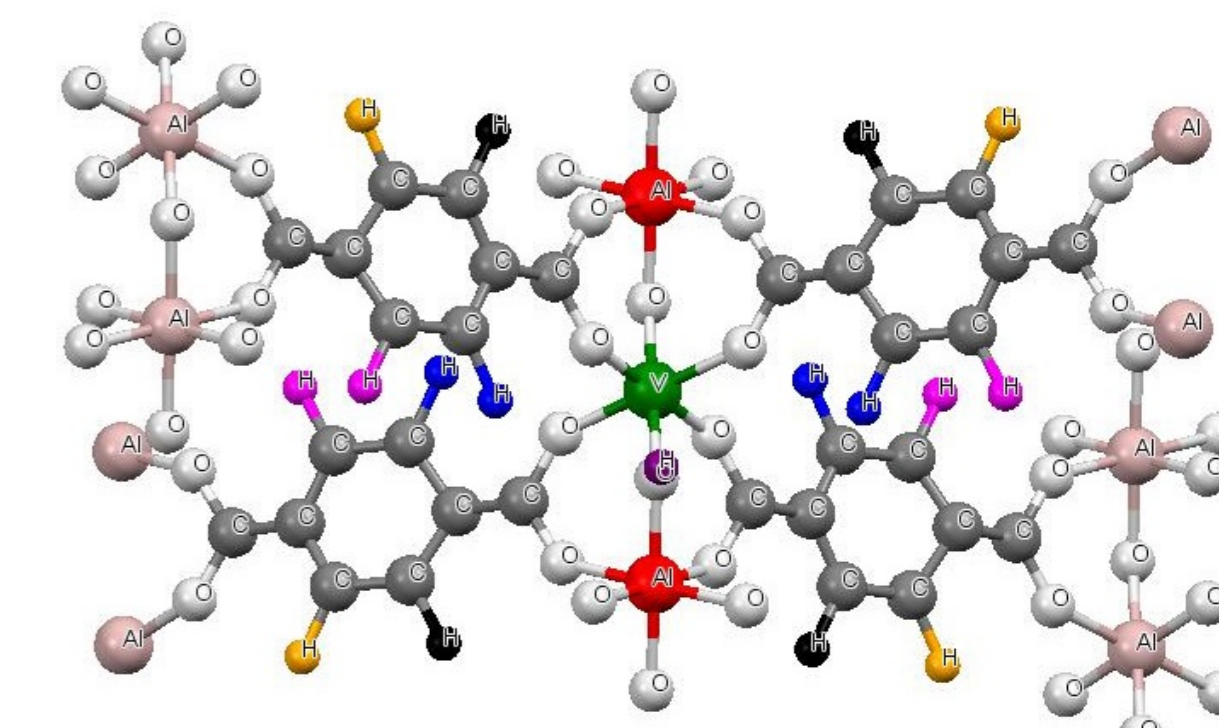
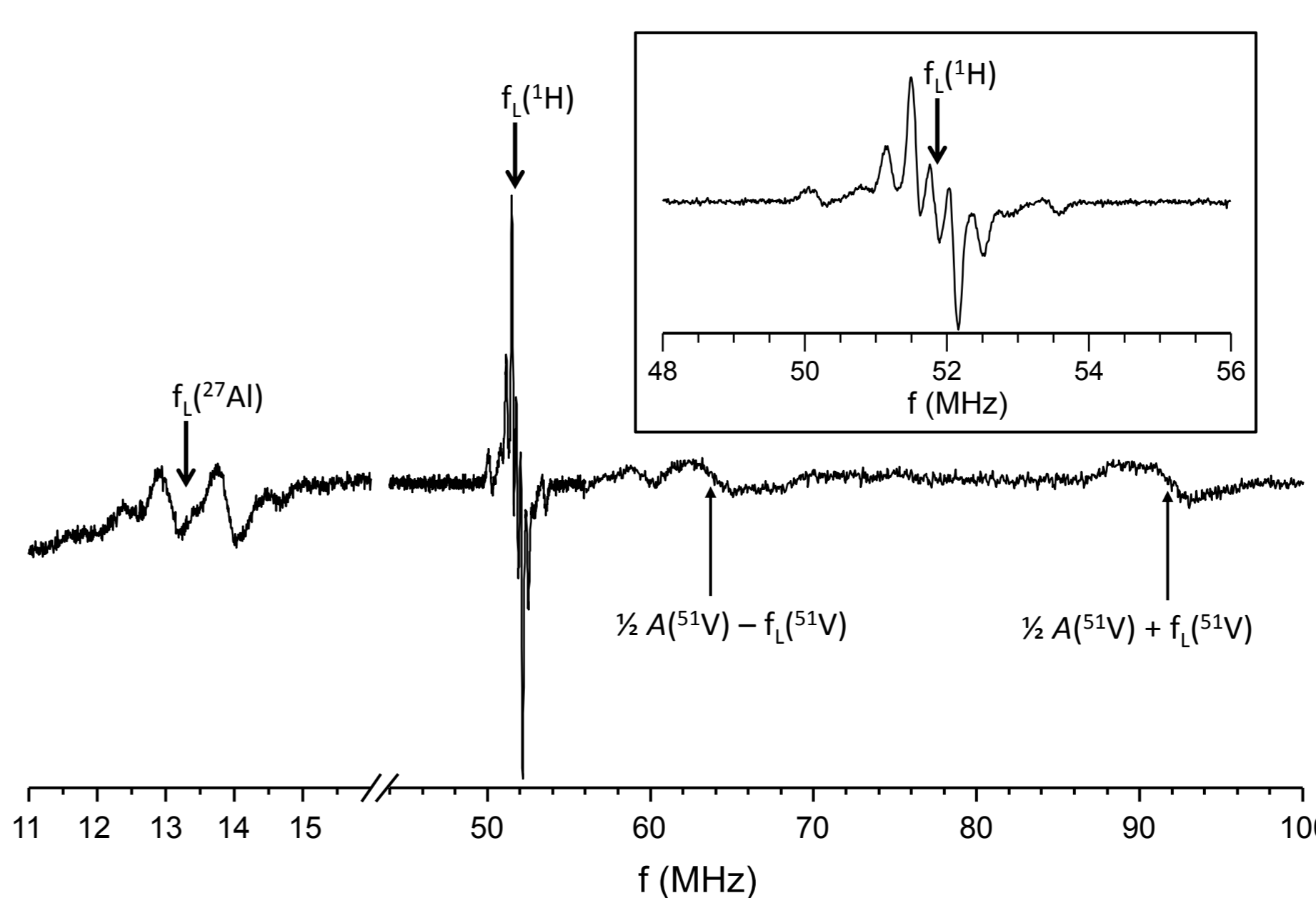


Nuclear spin of ⁵¹V is I = 7/2 → EPR signal splits into eight resonant lines



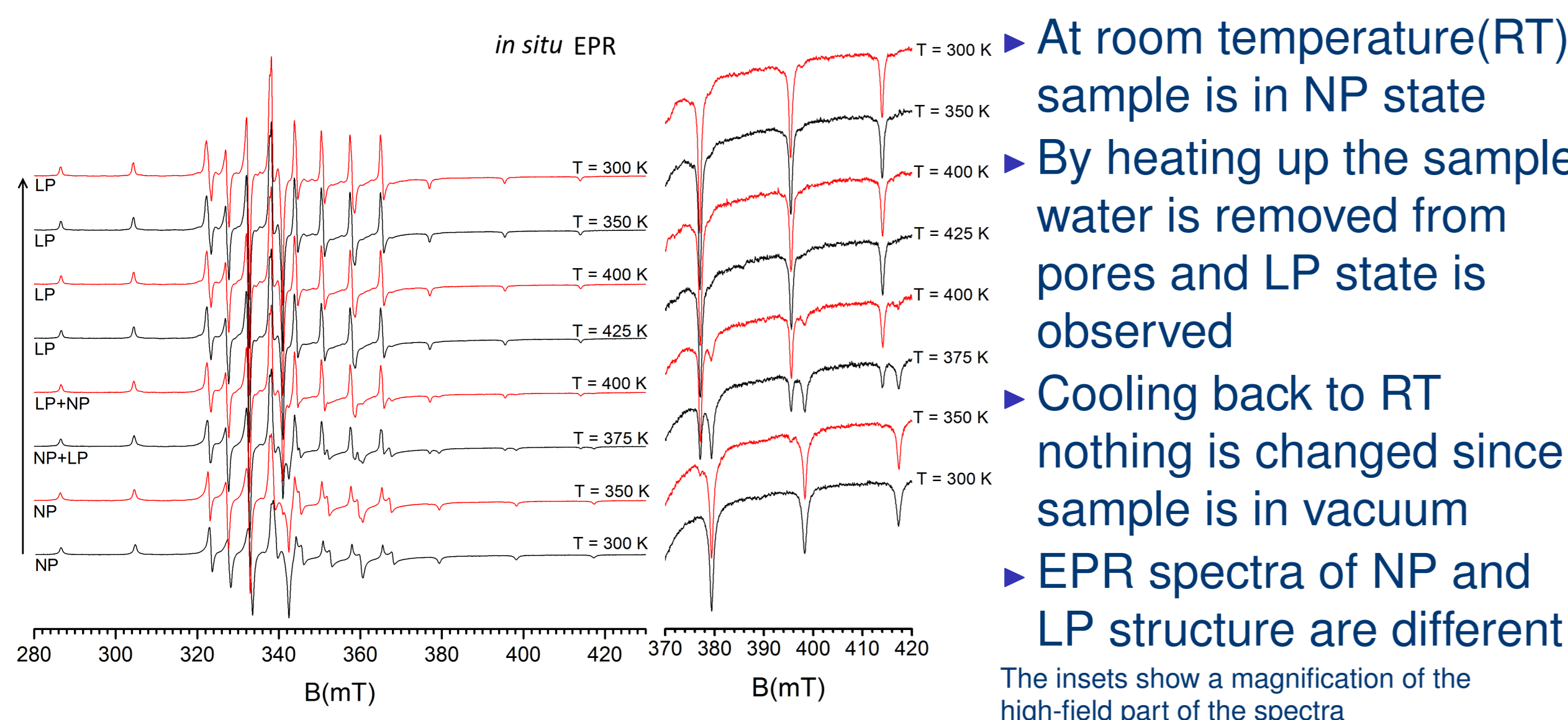
Is vanadium incorporated in the framework?

NMR like spectra called ENDOR, Electron Nuclear Double Resonance. Interaction of unpaired electron with central ⁵¹V nucleus (green), two ²⁷Al nuclei (red), nearest hydroxyl proton (purple) and 4 sets of 4 protons on the terephthalic linkers (blue, black, magenta and yellow)



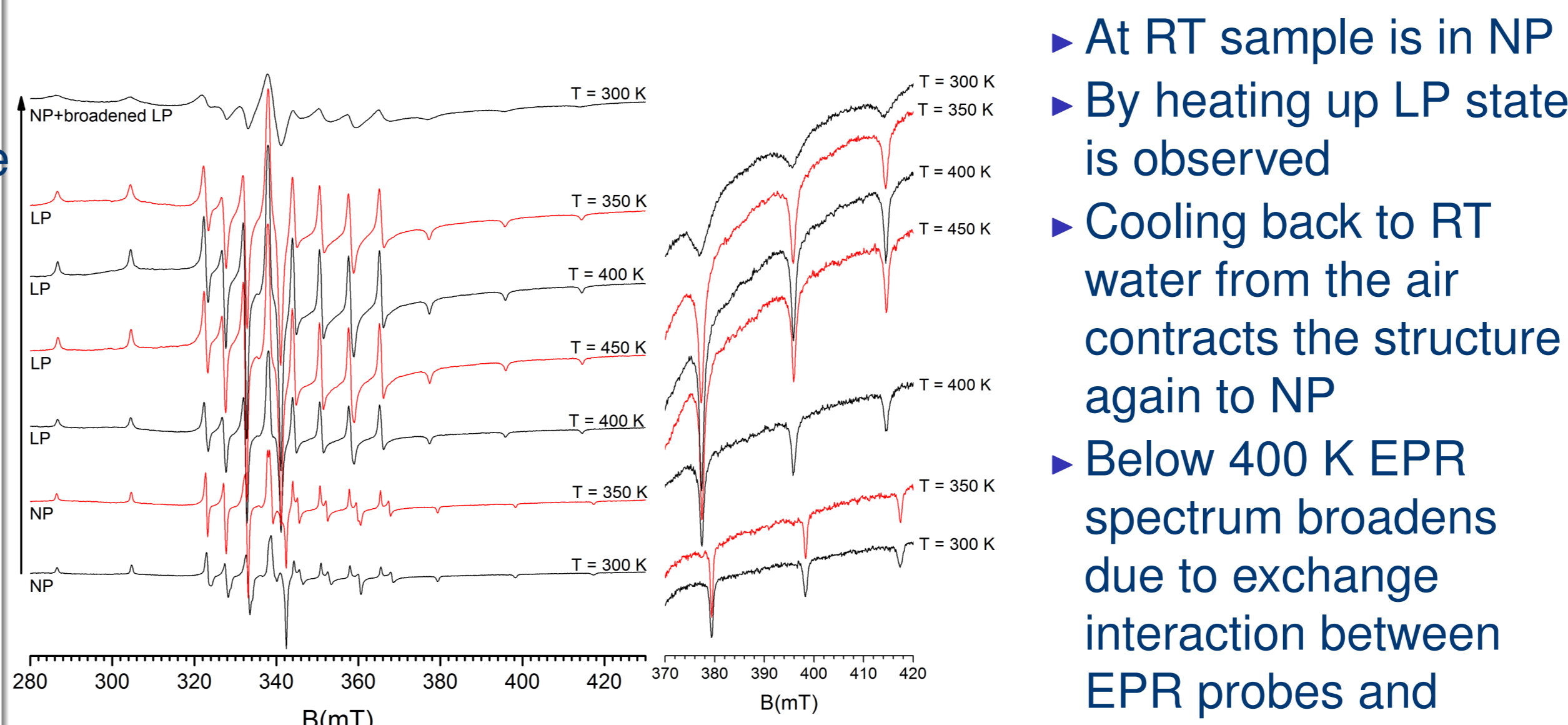
V^{IV}=O molecular ion replacing regular Al^{III}-OH unit in the MIL-53 framework

Breathing effect monitored *in situ* in vacuum



The insets show a magnification of the high-field part of the spectra

Breathing effect monitored *in situ* in air



Conclusions

- ▶ V^{IV}=O molecular ions replace regular Al^{III}-OH units in the MIL-53(Al) framework
- ▶ EPR active V^{IV}=O molecular ions act as local probes to detect phase transitions in the MIL-53(Al) framework
- ▶ EPR showed that exchange interaction between paramagnetic V^{IV}=O centers and O₂ molecules causes broadening of the LP EPR spectrum

References :

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

Acknowledgments :

Luka Luketin (Erasmus student)



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