Structural Insights into Metal-Organic Connectivity by Paramagnetic NMR

Lyle Walld[1], Kirill Levin[1], Daniel Padeanu[2], George Shimizu[2], Scott Kroeker[1]

1 = Department of Chemistry, University of Manitoba, 2 = Department of Chemistry, University of Calgary

Introduction

Metal-Organic Frameworks (MOFs) are an emerging class of materials with numerous applications in domains such as gas storage and separation, catalysis and bioimaging [1]. They consist of metallic centres with organic linkers between them, forming a 3D network. These MOFs are difficult to analyze through x-ray diffraction (XRD) methods, thus the hope is that Nuclear Magnetic Resonance (NMR) will provide meaningful insight into their structures.

However, many MOFs are paramagnetic, as many positive ions of transition metals contain unpaired electrons. Paramagnetic electrons introduce complications to NMR studies of such compounds. Along with these complications, opportunities to probe chemical structure through paramagnetic interactions arise.

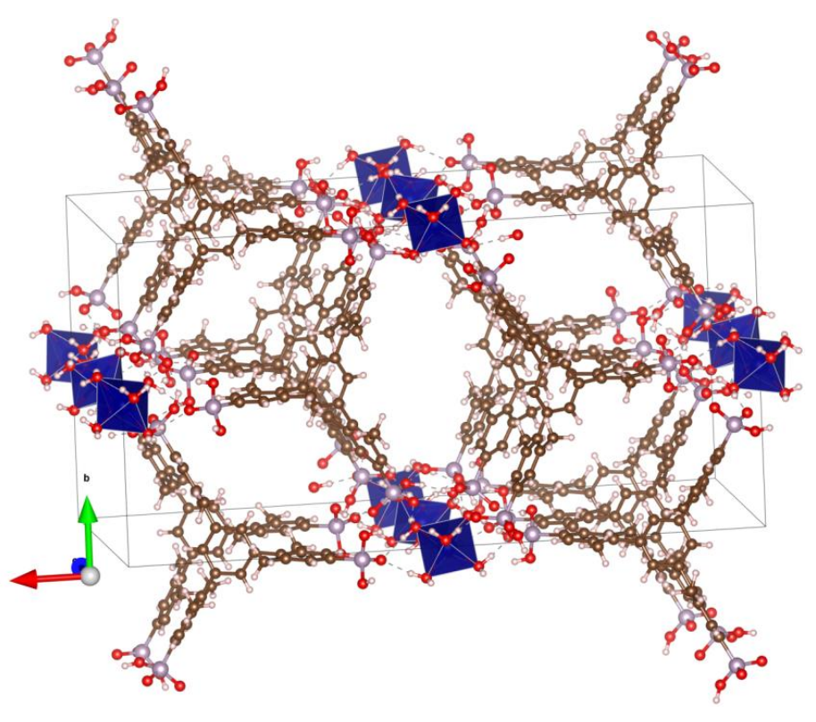


Figure 1: Typical MOF Structure

Purpose

The goal of this project is to make use of the sensitivity of NMR to unpaired electrons to gain insight into the packing structure of ligands in these materials, with the hope that paramagnetic NMR may be extended to a wider variety of MOFs.

Theory of Paramagnetic NMR

Most NMR is performed on diamagnetic compounds. The magnetic moment of paramagnetic electrons results in significant interactions with the nuclei in a material. These interactions drastically alter the NMR spectrum by two mechanisms.

Isotropic Hyperfine (Fermi):

A through-bond effect, which originates in unpaired-electron spin-density ($\rho_{\alpha\beta}$) having a probability to exist at a given nucleus. This interaction results in changes to the observed NMR shifts (δ_{obs}) according to:

$$\delta_{Fermi} = \frac{M(S+1)}{T}\rho_{\alpha\beta}$$

$$\delta_{obs} = \delta_{dia} + \delta_{Fermi}$$

where δ_{dia} is the diamagnetic shift, S is the total electron spin number, T is the temperature of the system, and M has a value of $23.5\ x\ 10^6$ ppm K au^{-1}.

Anisotropic Hyperfine (Dipolar):

The dipolar effect is a through-space interaction between nuclei and unpaired electrons with effects that include dramatic increases in nuclear relaxation rates.

The nuclear relaxation time, T_1, is a significant factor in terms of experimental NMR. Relaxation times vary drastically with interatomic distance r, as $T_1 \propto r^6$. A shorter relaxation period indicates a closer proximity to paramagnetic metal centres, r, the source of unpaired electrons. Nuclear T_1s were measured experimentally and compared with theory to gain structural insight.

$$\frac{1}{T_{1N}} = \frac{2S(S+1)\gamma_I^2 g^2 \beta^2}{15r^6}\omega(T_e)$$

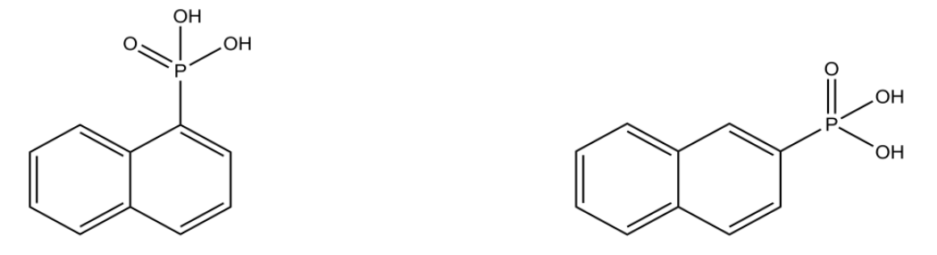
Methods

- **Apparatus Used:**
  - Bruker Avance III 500 Spectrometer
  - 1.3 mm Magic Angle Spinning (MAS) Probe
  - 40-60 kHz MAS Rate
- **Experiments Performed:**
  - ^{31}P, ^{13}C, ^{1}H Hahn-Echo
  - $^{13}C\{^1H\}$ REDOR used to distinguish carbons bonded to hydrogen from those not bonded to hydrogen.
  - Saturation Recovery and Inversion Recovery to measure T_1
  - CPMG to measure T_2, wherein a $\frac{\pi}{2}$ pulse is followed by a train of π pulses to measure the rate of longitudinal coherence delay, for which T_2 is the time constant.
- **Synthesis:**
  - Samples were synthesized by Daniel Padeanu and Dr. George Shimizu.

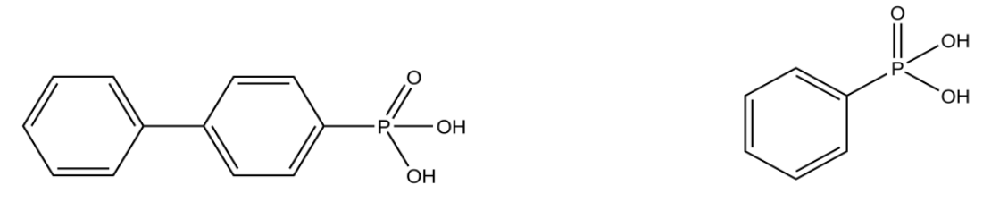
Structures

These samples consist of octahedral chromium nodes connected to phosphonate groups via water hydrogen bonds. The 3D framework is formed through phosphonate based organic linkers, see figure 2.

Unpaired electrons from the d^3 Cr^{3+} centres, are delocalized throughout the framework structure, and confer paramagnetic character on the nuclei of interest



a. 1-Naphthalene (1-Naph) Ligand **b. 2-Naphthalene (2-Naph) Ligand**



c. Biphenyl (BP) Ligand **d. Phenyl (PP) Ligand**

Figure 2: Ligands present in the structures analyzed

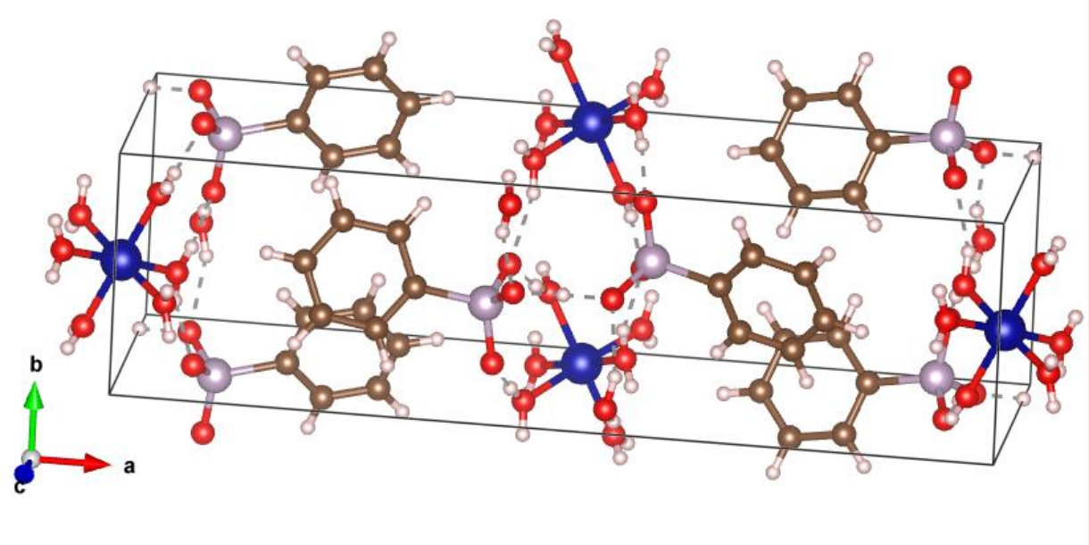


Figure 3: Phenyl based structure (PP), as determined by single-crystal X-ray diffraction

^{31}P MAS NMR

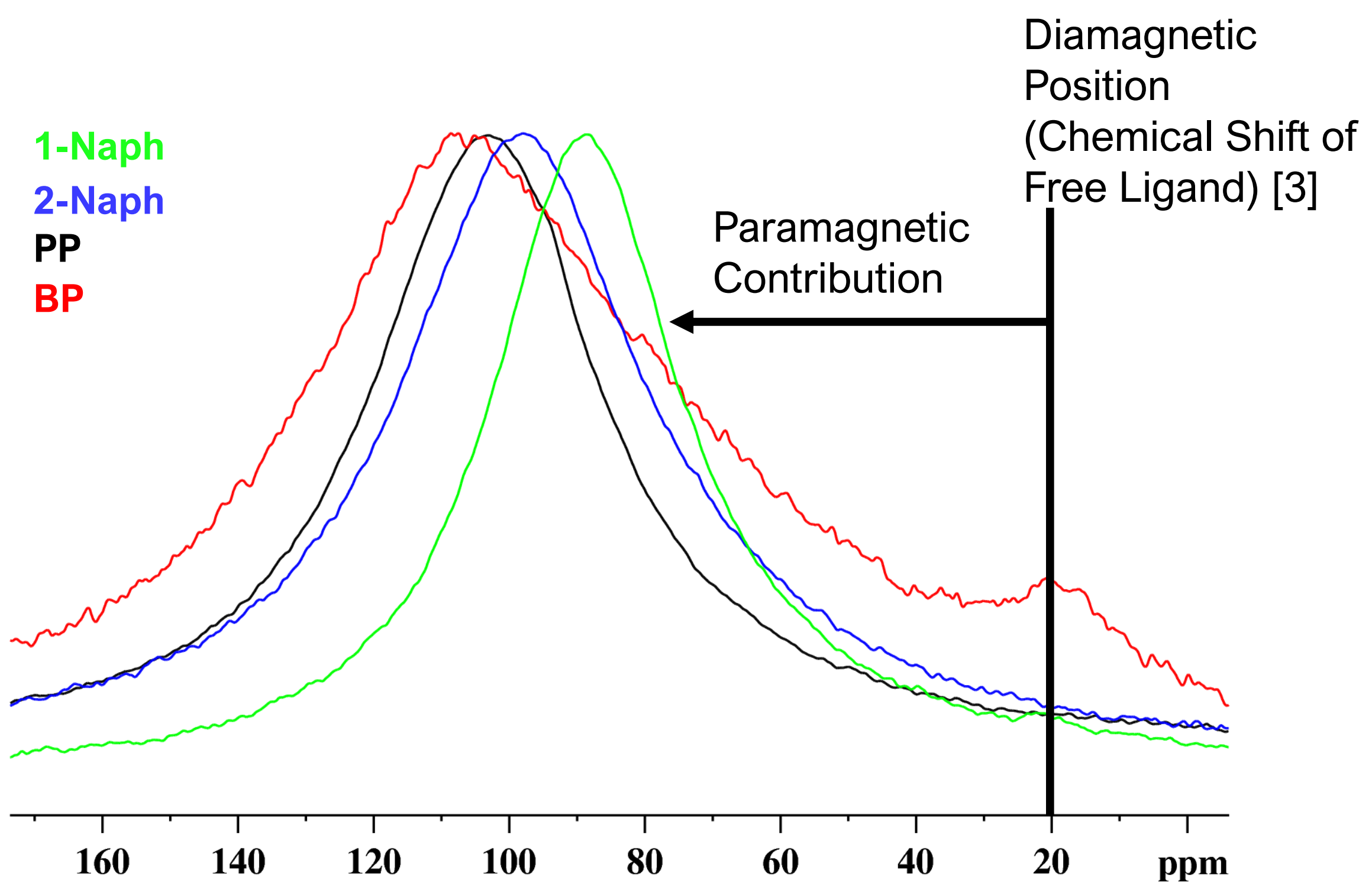


Figure 4: ^{31}P MAS NMR Spectra of four structures, with the approximate diamagnetic position labelled to demonstrate the paramagnetic contribution to shift

- The effects of the Fermi coupling shift the peaks to higher frequency, demonstrating the similar spin delocalization pathways and hence structural connectivity of these samples.

^{13}C MAS NMR

- The differences in aromatic ligand are the driving force behind the observed structural differences between these systems.
- ^{13}C NMR and $^{13}C\{^1H\}$ REDOR elucidate these differences.
- REDOR experiments were used to determine which carbon signals originate from atoms bonded to hydrogen atoms.

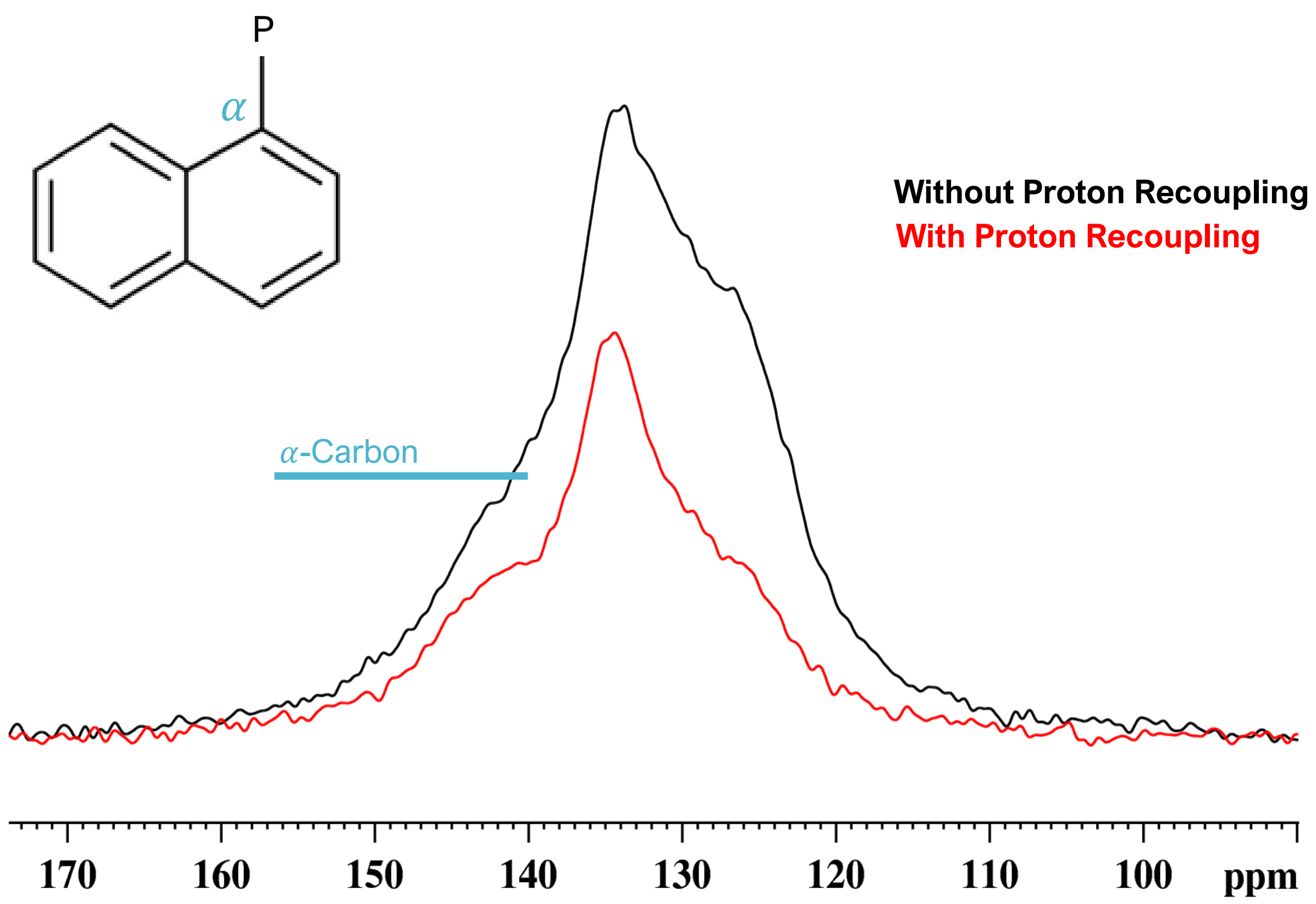


Figure 5: Peak Identification for 1-Naph Structure with $^{13}C\{^1H\}$ REDOR

- ^{13}C NMR spectra show larger shifts for carbons closer to the metal centre as evidenced by relaxation times and spin density maps.

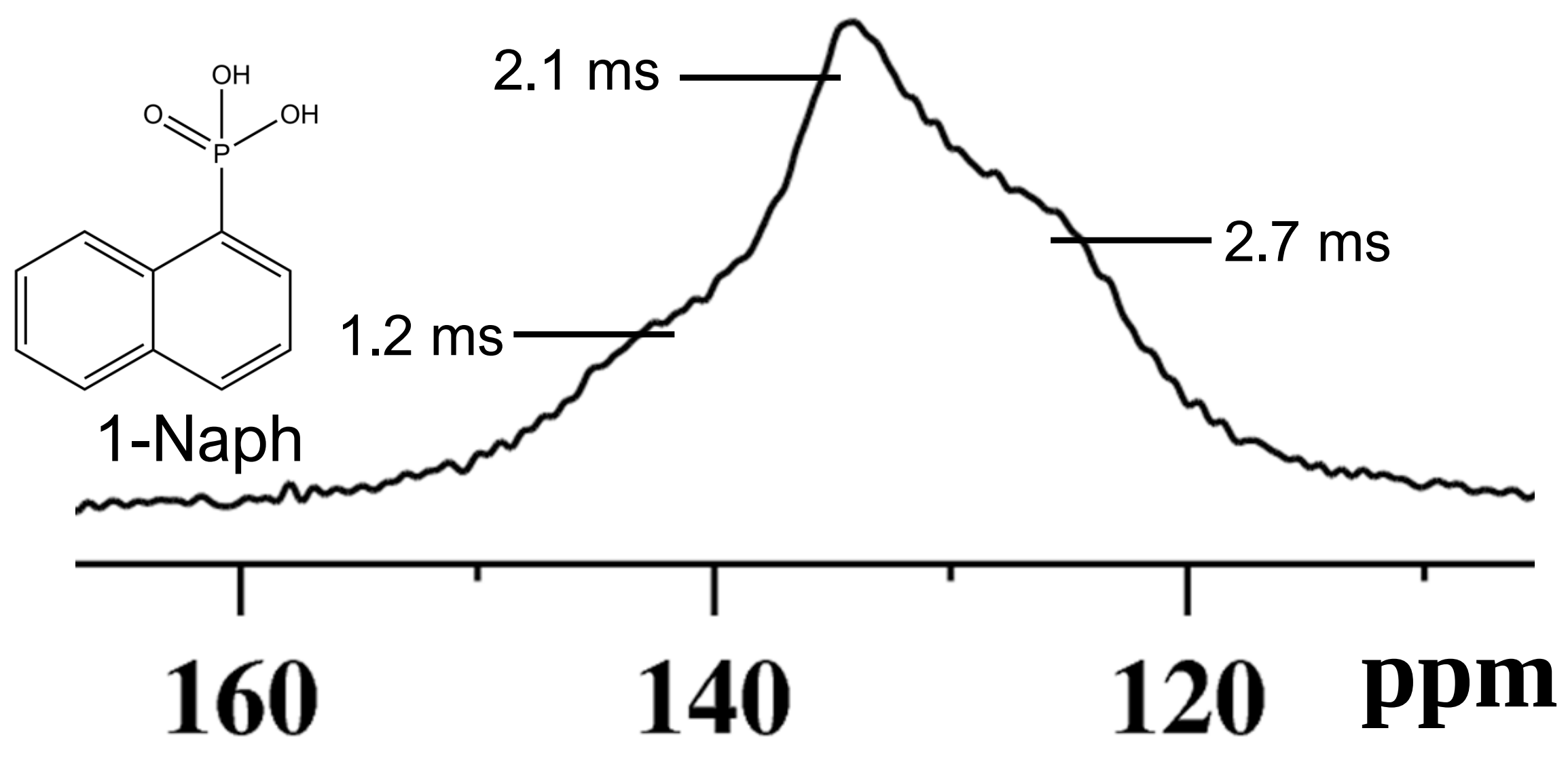


Figure 6: ^{13}C MAS NMR Spectra of 1-Naph, with peaks labelled with corresponding T_1 relaxation times. Uncertainty in T_1 taken as ±20%

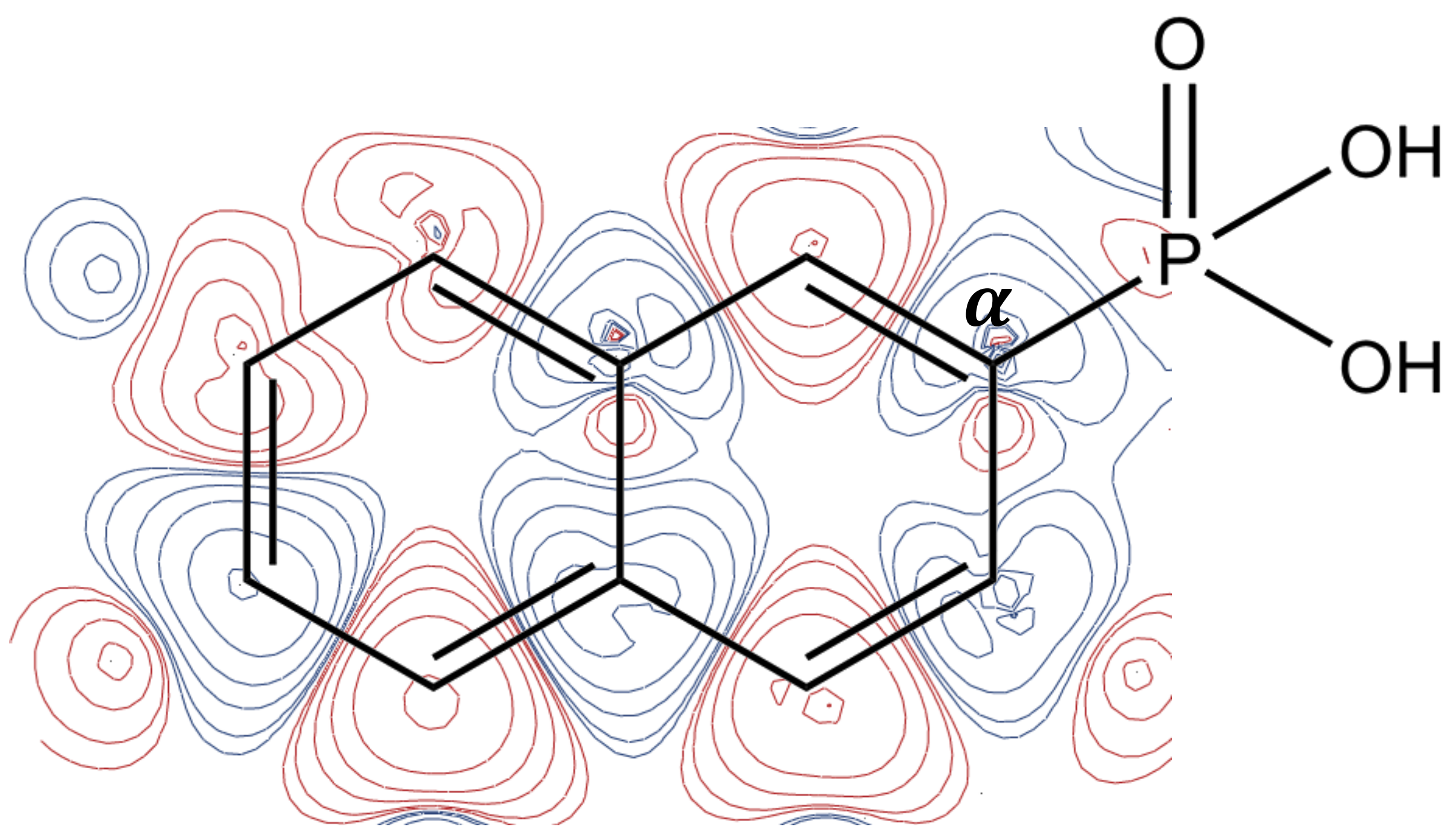


Figure 7: Spin Density Map of 2-Naph, as calculated by HSEH1PBE with 6-31G basis set applied to carbon atoms

- Blue colour of spin density contours at α carbon implies a positive Fermi shift, agreeing with the findings of $^{13}C\{^1H\}$ REDOR experiments, where the α carbon is shifted to higher frequencies.

Discussion

- ^{13}C assignments are in agreement with the crystal structures of 1-Naph, 2-Naph, and PP.
- Comparing with Figure 2b., this can be rationalized in terms of the measured relaxation times as well.
- The differences in packing arrangement under investigation originate in the degree of interdigitation, or overlap of neighboring sets of ligands, which is detectable via relaxation times.

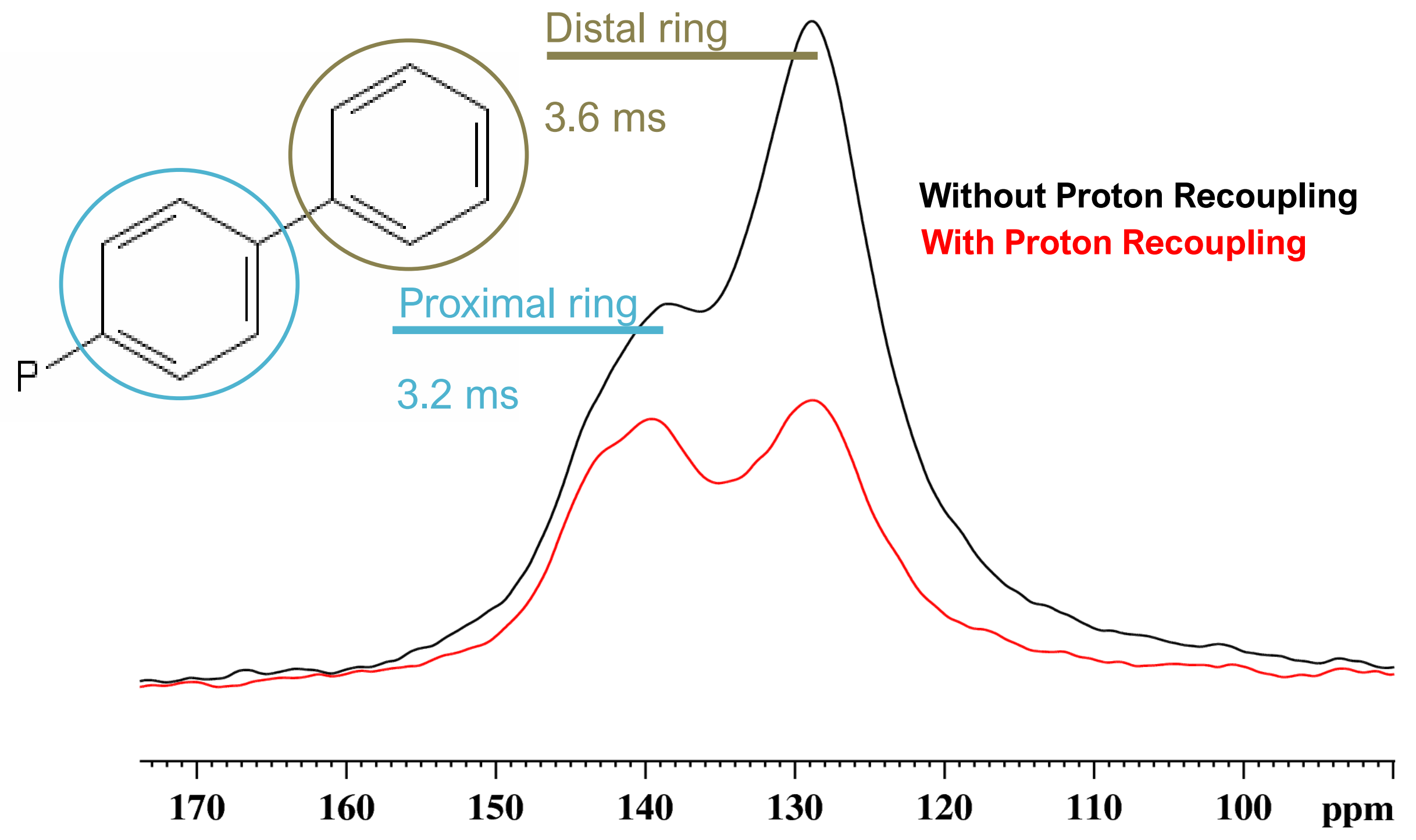


Figure 8: Peak Identification for BP Structure with $^{13}C\{^1H\}$ REDOR, and T_1 relaxation times

- No crystal structure could be obtained for BP, but structural predictions can be made based on NMR. The relaxation times can be used to gain insight into the packing arrangement.
- The degree of interdigitation of the biphenyl groups can be estimated based on the nuclear relaxation times of the peaks corresponding to each ring.
- Similar relaxation times of signals from neighboring phenyl rings suggests similar distance to a metal from either side of the biphenyl. This implies significant interdigitation in the structure. This is represented in Figure 9.

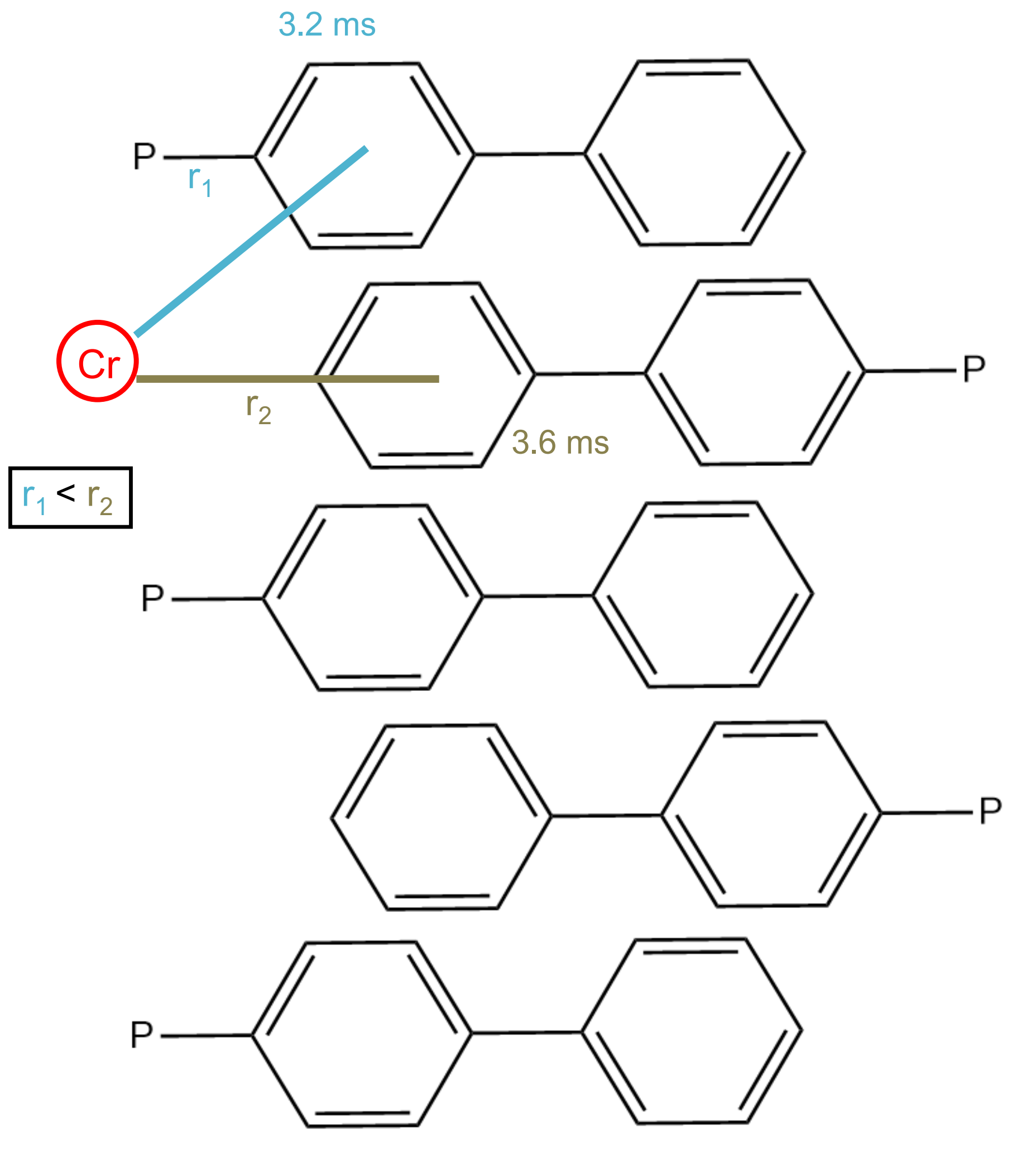


Figure 9: Suggested degree of interdigitation in BP structure

Conclusions

- The sensitivity of NMR peak shifts to paramagnetic electrons has been used to begin developing an understanding of metal-organic connectivity in MOFs.
- By comparison to other structures, insight has been gained on the packing arrangement of the biphenyl structure.
- A more quantitative model for interpreting paramagnetic relaxation times within these, and other periodic systems could potentially triangulate atomic positions.
- This sort of analysis can be extended to similar structures, such as other MOFs, to assist in the development of frameworks with specific and useful properties.

References

[1] Zhou, Hong-Cai, Long, Jeffrey R, and Yaghi, Omar M. “Introduction to Metal-Organic Frameworks.” *Chemical Reviews* 112.2 (2012): 673–674.

[2] La Mar, Gerd N., Horrocks, William DeW., and Holm, Richard Hadley. *NMR of Paramagnetic Molecules; Principles and Applications.* New York: Academic Press, 1973.

[3] Pretsch, Ernö., Bühlmann, Philippe., and Badertscher, Martin. *Structure Determination of Organic Compounds Tables of Spectral Data* . 4th, rev. and enlarged ed. Berlin, Heidelberg: Springer Berlin Heidelberg, 2009.

Acknowledgements

University of Manitoba
INNOVATION.CA
CANADA FOUNDATION FOR INNOVATION
FONDATION CANADIENNE POUR L'INNOVATION
NSERC
CRSNG
Manitoba