

# Characterization of Metals in Organometallic Catalysts using

# High Field Solid-State NMR Spectroscopy

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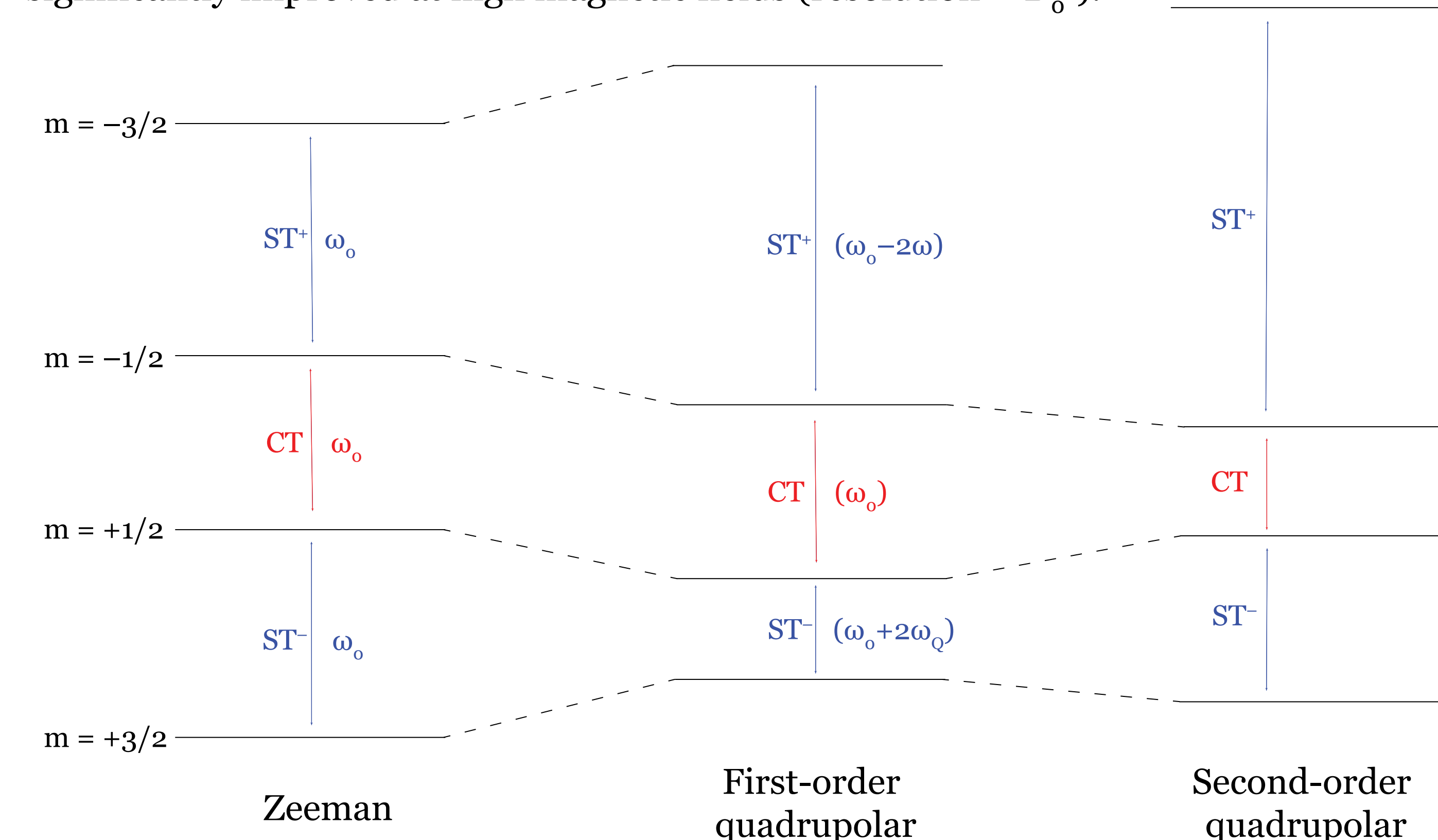
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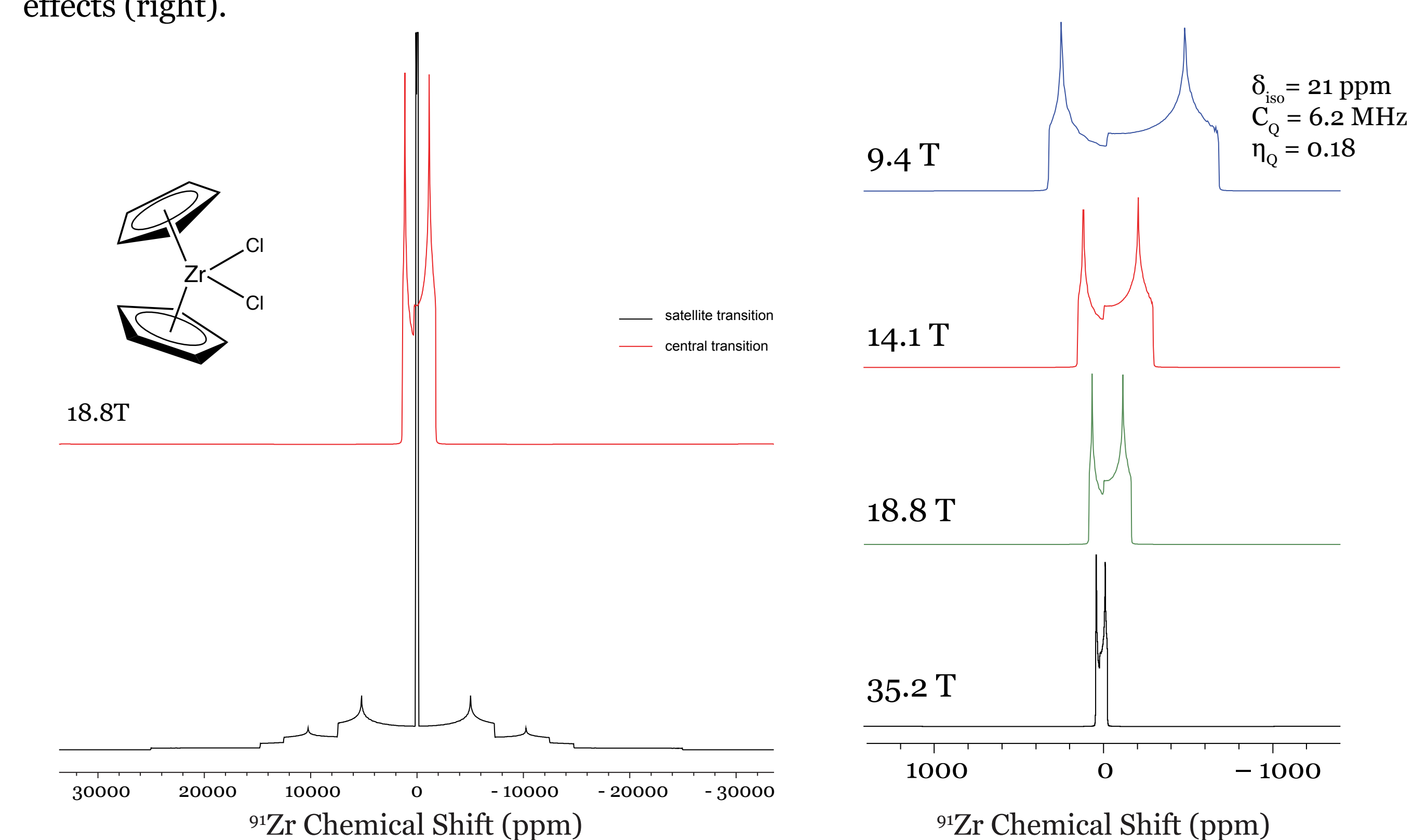
## Introduction

Catalytic materials are critical to improve the efficiency of chemical processes and meet global energy demands. The rational design and synthesis of catalysts relies on atomic-level characterization tools such as nuclear magnetic resonance (NMR) spectroscopy. The development and application of solid-state NMR techniques to study nuclei relevant to catalysis will benefit the design of better catalysts.

Solid-state NMR spectroscopy of metals in catalytically-relevant materials such as organometallic complexes will provide an atomistic picture of the local environment at the catalytic active site. However, solid-state NMR of metals which are important in catalysis such as titanium (<sup>47/49</sup>Ti), zirconium (<sup>91</sup>Zr) and molybdenum (<sup>95</sup>Mo) is challenging as they contain nuclei which have a nuclear spin  $I > 1/2$  - such nuclei show NMR spectra severely broadened by the quadrupolar interaction, which reduces the overall experimental sensitivity (Figure 1 and 2). However, the sensitivity and resolution of solid-state NMR spectra of half-integer quadrupolar nuclei can be significantly improved at high magnetic fields (resolution  $\propto B_0^2$ ).



**Figure 1.** Figure showing the energy levels of a spin  $I = 3/2$  quadrupolar nucleus under an applied magnetic field (left), under the first-order quadrupolar (center) and second-order quadrupolar effects (right).



**Figure 2.** <sup>91</sup>Zr solid-state NMR spectra of Cp<sub>2</sub>ZrCl<sub>2</sub> showing the relatively narrow linewidth of the central transition relative to the satellite transitions (left) and the magnetic field dependence (right). The <sup>91</sup>Zr chemical shift ( $\delta_{iso}$ ) and quadrupolar parameters ( $C_Q$ ,  $\eta_Q$ ) were extracted from reference [2].

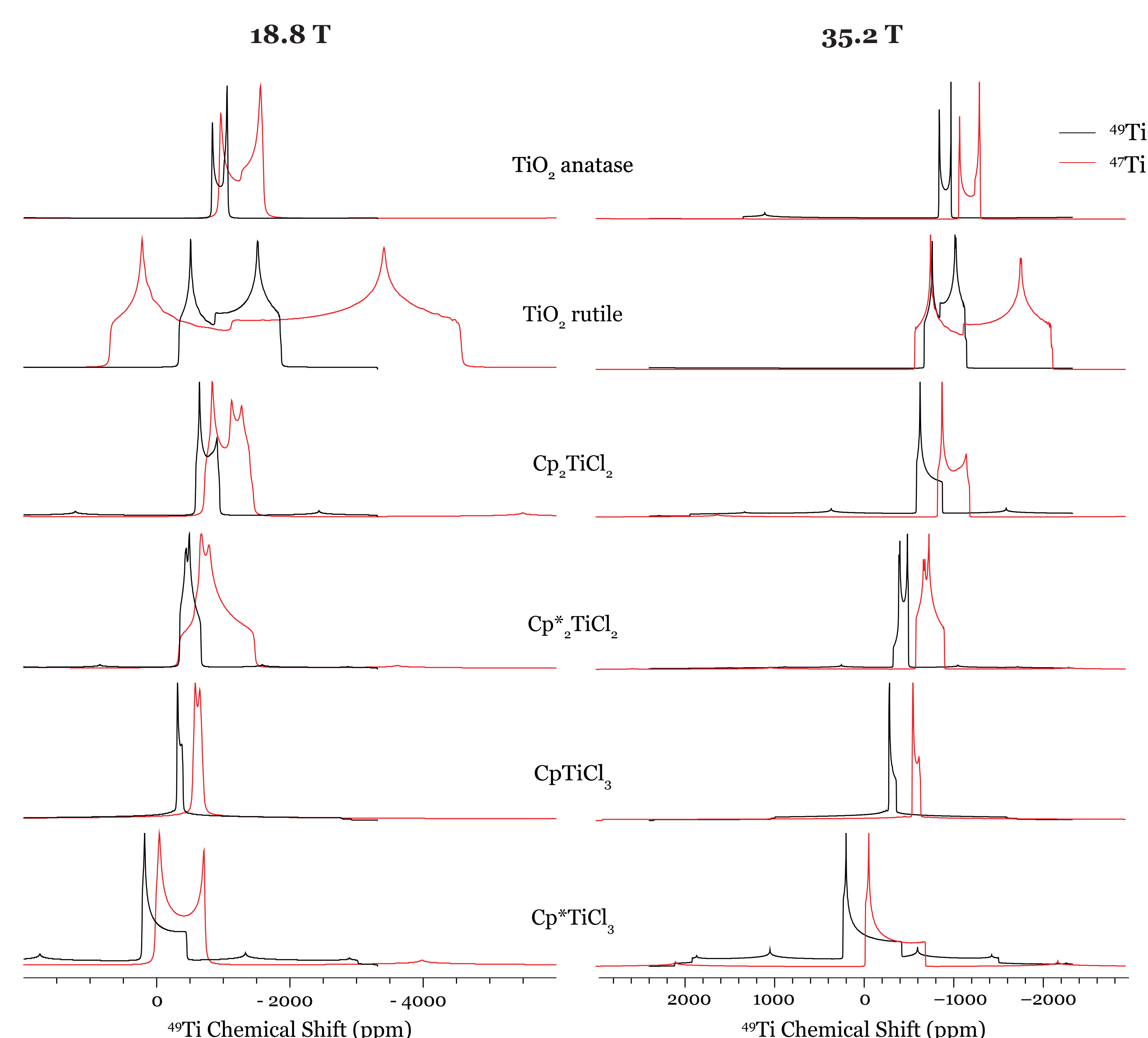
## <sup>47/49</sup>Ti Solid-State NMR Spectroscopy

In this work, we probe the local environments of titanium (Ti), zirconium (Zr), and molybdenum (Mo) in materials relevant to catalysis using solid-state NMR at high magnetic fields. The resolution of solid-state NMR spectra of half-integer quadrupolar nuclei such as <sup>47/49</sup>Ti, <sup>91</sup>Zr and <sup>95</sup>Mo improves as  $1/B_0^2$ .

Ti has two NMR-active isotopes <sup>47</sup>Ti ( $I = 5/2$ ) and <sup>49</sup>Ti ( $I = 7/2$ ) which have low natural abundance of 7.4 and 5.4 %, respectively, low gyromagnetic ratios and are close in Larmor frequency. As a result of these interactions, <sup>47/49</sup>Ti solid-state NMR spectra show poor sensitivity and resolution. Here we show that the linewidths of a series of Ti compounds can be substantially narrowed at high magnetic fields with examples at 18.8 and 35.2 T. We are presently applying this approach to materials containing Ti such as titania (anatase and rutile) and a Ti organometallic complex.

**Table 1.** Experimental <sup>49</sup>Ti chemical shift ( $\delta_{iso}$ ,  $\Omega$  and  $\kappa$ ) and quadrupolar ( $C_Q$ ,  $\eta_Q$ ) NMR parameters of titanium compounds along with the euler angles ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) between the two tensors. Values for TiO<sub>2</sub> and Titanocene compounds were extracted from references [3] and [4].

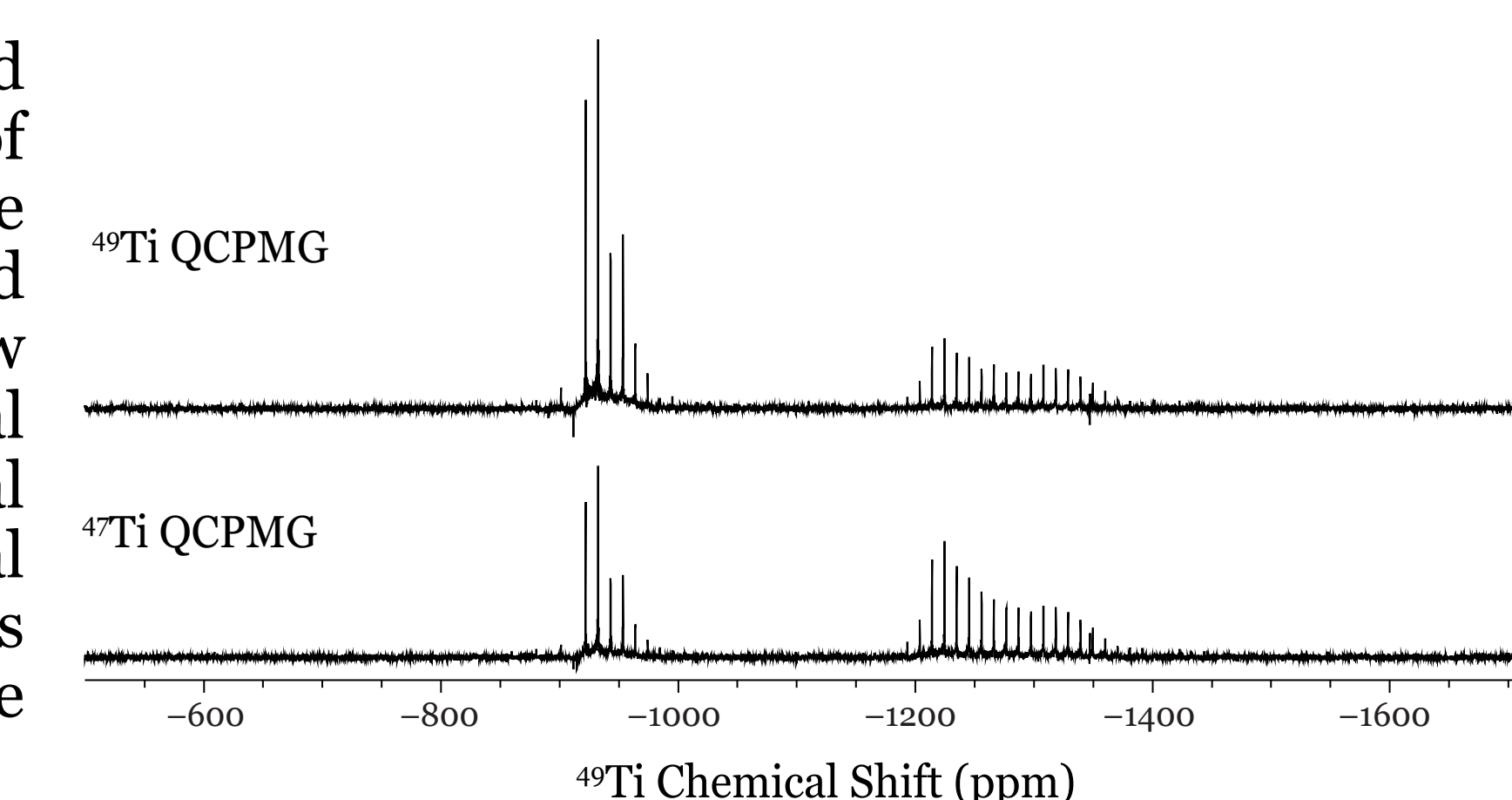
Sample	$\delta_{iso}$	$C_Q$	$\eta_Q$	$\Omega$	$\kappa$	$\alpha$	$\beta$	$\gamma$
TiO <sub>2</sub> - anatase	-927	4.9	0.06	120.9	0.9	254	179	97
TiO <sub>2</sub> - rutile	-881	13.9	0.2	60	0.0	80	110	81
Cp <sub>2</sub> TiCl <sub>2</sub>	-732	4.2	0.45	275	0.7	20	20	-10
Cp <sub>2</sub> *TiCl <sub>2</sub>	-449	5.5	0.72	165	-0.1	80	90	-5
CpTiCl <sub>3</sub>	-341	1.6	0.95	85	0.8	50	12	10
Cp*TiCl <sub>3</sub>	-33	3.0	0.35	650	0.9	30	0	0



**Figure 3.** Simulated static <sup>47/49</sup>Ti solid-state NMR spectra of Titania (anatase and rutile) and Titanocene complexes at 18.8 T (left) and 35.2 T (right) based on the experimental <sup>49</sup>Ti solid-state NMR parameters listed in Table 1. The <sup>47</sup>Ti chemical shifts were obtained by the relation <sup>47</sup>Ti (ppm) = <sup>49</sup>Ti (ppm) - 266, due to the small difference in their Larmor frequencies.  $C_Q(^{47}\text{Ti}) = 1.223 \times C_Q(^{49}\text{Ti})$  due to the difference in the nuclear quadrupole moments.

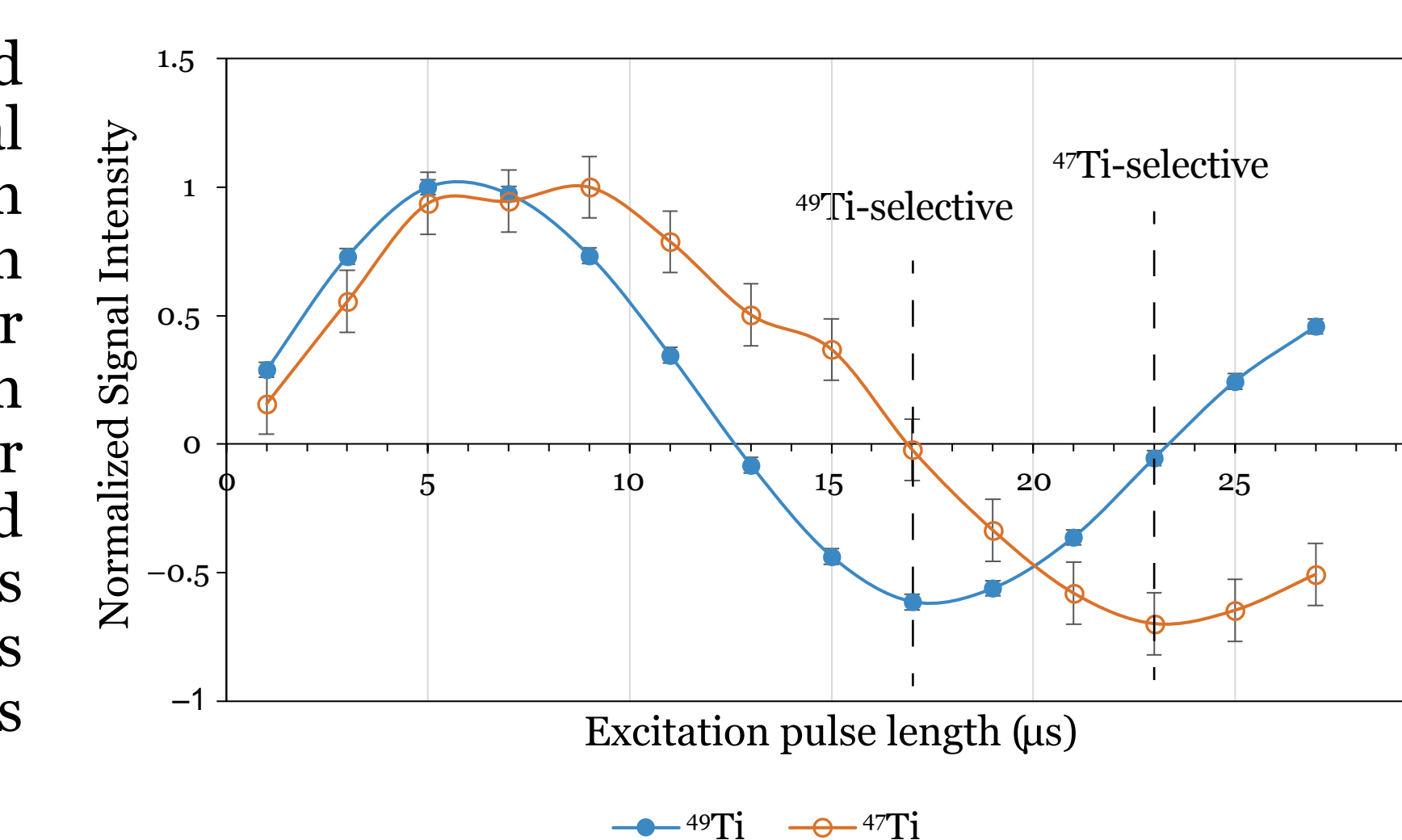
## Resolving <sup>49</sup>Ti and <sup>47</sup>Ti NMR Spectra

Figure 4 shows the <sup>49</sup>Ti and <sup>47</sup>Ti solid-state NMR spectra of TiO<sub>2</sub> anatase. Due to their close Larmor frequencies, <sup>47</sup>Ti and <sup>49</sup>Ti spectra frequently show overlap, which makes spectral analysis difficult. Traditional methods of using central transition selective 90° pulses show limited selectivity (Figure 4).



**Figure 4.** Experimental <sup>47/49</sup>Ti quadrupolar Carr Purcell Meiboom Gill (QCPMG) solid-state NMR spectra of TiO<sub>2</sub> anatase at 18.8 T and 16 kHz magic angle spinning (MAS) frequency. Central-transition selective 90° and 180° pulses for <sup>49</sup>Ti (top) and <sup>47</sup>Ti (bottom) were used.

Figure 5 shows the <sup>49</sup>Ti and <sup>47</sup>Ti solid-state NMR central transition selective nutation profiles. The nutation frequencies of half-integer quadrupolar nuclei depend on the spin  $I$  ( $I + 1/2$  times faster than the applied radiofrequency field). This result highlights pulse lengths at which <sup>49</sup>Ti and <sup>47</sup>Ti patterns can be selectively obtained.



**Figure 5.** Experimental <sup>47</sup>Ti (orange) and <sup>49</sup>Ti (blue) nutation curves using central-transition selective pulses, acquired with TiO<sub>2</sub> anatase at 18.8 T.

## Conclusions and Future Work

Here we demonstrate that high magnetic field solid-state NMR spectroscopy of metal sites is a powerful tool to characterize organometallic complexes relevant in catalysis. While magnetic field of 18.8 T cannot fully resolve <sup>47/49</sup>Ti solid-state NMR patterns, we expect that the resolution should be significantly improved at 35.2 T, which is the highest magnetic field for NMR in the world, available at NHMFL. The resolution can also be improved by nutation selective experiments.

The approaches developed for <sup>47/49</sup>Ti solid-state NMR in this study will be extended to <sup>91</sup>Zr and <sup>95</sup>Mo in the future. We are currently performing density functional theory (DFT) calculations on a variety of new Ti, Zr and Mo compounds to calculate their NMR properties prior to experiments. The understanding gained from NMR will aid the development of better catalysts.

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