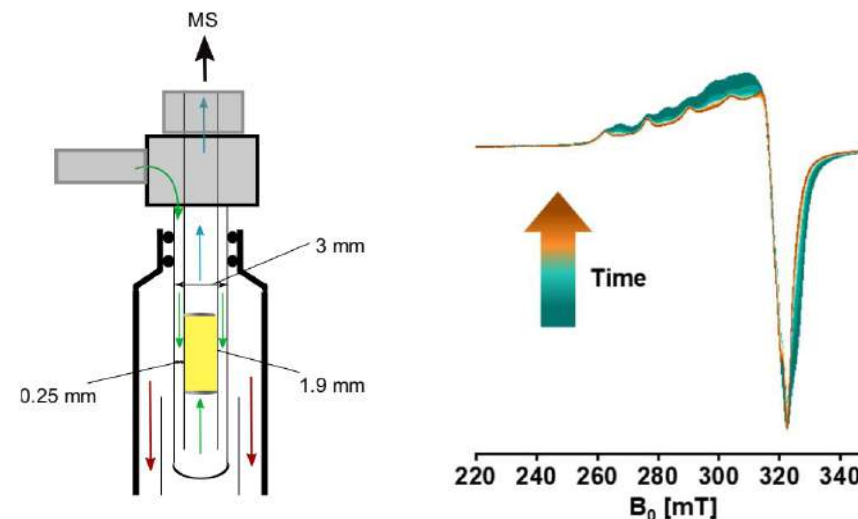


Electron paramagnetic resonance spectroscopy in catalysis

What we shall learn

- applicability of NMR, EPR, and paramagnetic NMR spectroscopy
- how EPR spectroscopy differs from NMR spectroscopy
- information accessible from EPR spectra
- scope and limitations of operando EPR
- scope and limitations of hyperfine spectroscopy
- EPR + DFT approach to spatial and electronic structure of active sites
- use of isotope labelling in detecting reactions



Instead of a lecture script

- EPR entry in Ullmann's Encyclopedia of Industrial Chemistry, [DOI: 10.1002/14356007.q09_q01](https://doi.org/10.1002/14356007.q09_q01)



NMR or EPR?

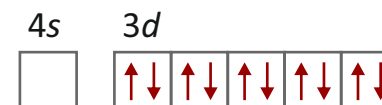
Closed-shell systems

- closed-shell molecules have only paired electrons
- they are diamagnetic
- EPR spectroscopy is not applicable and conventional NMR spectroscopy works

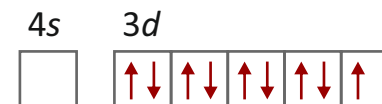
Open-shell systems

- open-shell molecules have at least one unpaired electron
- they are paramagnetic
- EPR spectroscopy is applicable *unless* the electron spin relaxes very fast
- paramagnetic NMR spectroscopy is applicable *if* the electron spin relaxes very fast
- typically, open-shell systems are more reactive

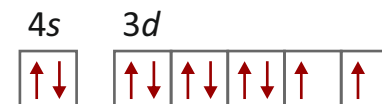
Cu(I) electron configuration $[\text{Ar}]3d^{10}$



Cu(II) electron configuration $[\text{Ar}]3d^9$



Ni(II) electron configuration $[\text{Ar}]4s^23d^8$



(high spin, Hund's rule)

How do unpaired electrons originate? (although chemical bonding involves electron pairing)

Strongly reactive systems

Homolytic bond scission



Electron transfer

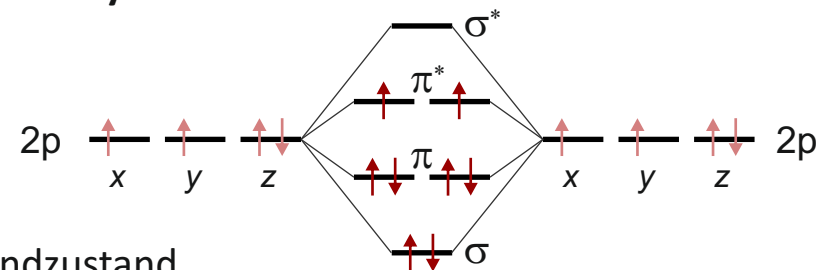


Coupled electron-proton transfer



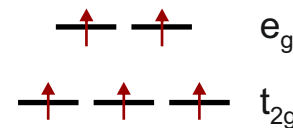
Weakly reactive systems

Orbital degeneracy

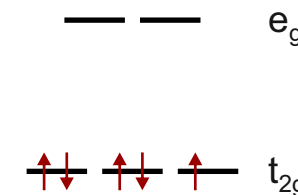


Triplettgrundzustand

Metal ions with odd number of electrons



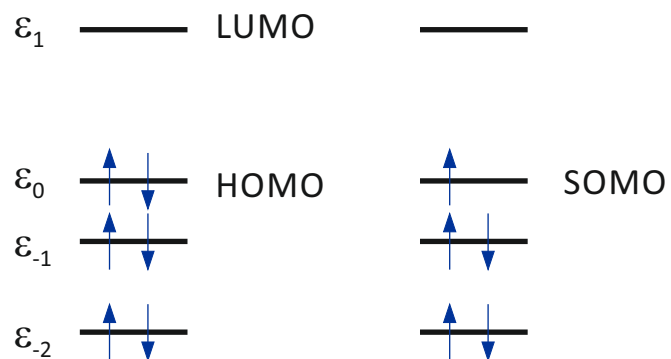
high spin



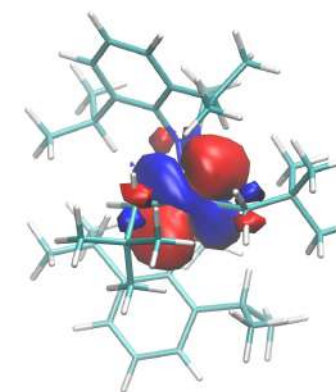
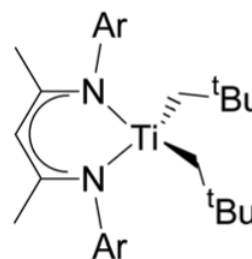
low spin

Where are the unpaired electrons?

The singly occupied molecular orbital (SOMO)



Ti(III) polymerization catalyst



- as a quantum object, an unpaired electron can be at several locations at once
- all these locations can be reactive “hot spots”

How can unpaired electrons be observed?

Electron spin - electron angular momentum contribution of pure quantum mechanical origin

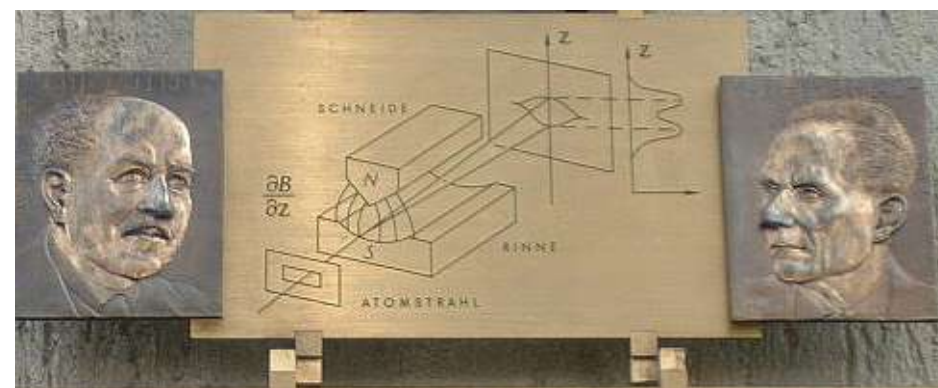
Classical physics: A homogeneous sphere with charge q and angular momentum J features magnetic dipole moment μ

$$\vec{\mu} = \frac{q}{2m} \vec{J}$$

Quantum physics: A correction factor $g \approx 2$ arises

$$\mu = -g \frac{e}{2m} \hbar S$$

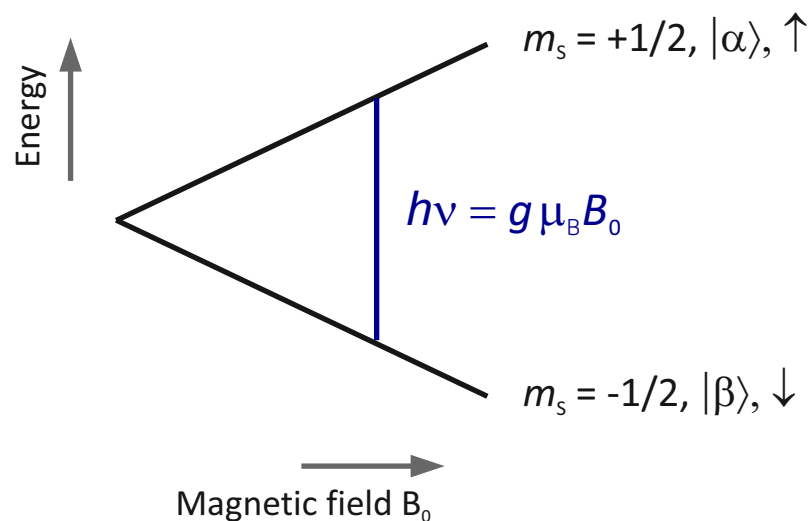
- the unpaired electron behaves as a tiny bar magnet



Stern-Gerlach experiment 1922

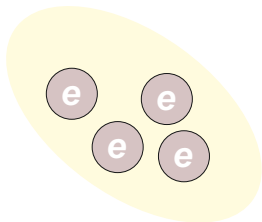
Electron paramagnetic resonance

Electron spin $S = 1/2$ in a magnetic field features two eigenstates of different energy



- frequency ν is in the microwave range (3-300 GHz)
- this corresponds to wave lengths between 10 cm and 1 mm
- by variation of the magnetic field at constant frequency we can find the resonance condition

- the tiny bar magnet can be flipped by microwave irradiation (oscillatory electromagnetic field)



Some are invisible

Kramers and non-Kramers ions

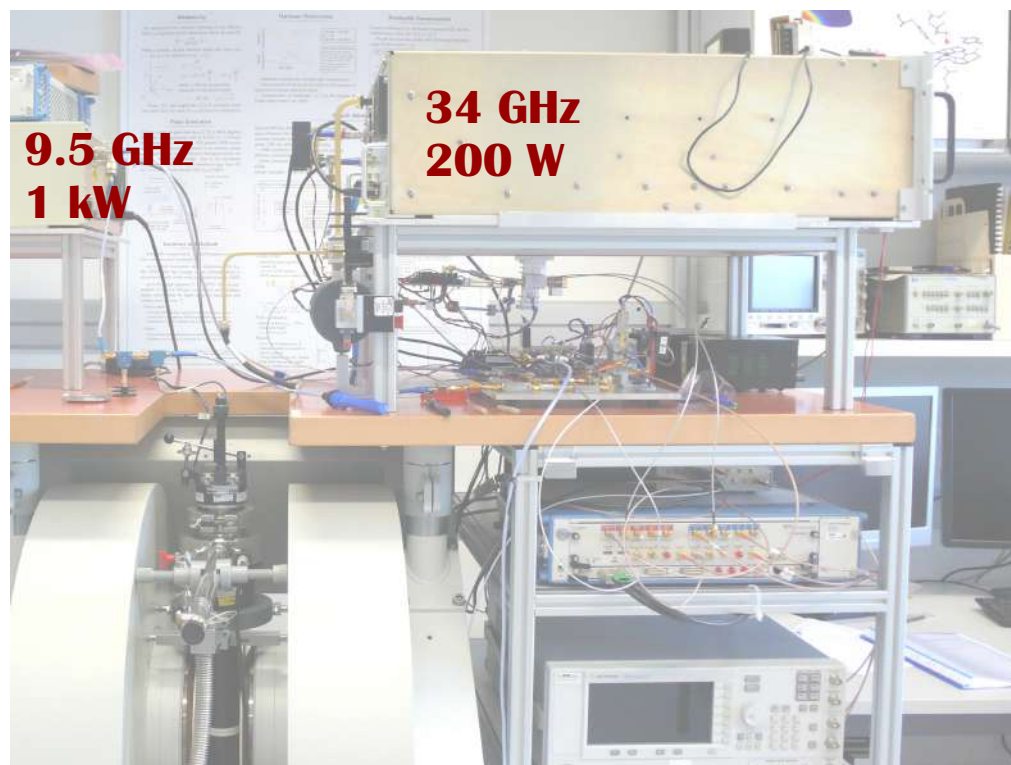
Zero-field splitting can be very large

- one contribution from dipole-dipole coupling of magnetic moments of the unpaired electrons
- one contribution from spin-orbit coupling
- sum may exceed typically accessible microwave frequency range at accessible magnetic fields

Non-Kramers ions

- for an *even number of unpaired electrons*, in general symmetry all transition frequencies may exceed the typically accessible microwave frequency range at zero field and at all accessible magnetic fields
- signals can be visible for systems with (nearly) axial symmetry
- convenient observation may require special microwave resonator geometry ("parallel mode EPR")

How does an EPR spectrometer look like?

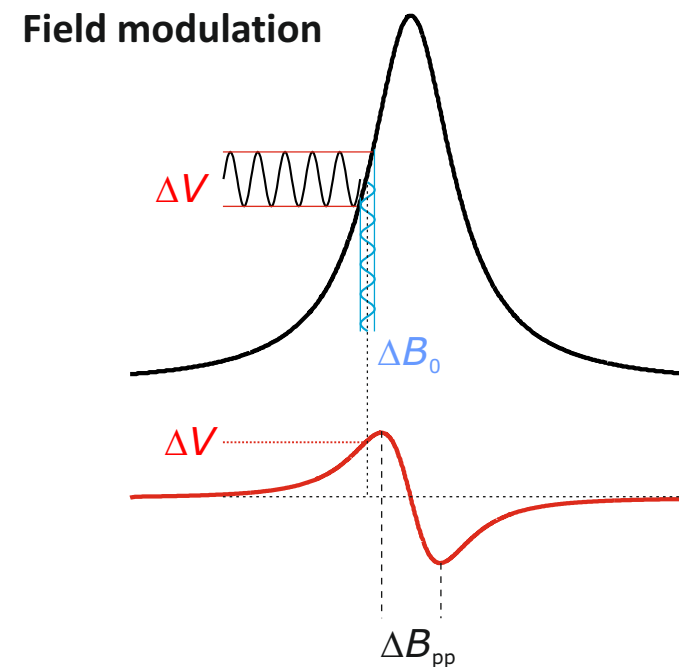
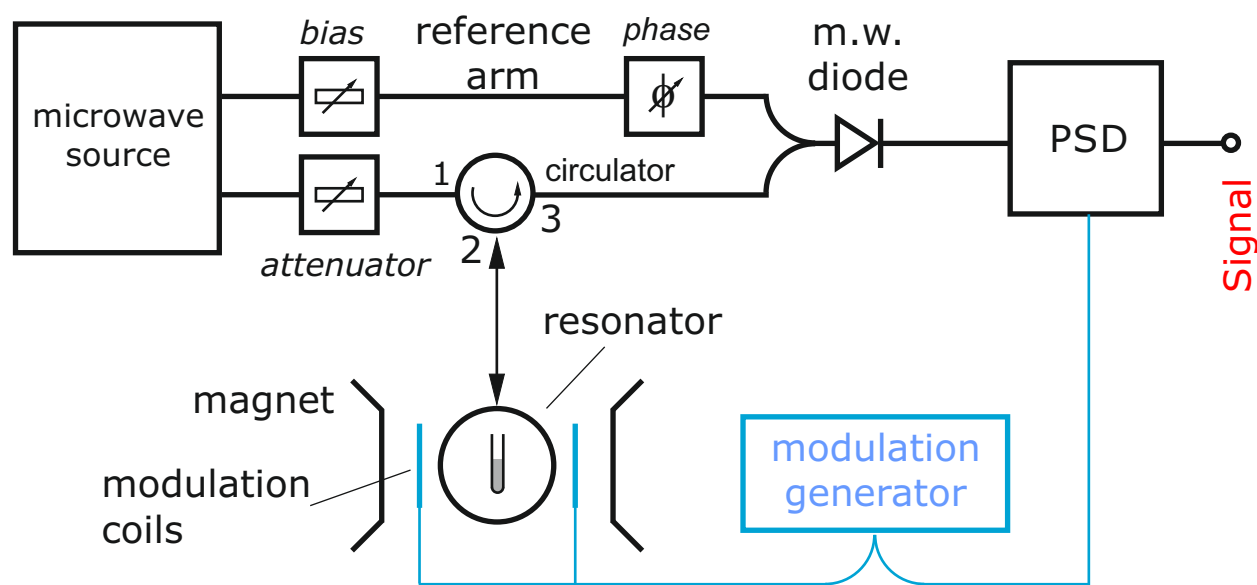


- superconducting magnet required at high frequencies (> 70 GHz)

**Electromagnet
0-1.5 T**

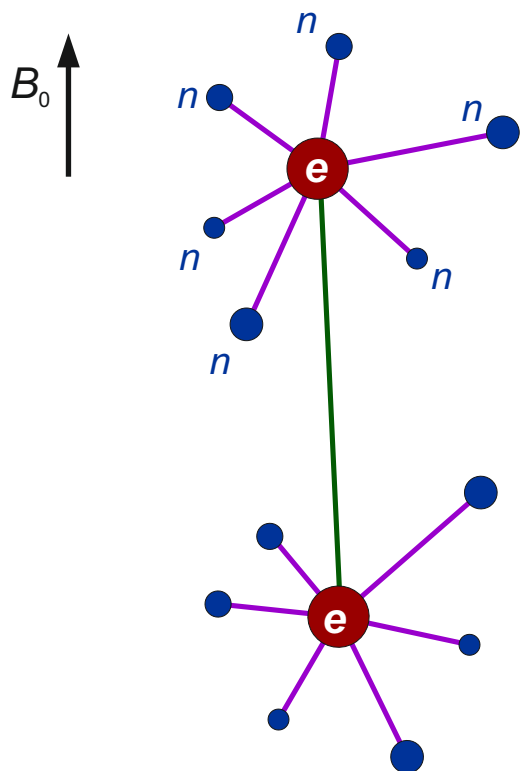
- high power amplifiers for pulsed EPR
- very fast electronics (sub-nanosecond resolution) for generating excitation waveforms

Continuous-wave EPR



- works at any electron spin relaxation time where the spectrum is resolved
- most sensitive technique for detecting EPR spectra of solids

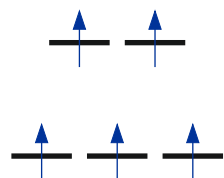
Interactions and the information inferred from them



Name	Information
electron Zeeman	fingerprinting of radical type or metal coordination
hyperfine	distribution of the SOMO (reactivity) distance of protons from the center of spin density
nuclear Zeeman	identification of nuclei that give rise to hfi
nuclear quadrupole	binding situation of the nucleus for $I > 1/2$ (chemical shift is not available)
zero-field	fingerprinting of triplet type or metal coordination spin state for metal ions (low or high spin)
exchange	orbital overlap (important for electron transfer)
dipole-dipole	distances in the nanometer range (15 - 100 Å) ⇒ structure

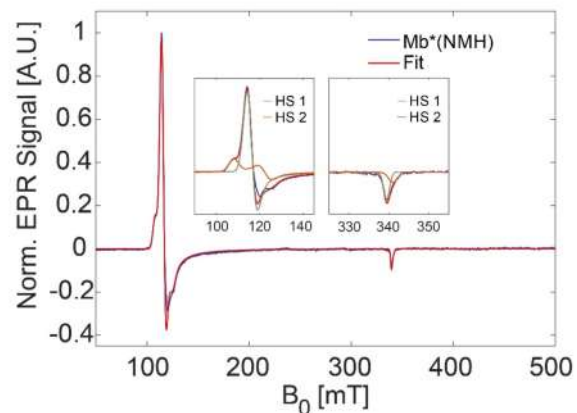
Distinguishing high-spin from low-spin complexes

Weak ligand field



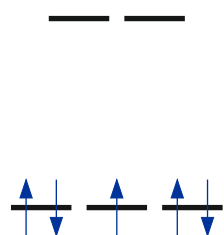
$S = 5/2$ (high spin Fe(III))

CW EPR before adding the substrate EDA

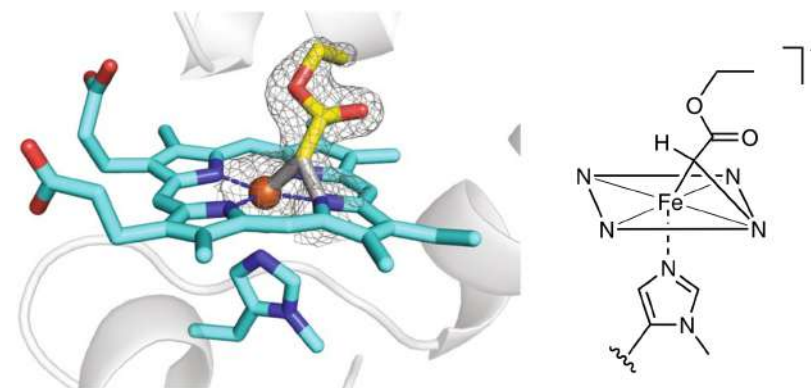
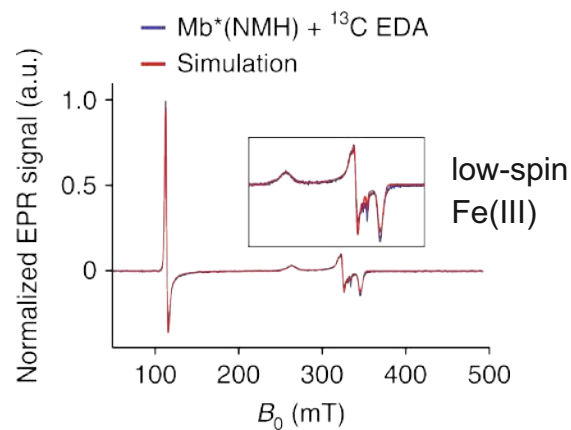


two high-spin Fe(III) species

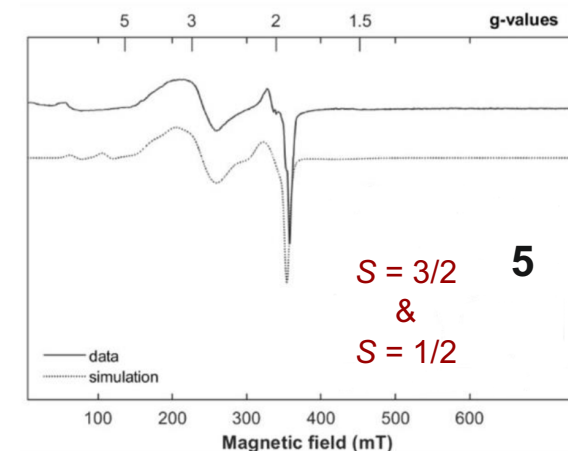
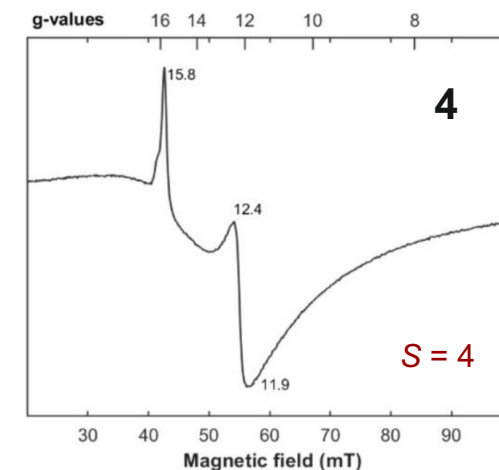
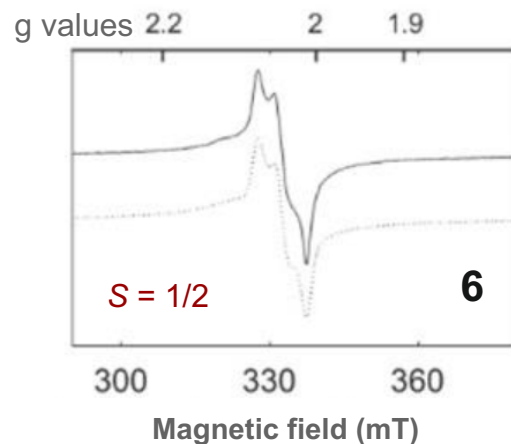
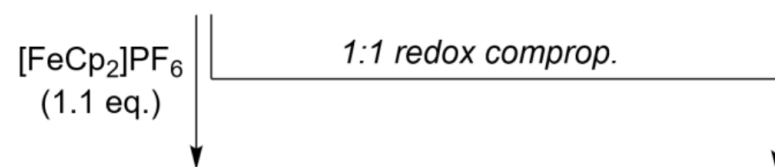
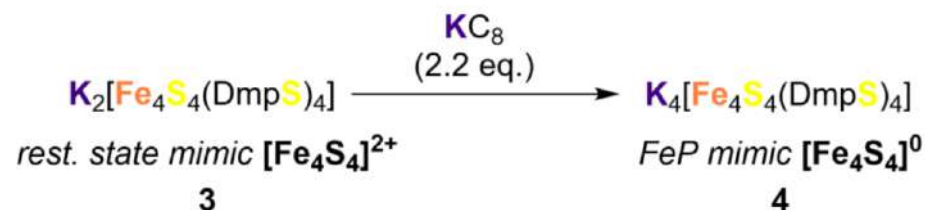
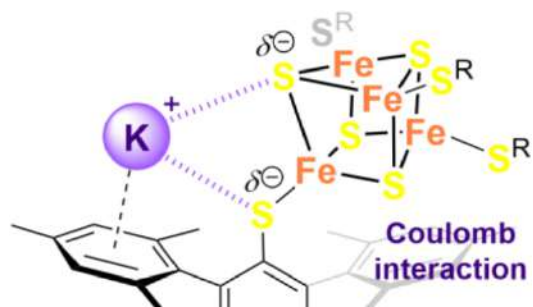
Strong ligand field



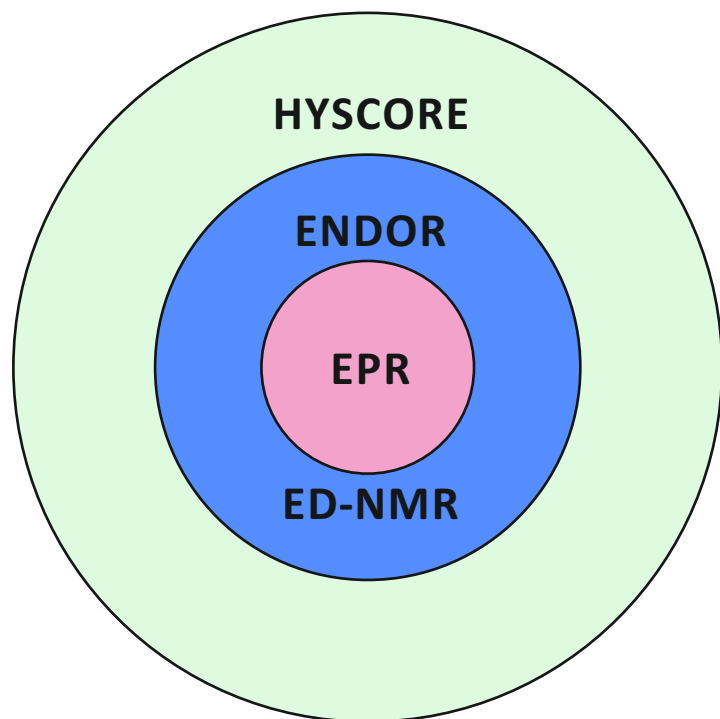
$S = 1/2$ (low spin Fe(III))



Fingerprinting and following oxidation state changes



Spatial and electronic structure: Measuring hyperfine interactions

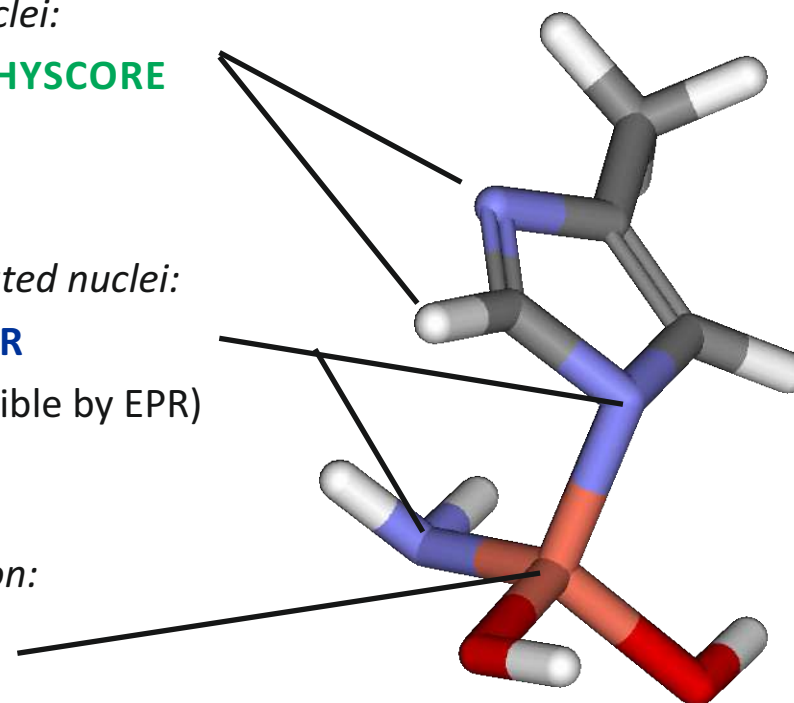


Example: Cu(II) complex

Remote nuclei:
ENDOR & HYSCORE

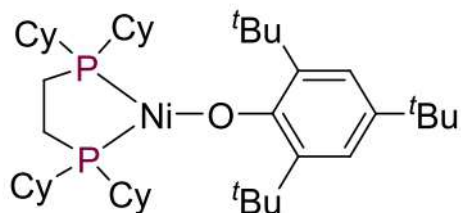
Directly coordinated nuclei:
ED-NMR, ENDOR
(sometimes possible by EPR)

Transition metal ion:
EPR

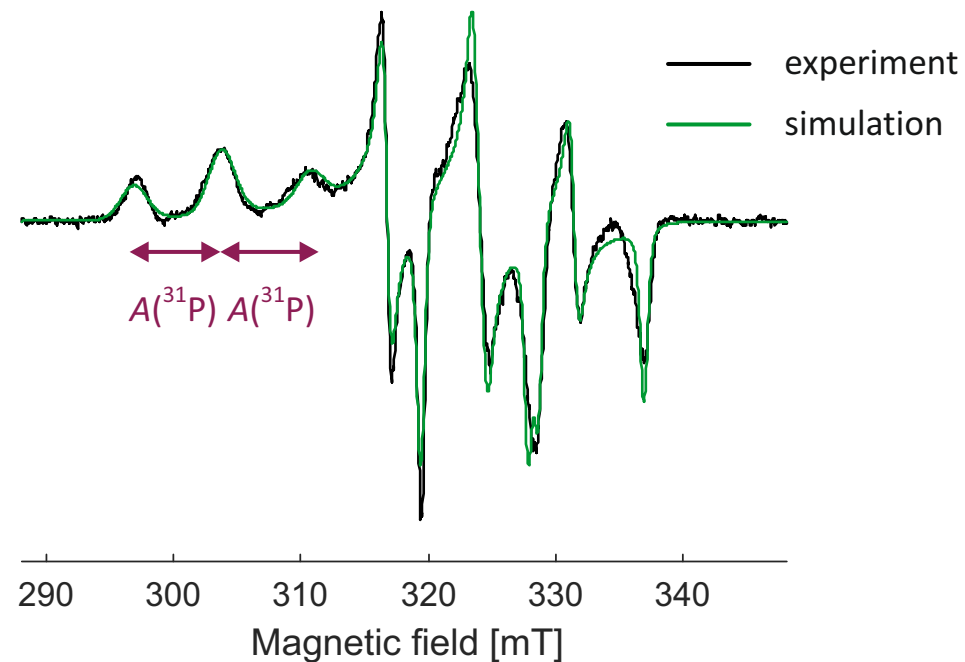


Large hyperfine interactions by CW EPR

^{31}P ligand hyperfine couplings in a Ni(I) complex

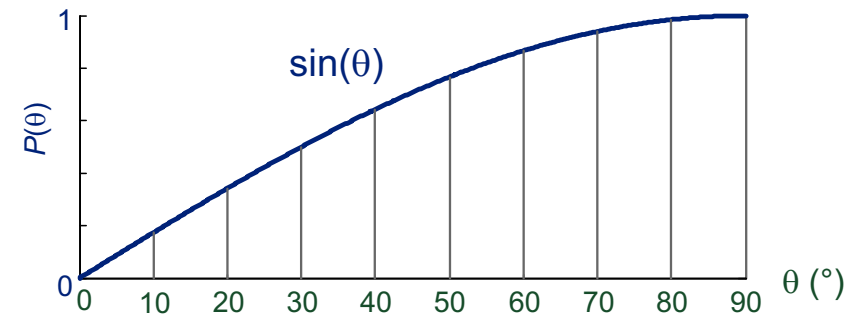
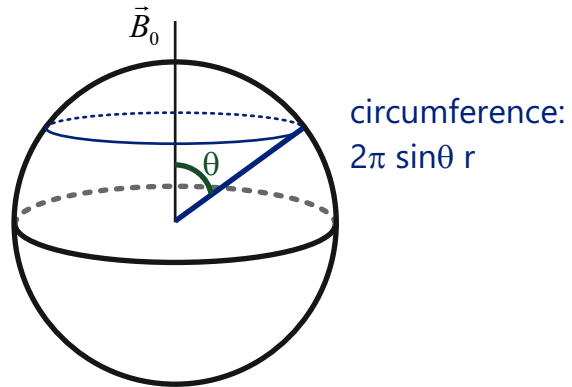


- as ^{31}P has spin $I = 1/2$ (as protons have), we expect a 1:2:1 hyperfine triplet
- in the solid state, complications arise from the combination of g and hyperfine anisotropy



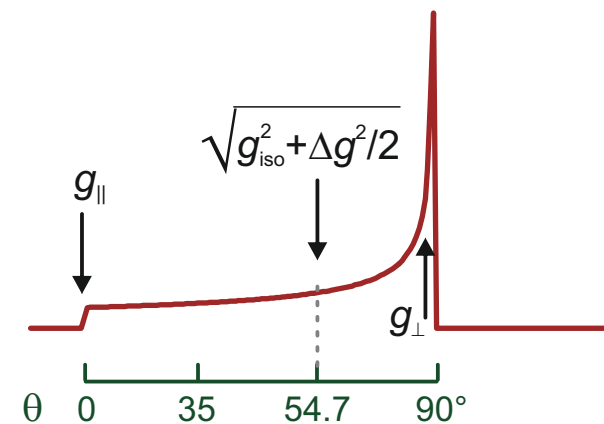
Understanding “powder” lineshapes - g anisotropy in axial symmetry

Equatorial orientations are more probable than polar (axial) orientations



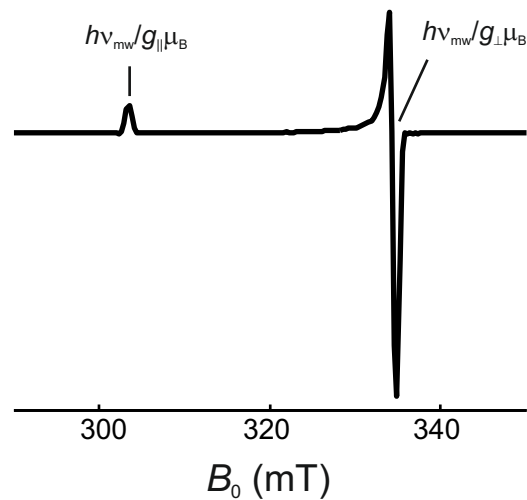
Intensity is higher at equatorial orientations corresponding to g_{\perp}

$$g_{\text{eff}} = \sqrt{\sin^2\theta g_{\perp}^2 + \cos^2\theta g_{\parallel}^2}$$

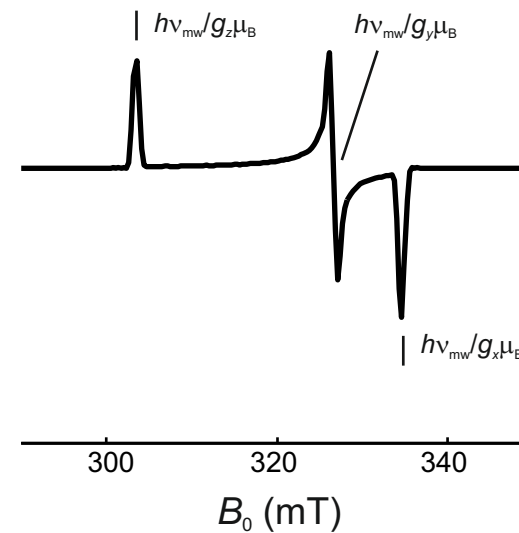


Understanding “powder” lineshapes - g anisotropy in CW EPR spectra

axial symmetry

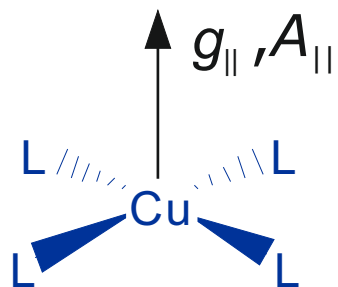


orthorhombic

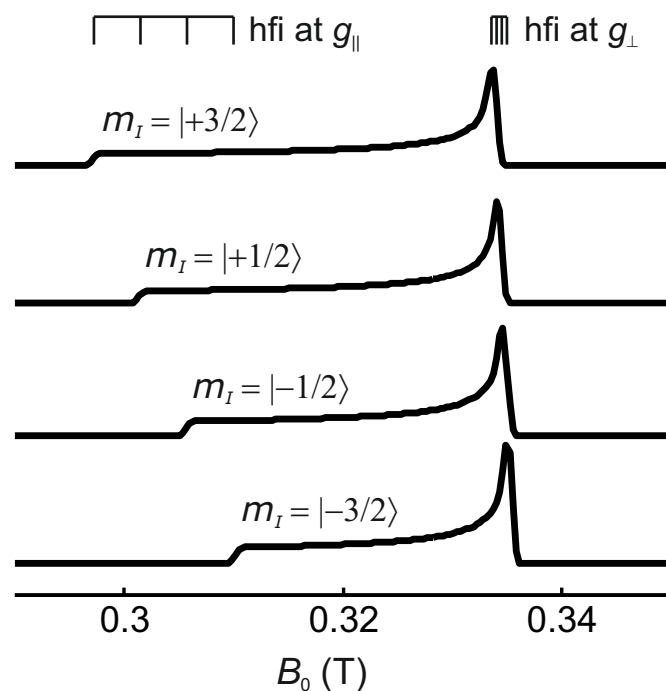


Understanding “powder” lineshapes - g and hyperfine anisotropy

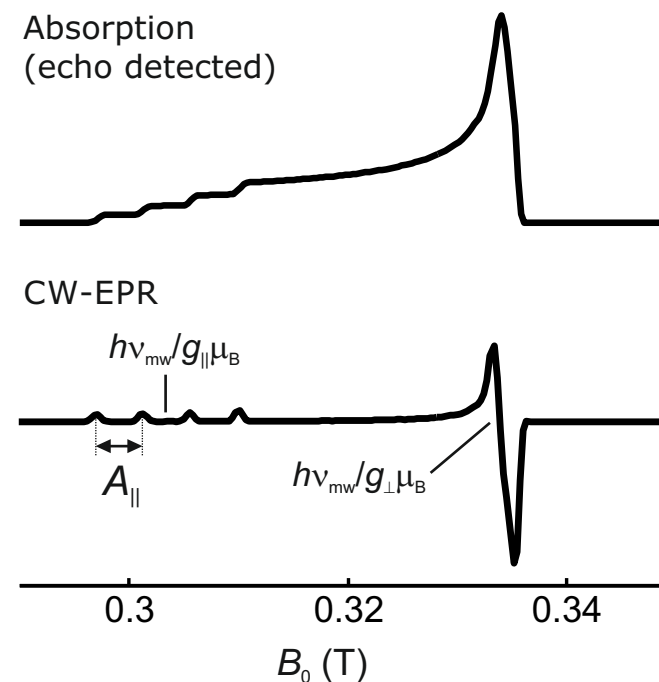
Example: Cu(II), $S = 1/2$, $I = 3/2$, axially symmetric g - and hyperfine tensor



Spectra of individual nuclear spin states



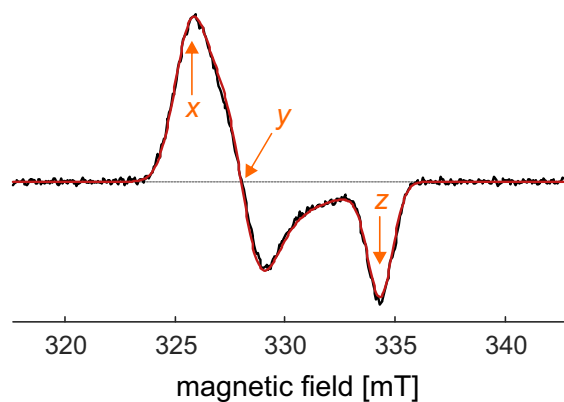
Total spectrum



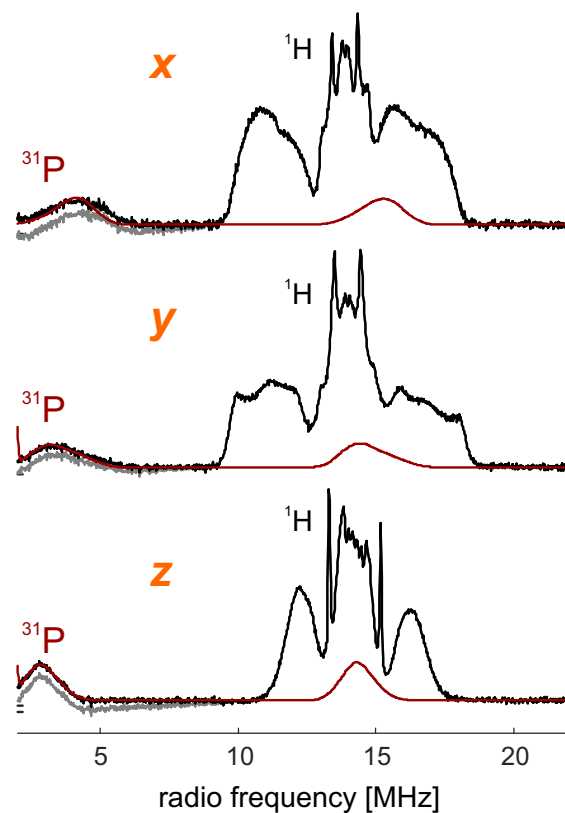
If ligand hyperfine couplings are too small: hyperfine spectroscopy



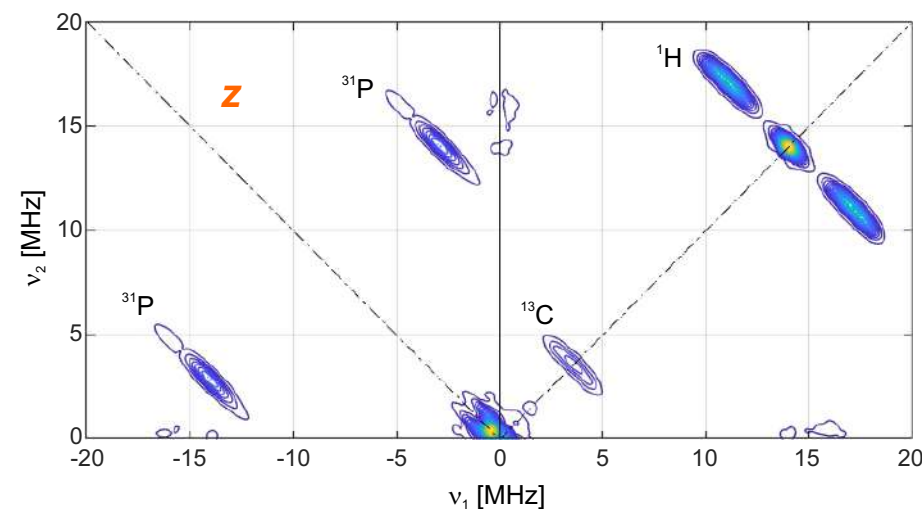
No hyperfine resolution in CW EPR



Electron-nuclear double resonance (ENDOR)



HYperfine Sublevel CORrELation spectroscopy (HYSCORE)



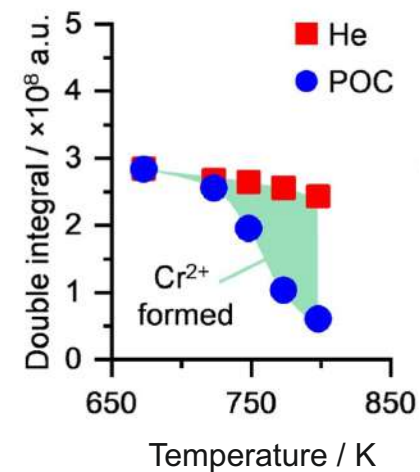
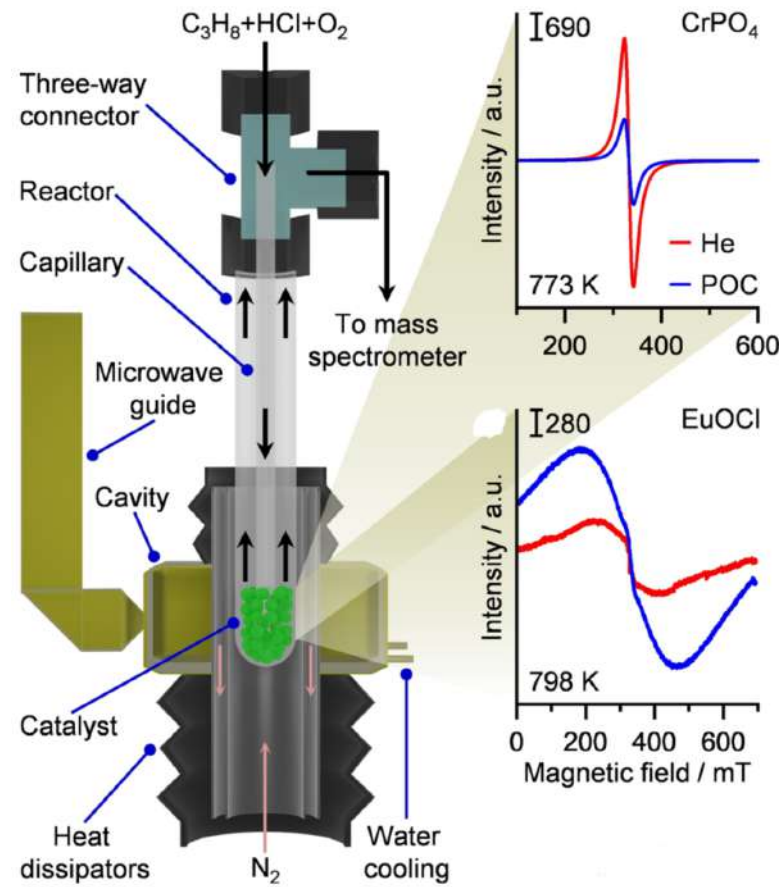
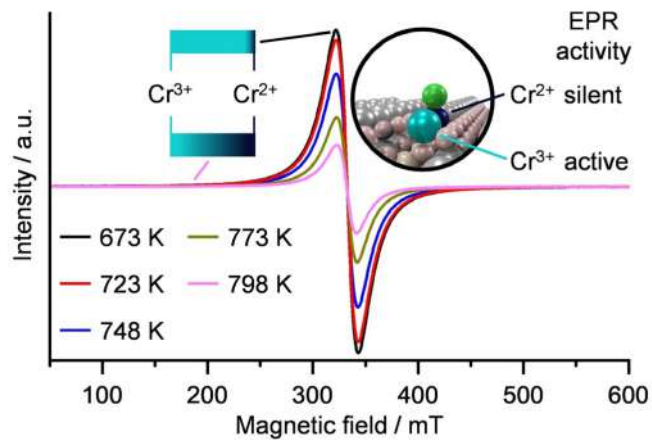
- when applicable, HYSCORE provides superior resolution and simplifies assignment



Operando EPR

Measure under reaction conditions

- high sample temperature
- resonator at ambient temperature (water-cooled)
- controlled reaction gas mixture
- on-line product analysis (mass spectrometry)

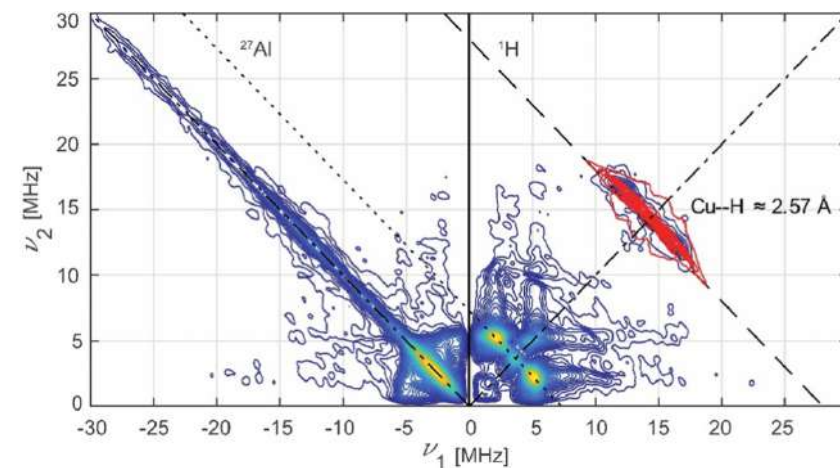
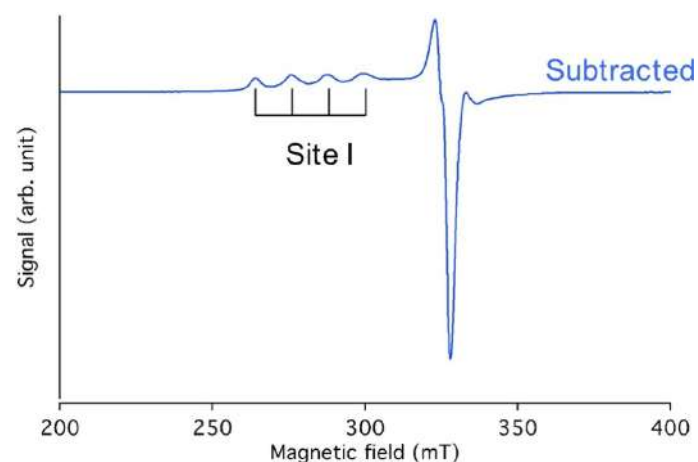
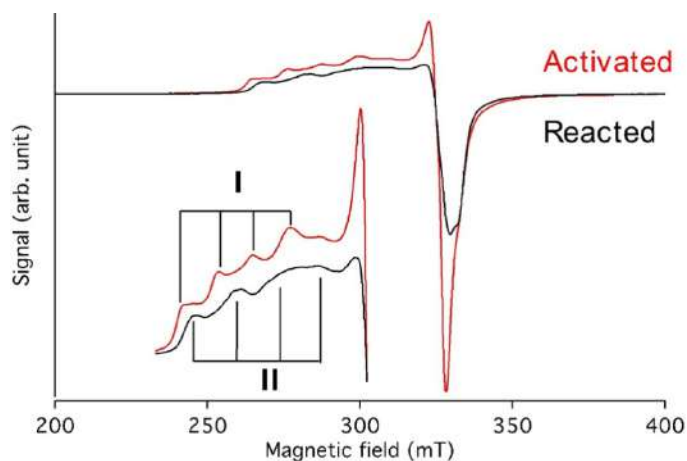
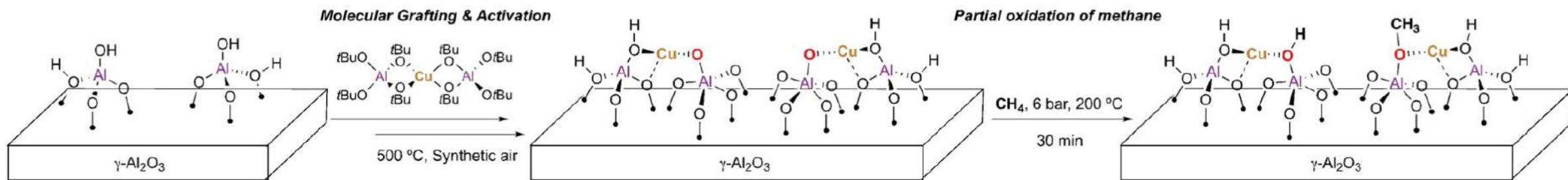




Angew. Chem. Int. Ed.
60, 16200-16207 (2021)

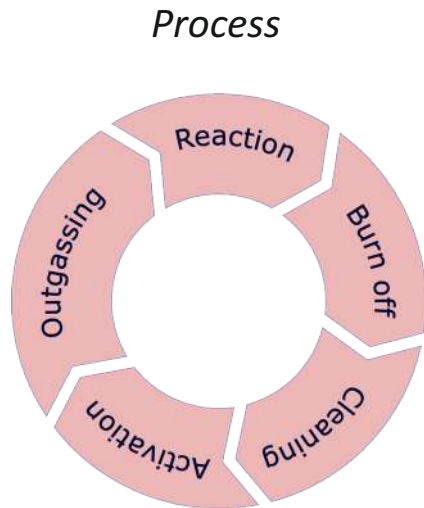
Identification of active species from difference spectra

Methanol from methane on γ -Al₂O₃

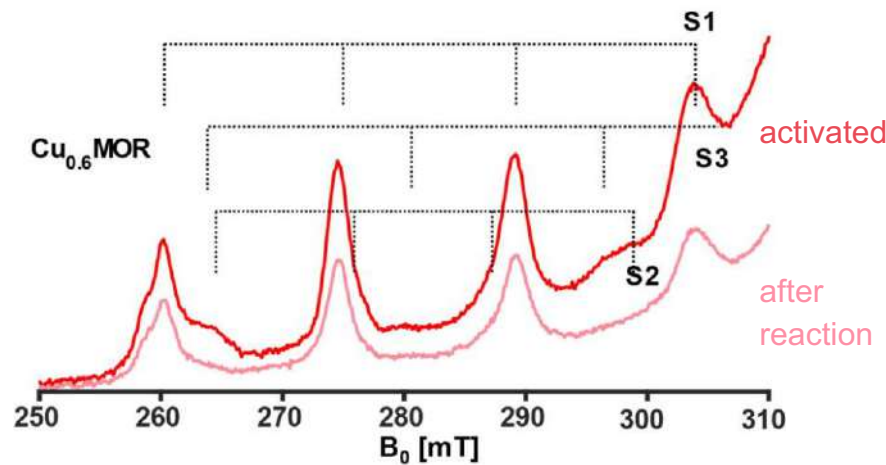


Distinguishing multiple active species by g factor and hyperfine interaction

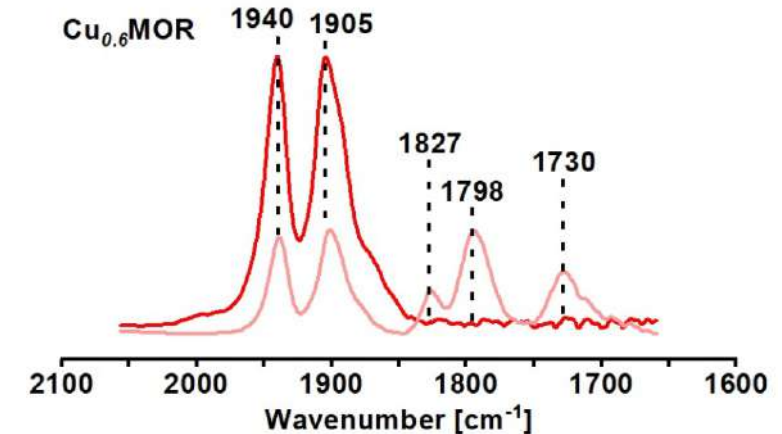
Methanol from methane on Cu-exchanged mordenite



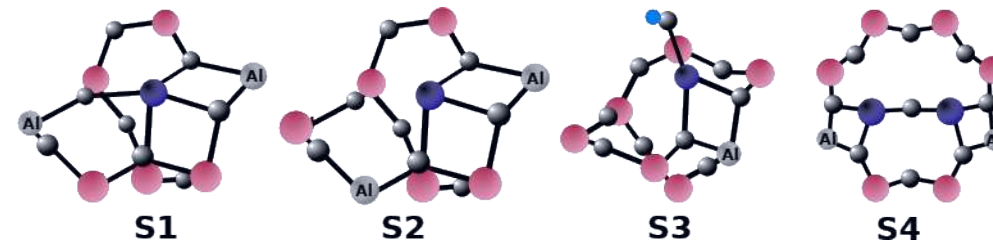
EPR spectroscopy



IR spectroscopy



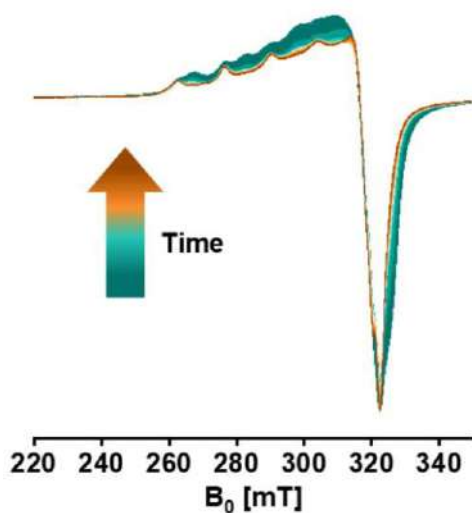
- UV-vis identifies an EPR-silent dimeric species S4 in a sample with high (5.2 wt%) copper loading



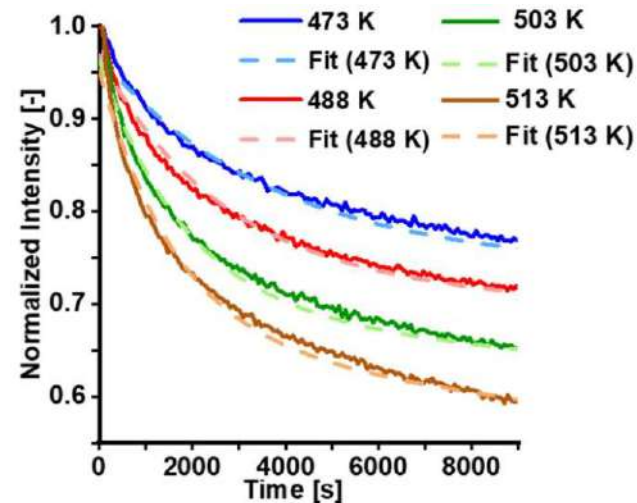
Combining techniques in a kinetic study

Methanol from methane on Cu-exchanged mordenite

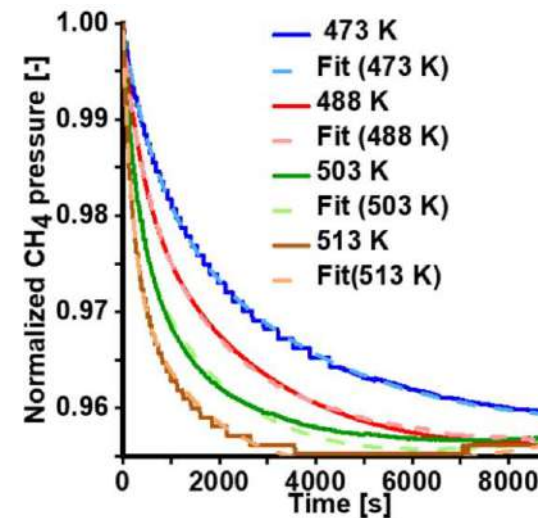
Operando EPR spectra



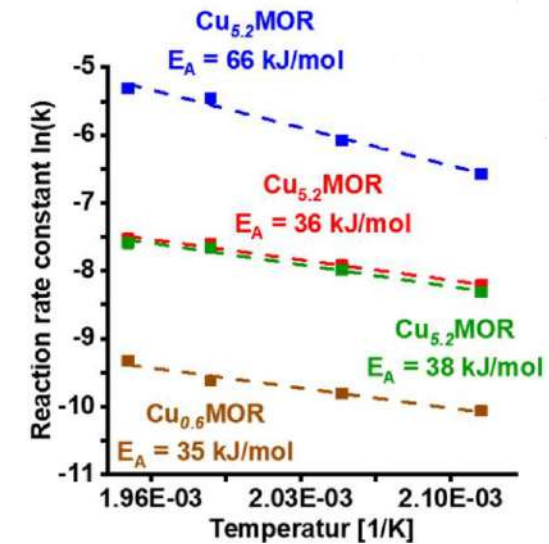
Operando EPR kinetics



Methane pressure kinetics



Arrhenius plots



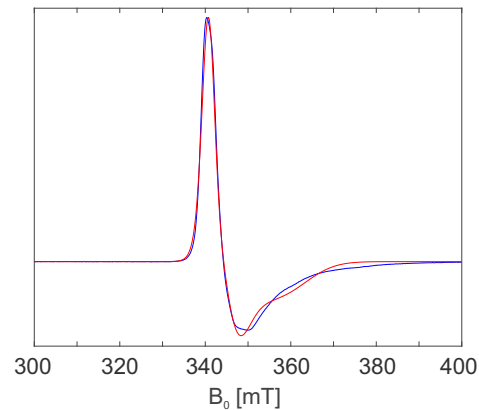
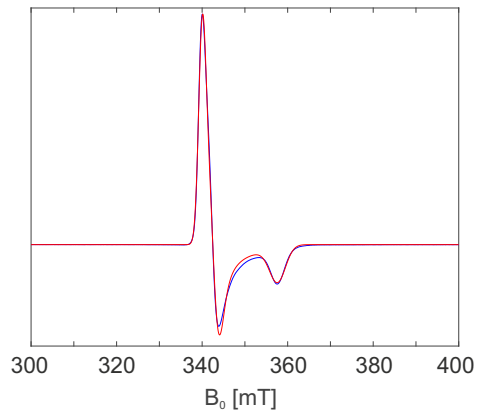
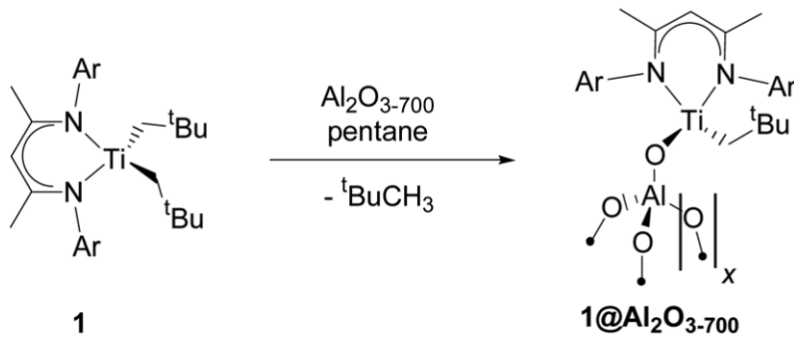
- kinetics data is consistent between samples and techniques (EPR and UV-vis)

- kCu-Dimer (CH₄ pressure)
- kCu-Monomer (EPR)
- kCu-Monomer (CH₄ pressure)
- kCu-Monomer (EPR)

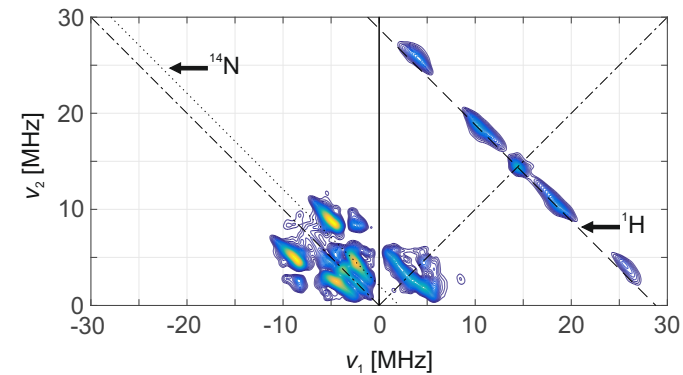


From molecular to surface species

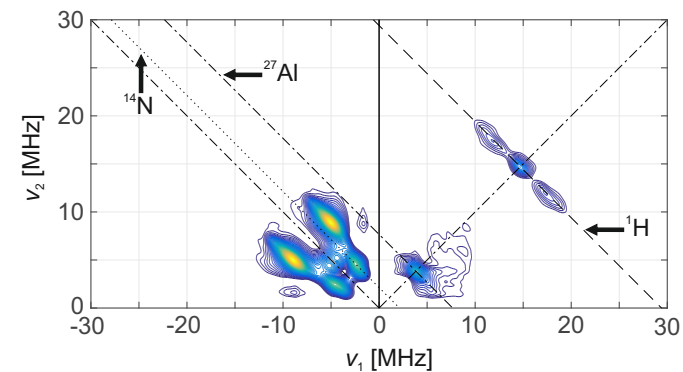
Surface organometallic chemistry



Molecular species 1



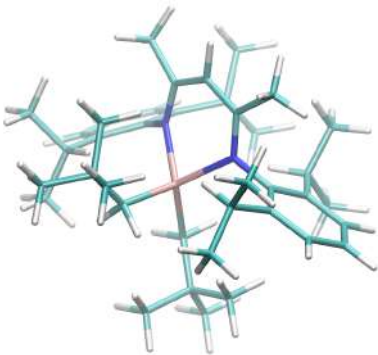
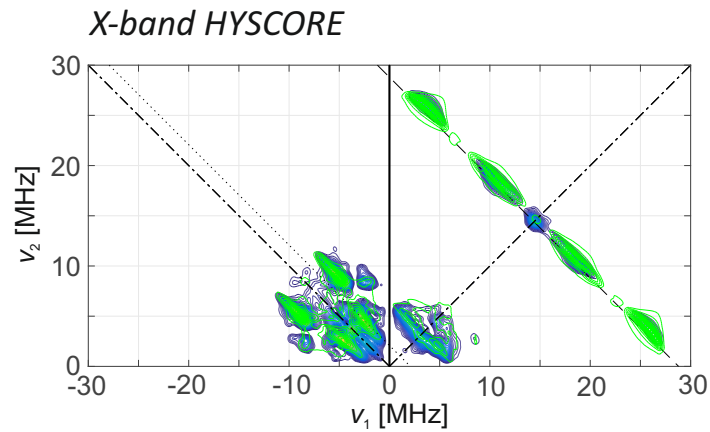
Surface species 1@ $\text{Al}_2\text{O}_{3-700}$



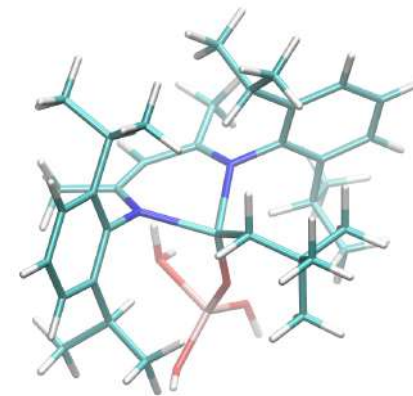
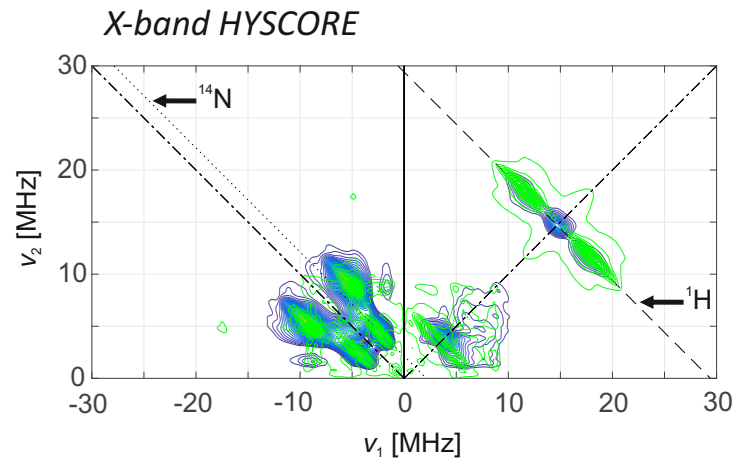
- proof that nacnac ligand remains attached

Structural models by EPR + DFT

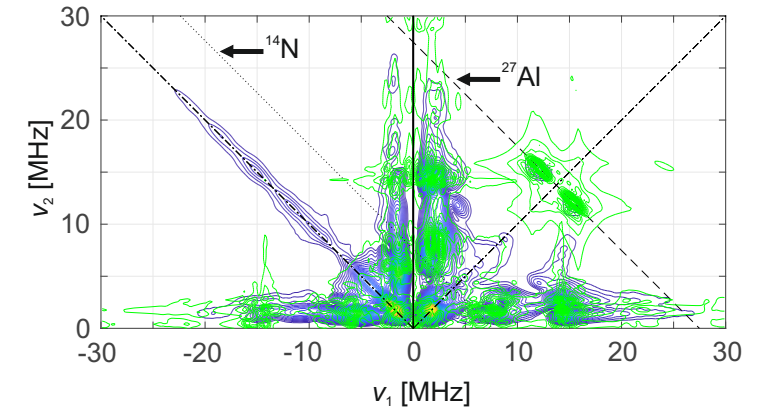
Molecular species 1



Surface species 1@Al₂O₃₋₇₀₀

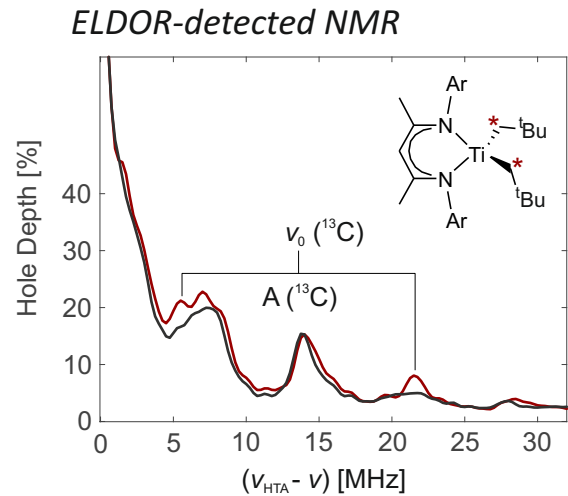


Q-band HYSCORE

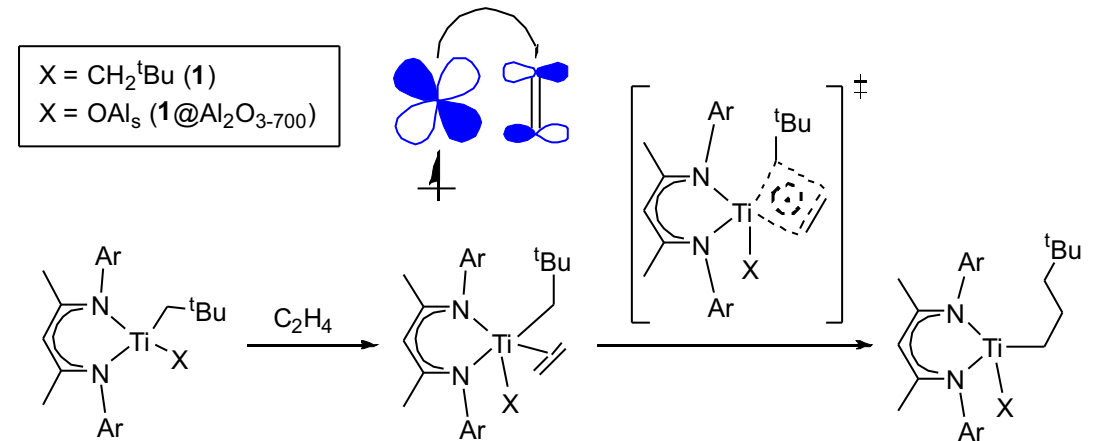


Verifying a reaction by isotope labelling

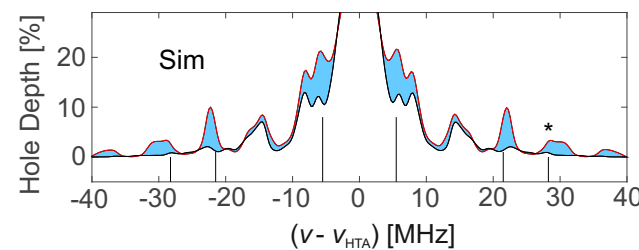
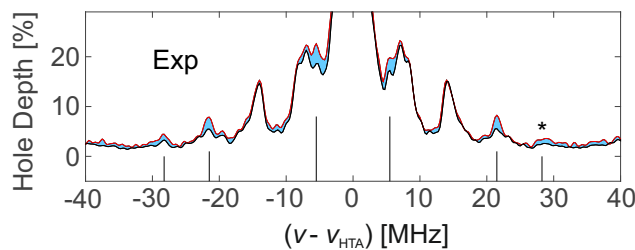
Reaction of $^{13}\text{CH}_2\text{-}^t\text{Bu}$ isotope-labelled molecular species **1*** with natural-isotope abundance ethylene



- ^{14}N features remain the same, merely a ligand exchange



ELDOR-detected NMR contrast **1*** to reacted **1***



- ethylene replaces ^tBu with $(\text{CH}_2\text{-CH}_2)_n\text{-}^t\text{Bu}$ probably only in part of the molecules
- evidence that a Ti(III) species catalyzes ethylene polymerization