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Spin-Polarized Structures and Solid-State NMR Spectroscopy of Paramagnetic Compounds**

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Solid-state NMR spectroscopy of paramagnetic compounds has a long standing tradition. Scientists such as McConnell,[1a] Fermi,[1b] or Van Vleck[1c] made important contributions more than half a century ago. Notably, it is impossible to distinguish different fields of science in this area because EPR and NMR spectroscopy, magneto chemistry, and quantum mechanics merge creating a new unit. High-resolution solid-state NMR spectroscopy offers a special view of the spin structure of solid matter, because, unlike magnetic-susceptibility measurements, very small spin densities can be traced on an atomic scale.[2,3] Such spin-density measurements are well documented, for example ^{1}H NMR spectroscopy of organic radicals, organometallic compounds, or inorganic coordination complexes.[3] Paramagnetic compounds are also used as chemical-shift thermometers in NMR spectroscopy because the isotropic chemical shift has a rather simple dependency on temperature.[4] $^{6/7}$Li NMR spectroscopy allowed different Li environments to be distinguished according to their coordination number in materials serving as electrodes.[5,6] The class of cyano metallates of the type $[\mathrm{Me(CN)_6}]^{n-}$ have attracted considerable interest, among them the compounds $\mathrm{Cd_3[Fe/Co(CN)_6]_2{\cdot}H_2O}$ by Lescouëzec et al.[7] highlighted herein. It is to be expected that the spin density of the spin center $\mathrm{Fe^{III}}$ is distributed to the surrounding atoms. Lescouëzec et al. were able to clarify by ^{13}C, ^{15}N, ^{113}Cd NMR spectroscopy how much spin density is distributed away from the spin center, the static disorder of the sample structure, and if spin-polarization mechanisms are active over three bonds.[7]

In this contribution the intention is to give the reader a look behind the scenes of solid-state NMR spectroscopy of paramagnetic compounds. The intention is to impart the conditions under which interesting insights can be expected and which approximations have to be made.

How are ^{113}Cd NMR and paramagnetism related? The ^{113}Cd nuclei as well as electrons have spin. The magnetic moment $\vec{\mu}$ is proportional to spin to which the magnetic moment of the unpaired electrons and the nucleus contribute. In an external magnetic field the nuclear Eigenstates are each split by hyperfine coupling to the total electronic magnetic moment into $(2J+1)$ sublevels where J is the total angular quantum momentum number. Ideally, the ^{113}Cd NMR resonance should then split into a $(2J+1)$ multiplet (see Figure 1).

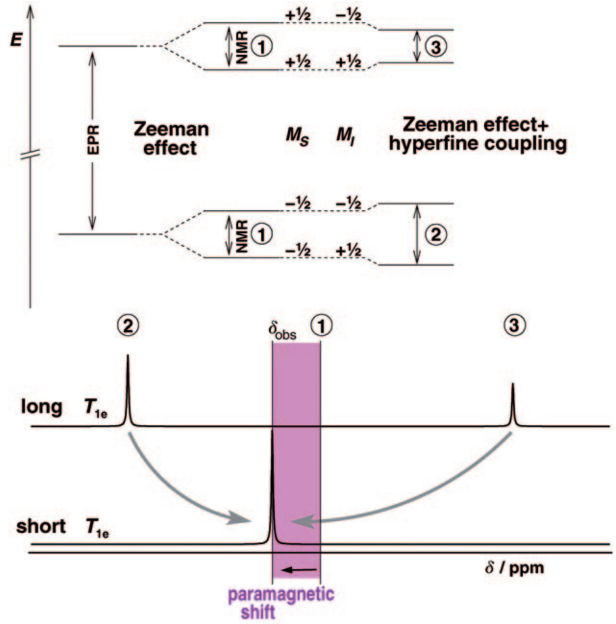

Figure 1. The paramagnetic shift as a consequence of hyperfine coupling and the Zeeman effect: qualitative energy-level diagram and NMR spectrum; the spin-lattice relaxation time of electron spin resonance transitions is T_{1e}; the magnetic quantum numbers electron spin ($S = {}^{1}/_{2}$) and nuclear spin ($I = {}^{1}/_{2}$) are M_S and M_I respectively.

In the presented sample the five d-electrons at the paramagnetic $\mathrm{Fe^{III}}$ centers are in a low-spin configuration.[8] The total electronic magnetic moment has contributions from electron-spin angular momentum and from orbital angular momentum. In octahedral crystal fields an incomplete suppression of the orbital angular momentum is expected. However, susceptibility measurements indicate (see the Supporting Information in Ref [7]), that at temperatures higher than room temperature the orbital contribution is still

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small. Hence the total electronic magnetic moment may be approximated with the spin-only formula and an electron spin $S = {}^1\!/_2$ to $-\beta_e 2\sqrt{\frac{1}{2}(1+\frac{1}{2})}$ in units of the Bohr magneton β_e.

In this case only the isotropic energy contribution $\hat{H}_{iso}$ is of interest because magic-angle-spinning proved to be sufficient to significantly reduce the anisotropic contributions. If both nuclear spin I and electronic spin J are quantized along the direction of the external magnetic field, then hyperfine coupling is proportional to the product of the z-components of the nuclear and electronic magnetic moments $\mu_{nuc,z}\mu_{e,z}$. The isotropic energy contribution $\hat{H}_{iso}$ defines the isotropic hyperfine coupling constant A_{iso}.[Eq. (1)].[9]

$$\hat{H}_{iso} = A_{iso}\, I_z\, J_z \tag{1}$$

The T_1 relaxation of electron spin is generally fast compared to the hyperfine coupling time scale, thus nuclei will behave as if exposed to an averaged magnetic hyperfine field. Consequently the doublet in the NMR spectrum collapses into a single resonance[2,3] (see Figure 1). Since the population of the different electronic Zeeman Eigenstates is temperature dependent, the observed chemical shift δ_{obs} of the NMR resonances will also be temperature dependent. Depending on the sign of the hyperfine coupling constant, chemical shift values moved to more positive or negative values are observed. Changes of a thousand ppm are not exceptional.

The task remains to quantitatively describe the temperature dependence of the magnetic moments and its outcome on the chemical shift. When, as in the current case, the electron Zemann effect is small relative to the thermal energy, the temperature dependence of the averaged magnetic moment $\langle\mu_z\rangle$ resembles the Curie law [Eq. (2)].[2]

$$\langle\mu_z\rangle = \frac{(\beta_e\, g_e)^2\, B_0}{3\,k\,T} S(S+1) \tag{2}$$

The contributions to the hyperfine coupling that need to be considered are: the magnetic dipole–dipole interaction through space ("pseudo-contact interaction"), and the Fermi contact interaction ("contact interaction") caused by electron density a the nucleus.[10] The contact interaction is dominated by s-electron contributions, which are the only ones to have a non-zero electron density at the nucleus. Hence it is predominantly local and isotropic in nature and sensitive to unpaired electron density in the s orbitals of the observed atom.

The paramagnetic contributions[10] to the isotropic chemical shift can be calculated as follows for the interaction with a single Fe^{III} center. The formula assumes an axial symmetric g-tensor, an electronic spin of $S = {}^1\!/_2$, the point-dipole approximation,[9] and normalization by the reference frequency of the chemical shift scale [Eq. (3)].

pseudo-contact shift :

$$\delta_{pseudo\text{-}contact} = \frac{\mu_0}{4\pi}\frac{\beta_e\, S(S+1)}{9\,k\,T}\frac{3\cos^2\theta - 1}{r^3}(g_\parallel^2 - g_\perp^2) \tag{3}$$

Note that the pseudo-contact shift critically depends on the g-tensor being anisotropic. In the described case the g-tensor of the Fe^{III} center is small ($g_\perp = 2.071$ and $g_\parallel = 2.345$) while the internuclear Cd–Fe distance r of 530 pm is big. Consequently the pseudo-contact contribution may safely be neglected, which helps because there are no experimental means to differentiate between pseudo-contact and contact interaction [Eq (4)]. Only the contact interaction is left. Apart from a few constants and the isotropic g-factor g_{av}, the only unknown variable is the spin density at the nucleus $\rho(N)$. The value of the spin density will change depending on the number of Fe^{III} centers and is a signed property. Systematic changes of its sign indicate that spin polarization mechanisms[3] need to be considered.

contact shift :

$$\delta_{contact} = \frac{\mu_0\,\beta_e^2\, g_{av}^2}{a_0^3}\frac{S(S+1)}{9\,k\,T}\rho(N) \tag{4}$$

In the present example[7,11] Lescouëzec et al. were able to show, that the spin of Fe^{III} polarizes its electronic environment which undergoes multiple sign changes (+/−/+/−) over the Fe^{III}-C-N-Cd^{II} bridge. Experimental reference data like these are a good basis to study cooperative magnetism on an atomic scale. It should be pointed out, that by the means of theoretical chemistry[12] g-tensors, hyperfine couplings, and zero-field splittings[9] can be calculated, thus enabling the prediction of chemical shift values for paramagnetic compounds and the study of spin-polarization mechanisms.

What can be learned from this example for the general application of solid-state NMR spectroscopy to paramagnetic problems? Numerous approximations must be made. Assumptions about the g-tensor, zero-field splitting, relaxation-time constants of the ESR transitions, and the magnetic moment of the electronic spin centers may be justified experimentally by ESR and susceptibility measurements. More difficult to handle are various contributions to the chemical shift. Experimentally we may distinguish a temperature-independent $\delta_{T=\infty}$ and a temperature-dependent part $\delta(T)$, assuming extrapolation to high temperature is feasible [Eq. (5)].

$$\delta_{obs}(T) \sim \delta_{T=\infty} + \delta(T) \tag{5}$$

Formally, the contributions to the temperature-independent part can be given as Equation (6).

$$\delta_{T=\infty} = \delta_{cs} + \delta_{vanVleck} + \delta_{Knight} \tag{6}$$

The first term is the closed-shell contribution δ_{cs}, which can be estimated from a similar diamagnetic compound, the second term is related to the temperature-independent Van Vleck paramagnetism,[1c] as for example in case of Eu^{III}, and the last term is the Knight shift, which is relevant for electric conductors and is caused by unpaired electrons close to the Fermi level. The last two terms can only be influenced by the choice of the sample.

The temperature-dependent part contains the contributions from the contact and pseudo-contact interaction [Eq. (7)].

$$\delta(T) = \delta_{pseudocontact} + \delta_{contact} \tag{7}$$

Clearly, every error made in the calculation of the pseudo-contact interaction and the temperature-independent contribution adds to the uncertainty of the experimentally determined spin density. Ideally suited samples are those in which the pseudo-contact interaction is well known (criteria: known crystal structure with high symmetry at the electronic spin center, simple magnetic structure, concentrated spin density at the metal atom) or close to zero (small g-tensor anisotropy, as for many organic radicals). Additionally diamagnetic reference compounds are required.

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