

Chapter 3

Motivation

The advantages of high-field EPR measurements have been extensively discussed in the literature. A small overview will be given here; extensive reviews of the topic can be found in (Budil et al. 1989, Ya. S. Lebedev 1990, K. Möbius 1993, T. F. Prisner 1997).

Most of the advantages generally attributed to EPR at high magnetic fields and high microwave frequencies can be directly derived from an inspection of the static spin Hamiltonian describing the interaction energies of an unpaired electron with a spin $S = 1/2$ and of the nuclei in a typical paramagnetic radical:

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_{Zeeman} + \mathcal{H}_{nuclearZeeman} + \mathcal{H}_{HFI} \\ &= \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} - \sum_i \mu_N \mathbf{B} \cdot g_{Ni} \cdot \mathbf{I}_i + \sum_i \mathbf{S} \cdot \mathbf{A}_i \cdot \mathbf{I}_i\end{aligned}\quad (3.1)$$

In the field-dependent Zeeman terms, \mathbf{B} is the external magnetic field vector, μ_B and μ_N are the electronic Bohr magneton and the nuclear magneton respectively, \mathbf{g} is the electron \mathbf{g} -tensor and g_{Ni} are the nuclear g -values, \mathbf{S} is the electron and \mathbf{I} the nuclear spin vector operator ($\mathbf{S} = (\mathbf{S}_x, \mathbf{S}_y, \mathbf{S}_z)$, analog for \mathbf{I}). In the field-independent hyperfine term, \mathbf{A}_i are the hyperfine tensors. Both summations are evaluated over all nuclei.

By varying the external magnetic field B , it is now possible to separate the influences of the different terms from each other. The difference in resonance field positions due to the electron Zeeman term for two different radicals with isotropic g -values g_1 and g_2 ($g_{iso} = (g_{xx} + g_{yy} + g_{zz})/3$) is given by:

$$\Delta B = \frac{hf}{\mu_B} \left(\frac{1}{g_1} - \frac{1}{g_2} \right) \quad (3.2)$$

This separation is a factor of 40 higher at 360 GHz EPR when compared to X-band EPR. As long as the intrinsic linewidth of the spectral lines does not increase by the same amount, this leads to increased spectral resolution. For samples containing only one radical species, in the case of unordered systems such as frozen solutions, the same effect will lead to enhanced spectral resolution of the so-called powder pattern originating from the orientation distribution of the molecules. For organic free radicals, the isotropic g -value is close to that of the free electron and the relative differences of the primary values $\Delta g/g_{iso}$ usually do not exceed $10^{-4} - 10^{-3}$. For X-band frequencies of 10 GHz, the separation of the turning points in the powder pattern associated to the canonical orientations of the molecule will therefore be between $\Delta B = 0.03 - 0.3$ mT. With the inhomogeneous EPR linewidth $\Delta B_{1/2}$ being dominated by field-independent factors such as unresolved hyperfine structure, the g -tensor anisotropy can not be resolved then.

A general sample-specific high resolution condition can therefore be expressed through:

$$B \frac{\Delta g}{g_{iso}} > \Delta B_{1/2}^{hfi} \quad (3.3)$$

— if the anisotropic Zeeman interaction exceeds the linewidth due to unresolved hyperfine interactions, this is considered “high-field EPR”. While for many samples, such as quinones and nitroxide radicals, this condition is met already with W-band EPR, for other systems such as chlorophyll radicals this is not yet the case. Especially in the case of samples that can not yet be

obtained in their deuterated forms, a further increase in the magnetic field B and the mw frequency f becomes necessary to achieve sufficient spectral resolution.

Once the powder spectrum of the \mathbf{g} -tensor can be resolved, it becomes possible to perform orientation-selective measurements, that otherwise would require single crystal samples. This is due to the fact that at the outer turning points of a powder spectrum, only those molecules with the \mathbf{g} -tensor primary axes aligned along the B -field axis contribute to the spectrum. For example, electron nuclear double resonance (ENDOR) measurements with the magnetic field tuned to such a turning point position will therefore also probe only these aligned molecules.

In the case of paramagnetic centers with electron spin $S > 1/2$, an additional field-independent term has to be included in the Hamiltonian, the fine structure or spin-spin coupling term

$$\mathcal{H}_{SS} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} \quad (3.4)$$

with the spin-spin coupling tensor \mathbf{D} (also called zero-field splitting tensor). For many high-spin systems, the zero-field splittings can exceed the Zeeman energy by an order of magnitude for X-band or even W-band EPR systems and therefore can not be detected (the system is “EPR-silent”). The energy of the microwave quantum therefore must be higher. This is another typical application of high-frequency EPR.

Another major motivation to go to higher microwave frequencies and higher fields is a possible increase in detection sensitivity. One reason for this is the increased Boltzmann polarization of the level populations due to the greater splitting of the Zeeman levels. As long as the total spin polarization is still small, the increase in polarization will scale linearly with the applied field. The absolute spin polarization at room temperature (300 K) is 0.2 % at X-band, 1.6 % at W-band and 5.5 % at 360 GHz. By going to even

higher frequencies, this factor therefore would still enhance the sensitivity. This is not the case for measurements at Helium temperatures: the temperature corresponding to the Zeeman energy is 17.3 K, therefore at these low temperatures the upper level is empty and increasing the frequency does not increase the EPR signal. In addition to the Boltzmann effect the energy $h\nu$ of a microwave quantum of frequency ν is larger at higher frequencies, such that the same amount of spins will lead to a larger signal.

A potential decrease in sensitivity can result for spectra of disordered samples when going to higher frequency. Since the intensity of a spectrum is spread over a wider range, the intensity of the signal peaks decreases. For detection of derivative spectra, this decrease has been estimated to scale with the detection frequency as $\nu^{1/2}$ (Ya. S. Lebedev 1990), so it is not expected to be dramatic.

In addition to these effects, many technical aspects come into play that can both enhance or lower the detection sensitivity. For samples that are available just in small sizes such as e.g. protein single crystals, equal resonator types at higher frequencies provide a better filling factor η and therefore a higher detection sensitivity.

In a real experiment, these advantages can be offset by the difficult task of building resonators with sufficiently high Q -factors. Further factors are lower power levels of the available sources, higher noise figures of detectors and higher power losses in transmission lines. As will be pointed out in the chapters dealing with the experimental setup (chapter 5) and with Gaussian optics techniques (chapter 4), many of these difficulties can be addressed. Since this is a work in progress, a final conclusion can not yet be drawn.

Other advantages of high-frequency EPR measurements have not yet been exploited in the current measurements, such as the increased possible time resolution and the sensitivity to a different timescale of motional effects. This will be addressed in future projects.