3.3: Spectral manifestation of the electron Zeeman interaction

Liquid solution

In liquid solution, molecules tumble due to Brownian rotational diffusion. The time scale of this motion can be characterized by a rotational correlation time τ_{rot} that in non-viscous solvents is of the order of $10\mathrm{ps}$ for small molecules, and of the order of $1\ \mathrm{ns}$ to $100\ \mathrm{ns}$ for proteins and other macromolecules. For a globular molecule with radius r in a solvent with viscosity η, the rotational correlation time can be roughly estimated by the Stokes-Einstein law

$$\tau_{\mathrm{r}} = \frac{4\pi\eta r^3}{3k_{\mathrm{B}}T} \tag{3.3.1}$$

If this correlation time and the maximum difference $\Delta\omega$ between the transition frequencies of any two orientations of the molecule in the magnetic field fulfill the relation $\tau_{\mathrm{r}}\Delta\omega \ll 1$, anisotropy is fully averaged and only the isotropic average of the transition frequencies is observed. For somewhat slower rotation, modulation of the transition frequency by molecular tumbling leads to line broadening as it shortens the transverse relaxation time T_2. In the slow-tumbling regime, where $\tau_{\mathrm{r}}\Delta\omega \approx 1$, anisotropy is incompletely averaged and line width attains a maximum. For $\tau_{\mathrm{r}}\Delta\omega \gg 1$, the solid-state spectrum is observed. The phenomena can be described as a multi-site exchange between the various orientations of the molecule (see Section 10.1.4), which is analogous to the chemical exchange discussed in the NMR part of the lecture course.

For the electron Zeeman interaction, fast tumbling leads to an average resonance field

$$B_{0,\mathrm{res}} = \frac{h\nu_{\mathrm{mw}}}{g_{\mathrm{iso}}\mu_{\mathrm{B}}} \tag{3.3.2}$$

with the isotropic g value $g_{\mathrm{iso}} = (g_x + g_y + g_z)/3$. For small organic radicals in non-viscous solvents at X-band frequencies around $9.5\mathrm{GHz}$, line broadening from g anisotropy is negligible. At W-band frequencies of $94\mathrm{GHz}$ for organic radicals and already at X-band frequencies for small transition metal complexes, such broadening can be substantial. For large macromolecules or in viscous solvents, solid-state like EPR spectra can be observed in liquid solution.

Solid state

For a single-crystal sample, the resonance field at any given orientation can be computed by Eq. (3.7). Often, only microcrystalline powders are available or the sample is measured in glassy frozen solution. Under such conditions, all orientations contribute equally. With respect to the

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Figure 3.3: Powder line shape for a g tensor with axial symmetry. (a) The probability density to find an orientation with polar angle θ is proportional to the circumference of a circle a angle θ on a unit sphere. (b) Probability density $P(\theta)$. The effective g value at angle θ is $\sqrt{g_\perp^2 + g_\parallel^2 + \cos(2\theta)\left(g_\parallel^2 - g_\perp^2\right)/2}$. (c) Schematic powder line shape. The pattern corresponds to $g_\perp > g_\parallel$ for a field sweep and to $g_\perp < g_\parallel$ for a frequency sweep. Because of the frame tilting, the isotropic value $g_{\mathrm{iso}} = \left(2g_\perp + g_\parallel\right)/3$ is not encountered at the magic angle, although the shift is small if $\Delta g = 2\left(g_\parallel - g_\perp\right)/3 \ll g_{\mathrm{iso}}$.

polar angles, this implies that ϕ is uniformly distributed, whereas the probability to encounter a certain angle θ is proportional to $\sin\theta$ (Figure 3.3). The line shape of the absorption spectrum is most easily understood for axial symmetry of the g tensor. Transitions are observed only in the range between the limiting resonance fields at $g_\parallel$ and $g_\perp$. The spectrum has a global maximum at $g_\perp$ and a minimum at $g_\parallel$.

In CW EPR spectroscopy we do not observe the absorption line shape, but rather its first derivative (see Chapter 7). This derivative line shape has sharp features at the line shape singularities of the absorption spectrum and very weak amplitude in between (Figure 3.4).

Concept 3.3.1 - Orientation selection.

The spread of the spectrum of a powder sample or glassy frozen solution allows for selecting molecules with a certain orientation with respect to the magnetic field. For an axial g tensor only orientations near the z axis of the g tensor PAS are selected when observing near the resonance field of $g_{\|}$. In contrast, when observing near the resonance field for $g_{\perp}$, orientations withing the whole xy plane of the PAS contribute. For the case of orthorhombic symmetry with three distinct principal values g_x, g_y, and g_z, narrow sets of orientations can be observed at the resonance fields corresponding to the extreme g values g_x and g_z (see right top panel in Figure 3.4). At the intermediate principal value g_y a broad range of orientations contributes, because the same resonance field can be realized by orientations other than $\phi = 90^\circ$ and $\theta = 90^\circ$. Such orientation selection can enhance the resolution of ENDOR and ESEEM spectra (Chapter 8) and simplify their interpretation.

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Figure 3.4: Simulated X-band EPR spectra for systems with only g anisotropy. The upper panels show absorption spectra as they can be measured by echo-detected field-swept EPR spectroscopy. The lower panels show the first derivative of the absorption spectra as they are detected by continuous-wave EPR. The unit-sphere pictures in the right upper panel visualize the orientations that are selected at the resonance fields corresponding to the principal values of the g tensor.

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