Lecture 7: Chemical shift, one-pulse experiment

General strategy

1. Define $\widehat{\rho}$ at $t = 0$

2. Describe evolution of $\widehat{\rho}$ using the relevant Hamiltonians
   usually several steps

3. Calculate the expectation value of the measured quantity (magnetization components in the x, y plane) as $\langle M_+ \rangle = \langle M_x + \mathrm{i} M_y \rangle = \mathcal{N} \mathrm{Tr}\left\{\widehat{\rho}\ \widehat{M}_+\right\}$

The procedure requires knowledge of

1. relation(s) describing the initial state of the system ($\widehat{\rho}(0)$)

2. all Hamiltonians ($\mathscr{H}$)

3. the operator representing the measurable quantity ($\widehat{M}_+$)

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Operator of measured quantity

$$M_+ = M_x + \mathrm{i} M_y$$

$$\hat{M}_+ = \mathcal{N}\gamma(\hat{I}_x + \mathrm{i}\hat{I}_y) = \mathcal{N}\gamma\hat{I}_+$$

$$\hat{M}_+ = \mathcal{N}\gamma\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

The procedure requires knowledge of

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Hamiltonian of static field $\vec{B}_0$

$$\widehat{H}_{0,\text{lab}} = -\gamma B_0 \widehat{I}_z$$

Hamiltonian of the radio-frequency field $\vec{B}_1$

Phase $= 0$ (x):

$$\widehat{H}_{1,\text{rot}} = (-\gamma B_0 - \omega_{\text{rot}})\widehat{I}_z - \gamma B_1 \widehat{I}_x = \Omega \widehat{I}_z + \omega_1 \widehat{I}_x$$

Phase $= \pi/2$ (y):

$$\widehat{H}_{1,\text{rot}} = (-\gamma B_0 - \omega_{\text{rot}})\widehat{I}_z - \gamma B_1 \widehat{I}_y = \Omega \widehat{I}_z + \omega_1 \widehat{I}_y$$

Chemical shift Hamiltonian

$$\begin{aligned}\hat{H}_\delta &= -\gamma(\hat{I}_x B_{\mathsf{e},x} + \hat{I}_y B_{\mathsf{e},y} + \hat{I}_z B_{\mathsf{e},z}) = -\gamma\begin{pmatrix}\hat{I}_x & \hat{I}_y & \hat{I}_z\end{pmatrix}\begin{pmatrix}B_{\mathsf{e},x}\\ B_{\mathsf{e},y}\\ B_{\mathsf{e},z}\end{pmatrix}\\ &= -\gamma\begin{pmatrix}\hat{I}_x & \hat{I}_y & \hat{I}_z\end{pmatrix}\begin{pmatrix}\delta_{xx} & \delta_{xy} & \delta_{xz}\\ \delta_{yx} & \delta_{yy} & \delta_{yz}\\ \delta_{zx} & \delta_{zy} & \delta_{zz}\end{pmatrix}\begin{pmatrix}B_{0,x}\\ B_{0,y}\\ B_{0,z}\end{pmatrix} = -\gamma\hat{\vec{I}}\cdot\underline{\delta}\cdot\vec{B}_0\end{aligned}$$

$$\hat{H} = \hat{H}_{0,\mathsf{lab}} + \hat{H}_{\delta,\mathsf{i}} + \hat{H}_{\delta,\mathsf{a}} + \hat{H}_{\delta,\mathsf{r}}$$

Chemical shift Hamiltonian

Isotropic component (independent of orientation):

$$\hat{H}_{\delta,\mathrm{i}} = -\gamma B_0 \delta_\mathrm{i} (\hat{I}_z)$$

Anisotropic (axially symmetric) component (depends on ϑ, φ):

$$\hat{H}_{\delta,\mathrm{a}} = -\gamma B_0 \delta_\mathrm{a} (3 \sin\vartheta \cos\vartheta \cos\varphi \hat{I}_x + 3 \sin\vartheta \cos\vartheta \sin\varphi \hat{I}_y + (3\cos^2\vartheta - 1)\hat{I}_z)$$

Rhombic (asymmetric) component (depends on ϑ, φ, χ):

$$\begin{aligned}\hat{H}_{\delta,\mathrm{r}} = -\gamma B_0 \delta_\mathrm{r} (\quad & (-\cos 2\chi \sin\vartheta \cos\vartheta \cos\varphi + \sin 2\chi \sin\vartheta \cos\vartheta \sin\varphi)\hat{I}_x + \\ & (-\cos 2\chi \sin\vartheta \cos\vartheta \sin\varphi - \sin 2\chi \sin\vartheta \cos\vartheta \cos\varphi)\hat{I}_y + \\ & ((\cos 2\chi \sin^2\vartheta)\hat{I}_z)\end{aligned}$$

Secular approximation

Molecular motions do not resonate with the precession frequency $-\gamma B_0$

$\Rightarrow$ $B_{\mathrm{e},x}\hat{I}_x$ and $B_{\mathrm{e},y}\hat{I}_y$ oscillate rapidly with frequency close to $-\gamma B_0$

$\vec{B}_0 \gg \vec{B}_\mathrm{e} \Rightarrow$ much faster oscillations than precession about $B_{\mathrm{e},x}$, $B_{\mathrm{e},y}$

effectively average to zero on timescale longer than $1/(\gamma B_0)$ ($\sim$ ns)

$\Rightarrow$Terms with $B_{\mathrm{e},x}\hat{I}_x$ and $B_{\mathrm{e},y}\hat{I}_y$ can be neglected on timescales $>$ ns

$$\hat{H} = -\gamma\hbar\frac{1}{2}\begin{pmatrix} B_0 + B_{\mathrm{e},z} & B_{\mathrm{e},x} - \mathrm{i}B_{\mathrm{e},y} \\ B_{\mathrm{e},x} + \mathrm{i}B_{\mathrm{e},y} & -(B_0 + B_{\mathrm{e},z}) \end{pmatrix}$$

Averaging in isotropic solvent

No orientation of the molecule is preferred

$\Rightarrow$ all values of χ are equally probable and independent of ϑ

$\Rightarrow \overline{\cos 2\chi} = 0$

$$
\begin{aligned}
Z_x &= \sin\vartheta\cos\varphi \\
Z_y &= \sin\vartheta\sin\varphi \\
Z_z &= \cos\vartheta
\end{aligned}
$$

$$Z_x^2 + Z_y^2 + Z_z^2 = 1 \Rightarrow \overline{Z_x^2 + Z_y^2 + Z_z^2} = 1 \Rightarrow \overline{3Z_z^2 - 1} = \overline{(3\cos^2\vartheta - 1)} = 0$$

Secular approximation

Isotropic component:

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Anisotropic (axially symmetric) component:

$$\hat{H}_{\delta,\mathrm{a}} = -\gamma B_0 \delta_\mathrm{a} (3 \sin\vartheta \cos\vartheta \cos\varphi \hat{I}_x + 3 \sin\vartheta \cos\vartheta \sin\varphi \hat{I}_y + (3\cos^2\vartheta - 1)\hat{I}_z)$$

Rhombic (asymmetric) component:

$$\begin{aligned}\hat{H}_{\delta,\mathrm{r}} = -\gamma B_0 \delta_\mathrm{r} (\quad & (-\cos 2\chi \sin\vartheta \cos\vartheta \cos\varphi + \sin 2\chi \sin\vartheta \cos\vartheta \sin\varphi)\hat{I}_x + \\ & (-\cos 2\chi \sin\vartheta \cos\vartheta \sin\varphi - \sin 2\chi \sin\vartheta \cos\vartheta \cos\varphi)\hat{I}_y + \\ & ((\cos 2\chi \sin^2\vartheta)\hat{I}_z)\end{aligned}$$

Averaging in isotropic solvent

Isotropic component:

$$\hat{H}_{\delta,\mathrm{i}} = -\gamma B_0 \delta_{\mathrm{i}} (\hat{I}_z)$$

Anisotropic (axially symmetric) component:

$$\hat{H}_{\delta,\mathrm{a}} = -\gamma B_0 \delta_{\mathrm{a}} (3 \sin\vartheta \cos\vartheta \cos\varphi \hat{I}_x + 3 \sin\vartheta \cos\vartheta \sin\varphi \hat{I}_y + (3\cos^2\vartheta - 1) \hat{I}_z)$$

Rhombic (asymmetric) component:

$$\begin{aligned}\hat{H}_{\delta,\mathrm{r}} = -\gamma B_0 \delta_{\mathrm{r}} (\quad & (-\cos 2\chi \sin\vartheta \cos\vartheta \cos\varphi + \sin 2\chi \sin\vartheta \cos\vartheta \sin\varphi) \hat{I}_x + \\ & (-\cos 2\chi \sin\vartheta \cos\vartheta \sin\varphi - \sin 2\chi \sin\vartheta \cos\vartheta \cos\varphi) \hat{I}_y + \\ & ((\cos 2\chi \sin^2\vartheta) \hat{I}_z)\end{aligned}$$

Secular approximation and averaging

Isotropic component:

$$\hat{H}_{\delta,\mathrm{i}} = -\gamma B_0 \delta_{\mathrm{i}} (\hat{I}_z)$$

Anisotropic (axially symmetric) component:

$$\hat{H}_{\delta,\mathrm{a}} = -\gamma B_0 \delta_{\mathrm{a}} (3 \sin\vartheta \cos\vartheta \cos\varphi \hat{I}_x + 3 \sin\vartheta \cos\vartheta \sin\varphi \hat{I}_y + (3\cos^2\vartheta - 1)\hat{I}_z)$$

Rhombic (asymmetric) component:

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Hamiltonian without radio waves ($\vec{B}_0$, δ_i)

$$\hat{H}_{0,\mathsf{lab}} = -\gamma B_0(1+\delta_\mathsf{i})\hat{I}_z = \omega_0\hat{I}_z$$
$$\hat{H}_{0,\mathsf{rot}} = (\omega_0 - \omega_{\mathsf{rot}})I_z = \Omega\hat{I}_z$$

Hamiltonian with radio waves ($\vec{B}_0$, δ_i, $\vec{B}_1$)

Phase = 0 (x):

$$\hat{H}_{1,\mathsf{rot}} = (-\gamma B_0 - \omega_{\mathsf{rot}})\hat{I}_z - \gamma B_1\hat{I}_x = \Omega\hat{I}_z + \omega_1\hat{I}_x$$

Phase = $\pi/2$ (y):

$$\hat{H}_{1,\mathsf{rot}} = (-\gamma B_0 - \omega_{\mathsf{rot}})\hat{I}_z - \gamma B_1\hat{I}_y = \Omega\hat{I}_z + \omega_1\hat{I}_y$$

Hamiltonian without radio waves ($\vec{B}_0$, δ_i)

$$\hat{H}_{0,\mathrm{lab}} = -\gamma B_0(1+\delta_\mathrm{i})\hat{I}_z = \omega_0 \hat{I}_z$$
$$\hat{H}_{0,\mathrm{rot}} = (\omega_0 - \omega_\mathrm{rot}) I_z = \Omega \hat{I}_z$$

Hamiltonian with radio waves ($\vec{B}_0$, δ_i, $\vec{B}_1$)

Phase = 0 (x), close to resonance $\Omega \ll \omega_1$:

$$\hat{H}_{1,\mathrm{rot}} = \Omega \hat{I}_z + \omega_1 \hat{I}_x \approx \omega_1 \hat{I}_x$$

Phase = $\pi/2$ (y), close to resonance $\Omega \ll \omega_1$:

$$\hat{H}_{1,\mathrm{rot}} = \Omega \hat{I}_z + \omega_1 \hat{I}_x \approx \omega_1 \hat{I}_y$$

The procedure requires knowledge of

1. the operator representing the measurable quantity ($\widehat{M}_+$)

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3. relation(s) describing the initial state of the system ($\widehat{\rho}(0)$)

Thermal equilibrium as the initial state

Classically, $\mathcal{E}_j = -\vec{\mu}_j \cdot \vec{B}_0 = -\mu B_0 \cos\vartheta_j = -\mu_{z,j} B_0$

Boltzmann: $P(\vartheta) = \mathrm{e}^{-\mathcal{E}(\vartheta)/k_\mathrm{B}T} \approx 1 - \mathcal{E}(\vartheta)/k_\mathrm{B}T$ for $\mathcal{E}(\vartheta) \ll k_\mathrm{B}T$

Quantum mechanically, $\mathcal{E}$ is eigenvalue of $\hat{H} = -\gamma B_0(1+\delta_\mathrm{i})\hat{I}_z \approx -\gamma B_0 \hat{I}_z$

$$\hat{\rho}^{\mathrm{eq}} = \begin{pmatrix} \frac{1}{2} + \frac{\gamma B_0 \hbar}{4k_\mathrm{B}T} & 0 \\ 0 & \frac{1}{2} - \frac{\gamma B_0 \hbar}{4k_\mathrm{B}T} \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{\gamma B_0 \hbar}{4k_\mathrm{B}T}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \mathscr{I}_t + \kappa \mathscr{I}_z$$

Mixed state: The two-dimensional density matrix does **not** imply that all magnetic moments are in one of two eigenstates!

Relaxation due to chemical shift anisotropy

Bloch - Wangsness - Redfield semiclassical theory

(spin magnetic moments classically, molecular environment classically)

$$R_1 = \frac{3}{4}b^2\left(\frac{1}{2}J(\omega_0) + \frac{1}{2}J(-\omega_0)\right) \approx \frac{3}{4}b^2 J(\omega_0)$$

$$R_2 = b^2\left(\frac{1}{2}J(0) + \frac{3}{8}J(\omega_0)\right) \approx R_0 + \frac{1}{2}R_1.$$

Same equations as derived classically

One pulse experiment

HOMEWORK: Sections 7.8 and 7.9

Conclusions

Density matrix evolves as

$$\hat{\rho}(t) \propto (\mathscr{I}_x \cos(\Omega t + \phi) + \mathscr{I}_y \sin(\Omega t + \phi) + \text{terms orthogonal to } \mathscr{I}_+,$$

Magnetization rotates during signal acquisition as

$$\langle M_+ \rangle = |M_+| \mathrm{e}^{-R_2 t} \mathrm{e}^{\mathrm{i}\Omega t} = |M_+| \mathrm{e}^{-R_2 t} \mathrm{e}^{\mathrm{i}\phi} (\cos(\Omega t) + \mathrm{i} \sin(\Omega t))$$

unimportant phase shift which is empirically corrected

Fourier transform gives a complex signal proportional to

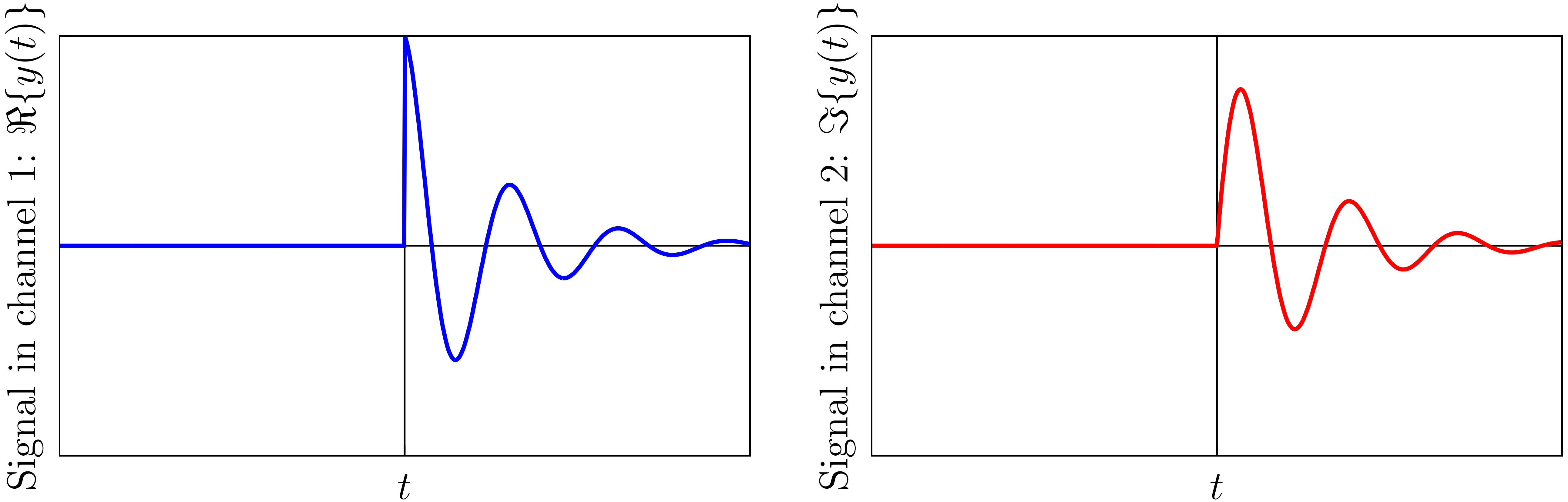
$$\frac{\mathcal{N}\gamma^2\hbar^2 B_0}{4k_\mathrm{B}T}\left(\frac{R_2}{R_2^2 + (\omega - \Omega)^2} - \mathrm{i}\,\frac{\omega - \Omega}{R_2^2 + (\omega - \Omega)^2}\right)$$

Signal

$$\hat{\rho}(t) \propto (\mathscr{I}_x \cos(\Omega t + \phi) + \mathscr{I}_y \sin(\Omega t + \phi) + \text{terms orthogonal to } \mathscr{I}_+,$$

cosine modulation of $\mathscr{I}_x$ = real component of signal

sine modulation of $\mathscr{I}_y$ = imaginary component of signal

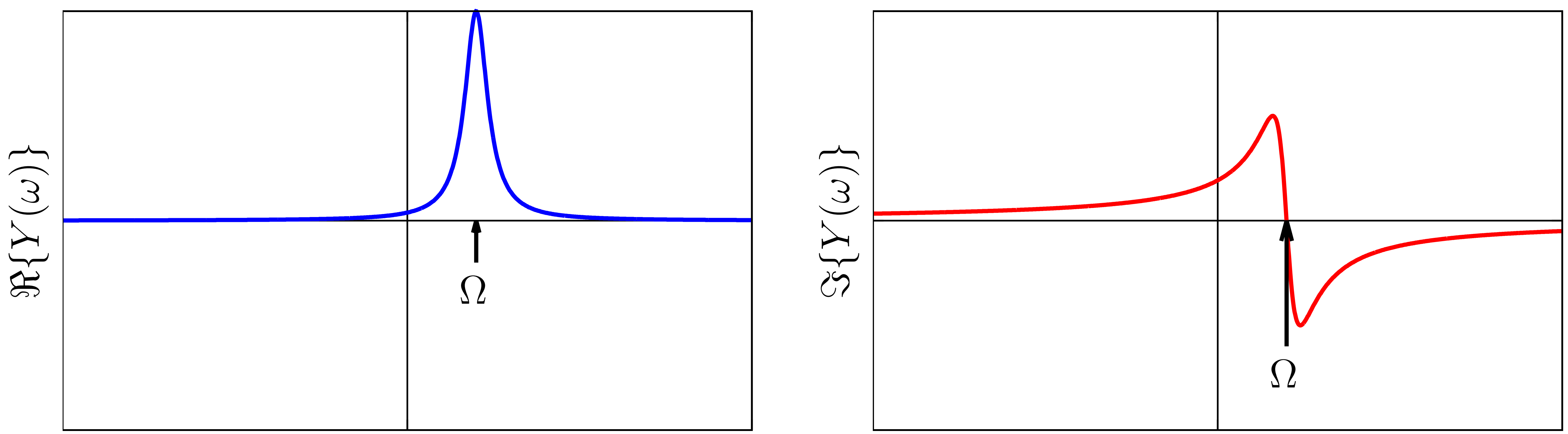


$$|M_+| e^{-R_2 t} e^{i\phi} (\cos(\Omega t) + i \sin(\Omega t))$$

Spectrum

After Fourier transformation:

$$\frac{\mathcal{N}\gamma^2\hbar^2 B_0}{4k_\mathrm{B}T}\left(\frac{R_2}{R_2^2+(\omega-\Omega)^2} - \mathrm{i}\,\frac{\omega-\Omega}{R_2^2+(\omega-\Omega)^2}\right)$$



Signal-to-noise ratio

$$\text{Signal/noise} = K\frac{\hbar^2 N|\gamma|^{5/2}B_0^{3/2}}{k_\mathrm{B}^{3/2}T_\mathrm{sample}^{3/2}}\cdot\underbrace{\frac{1-\mathrm{e}^{-R_2 t_{2,\mathrm{max}}}}{R_2\ t_{2,\mathrm{max}}^{1/2}}}_{\text{Relaxation}}$$

Relaxation: $\sim 1/R_2$ for long acquisition time $t_{2,\mathrm{max}}$

$1/R_2 \approx 6D^{\mathrm{rot}}/b^2$ for large rigid spherical molecules

$$6D^{\mathrm{rot}} = \frac{3k_\mathrm{B}T}{4\pi r^3\eta(T)},$$

$1/b^2 = \gamma^{-2}B_0^{-2}\delta_\mathrm{a}^{-2}$ for chemical shift anisotropy,

but chemical shift anisotropy is usually not dominant

$\Rightarrow$ High field/high γ **usually** advantageous (exception: ^{13}C=)