

Solutions

Repetition

a.

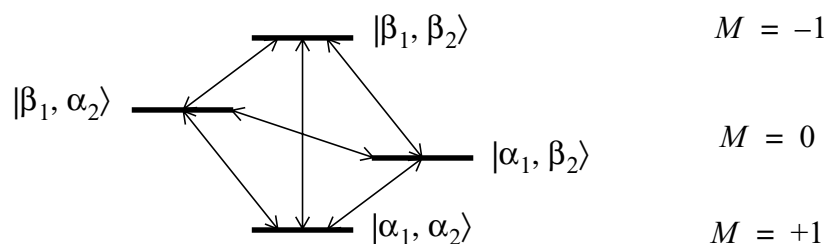


Figure 1: Energy level diagram and total magnetic quantum number for a two spin system.

- b. In a two spin system a total of 6 transitions are possible (See Figure 1). 1 double quantum, 1 zero-quantum and 4 single-quantum Transitions. Of these only the Single Quantum transitions are allowed because of the selection rule for Magnetic Resonance which states that changes of the total magnetic quantum number of are only allowed if:

$$\Delta M = M_i - M_j = \pm 1 \quad [1]$$

- c. The J-coupling (scalar coupling) is an *indirect* coupling between two nuclear spins, mediated though the electrons. The dipolar coupling is a *direct* coupling of the two magnetic moments.
- d. i) The J-coupling between two nuclear spins connected by one bond is determined by the Fermi-contact interaction between the electron and nuclei and the Pauli-principle which demands anti-parallel orientation of the spins, then J is usually positive and an anti-parallel orientation of the nuclear spins is favoured.
 ii) For a two-bond coupling, J is often negative because the exchange integral of overlapping orbitals is favouring parallel oriented electron spins. The corresponding nuclear spins are therefore oriented parallel.
- e. Nuclei having the same resonance frequency in nuclear magnetic resonance spectroscopy and also identical spin-spin interactions with the nuclei of a neighbouring group are magnetically equivalent. The spin-spin interaction between magnetically equivalent nuclei does not appear, and thus has no effect on the multiplicity of the respective NMR signals (*IUPAC Compendium of Chemical Terminology, 2nd edition 1997*). Nuclei which are related by molecular symmetry operations and have the same resonance frequency but different J coupling patterns are chemically equivalent.
 Note: Magnetically equivalent nuclei are always chemically equivalent but the reverse is

not true.

The spectrum of magnetically equivalent nuclei will not be influenced by its J coupling whereas in chemically equivalent nuclei this will be the case.

f. Four important effects that contribute to the chemical shielding are:

I) Diamagnetic effects. Electrons precessing in the magnetic field \vec{B}_0 generate a reaction field \vec{B}_d that counteracts \vec{B}_0 .

II) Paramagnetic effects. An amplification of the applied field \vec{B}_0 is achieved by (partially) excited electrons into a paramagnetic state by the applied field \vec{B}_0 .

III) Ring-current effects. The ring current within a π -system induced by the applied field \vec{B}_0 produces an additional field that reduces the applied field \vec{B}_0 inside the ring and enhances the applied field \vec{B}_0 outside the ring.

IV) Anisotropic neighbour effects. The electron density at a nucleus polarized by the electron density of its neighbouring atom leads to an induced dipolar moment and therefore to an additional field.

g. Each spin 1/2 can be described by a set of four basis operators $(\hat{E}, \hat{I}_x, \hat{I}_y, \hat{I}_z)$. The description of a two-spin system is constructed from all possible products consisting of an operator for spin one and an operator for spin two. This leads to a set of $4^2 = 16$ product operators.

h. The J-coupling Hamiltonian is the same in the laboratory frame and in the rotating frame as the scalar product of two vectors is independent of the coordinate system that the two individual vectors are described in.

Problem 1 : J coupling

a. The two-spin Hamiltonian for the two protons in the rotating frame is

$$\mathcal{H}'' = \Omega_1 \cdot \hat{I}_{1z} + \Omega_2 \cdot \hat{I}_{2z} + 2\pi J_{12} \cdot \vec{\hat{I}}_1 \vec{\hat{I}}_2 \quad [2]$$

with $\Omega_i = (1 - \sigma_{\text{iso}}^{(i)})\omega_0 - \omega_{\text{rf}}$.

b. Following the discussion in the script one gets four spectral peaks at frequencies:

$$\begin{aligned} \omega_{12, 34} &= \frac{\Omega_1 + \Omega_2}{2} \pm J_{12} - \sqrt{\left(\frac{\Omega_2 - \Omega_1}{2}\right)^2 + (\pi J_{12})^2} \\ \omega_{13, 24} &= \frac{\Omega_1 + \Omega_2}{2} \pm J_{12} + \sqrt{\left(\frac{\Omega_2 - \Omega_1}{2}\right)^2 + (\pi J_{12})^2} \end{aligned} \quad [3]$$

with intensities

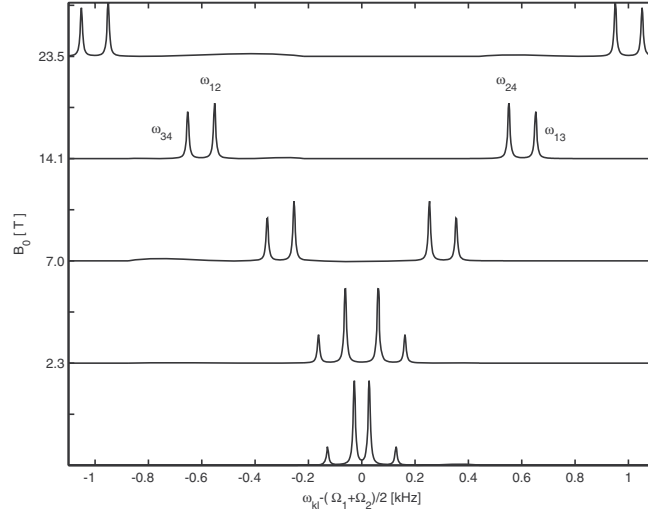


Figure 2: Spectral lines given with respect to $(\Omega_1 + \Omega_2)/2$

$$I_{(12, 24), (13, 34)} = \frac{1 \pm \sin 2\alpha}{4} \quad [4]$$

$$2\alpha = \text{atan}\left(\frac{2\pi J_{12}}{\Omega_1 - \Omega_2}\right)$$

- c. A relative chemical shift of $\sigma_{\text{iso}}^{(1)} - \sigma_{\text{iso}}^{(2)} = 2$ ppm and a coupling constant of $J_{12} = 16$ Hz is assumed (see Fig. 2). When varying the magnetic field $B_0 = -\omega_0/\gamma_{1\text{H}}$ ($\gamma_{1\text{H}} = 26.752 \cdot 10^7 \text{ radT}^{-1}\text{s}^{-1}$) then $\Omega_1 \pm \Omega_2$ are changed in eq. (3), while the coupling term J_{12} is field-independent. The absolute position of the center frequency $(\Omega_1 + \Omega_2)/2$ depends on the carrier frequency ω_{rf} which can be experimentally chosen, while the features of the spectrum remain the same.
- d. The parameter $k(\omega_0) = |(\Omega_1 - \Omega_2)/(2\pi J_{12})|$ tells about the appearance of the lines in the spectrum. For $k(60 \text{ MHz}) = 1.19$ the J-coupling is in the strongly coupled regime (weak static magnetic field), which is characterised by small intensities on outer lines and conjunction of the inner lines. $k(600 \text{ MHz}) = 11.94(1.19)$ is characteristic for weak coupling (strong B_0 field), where the intensities of the four peaks become equal for $\omega_0 \rightarrow \infty$.
- e. The spectra of a homonuclear dipolar-coupled spin pair consist in case of strong coupling of two (instead of one line) separated by $3d$, where d is the coupling constant. For weak coupling, the spectra consists of four lines with equal intensities.

Problem 2 : Off-resonance decoupling

- a. The Hamiltonian of a heteronuclear spin system is always a weak-coupling Hamiltonian. Therefore, the full Hamiltonian in the rotating frame under rf irradiation of the I spin reads

$$\mathcal{H}'' = \Omega_I \cdot \hat{I}_z + \Omega_S \cdot \hat{S}_z + 2\pi J_{IS} \cdot \hat{I}_z \hat{S}_z - \omega_{1I} \cdot \hat{I}_x \quad [5]$$

where the presence of \hat{I}_x is due to the rf irradiation.

- b. Since the rf irradiation is not on resonance ($\Omega_I \neq 0$), there is an effective field with magnitude $\sqrt{\Omega_I^2 + \omega_{1I}^2}$. The angle between the z axis and the effective field is $\alpha = \text{acot}\left(\frac{\Omega_I}{\omega_{1I}}\right)$.
- c. We rotate the coordinate system by an angle α around the y axis such that the z axis of the I spin is along the effective field direction. The Hamiltonian in the new coordinate system can be obtained by expressing the spin operators in the old coordinate system as a function of those in the new one (primed):

$$\begin{aligned} \hat{I}_x &= \hat{I}_x' \cos \alpha - \hat{I}_z' \sin \alpha \\ \hat{I}_y &= \hat{I}_y' \\ \hat{I}_z &= \hat{I}_x' \sin \alpha + \hat{I}_z' \cos \alpha \end{aligned} \quad [6]$$

The Hamiltonian in the new coordinate system thus reads

$$\begin{aligned} \hat{\mathcal{H}}'' &= (\Omega_I \cos \alpha + \omega_{1I} \sin \alpha) \hat{I}_z' + \Omega_S \hat{S}_z + 2\pi J_{IS} (\hat{I}_x' \sin \alpha + \hat{I}_z' \cos \alpha) \hat{S}_z \\ &\quad - (\omega_{1I} \cos \alpha - \Omega_I \sin \alpha) \hat{I}_x' \end{aligned} \quad [7]$$

- d. To calculate the scaling factor of the J coupling, we transform the Hamiltonian into an interaction frame around the effective field of the I spin. Now the effective field and \hat{I}_z' are along the same direction, we choose $\hat{\mathcal{H}}_0 = (\Omega_I \cos \alpha + \omega_{1I} \sin \alpha) \hat{I}_z'$. The transformation procedure is described step-by-step in the script.
- e. Since we are interested only on the scaling of the J coupling, we focus our attention on the coupling term, which contains both \hat{I}_z' and \hat{I}_x' . In the new rotating frame, only the part with \hat{I}_z' is time independent, because it commutes with $\hat{\mathcal{H}}_0$, while the part with \hat{I}_x' is time dependent. Therefore, the approximate effective Hamiltonian that describes the residual off-resonance coupling reads

$$\hat{\mathcal{H}}_J = 2\pi J_{IS} \cos(\alpha) \cdot \hat{I}_z' \hat{S}_z = 2\pi J_{IS} \cos\left[\text{acot}\left(\frac{\Omega_I}{\omega_{1I}}\right)\right] \cdot \hat{I}_z' \hat{S}_z = 2\pi J_{\text{eff}} \cdot \hat{I}_z' \hat{S}_z \quad [8]$$

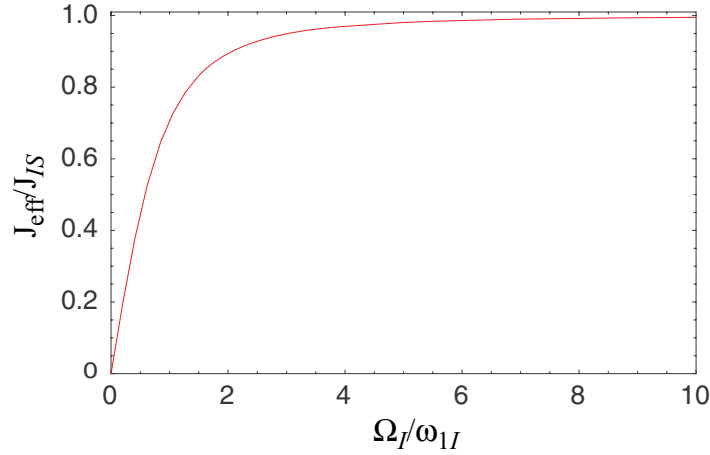


Figure 3: Residual coupling as a function of the chemical-shift offset of the spin I in units of the rf-field amplitude.

- f. The residual coupling as a function of Ω_I/ω_{1I} is plotted in Fig. 3. Notice that when $\omega_{1I} \gg \Omega_I$ J_{eff} goes to zero, while for $\Omega_I \gg \omega_{1I}$ J_{eff} reaches J_{IS} .
- g. When $\omega_{1I} \gg \Omega_I$, we can perform a Taylor expansion of the function in Eq. 8 such that

$$\cos\left[\text{acot}\left(\frac{\Omega_I}{\omega_{1I}}\right)\right] \cong \cos\left[\frac{\pi}{2} - \frac{\Omega_I}{\omega_{1I}}\right] \cong \frac{\Omega_I}{\omega_{1I}}. \quad [9]$$

The linear dependence for $\omega_{1I} \gg \Omega_I$ can also be noticed in Fig. 3.

Problem 3 : Operator representations

- a. Using the identities $\hat{I}_n^+ = \hat{I}_{nx} + i\hat{I}_{ny}$ and $\hat{I}_n^- = \hat{I}_{nx} - i\hat{I}_{ny}$ with $n = 1, 2$, we get
- $$\hat{I}_1^+\hat{I}_2^- + \hat{I}_1^-\hat{I}_2^+ = 2\hat{I}_{1x}\hat{I}_{2x} + 2\hat{I}_{1y}\hat{I}_{2y}$$

- b.

$$\begin{aligned} \hat{I}_1^+\hat{I}_2^- + \hat{I}_1^-\hat{I}_2^+ &= \hat{I}_1^+ \otimes \hat{I}_2^- + \hat{I}_1^- \otimes \hat{I}_2^+ \\ &= \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \otimes \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} \otimes \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \\ &= \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \end{aligned} \quad [10]$$

c. As can be found in the script on page 56:

$$\hat{T}_{10}^{(1,2)} = \frac{-1}{2\sqrt{2}}[\hat{I}_1^+\hat{I}_2^- - \hat{I}_1^-\hat{I}_2^+] \quad \Leftrightarrow \quad \hat{I}_1^+\hat{I}_2^- + \hat{I}_1^-\hat{I}_2^+ = -2\sqrt{2} \cdot \hat{T}_{10}^{(1,2)} \quad [11]$$

d. To generate the spherical spin-tensor operators in the spin space of two coupled spins, we have to calculate the tensor product of the two one-spin spherical tensor operators. This can be done using the general formula in the script (Eq. 2.45 on p. 53), which for the $\hat{T}_{10}^{(1,2)}$ term leads to (See also Eq. 2.47):

$$\hat{T}_{10}^{(1,2)} = \frac{1}{\sqrt{2}}(\hat{T}_{11}^{(1)}\hat{T}_{1,-1}^{(2)} - \hat{T}_{1,-1}^{(1)}\hat{T}_{11}^{(2)}) \quad [12]$$

Problem 4 : Tensor Rotations

a. A chemical shift tensor in its PAS in cartesian notation only has non zero elements on the diagonal of the 3x3 matrix (i.e. only the elements $\sigma_{xx}, \sigma_{yy}, \sigma_{zz}$ are non-zero). With ordering for the elements as described in the script (Eq. 1.38 on p. 19 and Eq. 2.68 on p. 59), this leads to:

$$\sigma^{(CS, PAS)} = \begin{bmatrix} 61 & 0 & 0 \\ 0 & 75 & 0 \\ 0 & 0 & 223 \end{bmatrix} \quad [13]$$

b. In spheric harmonic components in the PAS are defined as detailed in Eq. 2.69 on p. 60. For the case at hand the only non zero elements are:

$$\begin{aligned} \rho_{00}^{(CS, PAS)} &= -\sqrt{3}\bar{\sigma} = -\sqrt{3}\frac{\sigma_{xx} + \sigma_{yy} + \sigma_{zz}}{3} = -\sqrt{3} \cdot 119.67 \text{ ppm} = -207.27 \text{ ppm} \\ \rho_{20}^{(CS, PAS)} &= \sqrt{\frac{3}{2}}\delta = \sqrt{\frac{3}{2}}(\sigma_{zz} - \bar{\sigma}) = \sqrt{\frac{3}{2}} \cdot 103.33 \text{ ppm} = 126.56 \text{ ppm} \\ \rho_{2\pm 2}^{(CS, PAS)} &= \frac{-1}{2}\delta\eta = \frac{-1}{2} \cdot 14 \text{ ppm} = -7 \text{ ppm} \end{aligned} \quad [14]$$

c. We rotate by 90 degrees around the y-axis, for which the rotation matrix is :

$$R_y\left(\frac{\pi}{2}\right) = \begin{bmatrix} \cos\frac{\pi}{2} & 0 & -\sin\frac{\pi}{2} \\ 0 & 1 & 0 \\ \sin\frac{\pi}{2} & 0 & \cos\frac{\pi}{2} \end{bmatrix} \quad [15]$$

d. For this rotation the Euler angles are: $\left(0, \frac{\pi}{2}, 0\right)$

e.

$$\sigma^{(CS,new)} = R_y\left(\frac{\pi}{2}\right)\sigma^{(CS,PAS)}R_y^{-1}\left(\frac{\pi}{2}\right) = \begin{bmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} 61 & 0 & 0 \\ 0 & 75 & 0 \\ 0 & 0 & 223 \end{bmatrix} \cdot \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 223 & 0 & 0 \\ 0 & 75 & 0 \\ 0 & 0 & 61 \end{bmatrix}$$

[16]

$$f. \rho_{lm}^{(CS,new)} = \sum_{m'=-l}^{+l} \mathfrak{D}_{m'm}^l\left(0, \frac{\pi}{2}, 0\right)\rho_{lm'}^{(CS,PAS)} = \sum_{m'=-l}^{+l} d_{m'm}^l\left(\frac{\pi}{2}\right)\rho_{lm'}^{(CS,PAS)}$$

$$\rho_{00}^{(CS,new)} = \rho_{00}^{(CS,PAS)} = -207.27 \text{ ppm}$$

$$\begin{aligned} \rho_{20}^{(CS,new)} &= \sum_{m'=-2}^{+2} d_{m'0}^l\left(\frac{\pi}{2}\right)\rho_{2m'}^{(CS,PAS)} \\ &= \sqrt{\frac{3}{8}}\sin\left(\frac{\pi}{2}\right)^2\rho_{2-2}^{(CS,PAS)} + \frac{3\cos\left(\frac{\pi}{2}\right)^2 - 1}{2}\rho_{20}^{(CS,PAS)} + \sqrt{\frac{3}{8}}\sin\left(\frac{\pi}{2}\right)^2\rho_{22}^{(CS,PAS)} \\ &= \left(\sqrt{\frac{3}{2}} \cdot -7\right) + \left(-\frac{1}{2} \cdot 126.56\right) = -71.85 \text{ ppm} \end{aligned}$$

$$\begin{aligned} \rho_{2\pm 1}^{(CS,new)} &= \sum_{m'=-2}^{+2} d_{m'\pm 1}^l\left(\frac{\pi}{2}\right)\rho_{2m'}^{(CS,PAS)} \\ &= \frac{1}{2}\left(1 \mp \cos\left(\frac{\pi}{2}\right)\right)\sin\left(\frac{\pi}{2}\right)\rho_{2-2}^{(CS,PAS)} + \left(\pm\sqrt{\frac{3}{8}}\right)\sin\left(2\frac{\pi}{2}\right)\rho_{20}^{(CS,PAS)} \\ &\quad - \frac{1}{2}\left(1 \pm \cos\left(\frac{\pi}{2}\right)\right)\sin\left(\frac{\pi}{2}\right)\rho_{22}^{(CS,PAS)} \\ &= 0 \end{aligned} \tag{17}$$

$$\begin{aligned} \rho_{2\pm 2}^{(CS,new)} &= \sum_{m'=-2}^{+2} d_{m'\pm 2}^l\left(\frac{\pi}{2}\right)\rho_{2m'}^{(CS,PAS)} \\ &= \frac{1}{4}\left(1 \mp \cos\left(\frac{\pi}{2}\right)\right)^2\rho_{2-2}^{(CS,PAS)} + \sqrt{\frac{3}{8}}\sin\left(\frac{\pi}{2}\right)^2\rho_{20}^{(CS,PAS)} \\ &\quad + \frac{1}{4}\left(1 \pm \cos\left(\frac{\pi}{2}\right)\right)^2\rho_{22}^{(CS,PAS)} \\ &= \left(\frac{1}{2} \cdot -7\right) + \left(\sqrt{\frac{3}{8}} \cdot 126.56\right) = 74 \text{ ppm} \end{aligned}$$

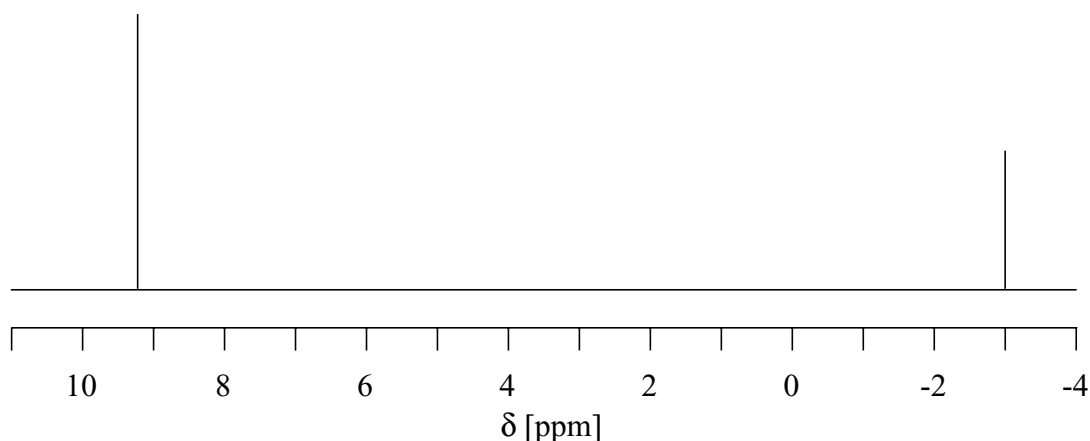


Figure 4: Schematic spectrum of [18]-annulene at 213 K. The signals at 9.17 ppm and -2.96 ppm are due to the outer and inner protons respectively.

Problem 5 : Chemical Shift

- There are 18 protons in a molecule of [18]-annulene: six on the inside of the ring and 12 on the outside. These two sets have separate chemical shifts and the two signals have relative intensities of 1:2. In both cases the chemical shift is dominated by the ring current of the aromatic electrons. Those protons on the outside of the ring are shifted downfield (less shielded), while those on the inside are shifted upfield (more shielded). The values of the chemical shift are $\delta=9.17$ ppm and $\delta=-2.96$ ppm relative to TMS for the protons outside and inside the ring respectively (From Y. Gaoni *et al.*, *Proc. Chem. Soc.*, **1964**, 397 and C.D. Stevenson *et al.*, *J. Am. Chem. Soc.*, **2000**, 122, 722.) In principle one would also expect a fine structure due to the J-coupling. This is in fact observed but because the molecule is not completely planar (and therefore the protons are not equivalent) the multiplets are not as expected. The resonance for the outer protons shows a quartet and the resonance for the inner protons shows a pentet. A sketch of the spectrum (without J-coupling) is shown in figure 4.
- The signal for the outer protons is found upfield from the signal of benzene. The larger size of the conjugated ring of [18]-annulene generates a larger ring current and causes a more pronounced de-shielding effect on the outer protons

Problem 6 : Single Crystal and MAS

- The Hamilton operator of a spin system in a single crystal is given by:

$$\hat{H} = \gamma \hat{\mathbf{I}} \cdot \underline{\sigma} \cdot \mathbf{B} \quad [18]$$

Evaluation of this expression gives:

$$\hat{H} = \gamma B_0 (\hat{I}_x \sigma_{xz} + \hat{I}_y \sigma_{yz} + \hat{I}_z \sigma_{zz}) \quad [19]$$

In the high field approximation the terms containing \hat{I}_x and \hat{I}_y are time dependent in the rotating frame and are averaged to zero and the Hamiltonian simplifies to $\hat{H} = \gamma B_0 \hat{I}_z \sigma_{zz}$. The orientation of the single crystal is such that the principle components of the CSA lie along x , y and z in the laboratory frame. Combined with the convention for ordering the principle components of the chemical shift tensor, this means that $\sigma_{zz} = \sigma_{33} = 106$ ppm and therefore the resonance frequency is 106 ppm.

b. The CSA-tensor after a rotation $R(\gamma)$ is given by:

$$\underline{\sigma}(\gamma) = \underline{R}(\gamma) \underline{\sigma} \underline{R}(-\gamma) \quad [20]$$

Again we only need the $\sigma_{zz}(\gamma)$ to calculate the resonance frequency (see 4A.):

$$\begin{bmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \sigma_{zz}(\gamma) \end{bmatrix} = \begin{bmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ R_{31}(\gamma) & R_{32}(\gamma) & R_{33}(\gamma) \end{bmatrix} \begin{bmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{bmatrix} \begin{bmatrix} \cdot \cdot R_{13}(-\gamma) \\ \cdot \cdot R_{23}(-\gamma) \\ \cdot \cdot R_{33}(-\gamma) \end{bmatrix} \quad [21]$$

After multiplication and the application of some basic trigonometric functions we obtain:

$$\begin{aligned} \sigma_{zz}(\gamma) &= \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) + \left(\frac{4}{9}\sigma_{zz} - \frac{4}{9}\sigma_{xx}\right)\cos(\gamma) + \left(\frac{2}{9}\sigma_{zz} + \frac{1}{9}\sigma_{xx} - \frac{1}{3}\sigma_{yy}\right)\cos(2\gamma) \\ &= \sigma_{iso} + \sigma_1 \cos(\gamma) + \sigma_2 \cos(2\gamma) \end{aligned} \quad [22]$$

and with $\sigma_{xx} = 239$ ppm, $\sigma_{yy} = 184$ ppm and $\sigma_{zz} = 106$ ppm, we calculate

$$\sigma_{iso} = 176.333 \text{ ppm}$$

$$\sigma_1 = -59.111 \text{ ppm}$$

$$\sigma_2 = -11.222 \text{ ppm}$$

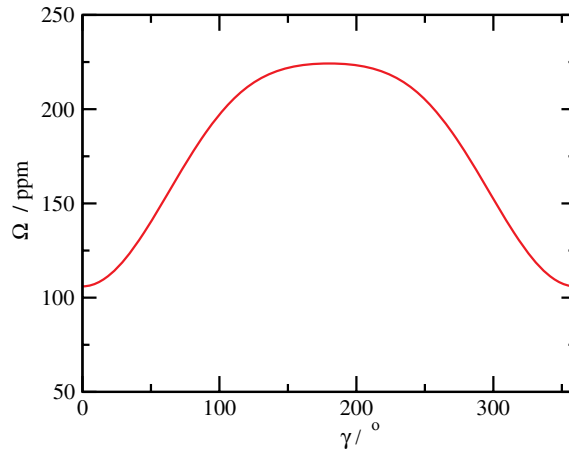


Figure 5: Rotation plot illustrating the dependence of the observed chemical shift on the rotation around the magic angle.

- c. The isotropic chemical shift can be written as:

$$\sigma_{iso} = \frac{1}{3} \text{Trace}\{\underline{\sigma}\} = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) = 176.333 \text{ ppm}$$

and is thus equal to σ_{iso} in b.

- d. In a powdered sample all orientations of the chemical shift tensor with respect to the magnetic field are equally likely. Each of these orientations will give rise to a different resonance frequency because of the rotation from the PAS to the LAB frame of reference with the set of angles (α, β, γ) . The spectrum will be a superposition of all these orientations. Mathematically this means that we need to integrate over all angles:

$$s(t) = \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} s(\alpha, \beta, \gamma, t) \delta\alpha \sin\beta \delta\beta \delta\gamma \quad [23]$$

This gives rise to the spectrum in figure 6.

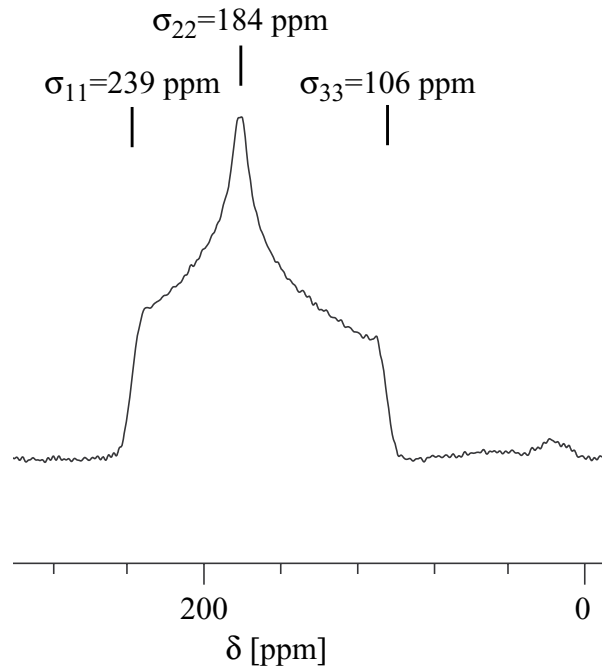


Figure 6: Powder spectrum of $^{13}\text{C}_1$ -alanine. The sample was ^{13}C enriched to 99% at the carbonyl position. A small signal around 20 ppm can be seen for the methyl group at natural abundance (1.1%).

- e. If we rotate continuously the expression for $\sigma_{zz}(\gamma)$ as derived in b becomes time dependent (because the rotation angle γ is now time dependent with angular velocity ω_r). Replacing γ with $\gamma(t) = 2\pi\omega_r \cdot t$ gives:

$$\sigma_{zz}(\gamma(t)) = \sigma_{iso} + \sigma_1 \cos(2\pi\omega_r \cdot t) + \sigma_2 \cos(4\pi\omega_r \cdot t) \quad [24]$$

The actual value of the chemical shift comes from integrating over γ , so if the rotation frequency is fast compared to the anisotropy of the chemical shift tensor, the time dependent terms can be neglected and the value is equal to the isotropic chemical shift.

In a (much) more advanced treatment of the problem, which is (almost) beyond the scope of this course, it is possible to deal with the situation when the approximation is not valid (i.e. for lower rotation frequencies). In this case the signal can be calculated by evaluating:

$$s(t_2) = \langle \hat{I}^+(t_2) \rangle = \text{tr}\{\hat{\sigma}(t_2)\hat{I}^+\} \quad [25]$$

In the last equation $\hat{\sigma}(t_2)$ is the density operator at time t_2 and it is the solution of the Liouville-von Neumann equation with a time-dependent Hamiltonian.

$$\hat{\sigma}(t_2) = \hat{T} \exp\left(2\pi i \int_0^{t_2} \hat{H}(t) dt\right) \sigma(0) \exp\left(-2\pi i \int_0^{t_2} \hat{H}(t) dt\right) \quad [26]$$

Going through the calculation leads to an equation of the following form:

$$s(t_2) \propto \exp\left(-i2\pi \int_0^{t_2} (-\omega_0)\sigma_{zz}(t)dt\right) \quad [27]$$

Substituting $\sigma_{zz}(\gamma(t))$ and evaluating the integral leads to three terms in the exponent:

$$s(t_2) \propto \exp\left(-i2\pi\left((-\omega_0)\sigma_{iso}t_2 + \left(\frac{-\omega_0\sigma_1}{2\pi\omega_r} \sin(2\pi\omega_r \cdot t_2)\right) + \left(\frac{-\omega_0\sigma_2}{4\pi\omega_r} \sin(4\pi\omega_r \cdot t_2)\right)\right)\right)$$

The first term, $(-\omega_0)\sigma_{iso}t_2$, is the isotropic chemical shift.

The second term (which we neglected in the case of fast rotation) is more complicated because the frequency of the signal is itself a time dependent sine function:

$$\exp\left(\frac{i\omega_0\sigma_1}{\omega_r} \sin(2\pi\omega_r \cdot t_2)\right)$$

One of the ways to evaluate this part of the signal function is to expand it as an infinite sum over Bessel functions (Note that the sum goes from $-\infty$ and not from 0 as in the question):

$$\exp(i \cdot z \cdot \sin(\theta)) = \sum_{k=-\infty}^{\infty} (i)^k \cdot J_k(z) \cdot \exp\left(ik\left(\theta + \frac{\pi}{2}\right)\right)$$

Using these expansion we see that the signal consists of infinitely many, equidistantly spaced, frequency components each with an amplitude given by a Bessel function:

$$k \cdot \theta = 2\pi k \cdot \omega_r \cdot t_2 \quad \text{and} \quad z = \frac{\omega_0\sigma_1}{\omega_r}$$

In the limit of fast spinning $\omega_r \gg \omega_0\sigma_1 \Rightarrow z \approx 0$: $J_0(z) \approx 1$ and $J_k(z) \approx 0$ for

$k = [\pm 1, \pm 2, \pm 3, \dots]$ and no contribution to the signal occurs except for a single component at zero frequency. On the other hand for very large values of k and reasonable values of z (say $1 < z < 10$) the values for the Bessel function approaches zero (e.g. $J_{10}(5) = 0.0015$). This means that higher order sidebands have almost no intensity.

For the third term the same as for the second term is valid except that:

$$k \cdot \theta = 4\pi k \cdot \omega_r \cdot t_2 \quad \text{and} \quad z = \frac{\omega_0\sigma_2}{2\omega_r}$$

The spectrum at different rotation frequencies for Alanine are shown in figure 7. These spectra are for a powder but the spectrum for a single orientation would look the same

except for different intensities and phases of the spinning sidebands. Note that the signal to noise ratio at lower spinning speeds becomes worse because the integral of the signal is constant but is divided over more lines.

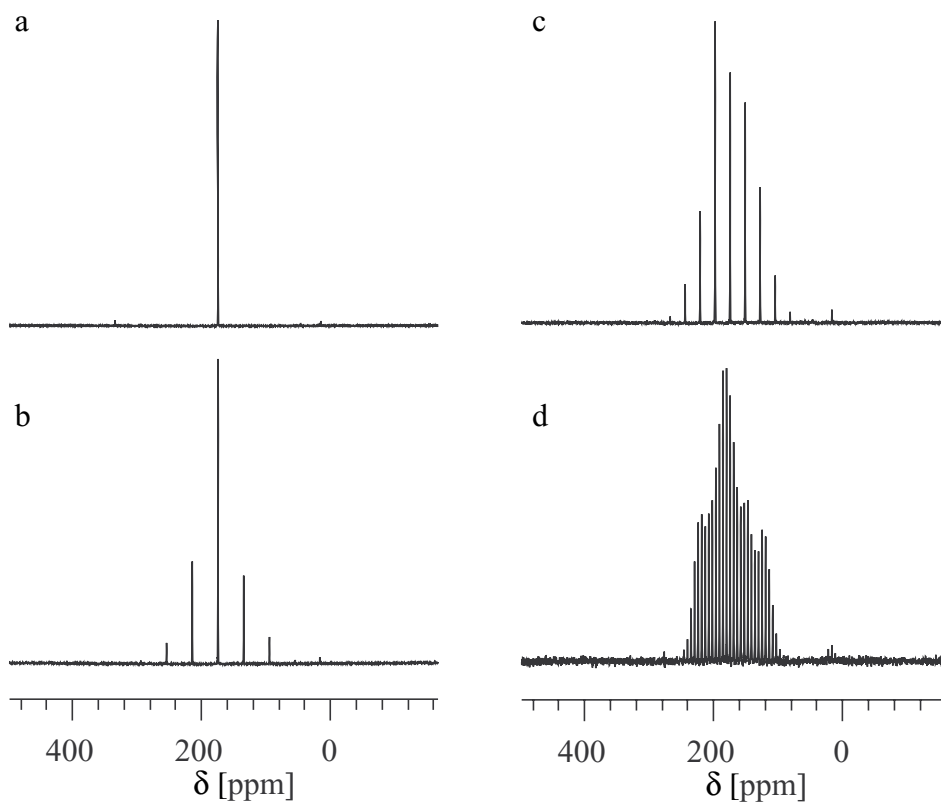


Figure 7: MAS spectra of $^{13}\text{C}_1$ -alanine at $\omega_r/2\pi = 12.00, 3.00, 1.75,$ and 0.41 kHz (a-d). All spectra are the sum of 16 scans.