Supporting Information

^{2}H NMR lineshape calculations of CD$_3$ groups of decamethylzincocene in the presence of methyl group rotations, Zn tautomerism and ring rotations.

In this section, we will present the results of model calculations of ^{2}H NMR lineshapes of methyl-deuterated decamethylzincocene in the presence of various molecular motions. The basic theory of solid state ^{2}H NMR is well-known[1,2] and it is only briefly summarized here. The leading interaction in ^{2}H solid-state NMR is the ^{2}H quadrupolar interaction. In the usual high field approximation, the first-order quadrupolar interaction is characterized by the Hamiltonian

$$\hat{H}_Q = 2\pi v_Q (\vartheta, \varphi)\left(\hat{I}_Z^2 - \frac{2}{3} \right), \tag{1}$$

where the orientation dependent resonance frequencies v_Q of the two transitions are given as

$$v_Q (\vartheta, \varphi) = \pm \frac{3}{4} \frac{eQeq}{\hbar}\left(\frac{1}{2} \right)\left(3\cos^2 \vartheta - 1 - \eta \sin^2 \vartheta \cos 2\varphi \right) = q_{ZZ} \frac{1}{2}\left(3\cos^2 \vartheta - 1 - \eta \sin^2 \vartheta \cos 2\varphi \right). \tag{2}$$

Here, η is the asymmetry parameter and q_{zz} the strength of the quadrupolar interaction.

While in single crystals only two lines at $\pm v_Q$ are observable, in a nonoriented powder sample the average over all possible orientations has to be calculated. Assuming for simplicity that the transversal relaxation time T_2 is orientation independent, the spectrum can be calculated as a superposition of simple Lorentzians:

$$I(v) = \int_0^\pi d\vartheta \sin \vartheta \int_0^{2\pi} d\vartheta \left(\frac{T_2}{1 + 4\pi^2 T_2 \left(v - v_Q (\vartheta, \varphi) \right)^2} + \frac{T_2}{1 + 4\pi^2 T_2 \left(v + v_Q (\vartheta, \varphi) \right)^2} \right) \tag{3}$$

The quadrupolar coupling constant q_{cc} = 4/3q_{zz} is a measure for the strength of the quadrupolar interaction. Because of the large spectral width, the ^{2}H NMR spectra are measured with the solid echo sequence [90°$_y$-τ-90°$_x$-τ-$\langle I_x \rangle$]. If the molecule undergoes fast reorientations the value of the quadrupolar tensor and thus also the quadrupolar coupling in general are changed, depending on the type and speed of the motion. If the motions are fast in the NMR time scale, a relatively simple scenario is found: fast isotropic reorientations of the molecule cause a complete averaging of the quadrupolar tensor ($q_{cc\ (iso)}$ = 0). Anisotropic rotations or rotational jump diffusions around a C_5-axis, reduce the value of q_{zz} to $q_{zz\ (rot)}$ = 1/2q_{zz}. In these situations the normalized line shape of the solid echo spectrum is identical to the FID spectrum. This is no longer the case if the correlation time of the motion is in the NMR time scale. Here, the lineshape of the solid echo spectrum becomes a function of the pulse spacing τ and has to be calculated by standard NMR methods.[2]

First we will consider the effect that a CD$_3$ rotation will produce in the ^{2}H NMR spectra as a function of the D jump rates. The intrinsic value for the quadrupolar coupling constant of a rigid CD$_3$ group is q_{cc} = 167 ± 1 kHz.[3] In Figure S1 the calculated ^{2}H NMR spectra for such a group subject to 3-fold 120° jumps are shown as a function of the rate constants k_{met} of this process. The simulations were performed considering echo delays of τ = 30 μs, an asymmetry factor η = 0 and a transversal relaxation T_2 = 0.15 s. From this simulation a reduction of the q_{cc} is observed from 167 kHz in the slow (<5×10^3 sec^{-1}) regime to 58 kHz at high rates (>1×10^7 sec^{-1}).

Let us now consider, in a second step, the effect that an η^1-η^5 interconversion or Zn tautomerism between states A and B in Figure 2 would have on the spectra, in the presence of CD$_3$ rotations which are faster than 1×10^7 sec^{-1}. We consider the case where ring rotations are absent. Furthermore, we assume a degenerate interconversion with an equilibrium constant of K_{AB} = 1. The result of this simulation is shown in Figure S2. No effect is observed in the

Figure for the case of slow exchange with $k_{inv} = k_{AB} = k_{BA} < 1 \times 10^3$ sec^{-1}. The solid line of Figure S2a corresponds to the case depicted to the motion of a given Cp* ring defined in Figure S2. The overall spectrum obtained by the sum of all slightly different contributions of the different methyl group sites. In approximation, the calculated lineshape can be approximated by a normal Pake doublet characterized by the value of q_{cc} = 53 kHz, as represented by the dotted line in Figure S2a. This procedure is justified because fairly slow ring rotations will lead to a coalescence of the solid into the dotted lineshape in the figure. We obtain a reduction of only Δq_{cc} = -5 kHz arising from a degenerate Zn tautomerism.

In order to estimate the reduction δq_{cc} for the non-degenerate case we assume that

$$\delta q_{cc} = \frac{2K_{AB}}{1 + K_{AB}} \Delta q_{cc} .$$

(4)

Thus, if K_{AB} were zero, no effect of the η^1-η^5 interconversion on the ^{2}H NMR lineshapes would be observed.

We will consider now in a third step the effect that additional 5-fold rotations would have in the spectra obtained in Figure S2a. This would correspond to a situation in which the CD$_3$ rotations are much faster than the Cp* rotations. For this simulation, we will consider as the starting point the spectrum represented by the dotted line of Figure S2a. This spectrum was characterized by q_{cc} = 53 kHz and η = 0. In Figure S3a, the result of this simulation is shown, in which planar 5-fold rotations were considered. The ^{2}H NMR signal obtained at rotational rates higher than 1×10^7 sec^{-1} are characterized with a q_{cc} value of 27 kHz, this implies a q_{zz} reduction of ½ as predicted in the theoretical section for planar rotations.

In contrast to an η^5 bonded Cp* ring, a 5-fold planar rotation is a poor approximation to describe the corresponding rotation of an η^1 bonded Cp* ring. As a first approximation, we move the methyl groups out of the molecular plane by an angle of 24°. The conical angle with the ring axis is then 76°. The effect of a 5-fold conical rotation on the ^{2}H NMR lineshapes of

the methyl groups is illustrated in Figure S3b. As before, the calculations were performed considering echo delay of $\tau = 30$ μs, an asymmetry factor $\eta = 0$, a value of $T_2 = 0.15$ s and an intrinsic quadrupolar coupling constant $q_{cc} = 53$ kHz. The lineshapes are somewhat different from those for the 5-fold planar rotation. The transition from the slow to the fast exchange regime occurs at the same rate constants of about 2×10^6 sec^{-1}, as in the 5-fold planar rotation. However, the effective coupling constant in the fast exchange limit, $q_{cc} = 23$ kHz is smaller than for the 5-fold planar rotation, where the corresponding values is 27 kHz.

So far, we have considered only a deuterated methyl group in a single Cp* ring. Now, let us study the methyl group ^{2}H line shapes in the presence of a combined fast non-degenerate Zn tautomerism and 5-fold planar rotations of both Cp* rings X and Y as illustrated in Figure S4. In analogy to complex H-transfers,[4] one can derive the following equation for the average planar rotation rate constants of both rings

$$k_{rot}^X = \frac{K_{AB}}{K_{AB}+1}k_1 + \frac{1}{K_{AB}+1}k_5 \qquad (5)$$

$$k_{rot}^Y = \frac{K_{AB}}{K_{AB}+1}k_5 + \frac{1}{K_{AB}+1}k_1 .$$

where k_1 and k_5 are the intrinsic rate constants of the 5-fold planar rotations of the η^1-Cp* and η^5-Cp* rings.

The results of the calculations are depicted in Figure S4, where the spectral parameters were the same as in Figure S3. Figure S4a illustrates the slow ring rotation regime, where k_1 and k_5 and hence k_{rot}^X and k_{rot}^Y are small as compared to $q_{cc} = 53$ kHz. The spectrum in Figure 8c can be obtained in different ways. Either, both k_1 and k_5 are very large, or only one of these constants is large and the other small, but the equilibrium constant K_{AB} is close to 1. Then, both rings contribute a lineshape exhibiting the same effective reduced quadrupole coupling constant of 23 kHz. Generally, both rings contribute different lineshapes, as K_{AB} is not 1 in

the non-degenerate case. A particular example is depicted in Figure S3b. Here, either the 5-fold planar η^1 or η^5 rotation is fast, the other slow. According to eq **Error! Reference source not found.**, two different lineshape contributions result, a reduced Pake doublet for the ring present dominantly in the rapidly rotating and the other in the slowly rotating form.

Figure captions

Figure S1. Calculated ^{2}H NMR spectra for a CD_3 unit as a function of the rotational rates as explained in the text.

Figure S2. The effect, of fast (a), and slow (b) Zn tautomerism rates, in the ^{2}H NMR spectrum obtained for fast rotating methyl groups is shown.

Figure S3. Calculated ^{2}H NMR spectra for a fast rotating CD_3 unit which is subject to additional (a) planar 5-fold rotations and (b) conical 5-fold rotations.

Figure S4. The effect of the possible combinations of slow-fast k_1/k_5 rates and equilibrium constant values K_{AB} in the ^{2}H NMR spectra of the system of **I** shown in the figure, are calculated. For more details see text.
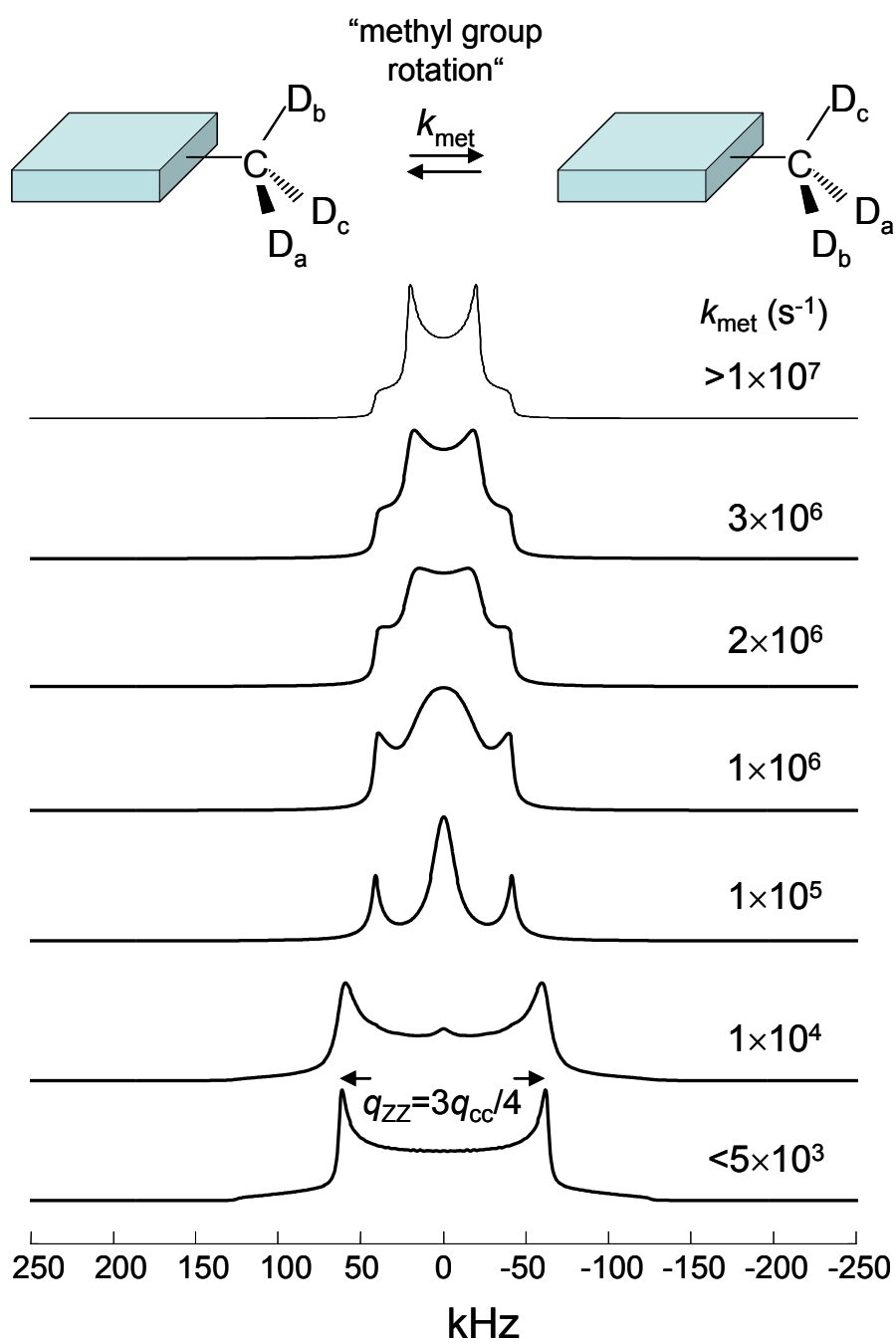
Figure S1:

"methyl group rotation"

k_{met}

D_b
D_c
D_a
C

D_c
D_a
D_b
C

k_{met} (s^{-1})

$>1\times10^7$

3×10^6

2×10^6

1×10^6

1×10^5

1×10^4

$q_{ZZ}=3q_{cc}/4$

$<5\times10^3$

250 200 150 100 50   0   -50 -100 -150 -200 -250

kHz

Figure S2:

Figure S3:

Figure S4:

ring **X**

k_5

Zn   A $\xrightleftharpoons[k_{BA}]{k_{AB}}$ B   **Zn** k_1

k_1 k_5

ring **Y**

rings **X,Y**

$k_1 , k_5 \quad q_{cc}$

$k_1 \quad q_{cc}, k_5 << q_{cc}, K_{AB} \quad 1$

c

$k_5 \quad q_{cc}, k_1 << q_{cc}, K_{AB} \quad 1$

ring **X**

$k_1 \quad q_{cc}, k_5 << q_{cc}, K_{AB} \neq 1$

ring **Y**

$k_5 \quad q_{cc}, k_1 << q_{cc}, K_{AB} \neq 1$

b

$q_{ZZ}=3q_{cc}/4$

rings **X,Y**

$k_1 , k_5 \quad q_{cc}$

a

100 80 60 40 20 0 -20 -40 -60 -80 -100

kHz
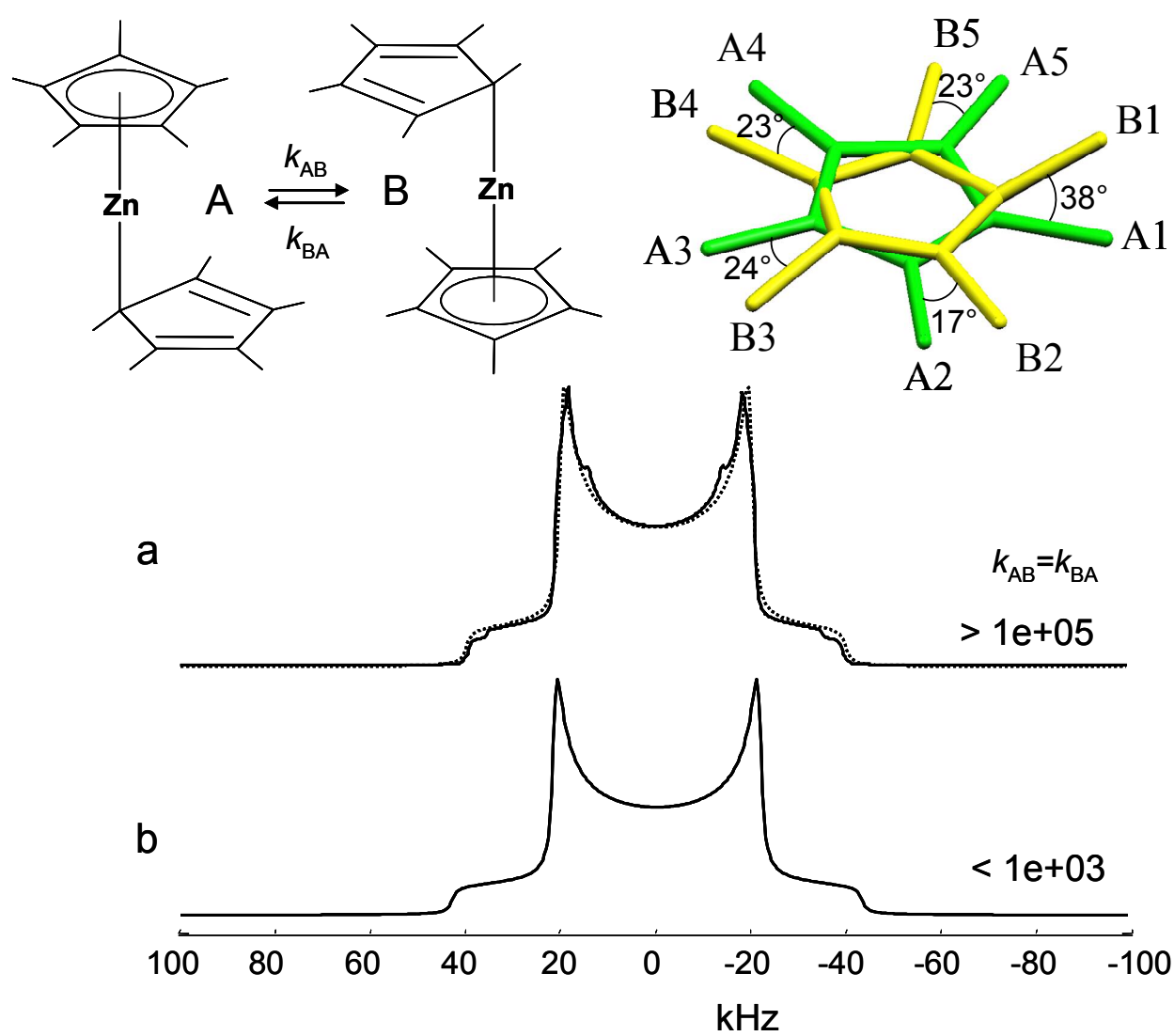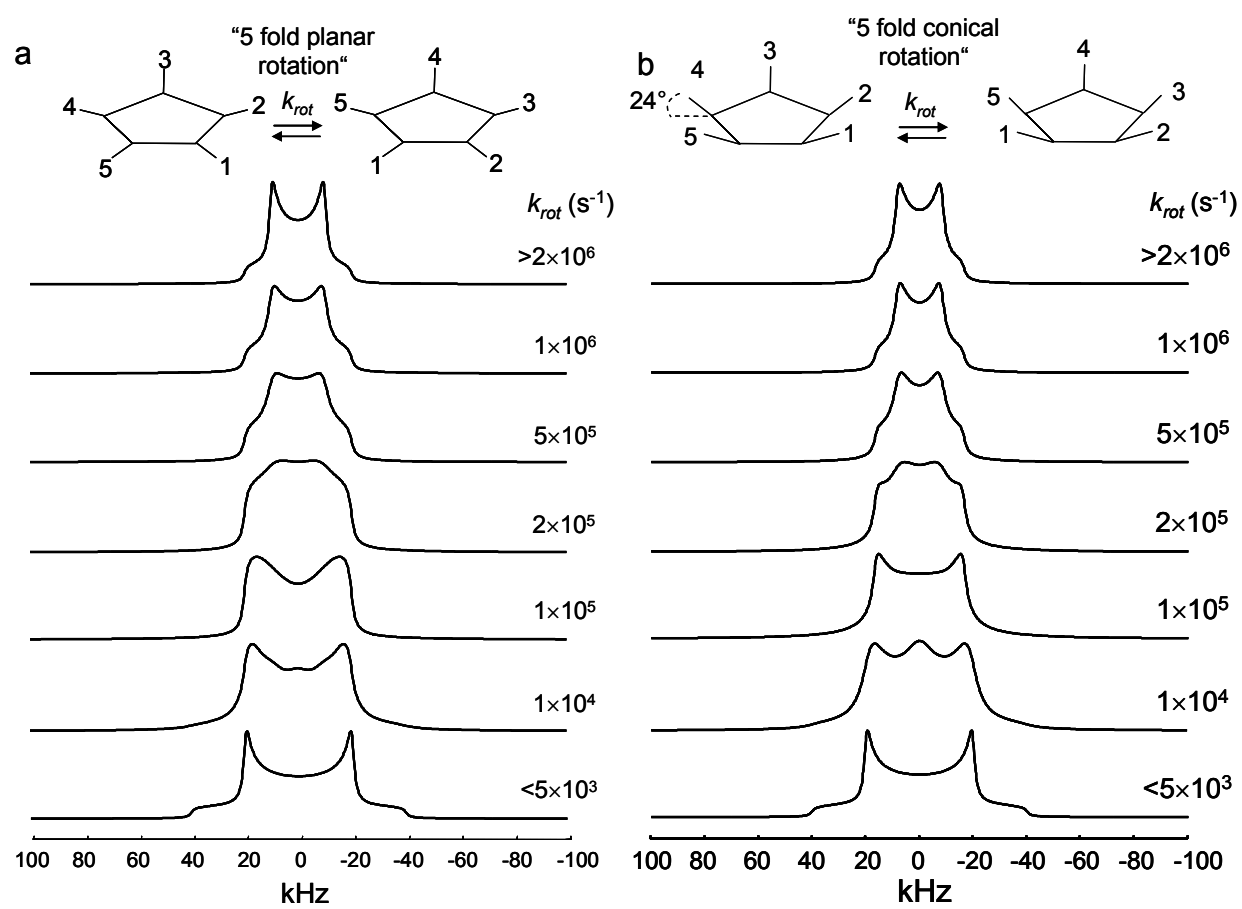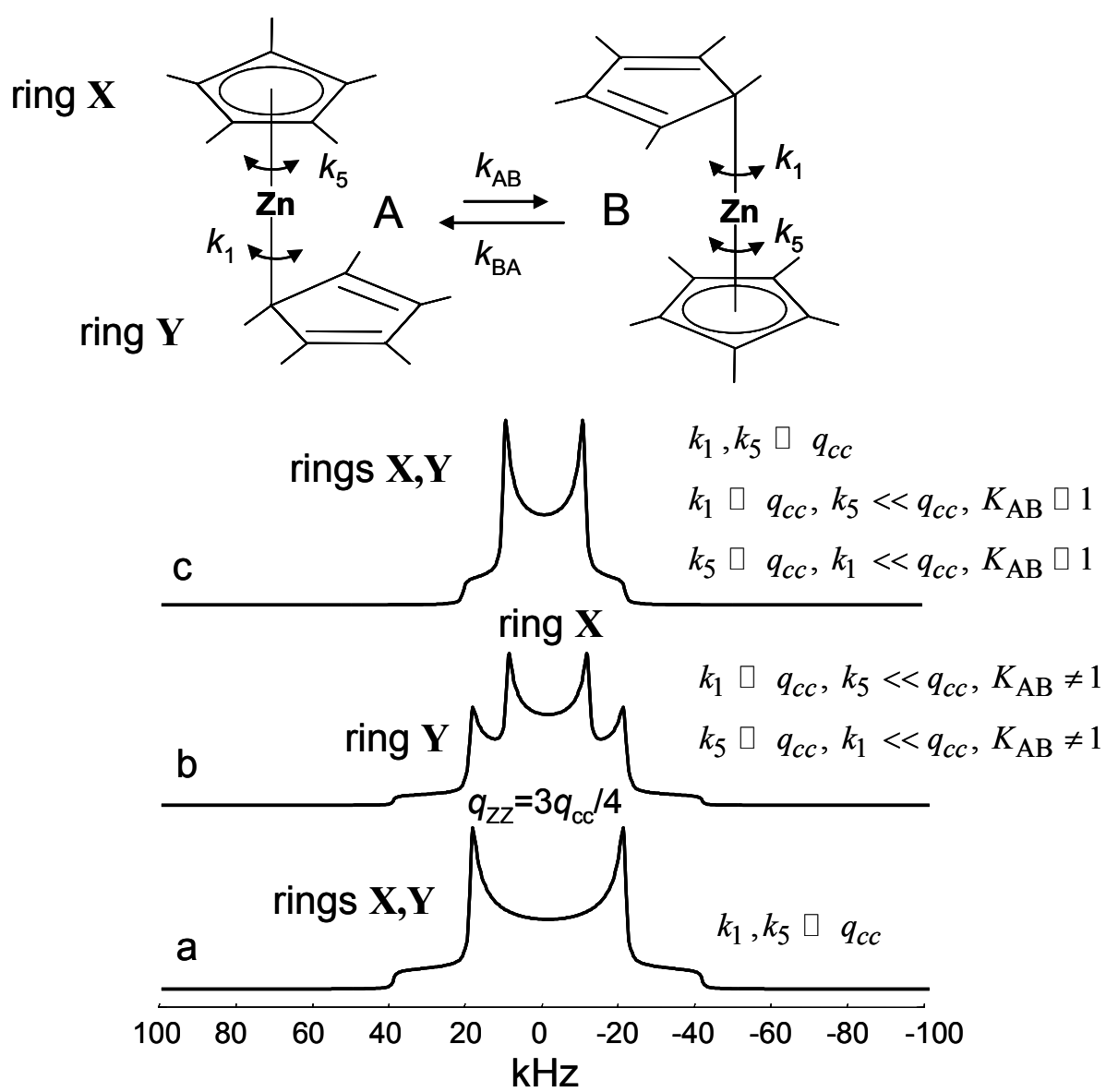
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