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The Origin of Mirror Symmetry in High-Resolution NMR Spectra

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Abstract

A correlation between the symmetry of NMR spectra, including higher-order spectra, and the properties of the spin system has been established. It is shown that for a spectrum to be symmetric about the mid-resonance frequency (ν_0), two conditions must be satisfied: the resonant frequencies of the spins must be symmetrically positioned about ν_0, and the J-coupling matrix must be symmetric about the secondary diagonal. The results were validated by calculating theoretical spectra for 3-, 4-, 5-, and 6-spin systems.

Keywords

symmetric NMR spectra, spin systems theory, NMR spectra simulation

1. Introduction

Some high-resolution NMR spectra exhibit symmetry, which can be reasonably categorized into two types: (1) the symmetry of a first-order multiplet about its resonant frequency, and (2) the symmetry of the entire spectrum of a spin system about its spectral center of mass, as observed, for example, in AB (Pople et al., 1959, p.122; Hoffman et al., 1971, p.57; Gunter, 2013, p.166) and AA'XX' (Pople et al., 1959, p.142; Hoffman et al., 1971, p.110; Gunter, 2013, p.197) spin systems. The first type of symmetry is readily explained by the fact that the coupled nuclei exist in different spin states, that contribute equally to the spectral density on either side of the resonant frequency, regardless of the nuclei spin quantum numbers.

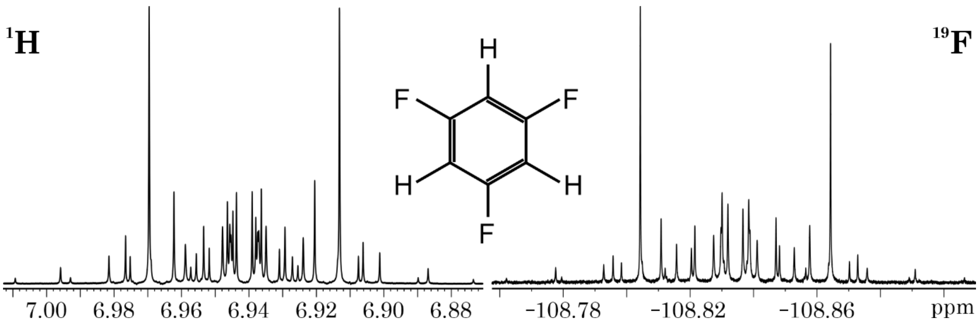

Figure 1. ^{1}H (300.13 MHz) and ^{19}F (282.40 MHz) spectra of 1,3,5-trifluorobenzene.

The second type of symmetry is an intrinsic property of the entire spin system. For instance, the spectra of AB (AX) and AA'BB' (AA'XX') systems exhibit symmetry about their mid-resonance frequency, $\nu_0=(\nu_A+\nu_B)/2$. At first glance, one might expect the AA'A"XX'X" spin system with C_{3V} symmetry (as in 1,3,5-trifluorobenzene, see Figure 1) to also be symmetric about $(\nu_H+\nu_F)/2$; however, this is not observed in practice (Cheshkov and Sinitsyn, 2020).

In general, high-resolution NMR spectra do not exhibit symmetry around the mid-resonance frequency. It is worth considering how this type of spectrum symmetry can arise.

2. Theory

Figure 2 shows the spectra of two ABC spin systems with different signs of resonant frequencies. It is readily apparent that the spectra of these spin systems are mirror images of each other. Inverting the order of the resonant frequencies while maintaining the differences between them produces a reflected spectrum, which can be thought of as reversing the direction of the frequency axis.

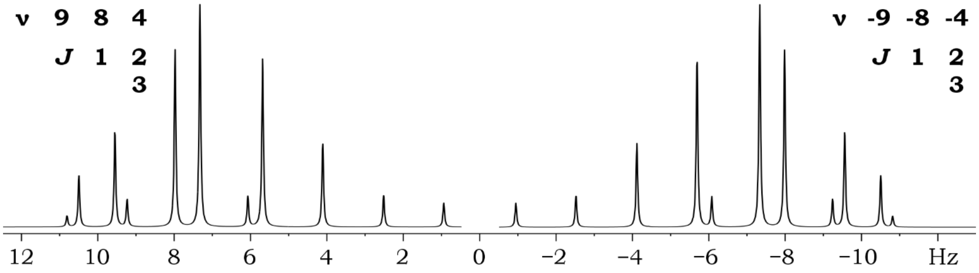

Figure 2. Spectra of two ABC spin systems, with different signs of resonant frequencies.

To demonstrate how this spectral symmetry can be achieved for a single spin system, the parameter matrices of the considered ABC spin systems are rewritten according to the sequence of their resonant frequencies:

$$\begin{array}{ccc} \nu_1 & \nu_2 & \nu_3 \\ 9 & 8 & 4 \\ & J_{12} & J_{13} \\ & 1 & 2 \\ & & J_{23} \\ & & 3 \end{array} \qquad \begin{array}{ccc} -\nu_3 & -\nu_2 & -\nu_1 \\ -4 & -8 & -9 \\ & J_{23} & J_{13} \\ & 3 & 2 \\ & & J_{12} \\ & & 1 \end{array}$$

It can be shown that reversing the sequence of resonant frequencies results in a reflection of the J-coupling matrix about its secondary diagonal, while the coupling constants on the secondary diagonal remain unchanged. If for a certain spin system, the parameter matrix is constructed in such a way that the resonant frequencies are symmetric about the mid-resonance frequency (ν_0) and the J-coupling matrix is symmetric about the secondary diagonal, then reversing the order of the resonant frequencies will not alter the spectrum (Figure 3). Moreover, the spectrum itself will be symmetric about ν_0. Thus, a J-coupling matrix symmetric about the secondary diagonal remains invariant under a reversal of the spin order. The secondary diagonal contains the coupling constants between spin pairs that are interchanged upon order reversal,

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i.e., the first and the last, the second and the penultimate, and so forth. The resonant frequencies of these spins must be symmetrically arranged about the mid-resonance frequency ν_0, in other words, they must be "equilibrated".

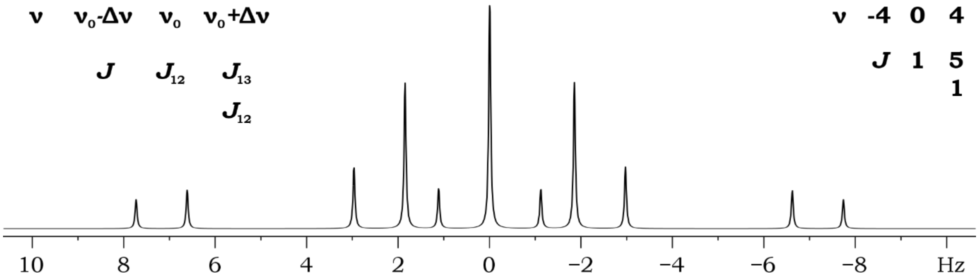


Figure 3. Spectrum of ABC spin system with symmetry about mid-resonance frequency.

3. Results and discussion

Below, in Figure 4, we present several theoretically calculated spectra that are symmetric about the mid-resonance frequency for spin systems with different numbers of spins (4, 5, and 6). All these spin systems possess parameter values that meet the conditions outlined above.

In practice, the secondary diagonal symmetry of J-coupling matrix may not be immediately apparent, as its representation depends on the order of the spins, which in general can be arbitrary. Therefore, it may be necessary to find a specific ordering of the spins that results in a J-coupling matrix with this symmetry, provided such an ordering exists. Spin reordering is effectively a permutation operation, which corresponds to conjugating (in the group theory sense) the Hamiltonian (along with other spin operators and the J-coupling matrix) by a permutation matrix, an operation under which the spectrum remains invariant.

3.1. Some practical aspects and exceptions

It is well-established that o-dichlorobenzene (ODCB) exhibits a mid-resonance symmetrical ^{1}H NMR spectrum, corresponded to AA'XX' spin system. When the resonant frequencies are arranged in the order {O_1, O'_2, M_3, M'_4}, the resulting J-coupling matrix does not possess symmetry about the secondary diagonal (Figure 5, a). However, reordering the spins as {O_1, M_3, M'_4, O'_2} reveals the underlying secondary diagonal symmetry (Figure 5, b).

This symmetry is preserved upon permuting only the ortho-protons to {O'_2, M_3, M'_4, O_1} or only the meta-protons to {O_1, M'_4, M_3, O'_2}. These permutations (Figure 5, c) result in swapping the coupling constants J_O (J_{AX}) and J_M ($J_{AX'}$), while leaving the spectrum unchanged. The invariance of the spectrum to this swap is a direct consequence of its dependence on the magnitudes $|J_O+J_M|$ and $|J_O-J_M|$.

Furthermore, calculation of the spin energy levels, transition frequencies, and intensities confirms that the spectrum is also determined by $|J_P+J_{O'}|$ and $|J_P-J_{O'}|$. Consequently, interchanging the coupling constants J_P ($J_{AA'}$) and $J_{O'}$ ($J_{XX'}$) leaves the spectrum unaltered (Figure 5, d and e). This interchange is equivalent to swapping the resonance frequencies ν_O (ν_A) and ν_M (ν_X) (Figure 5, f and g).

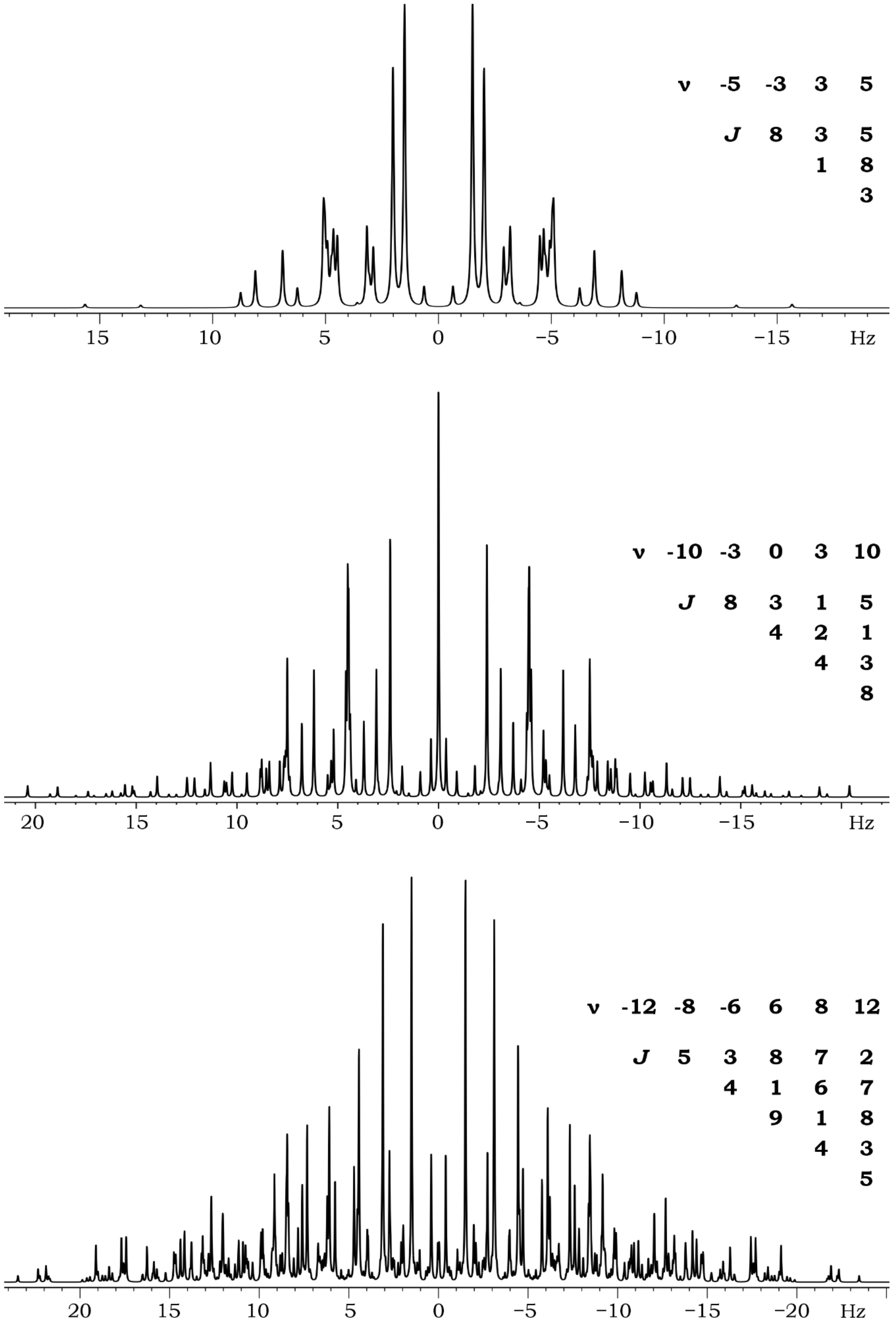
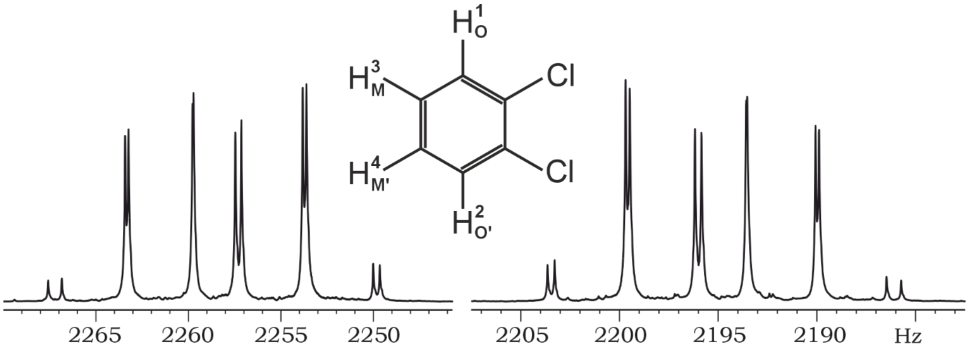


Figure 4. Some examples of theoretically calculated mid-resonance symmetric spectra for 4, 5 and 6-spin systems.



a	1	2	3	4
	2	1	4	3
ν	ν_O	ν_O	ν_M	ν_M
	J	J_P	J_O	J_M
			J_M	J_O
				$J_{O'}$

b	1	3	4	2
	2	4	3	1
ν	ν_O	ν_M	ν_M	ν_O
	J	J_O	J_M	J_P
			$J_{O'}$	J_M
				J_O

c	1	4	3	2
	2	3	4	1
ν	ν_O	ν_M	ν_M	ν_O
	J	J_M	J_O	J_P
			$J_{O'}$	J_O
				J_M

d				
ν	ν_O	ν_M	ν_M	ν_O
	J	J_O	J_M	$J_{O'}$
			J_P	J_M
				J_O

e				
ν	ν_O	ν_M	ν_M	ν_O
	J	J_M	J_O	$J_{O'}$
			J_P	J_O
				J_M

f				
ν	ν_M	ν_O	ν_O	ν_M
	J	J_O	J_M	J_P
			$J_{O'}$	J_M
				J_O

g				
ν	ν_M	ν_O	ν_O	ν_M
	J	J_M	J_O	J_P
			$J_{O'}$	J_O
				J_M

h				
ν	ν_M	ν_O	ν_O	ν_M
	J	J_O	J_M	$J_{O'}$
			J_P	J_M
				J_O

i				
ν	ν_M	ν_O	ν_O	ν_M
	J	J_M	J_O	$J_{O'}$
			J_P	J_O
				J_M

Figure 5. ODCB chemical structure with atom numbering, ^{1}H NMR spectrum (300.13 MHz), and spin system matrices. $J_O={}^3J_{OM}={}^3J_{O'M'}$, $J_{O'}={}^3J_{MM'}$, $J_M={}^4J_{OM'}={}^4J_{O'M}$, $J_P={}^5J_{OO'}$.

Thus, six spin system matrices (Figure 5, b-g) and the two additional permuted matrices (Figure 5, h and i) yield identical spectra. The *J*-coupling part of all these matrices exhibits symmetry about the secondary diagonal.

Considering the equilibration of resonant frequencies, one might note that the resonant frequencies within spin pairs {O_1, O'_2} and {M_3, M'_4} should have been equilibrated about $\nu_0=(\nu_A+\nu_X)/2$. However, it is obvious that this condition cannot be met. Yet, due to the additional spectral invariance under the permutation of ν_O and ν_M, spectral equilibration about ν_0 is still observed.

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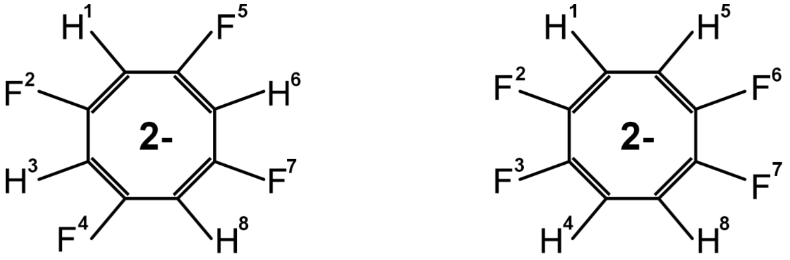
For the case of AA'XX' spin system with chemically equivalent spins, two further equilibration schemes are possible: {ν_A, ν_A, ν_X, ν_X} и {ν_A, ν_X, ν_A, ν_X}. Both yield spectra symmetric about $(\nu_A+\nu_X)/2$, but they are not realized in practice, as they require the equality $J_{AA}=J_{XX}$.

Another family of mid-resonance symmetric spectra originates from spin systems with two groups of magnetically equivalent nuclei A_nB_n (A_nX_n). In general, the *J*-coupling matrix in such systems lacks secondary diagonal symmetry because the coupling constant between the A nuclei can differ from the coupling constant between the B (or X) nuclei. However, the theoretical spectrum is independent of coupling between magnetically equivalent nuclei. The spectrum depends only on the inter-group couplings, which are all equal to the same value J_{AB} (J_{AX}). Thus, the part of the *J*-coupling matrix that contains these coupling constants and defines the spectrum does indeed possess secondary diagonal symmetry.



$$\begin{array}{cccccccc}
\nu_{H1} & \nu_{F2} & \nu_{H3} & \nu_{F4} & \nu_{F5} & \nu_{H6} & \nu_{F7} & \nu_{H8} \\
 & {}^3J_{HF} & {}^4J_{HH} & {}^5J_{HF} & {}^3J_{HF} & {}^4J_{HH} & {}^5J_{HF} & {}^6J_{HH} \\
 & & {}^3J_{HF} & {}^4J_{FF} & {}^4J_{FF} & {}^5J_{HF} & {}^6J_{FF} & {}^5J_{HF} \\
 & & & {}^3J_{HF} & {}^5J_{HF} & {}^6J_{HH} & {}^5J_{HF} & {}^4J_{HH} \\
 & & & & {}^6J_{FF} & {}^5J_{HF} & {}^4J_{FF} & {}^3J_{HF} \\
 & & & & & {}^3J_{HF} & {}^4J_{FF} & {}^5J_{HF} \\
 & & & & & & {}^3J_{HF} & {}^4J_{HH} \\
 & & & & & & & {}^3J_{HF}
\end{array}
\qquad
\begin{array}{cccccccc}
\nu_{H1} & \nu_{F2} & \nu_{F3} & \nu_{H4} & \nu_{H5} & \nu_{F6} & \nu_{F7} & \nu_{H8} \\
 & {}^3J_{HF} & {}^4J_{HF} & {}^5J_{HH} & {}^3J_{HH} & {}^4J'_{HF} & {}^5J_{HF} & {}^6J_{HH} \\
 & & {}^3J_{FF} & {}^4J_{HF} & {}^4J'_{HF} & {}^5J_{FF} & {}^6J_{FF} & {}^5J_{HF} \\
 & & & {}^3J_{HF} & {}^5J_{HF} & {}^6J_{FF} & {}^5J_{FF} & {}^4J'_{HF} \\
 & & & & {}^6J_{HH} & {}^5J_{HF} & {}^4J'_{HF} & {}^3J_{HH} \\
 & & & & & {}^3J_{HF} & {}^4J_{HF} & {}^5J_{HH} \\
 & & & & & & {}^3J_{FF} & {}^4J_{HF} \\
 & & & & & & & {}^3J_{HF}
\end{array}$$

Figure 6. Spin system matrices for 1,3,5,8- and 1,2,5,6-tetrafluoro substituted cyclooctatetraene dianions.

For the 1,3,5-trifluorobenzene, AA'A"XX'X" spin system with C_{3V} symmetry the exhaustive enumeration of all possible *J*-coupling matrix representations was performed. This yielded 120 unique matrices out of 720 (=6!) total permutations, with each unique matrix occurring 6 times, corresponding to the 6 symmetry elements of the C_{3V} point group. Accounting for the symmetry between the H(A) and F(X) spin subsystems further reduces the number of unique matrix types to 60, and none of the resulting matrices exhibited symmetry about the secondary diagonal (Table S1). The absence of this symmetry type is, again, a consequence of the inequality $J_{AA'} \neq J_{XX'}$. Nevertheless, the high symmetry of the spin system results in symmetric signal patterns for the ^{1}H(A) signal about ν_A and for the ^{19}F(X) signal about ν_X.

The eight-spin systems AA'A"A'"XX'X"X'" of the aromatic 1,3,5,8-tetrafluorocyclooctatetraene and 1,2,5,6-tetrafluorocyclooctatetraene dianions possess *J*-coupling matrices that are symmetric about the secondary diagonal (Figure 6) which itself contains the homonuclear coupling constants $J_{AA'}$ and $J_{XX'}$. However, unlike ODCB, the theoretical spectra of these spin systems are not invariant under permutation of the ν_A and ν_X frequencies and, consequently, do not exhibit symmetry about the mid-resonance frequency.

4. Conclusion

The properties that a spin system must possess for its NMR spectrum to be symmetric about the mid-resonance frequency ν_0 have been identified. We believe these findings are of fundamental importance to the theory of spin system spectra.

All theoretical spectra were simulated using the ANATOLIA NMR software (Cheshkov et al., 2018).

5. Supplement: The supplementary material contains a complete listing of all possible *J*-coupling matrix types resulting from spin permutations in 1,3,5-trifluorobenzene (Table S1).

6. Author contribution: D.A.C. and D.O.S. contributed equally to the conceptualization, methodology, investigation, formal analysis, and writing (both original draft and review & editing) of this manuscript.

6. Competing interests: The authors have declared that they have no competing interests.

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