The Origin of Mirror Symmetry in High-Resolution NMR Spectra

Dmitry A. Cheshkov[1], Dmitry O. Sinitsyn[2]
[1]State Scientific Research Institute of Chemistry and Technology of Organoelement Compounds, 38 Shosse Entuziastov, 105118 Moscow, Russia
[2]Russian Center of Neurology and Neurosciences. 80 Volokolamskoe shosse, 125367 Moscow, Russia
E-mail: dcheshkov@gmail.com[1], d_sinitsyn@mail.ru[2]

Moscow, 2025

Abstract

A correlation between the symmetry of high-field 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: 1) the resonan~~t~~ce frequencies of the spins must be symmetrically positioned about ν_0, and 2) ~~the *J*-coupling matrix must be symmetric about the secondary diagonal.~~ there must exist at least one spin ordering with a monotonic increase (or decrease) of resonance frequencies such that the spectrum is invariant under reflection of the *J*-coupling matrix about its anti-diagonal (one way to satisfy this condition is for the *J*-coupling matrix to be explicitly persymmetric). 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

This study investigates the spectral properties of the high-field (or ‘high-resolution’ in the classical sense) spin Hamiltonian under the condition $\nu \gg J$. However, for weak magnetic fields, comparable to or below the Earth's field, the following reasoning becomes inapplicable.

Some high-resolution high-field NMR spectra exhibit symmetry, which can be reasonably categorized into two types: (1) the symmetry of a first-order multiplet about its resonan~~t~~ce frequency, and (2) the symmetry of the entire spectrum of a spin system about its spectral center of mass (mirror-symmetric spectrum), as observed, for example, in AB (Pople et al., 1959, p.122; Hoffman et al., 1971, p.57; Gunter, 2013, p.166), A_nB_n (Corio, 1966; p.254), 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 resonan~~t~~ce frequency, regardless of the nuclei spin quantum numbers.

The second type of symmetry is an intrinsic property of the entire spin system. For instance, the spectra of AB (AX), A_nB_n (A_nX_n) 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 mirror-symmetric ~~about (ν_H+ν_F)/2~~, however, this is not observed in practice (Cheshkov and Sinitsyn, 2020).

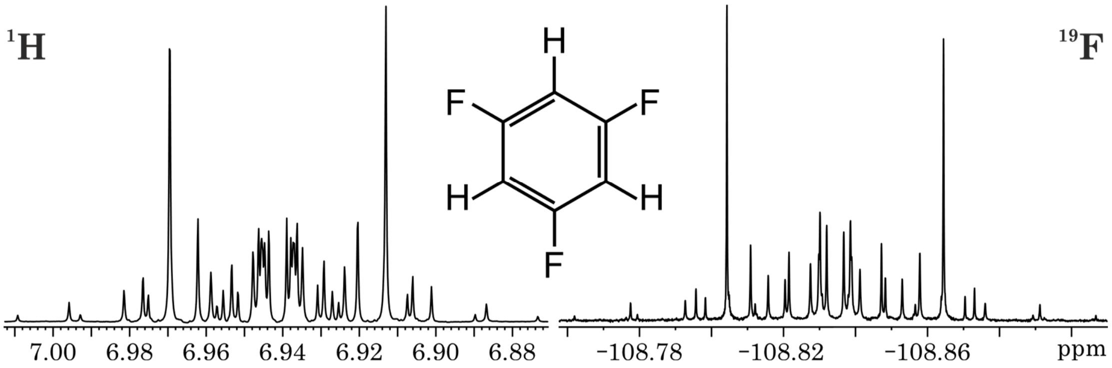


Figure 1. ^{1}H (300.13 MHz) and ^{19}F (282.40 MHz) spectra of 1,3,5-trifluorobenzene.

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 resonan~~t~~ce frequencies. It is readily apparent that the spectra of these spin systems are mirror images of each other. Inverting the order of the resonan~~t~~ce frequencies while maintaining the differences between them produces a reflected spectrum, which can be thought of as reversing the direction of the frequency axis.

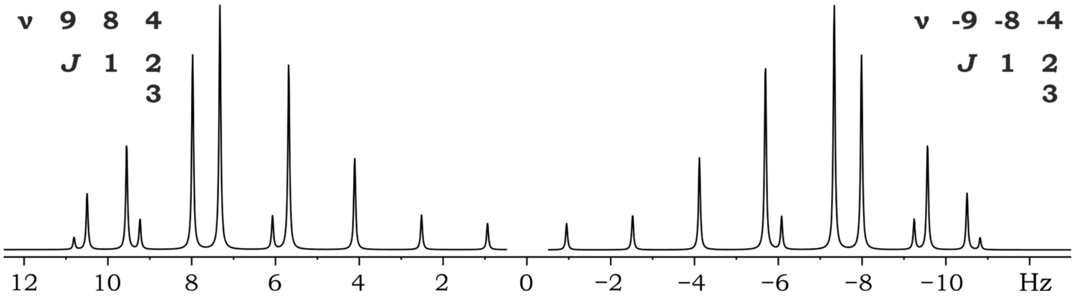


Figure 2. Spectra of two ABC spin systems, with different signs of resonan~~t~~ce frequencies.

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 resonan~~t~~ce frequencies:

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

It can be shown that reversing the sequence of resonan~~t~~ce frequencies results in a reflection of the J-coupling matrix about its ~~secondary~~ anti-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 resonan~~t~~ce frequencies are symmetric about the mid-resonance frequency (ν_0) and the J-coupling matrix is symmetric about the ~~secondary~~ anti-diagonal, i.e. persymmetric (or even bisymmetric), then reversing the order of the resonan~~t~~ce frequencies will not alter the spectrum (Figure 3). Moreover, the spectrum itself will be symmetric about ν_0. Thus, a persymmetric J-coupling matrix ~~symmetric about the secondary diagonal~~ remains invariant under a reversal of the spin order. The ~~secondary~~ anti-diagonal itself contains the coupling constants between spin pairs that are interchanged upon order reversal, i.e., the first and the last, the second and the penultimate, and so forth. The resonan~~t~~ce frequencies of these spin~~s~~ pairs must be symmetrically arranged about the mid-resonance frequency ν_0, in other words, they must be "equilibrated".

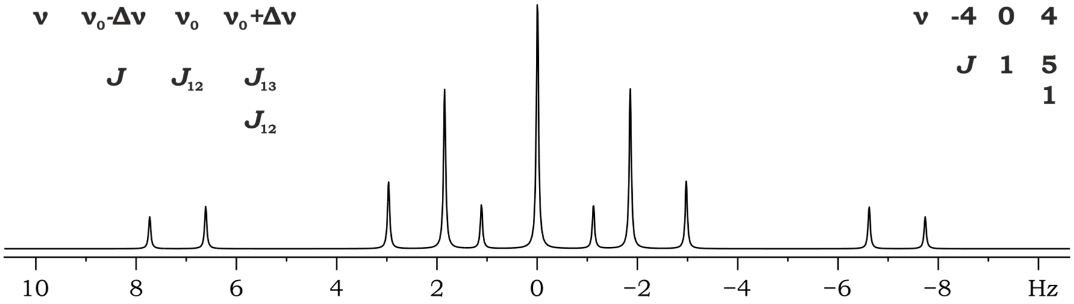


Figure 3. Mirror-symmetry ~~S~~spectrum of ABC spin system ~~with about mid-resonance frequency~~.

3. Results and discussion

Below, in Figure 4, we present several theoretically calculated mirror-symmetric spectra ~~that are mirror-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~~

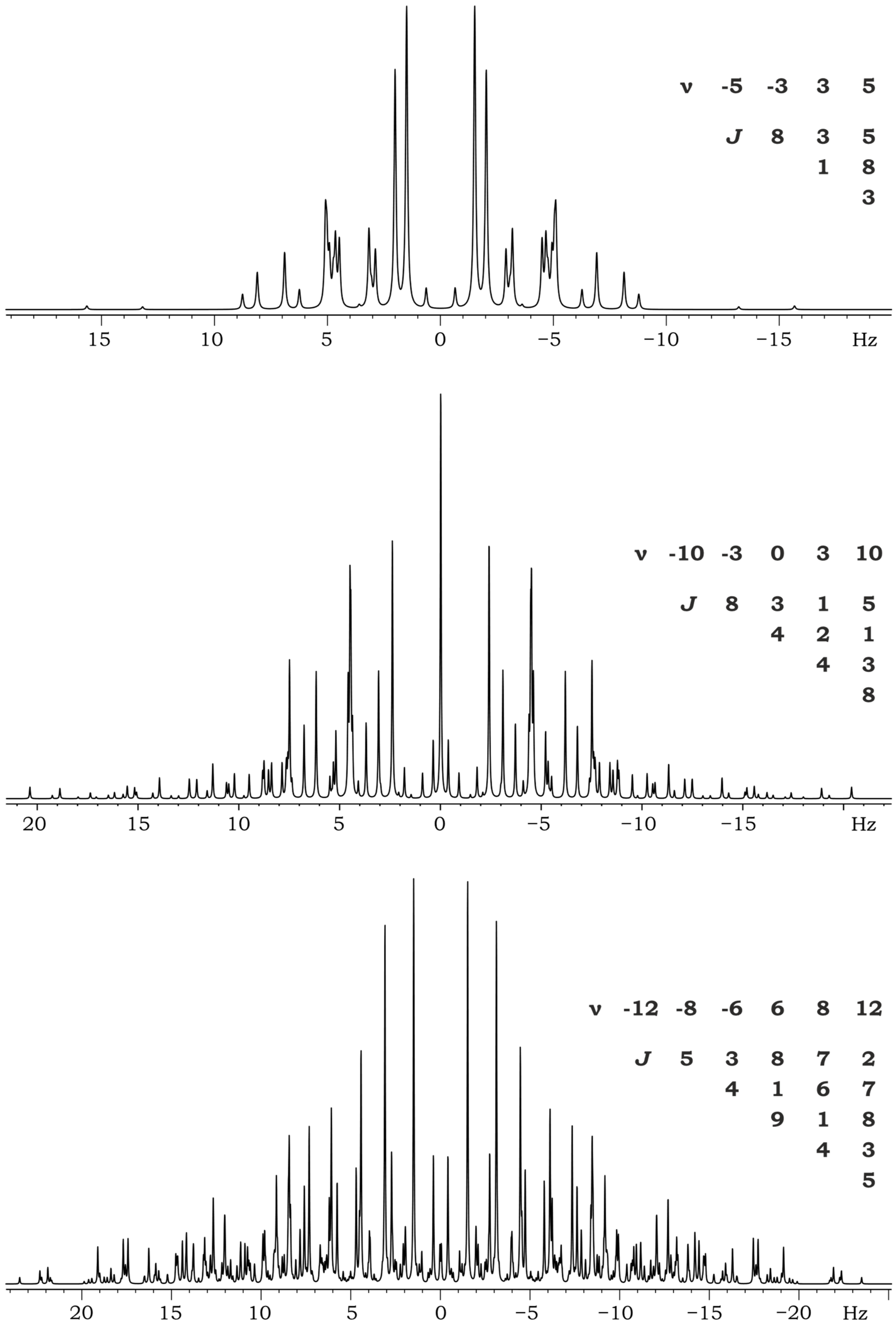
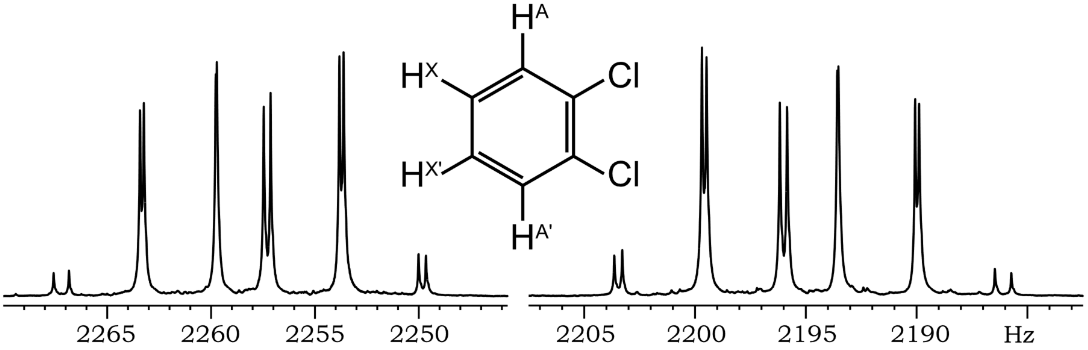


Figure 4. Some examples of theoretically calculated ~~mid-resonance~~ mirror-symmetric spectra for 4, 5 and 6-spin systems.



a	A	A'	X	X'
ν	ν_A	ν_A	ν_X	ν_X
J		$J_{AA'}$	J_{AX}	$J_{AX'}$
			$J_{AX'}$	J_{AX}
				$J_{XX'}$

b				
ν	ν_A	ν_A	ν_X	ν_X
J		$J_{XX'}$	J_{AX}	$J_{AX'}$
			$J_{AX'}$	J_{AX}
				$J_{AA'}$

c	A	A'	X'	X
ν	ν_A	ν_A	ν_X	ν_X
J		$J_{AA'}$	$J_{AX'}$	J_{AX}
			J_{AX}	$J_{AX'}$
				$J_{XX'}$

d				
ν	ν_A	ν_A	ν_X	ν_X
J		$J_{XX'}$	$J_{AX'}$	J_{AX}
			J_{AX}	$J_{AX'}$
				$J_{AA'}$

e				
ν	ν_X	ν_X	ν_A	ν_A
J		$J_{AA'}$	J_{AX}	$J_{AX'}$
			$J_{AX'}$	J_{AX}
				$J_{XX'}$

f	X	X'	A	A'
ν	ν_X	ν_X	ν_A	ν_A
J		$J_{XX'}$	J_{AX}	$J_{AX'}$
			$J_{AX'}$	J_{AX}
				$J_{AA'}$

g				
ν	ν_X	ν_X	ν_A	ν_A
J		$J_{AA'}$	$J_{AX'}$	J_{AX}
			J_{AX}	$J_{AX'}$
				$J_{XX'}$

h	X	X'	A'	A
ν	ν_X	ν_X	ν_A	ν_A
J		$J_{XX'}$	$J_{AX'}$	J_{AX}
			J_{AX}	$J_{AX'}$
				$J_{AA'}$

Figure 5. ODCB chemical structure with spins labeling ~~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=$^5J_{OO'}$.~~

3.1. Spectral Mirror Symmetry of AA'XX' (AA'BB') and A_nX_n (A_nB_n) Spin Systems

It is well-established that o-dichlorobenzene (ODCB) exhibits a ~~mid-resonance~~ mirror-symmetric~~al~~ ^{1}H NMR spectrum, corresponding~~ed~~ to an AA'XX' spin system (Figure 5).

~~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).~~

~~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.~~

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

From the algebraic properties of the AA'XX' spin system Hamiltonian, it follows that the spectrum depends only on the sums and absolute differences of the coupling constant pairs $\{J_{AA'}$ and $J_{XX'}\}$ and $\{J_{AX}$ and $J_{AX'}\}$. Consequently, the spectrum is invariant under permutation of the values within these pairs. Crucially, interchanging $J_{AA'}$ and $J_{XX'}$ is equivalent to interchanging the resonance frequencies ν_A and ν_X. Because the spectrum is fully determined by two resonance frequencies and remains invariant under their permutation (i.e., reversal of the resonance-frequency order), it must possess mirror symmetry.

The existence of three independent permutations within parameter pairs gives rise to eight distinct combinations of spin-system parameters corresponding to the same NMR spectrum (Fig. 5). Four of these combinations can be represented as a result of spin reordering (Fig. 5, a, c, f, h), while the others contain "non-physical" permutations of parameter values. Notably, none of these *J*-coupling matrices possess symmetry with respect to the anti-diagonal. However, *J*-coupling matrix **b** (Fig.5) is the anti-diagonal reflection of matrix **a** (Fig.5). This observation leads to more general criteria for mirror symmetry:

If there exists a spin ordering in which resonance frequencies monotonically ordered increasingly (or decreasingly) and in this order the spectrum is invariant under the reflection of the *J*-coupling matrix about the anti-diagonal, then the spectrum will be mirror-symmetric.

The coupling constants that map onto each other above and below the anti-diagonal can either be equal or form "balanced pairs" (actually, balance each other). In fact, in the AA'XX' (AA'BB') spin system, the constants $J_{AA'}$ and $J_{XX'}$ should be considered as “equivalent” under anti-diagonal reflection. Therefore, when analyzing symmetric spin systems with chemically equivalent but magnetically non-equivalent spin groups, one must first identify all such balanced pairs of coupling constants and treat them as equivalent in assessing the symmetry of the *J*-coupling matrix.

Another family of ~~mid-resonance~~ mirror-symmetric spectra originates from spin systems with two groups of magnetically equivalent nuclei A_nX_n (A_nB_n), the mirror symmetry of which was proved by Corio (Corio, 1966; p.254). In general, the *J*-coupling matrix in such systems lacks ~~secondary diagonal~~ persymmetry because the coupling constant between the A nuclei can differ from the coupling constant between the X (or B) 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_{AX} (J_{AB}). Thus, the part of the J-coupling matrix that contains these coupling constants and defines the spectrum does indeed possess ~~secondary diagonal~~ persymmetry.

~~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 $J_{\mathrm{AA'}} \neq J_{\mathrm{XX'}}$. 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}.~~

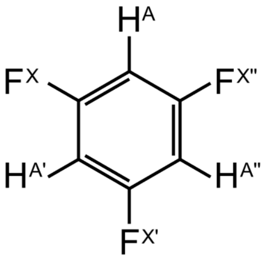
~~The eight-spin AA'A"A'''XX'X"X''' systems of the aromatic 1,3,5,8- and 1,2,5,6-tetrafluorocyclooctatetraene dianions possess J-coupling matrices that are symmetric about the secondary diagonal (Figure 6) which itself contains the homonuclear coupling constants $J_{\mathrm{AA'}}$ and $J_{\mathrm{XX'}}$.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

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

3.2. Spectral Asymmetry of Some Symmetric [A'X']$_{\mathrm{n}}$ ([A'B']$_{\mathrm{n}}$) Spin Systems

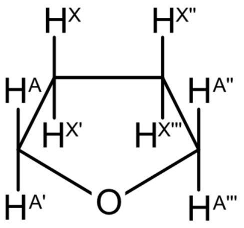
Five representative examples of highly symmetric [A'X']$_{\mathrm{n}}$ spin systems are shown in Figure 6. The condition of resonance frequency balance requires ordering spins by their resonance frequencies in ascending or descending order. However, within groups of chemically equivalent spins an additional ordering is required. The chemical equivalence of spin groups, determined by spin permutation symmetry, results in the topological equivalence of the coupling networks of the [A']$_{\mathrm{n}}$ and [X']$_{\mathrm{n}}$ subsystems. Therefore, the most symmetric form of the J-coupling matrix can be achieved by a consistent ordering of chemically equivalent spins from different groups such that the equality $J_{\mathrm{AX}} = J_{\mathrm{A'X'}} = J_{\mathrm{A''X''}} = J_{\mathrm{A'''X'''}}$ holds. For 1,3,5-trifluorobenzene and the 1,3,5,7-tetrafluorosubstituted cyclooctatetraene dianion, this ordering coincides with the molecular canonical topological order. Accordingly, in all examples of J-coupling matrices presented in Fig. 6, the chemically equivalent spins were ordered using the described scheme.

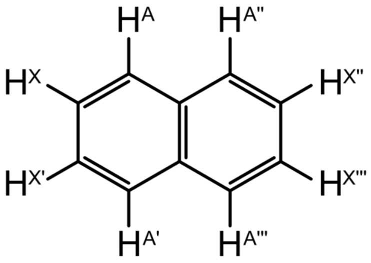
D_3-symmetric [A'X']$_3$ spin system of 1,3,5-trifluorobenzene

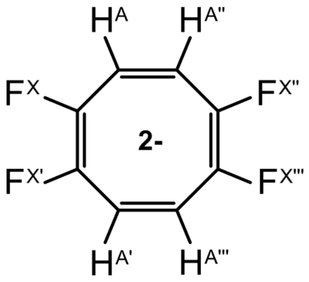


	A	A'	A''	X	X'	X''
ν	ν_A	ν_A	ν_A	ν_X	ν_X	ν_X
J		$J_{AA'}$	$J_{AA'}$	J_{AX}	$J_{AX'}$	J_{AX}
			$J_{AA'}$	J_{AX}	J_{AX}	$J_{AX'}$
				$J_{AX'}$	J_{AX}	J_{AX}
					$J_{XX'}$	$J_{XX'}$
						$J_{XX'}$

C_{2V}-symmetric [A'X']$_4$ spin systems

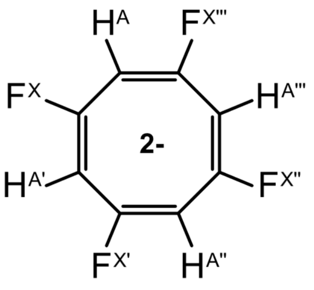






	A	A'	A''	A'''	X	X'	X''	X'''
ν	ν_A	ν_A	ν_A	ν_A	ν_X	ν_X	ν_X	ν_X
J		$J_{AA'}$	$J_{AA''}$	$J_{AA'''}$	J_{AX}	$J_{AX'}$	$J_{AX''}$	$J_{AX'''}$
			$J_{AA'''}$	$J_{AA''}$	$J_{AX'}$	J_{AX}	$J_{AX'''}$	$J_{AX''}$
				$J_{AA'}$	$J_{AX''}$	$J_{AX'''}$	J_{AX}	$J_{AX'}$
					$J_{AX'''}$	$J_{AX''}$	$J_{AX'}$	J_{AX}
						$J_{XX'}$	$J_{XX''}$	$J_{XX'''}$
							$J_{XX'''}$	$J_{XX''}$
								$J_{XX'}$

D_4-symmetric [A'X']$_4$ spin system



	A	A'	A''	A'''	X	X'	X''	X'''
ν	ν_A	ν_A	ν_A	ν_A	ν_X	ν_X	ν_X	ν_X
J		$J_{AA'}$	$J_{AA''}$	$J_{AA'}$	J_{AX}	$J_{AX'}$	$J_{AX'}$	J_{AX}
			$J_{AA'}$	$J_{AA''}$	J_{AX}	J_{AX}	$J_{AX'}$	$J_{AX'}$
				$J_{AA'}$	$J_{AX'}$	J_{AX}	J_{AX}	$J_{AX'}$
					$J_{AX'}$	$J_{AX'}$	J_{AX}	J_{AX}
						$J_{XX'}$	$J_{XX''}$	$J_{XX'}$
							$J_{XX'}$	$J_{XX''}$
								$J_{XX'}$

Figure 6. Some examples of symmetric [A'X']$_n$ ([A'B']$_n$) spin systems.

In all considered spin systems, the *J*-coupling matrices exhibit high symmetry, with the inter-group coupling blocks being persymmetric. Unlike the AA'BB' case, due to the algebraic properties of the Hamiltonian, there is no balancing of topologically equivalent homonuclear coupling constant pairs in these systems. Specifically, the constant pairs $\{J_{AA'}, J_{XX'}\}$, $\{J_{AA''}, J_{XX''}\}$, and $\{J_{AA'''}, J_{XX'''}\}$ do not form balanced pairs. Consequently, the spectra are not invariant under the permutation of constants within these pairs nor under the permutation of ν_A and ν_X, and therefore do not possess mirror symmetry, despite the high symmetry of the spin systems themselves.

Nevertheless, in the case of 1,3,5-trifluorobenzene, the high symmetry of the $[A'X']_3$ spin system results in symmetric signal patterns for the $^1H(A)$ signal about ν_A and for the $^{19}F(X)$ signal about ν_X separately.

4. Conclusion

The properties that a spin system must possess for its high-field 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). For an in-depth theoretical analysis of spectral mirror symmetry, see DOI: 10.13140/RG.2.2.19473.90724.

~~**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).~~

5~~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.

7. Acknowledgments: The authors thank Dr. Alexey S. Kiryutin for helpful discussion.

8. References

Cheshkov, D. A. and Sinitsyn, D. O., Total lineshape analysis of high-resolution NMR spectra, in: Annual Reports on NMR Spectroscopy, vol. 100, edited by: Webb, G. A., Academic Press, 61-96, https://doi.org/10.1016/bs.arnmr.2019.11.001, 2020.

Cheshkov, D. A., Sheberstov, K. F., Sinitsyn, D. O., and Chertkov, V. A.: ANATOLIA: NMR software for spectral analysis of total lineshape, Magn. Reson. Chem., 56, 449-457, https://doi.org/10.1002/mrc.4689, 2018. https://github.com/dcheshkov/ANATOLIA/

Gunter H.: NMR Spectroscopy: basic principles, concepts and applications in chemistry, 3rd ed., Wiley-VCH, ISBN: 978-3-527-33000-3, 2013.

Hoffman, R. A., Forsen, S., Gestblom, B., Analysis of NMR spectra – A guide for chemists in NMR Basic Principles and Progress, vol. 5, edited by: Diehl, P., Fluck, E., Kosfeld, R., Springer, Berlin, Heidelberg, N.Y., https://doi.org/10.1007/978-3-642-65205-9, 1971.

Corio, P. L.: Structure of High-Resolution NMR spectra, Academic Press, ISBN: 978-0124142831, 1966.

Pople, J. A., Schneider, W. G., Bernstein, H. J., High Resolution Nuclear Magnetic Resonance, McGraw-Hill, ISBN: 978-0070505162, 1959.