

Symmetry Properties of Indirect Nuclear Spin–Spin Coupling Tensors: First Principles Results for ClF₃ and OF₂

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Indirect spin–spin coupling tensors, \mathbf{J} , are of widespread importance in NMR spectroscopy. For example, a great deal of recent experimental and theoretical work has focused on the characterization of \mathbf{J} couplings observed across hydrogen bonds in proteins, RNA, and related model compounds.¹ Much work has focused solely on the isotropic portion of the \mathbf{J} tensor; however, this tensor is composed of nine elements. Given the fundamental importance of \mathbf{J} coupling, it is of utmost interest to more fully understand the influence of local molecular symmetry on the properties of the *complete* coupling tensor.

The original theory of \mathbf{J} coupling was advanced by Ramsey.² As described elsewhere, \mathbf{J} may be decomposed into three parts: isotropic (J_{iso}), symmetric (\mathbf{J}^{sym}), and antisymmetric ($\mathbf{J}^{\text{antisym}}$).^{3–6} The isotropic portion is defined as one-third the trace of the tensor. The symmetric portion of the tensor, which is constructed from \mathbf{J} and its transpose,

$$\mathbf{J}^{\text{sym}} = (\mathbf{J} + \mathbf{J}^t)/2 - J_{\text{iso}}\mathbf{1} \quad (1)$$

may possess up to five independent elements. In its principal axis system (PAS), $\mathbf{J}^{\text{sym}} + J_{\text{iso}}\mathbf{1}$ is diagonal and has up to three independent elements, J_{11} , J_{22} , and J_{33} , ordered according to the convention $|J_{33} - J_{\text{iso}}| \geq |J_{11} - J_{\text{iso}}| \geq |J_{22} - J_{\text{iso}}|$.⁷ The diagonalization of $\mathbf{J}^{\text{sym}} + J_{\text{iso}}\mathbf{1}$ yields its orientation in the molecular framework, defined by three Euler angles. The anisotropy, ΔJ , of the tensor is defined as^{4,6,7}

$$\Delta J = J_{33} - (J_{11} + J_{22})/2 \quad (2)$$

and the asymmetry as⁷

$$\eta = (J_{22} - J_{11})/(J_{33} - J_{\text{iso}}) \quad (3)$$

where $0 \leq \eta \leq 1$. Typically, the asymmetry of \mathbf{J} has been ignored or it has been assumed that \mathbf{J} possesses axial symmetry, that is, $\eta = 0$. While this is true for couplings that involve nuclei lying

on a C_n ($n \geq 3$) axis, in the general case there is no basis to arrive at this conclusion.⁵

The antisymmetric portion of \mathbf{J} may have up to three independent elements and is defined as

$$\mathbf{J}^{\text{antisym}} = (\mathbf{J} - \mathbf{J}^t)/2 \quad (4)$$

It has long been known that for powdered samples containing tightly coupled (AB) spin systems observed under conditions of magic-angle spinning, $\mathbf{J}^{\text{antisym}}$ should affect the observed spectrum.⁸ Nevertheless, no experimental determinations of $\mathbf{J}^{\text{antisym}}$ exist.

Ab initio methods for the calculation of \mathbf{J} have been recently reviewed.⁹ Recent studies have established the success of multiconfigurational self-consistent field (MCSCF) methods with large basis sets for predicting both J_{iso} and ΔJ in small molecules.^{10–12} Here, we apply these methods to determine the *complete* coupling tensors $\mathbf{J}^{(35\text{Cl}, 19\text{F}_{\text{eq}})}$, $\mathbf{J}^{(35\text{Cl}, 19\text{F}_{\text{ax}})}$, and $\mathbf{J}^{(19\text{F}_{\text{eq}}, 19\text{F}_{\text{ax}})}$ for chlorine trifluoride, ClF₃, and $\mathbf{J}^{(19\text{F}, 17\text{O})}$ for oxygen difluoride, OF₂. Atomic coordinates used in the calculations were taken from the experimental equilibrium geometries for ClF₃¹³ and OF₂.¹⁴ All MCSCF calculations were carried out using DALTON¹⁵ on an IBM RS/6000 workstation. We have carried out a number of calculations using complete active space (CAS) wave functions and restricted active space (RAS) wave functions with a range of basis sets of the cc-pVXZ, aug-cc-pVXZ, and cc-pCVXZ types ($X = \text{D, T, Q}$).¹⁶ The highest-quality results are presented in Table 1.

Experimental isotropic coupling constants are available for comparison with the calculations: $J_{\text{iso}}^{(35\text{Cl}, 19\text{F})}$ in ClF₃ is ± 260 Hz¹⁷ (a weighted average of the chlorine coupling to the two nonequivalent types of fluorine); $J_{\text{iso}}^{(19\text{F}_{\text{eq}}, 19\text{F}_{\text{ax}})}$ in ClF₃ is ± 403

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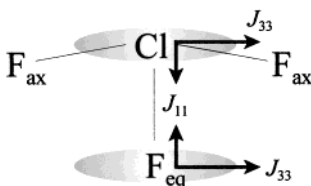
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Table 1: Calculated Indirect Spin–Spin Coupling Tensors in Chlorine Trifluoride and Oxygen Difluoride

	$J_{\text{iso}}/$ Hz	$\Delta J/$ Hz	η	$J_{11}/$ Hz	$J_{22}/$ Hz	$J_{33}/$ Hz	$ J_{\text{antisym}} /$ Hz ^a
$\mathbf{J}({}^{35}\text{Cl}, {}^{19}\text{F}_{\text{eq}})$ in ClF_3 ^b	195	769	0.19	−109	−13	708	0
$\mathbf{J}({}^{35}\text{Cl}, {}^{19}\text{F}_{\text{ax}})$ in ClF_3 ^b	164	633	0.66	−185	92	586	150 ^c
$\mathbf{J}({}^{19}\text{F}_{\text{eq}}, {}^{19}\text{F}_{\text{ax}})$ in ClF_3 ^b	404	720	0.40	68	260	884	292 ^c
$\mathbf{J}({}^{19}\text{F}, {}^{17}\text{O})$ in OF_2 ^d	−309	−933	0.42	133	−129	−931	109 ^e

^a We report the absolute value of the nonzero antisymmetric component of the coupling tensor. Note that for two coupled nuclei A and B, $\mathbf{J}_{\text{antisym}}(\text{A}, \text{B}) = -\mathbf{J}_{\text{antisym}}(\text{B}, \text{A})$. ^b MCSCF calculation using a RAS wave function (orbital symmetries A_1, B_2, B_1, A_2): 5210 (inactive), 0000 (RAS1), 6431 (RAS2), 3221 (RAS3); up to two electrons were allowed to be excited into RAS3; cc-pVQZ basis set (224 orbitals); total MCSCF energy: −757.970183623 hartrees. ^c This value is the $|J_{\text{yz}}| = |J_{\text{yx}}|$ component of the \mathbf{J} tensor in a coordinate system where the molecule lies in the xy plane with the unique Cl–F_{eq} bond along the y axis. ^d MCSCF calculation using a RAS wave function (orbital symmetries A_1, B_2, B_1, A_2): 2010 (inactive), 0000 (RAS1), 4231 (RAS2), 2121 (RAS3); up to two electrons were allowed to be excited into RAS3; cc-pCVQZ basis set (252 orbitals); total MCSCF energy: −273.817988604 hartrees. ^e This value is the $|J_{\text{yz}}| = |J_{\text{yx}}|$ component of the \mathbf{J} tensor in a coordinate system where the molecule lies in the yz plane with its C_2 axis along the y axis.

**Figure 1.** Orientation of the symmetric portion of the $\mathbf{J}({}^{35}\text{Cl}, {}^{19}\text{F}_{\text{eq}})$ tensor in ClF_3 . Note that the largest component, J_{33} , is perpendicular to the Cl–F_{eq} bond axis. J_{22} is perpendicular to the plane of the molecule.

Hz;^{17–18} $J_{\text{iso}}({}^{19}\text{F}, {}^{17}\text{O})$ in OF_2 is $\pm(300 \pm 30)$ Hz.¹⁹ Our calculations accurately reproduce the latter two values (+404 Hz and −309 Hz, respectively) and provide the sign of these two couplings. For the Cl–F couplings, we obtain a calculated, weighted-average value of 174 Hz, which is less than the experimental value by 86 Hz. We note, however, that the dual-spin probe relaxation technique used to determine experimentally the average $J_{\text{iso}}({}^{35}\text{Cl}, {}^{19}\text{F})$ for ClF_3 relies on several assumptions, which makes the method subject to errors. Furthermore, intermolecular interactions could be significant.¹⁸

For all of the couplings reported here, the \mathbf{J} tensor exhibits a significant asymmetry, η . The $\mathbf{J}({}^{35}\text{Cl}, {}^{19}\text{F}_{\text{eq}})$ tensor in ClF_3 is expected to exhibit the lowest asymmetry because the internuclear vector lies in a mirror plane and on a C_2 axis. We report a value of 0.19. In a diatomic molecule, by comparison, the internuclear vector lies on a C_∞ axis and \mathbf{J} is axially symmetric. The $\mathbf{J}({}^{35}\text{Cl}, {}^{19}\text{F}_{\text{ax}})$ tensor in ClF_3 , for which the internuclear vector lies in a mirror plane, exhibits an asymmetry of 0.66. The situation is similar in OF_2 , where $\eta = 0.42$ for $\mathbf{J}({}^{19}\text{F}, {}^{17}\text{O})$. Thus, except for spin pairs in symmetric environments, ΔJ cannot be defined simply as $J_{\parallel} - J_{\perp}$.

When a coupling tensor exhibits asymmetry, it is important to specify its orientation with respect to the molecular framework. Shown in Figure 1 is the orientation of the symmetric portion of $\mathbf{J}({}^{35}\text{Cl}, {}^{19}\text{F}_{\text{eq}})$. For both $\mathbf{J}({}^{35}\text{Cl}, {}^{19}\text{F}_{\text{eq}})$ and $\mathbf{J}({}^{35}\text{Cl}, {}^{19}\text{F}_{\text{ax}})$, J_{33} is oriented perpendicular (or approximately perpendicular) to the vector connecting the two coupled nuclei. In contrast, for $\mathbf{J}({}^{35}\text{Cl}, {}^{19}\text{F}_{\text{eq}})$, the magnitude of the coupling along the Cl–F bond is only −109 Hz, or about 56% of J_{iso} . Such an orientation is consistent with the calculated and experimental orientation for chlorine monofluoride.¹⁰ For OF_2 , the calculations indicate that

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Table 2: Percentage Contributions of the Various Coupling Mechanisms to J_{iso} in ClF_3 and OF_2 ^a

	DSO/%	PSO/%	FC/%	SD/%
$J_{\text{iso}}({}^{35}\text{Cl}, {}^{19}\text{F}_{\text{eq}})$ in ClF_3	0.13	107	−93	86
$J_{\text{iso}}({}^{35}\text{Cl}, {}^{19}\text{F}_{\text{ax}})$ in ClF_3	0.12	39	31	29
$J_{\text{iso}}({}^{19}\text{F}_{\text{eq}}, {}^{19}\text{F}_{\text{ax}})$ in ClF_3	−0.01	30	15	55
$J_{\text{iso}}({}^{19}\text{F}, {}^{17}\text{O})$ in OF_2	0.13	82	−47	65

^a Computational methods are the same as those given in the footnotes to Table 1.

the J_{33} component of $\mathbf{J}({}^{19}\text{F}, {}^{17}\text{O})$ makes an angle of 44° with the molecular C_2 axis, such that J_{33} is approximately perpendicular (85°) to the internuclear vector. J_{22} is perpendicular to the molecular plane. Such an orientation is consistent with those observed in ClF_3 and ClF .

Although the existence of antisymmetric elements of nuclear magnetic shielding tensors, σ , has been established,²⁰ experimental evidence for $\mathbf{J}_{\text{antisym}}$ has never been demonstrated. The results shown in Table 1 indicate that not only do antisymmetric components of \mathbf{J} exist, but *there is no reason to presume that these components will be small compared to their symmetric counterparts*. For the couplings studied here, the calculated antisymmetric component of \mathbf{J} is of the same order of magnitude as the principal components of \mathbf{J}^{sym} . This is in contrast to statements made by Abragam.^{21–22} Only for $\mathbf{J}({}^{35}\text{Cl}, {}^{19}\text{F}_{\text{eq}})$ in ClF_3 are all of the antisymmetric components zero; this arises due to the local C_{2v} symmetry, in agreement with the symmetry rules developed by Buckingham et al.^{4,23}

The existence of both asymmetry and antisymmetry in the \mathbf{J} tensor is a direct consequence of significant non-Fermi contact (FC) coupling mechanisms. Shown in Table 2 are the relative contributions of each coupling mechanism to the total isotropic coupling constants for ClF_3 and OF_2 . Many researchers make the assumption that \mathbf{J} couplings are dominated by the FC mechanism. While this is true for selected pairs of nuclei in certain environments, in general all of the coupling mechanisms, spin–orbit (diamagnetic, DSO and paramagnetic, PSO), spin-dipolar (SD), and FC, may play an important role (Table 2). We note specifically the importance of the SD mechanism, which has been neglected in many recent DFT calculations of \mathbf{J} .

In summary, results from high-level ab initio calculations on ClF_3 and OF_2 have provided important information about the symmetry properties of the \mathbf{J} tensor and confirmed some of the predictions of Buckingham et al.^{4,23} which relate the local molecular symmetry to the number of unique elements in the \mathbf{J} tensor. Given the absence of experimental determinations of $\mathbf{J}_{\text{antisym}}$, MCSCF calculations are well-suited to predict this property and should be useful in selecting appropriate candidates for experimental work. It is hoped that the present study will encourage workers to carefully consider all contributions to the total \mathbf{J} tensor.

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