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Periodic Trends in Indirect Nuclear Spin−Spin Coupling Tensors: Relativistic Density Functional Calculations for Interhalogen Diatomics

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Abstract: There have been significant advances in the calculation and interpretation of indirect nuclear spin−spin coupling (**J**) tensors during the past few years; however, much work remains to be done, especially for molecules containing heavy atoms where relativistic effects may play an important role. Many **J** tensors cannot be explained based solely on a nonrelativistic Fermi-contact mechanism. In the present work, the relativistic zeroth-order regular approximation density-functional (ZORA-DFT) implementation for the calculation of **J** has been applied to the complete series of homonuclear and heteronuclear diatomic halogen molecules: F_2, Cl_2, Br_2, I_2, At_2, ClF, BrF, IF, ClBr, ClI, and BrI. For all of these compounds, the reduced isotropic coupling constant (K_{iso}) is positive and the reduced anisotropic coupling constant (ΔK) is negative. With the exception of molecular fluorine, the magnitudes of K_{iso} and ΔK are shown to increase linearly with the product of the atomic numbers of the coupled nuclei. ZORA-DFT calculations of **J** for F_2 and ClF are in excellent agreement with the results obtained from multiconfigurational self-consistent-field calculations. The relative importance of the various coupling mechanisms is approximately constant for all of the compounds, with the paramagnetic spin−orbit term being the dominant contributor to K_{iso}, at approximately 70−80%. Available experimental stimulated resonant Raman spectroscopy data are exploited to extract the complete $\mathbf{J}(^{127}I,^{127}I)$ tensor for iodine in two rotational states. The dependence of K_{iso} and ΔK on bond length and rovibrational state is investigated by using calculated results in combination with available experimental data. In addition to providing new insights into periodic trends for **J** coupling tensors, this work further demonstrates the utility of the ZORA-DFT method and emphasizes the necessity of spin−orbit relativistic corrections for **J** calculations involving heavy nuclei.

Introduction

Indirect nuclear spin−spin coupling (**J**) tensors are of paramount importance in nuclear magnetic resonance (NMR) spectroscopy.[1,2] Recent applications have involved the detection of **J** couplings across hydrogen bonds in nucleic acid base pairs[3,4] and proteins,[5,6] and the characterization of inorganic semiconducting materials.[7,8] As for the nuclear magnetic shielding interaction, the **J** coupling interaction is orientation-dependent, and wholly described by a second-rank tensor. The symmetric part of the **J** tensor may be decomposed into two parts: an isotropic part described by the coupling constant J_{iso}, which is familiar from solution NMR, and an anisotropic part described by ΔJ.[9−11] For molecules with high symmetry such as diatomics, ΔJ may be written as the difference between the coupling along the bond axis and the coupling perpendicular to the bond axis, i.e., $J_{\|} - J_{\perp}$.

Recently, there have been substantial improvements in first-principles calculations of **J** couplings.[12−22] Our ongoing ab initio study of **J** tensors[23−26] has focused on examining periodic trends

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and the relative importance of the various coupling mechanisms in small systems using complete active space and restricted active space wave functions as part of the multiconfigurational linear response module in the Dalton Quantum Chemistry program.[27] While these ab initio techniques have yielded results which are in excellent agreement with available experimental data, they are time-consuming and limited to small systems composed of relatively light atoms. Density functional theory (DFT) methods for calculating NMR properties allow for relatively large or heavy systems to be treated more rapidly.[28] Malkina et al. have described their implementation of a DFT method for calculating **J** tensors using Gaussian-type orbitals.[29] An alternative implementation was subsequently applied with Slater-type basis sets to demonstrate the feasibility of calculating **J** couplings to transition metal nuclei.[30,31] Recently, several new DFT techniques for calculating **J** tensors have been developed, including a zeroth-order regular approximation (ZORA) DFT method.[32−36] The more recent implementations have included the spin-dipolar (SD) term in the calculations; this term, which is known to be important in many cases, had been neglected in earlier DFT treatments.

In the present work, we extend our study of periodic trends and properties of **J** tensors in diatomics[23] to examine heavier systems where relativistic effects play an important role. For this purpose, the ZORA-DFT method[33,34] has been employed. Previous ZORA-DFT results have reinforced the importance of considering the SD contribution to **J** tensors, and established the sensitivity of heavy-atom couplings to spin−orbit relativistic effects. Interhalogen coupling constants are particularly interesting, based on the previously reported experimental results for ClF,[37] BrF,[38] and IF,[38] which indicate significant anisotropy in **J**. Recent calculations on these molecules[23,34] and others[24] indicate that the Fermi-contact mechanism, in most cases, is a relatively minor contributor to **J**. The present work endeavors to provide a combined theoretical and experimental basis for periodic trends in homonuclear and heteronuclear interhalogen coupling constants. It will also serve as a first step toward a proper interpretation of interhalogen coupling constants in more complex polyatomic molecules.[39−46]

Another goal of this work is to take advantage of the highly precise indirect nuclear spin−spin coupling tensors for the homonuclear diatomic iodine which are available from molecular beam magnetic resonance spectroscopy,[47] and more recently from stimulated resonant Raman spectroscopy.[48] These methods have generally been overlooked as excellent sources of data for comparison with theoretical calculations. The agreement between experimental **J** coupling tensors available for light heteronuclear diatomics from the hyperfine structure in molecular beam electric resonance[49,50,51] or high-resolution microwave spectroscopy experiments[52] and high-level multiconfigurational SCF calculations has recently been established.[23]

Computational Details

Indirect nuclear spin−spin coupling tensors were calculated by using the CPL spin-spin coupling module[30,31,33,34] of the Amsterdam Density Functional program[53,54] running on an IBM RS6000 workstation or a PC with an AMD Athlon microprocessor. The couplings are calculated based on the relativistic ZORA-DFT implementation described in refs 33 and 34. The Fermi-contact (FC), SD, diamagnetic, and paramagnetic spin−orbit (DSO and PSO) coupling mechanisms were included in the calculations. In the ZORA-DFT implementation, the FC and SD terms are not separated, and this sum term is labeled "FC + SD". The FC + SD term contains the well-known FC − SD cross term, and also part of the (FC + SD) − PSO cross term. Likewise, the "PSO" term that is computed contains the remaining part of the (FC + SD) − PSO cross term. Note that the (FC + SD) − PSO term is exactly zero in the nonrelativistic or scalar relativistic limit where no spin−orbit coupling is present. However, it has been demonstrated that, e.g., for TlI, it can represent the largest individual contribution to the isotropic coupling

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Table 1. Experimental and Calculated[a] Indirect Nuclear Spin−Spin Coupling Data for the Ground $^1\Sigma_g^+$ Electronic State of Iodine, $^{127}I_2$

method	basis set or rovibrational state	c_3/Hz	R_{DD}/Hz	ΔJ/Hz	c_4 (= J_{iso})/Hz	ΔK/ 10^{20} N A^{-2} m^{-3}	K_{iso}/ 10^{20} N A^{-2} m^{-3}
scalar-GGA	ZORA IV			−6536	6254	−1345	1287
scalar-GGA	ZORA V			−5663	5418	−1165	1115
so-GGA	ZORA IV			−5535	4791	−1139	986
so-GGA	ZORA V			−4941	4263	−1017	877
experiment	$v = 0, J = 13$	1528 ± 18	256.77	−3814 ± 54	3708 ± 22	−785 ± 11	763 ± 5
experiment	$v = 0, J = 15$	1519 ± 18	256.76	−3787 ± 54	3701 ± 23	−779 ± 11	762 ± 5

[a] Calculated values are at the equilibrium bond length.

constant[34,55] and only upon inclusion of spin−orbit coupling (and the respective cross terms) can reasonable agreement with experiment be achieved. In all of the molecules studied in the present work, the DSO term is negligible. All DFT calculations used the VWN[56] + Becke88[57] and Perdew86[58] generalized gradient approximation (GGA) as described in ref 34. Relativistic spin−orbit calculations were performed for all molecules (so-GGA), and scalar relativistic calculations (scalar-GGA) were carried out for some molecules for comparison purposes. The triple-polarized ADF ZORA IV and ZORA V Slater-type basis sets available within the ADF package were used. A missing 5d polarization function with exponent 1.900 was added to the iodine basis set, which was found to yield slightly improved results for the computed coupling tensors. Experimental equilibrium bond lengths were obtained from the compilation of Huber and Herzberg,[59] except for ClF,[60] Cl_2,[61] and I_2.[62] A reliable theoretical bond length of 2.987 Å was used for At_2.[63]

Some calculations for F_2 and ClF were also carried out by using the multiconfigurational self-consistent-field (MCSCF) method,[64] as implemented in the DALTON quantum chemistry package.[27] Restricted active space (RAS) wave functions[65] were chosen based on the MP2 natural orbital occupation numbers.[66] The $D_{\infty h}$ symmetry of F_2 was represented in the D_{2h} point group in DALTON. The RAS used for F_2 was 10001000(inactive), 00000000(RAS1), 21101110(RAS2), and 32213221 (RAS3), where the eight digits refer to orbitals of A_g, B_{3u}, B_{2u}, B_{1g}, B_{1u}, B_{2g}, B_{3g}, and A_u symmetries, respectively. The $C_{\infty v}$ symmetry of ClF was represented in the C_{2v} point group in DALTON. The RAS used for ClF was 4110(inactive), 0000(RAS1), 3220(RAS2), and 4331(RAS3), where the four digits refer to orbitals of A_1, B_1, B_2, and A_2 symmetries, respectively. The cc-pCVQZ basis set was used for F_2, and the aug-cc-pVQZ basis set was used for ClF.[67] For both molecules, up to two electrons were allowed to be excited into RAS3.

For both computational methods, derivatives of the spin−spin coupling tensors were determined by carrying out calculations in the vicinity of the equilibrium bond length, e.g., r_e, $r_e \pm 0.01$ Å, $r_e \pm 0.02$ Å.[23] The resulting data were then fit to a linear equation.

When comparing several different spin pairs, it is convenient to use a *reduced* coupling tensor, **K**, that is equal to $4\pi^2\mathbf{J}/\gamma_N\gamma_{N'}h$. Here, γ_N and $\gamma_{N'}$ are the magnetogyric ratios of the coupled nuclei N and N′. The units for **K** are N A^{-2} m^{-3} or, equivalently, T^2 J^{-1}.

Results and Discussion

Shown in Table 1 are the available magnetic hyperfine data for the ground $^1\Sigma_g^+$ electronic state of molecular iodine, I_2.[48] Stimulated Raman spectroscopy has provided the hyperfine parameters d and δ, which are equivalent to the parameters c_3 and c_4, respectively, used in the molecular beam literature.[50,51,68] The procedures outlined in ref 23 have been applied to determine the complete indirect nuclear spin−spin coupling tensor for iodine. The parameter d is equal to the effective dipolar coupling constant, R_{eff}, which is defined below:

$$d = c_3 = R_{eff} = R_{DD} - \frac{\Delta J}{3} \tag{1}$$

The parameters δ and c_4 are equal to J_{iso}. Wallerand et al.[48] were able to determine values for c_3 and c_4 for two rovibrational states ($v = 0$, $J = 13$ and $v = 0$, $J = 15$). The rovibrationally averaged value of the direct dipolar coupling constant, $R_{DD} = (\mu_0/4\pi)(\hbar\gamma_N\gamma_{N'}\langle r_{NN'}^{-3}\rangle/2\pi)$, is determined by using the equilibrium bond length of 2.66614 Å[62] and the averaging procedure described in ref 23. As shown in Table 1, there is a slight rotational dependence of the two hyperfine constants; however, the values for the two rotational states are identical within experimental error. We note that analogous experimental data have also been discussed for the excited electronic $B^3\Pi_{0_u^+}$ state of iodine.[69,70] The iodine data are particularly interesting from an NMR spectroscopist's point of view, since coupling between magnetically equivalent nuclei is not typically observed in NMR experiments. It is important to note that the negative experimental value of ΔJ implies that the largest component of the **J** tensor lies perpendicular to the bond axis rather than along it (Figure 1). This orientation for **J** is consistent for all of the interhalogen couplings discussed herein (vide infra).

Molecular beam magnetic resonance spectroscopy was applied in 1980 by Yokozeki and Muenter[47] to provide values of c_3 and c_4 similar to those shown in Table 1; however, the Raman study has improved the precision to which these parameters are

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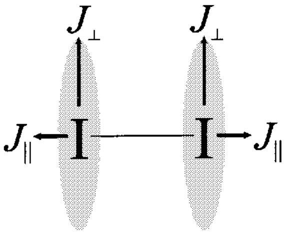

Figure 1. Experimental orientation of the **J**(^{127}I,^{127}I) tensor for molecular iodine in its ground electronic state. The larger component of the coupling tensor lies perpendicular to the bond axis, $J_\perp = 4979$ Hz, and the smaller component lies along the bond axis, $J_\parallel = 1165$ Hz (values for the $v = 0$, $J = 13$ state).

known. In 1981, Pyykkö and Wiesenfeld[71] attempted to calculate the **K** coupling tensors for molecular iodine using the relativistically parametrized extended Hückel (REX) method, and compared their results to the molecular beam data.[47] The REX method provided a value of -99.7×10^{20} N A^{-2} m^{-3} for K_{iso}, which is clearly of the wrong sign and magnitude when compared to the experimental data (Table 1).

The indirect nuclear spin−spin coupling tensor for molecular iodine therefore represents a stringent test of the ZORA-DFT method, especially given the very small errors associated with the experimental data. It is important to emphasize that the experimental data are for relatively isolated molecules in the gas phase (1 mTorr pressure) and the resulting lack of intermolecular effects make the data ideal for comparisons with calculated results, which are carried out on isolated single molecules. The results of scalar and spin−orbit relativistic calculations of the **K** tensor for iodine are presented in Table 1. The fact that the sign and order of magnitude of both K_{iso} and ΔK are reproduced by the calculations is an important success. For many years, it was a formidable challenge to even reproduce the sign of K_{iso} in a molecule as small as hydrogen fluoride.[72,73] For the scalar relativistic calculation on I_2 with the ZORA IV basis set, the isotropic and anisotropic coupling constants are overestimated by approximately 70%. However, the improvement obtained when spin−orbit relativistic effects are included and the ZORA V basis set is used is remarkable; the calculated equilibrium value of J_{iso}, 4263 Hz, overestimates the experimental $v = 0$ values by only 15%. Similarly, the agreement between the experimental and calculated values of ΔJ improves substantially when spin−orbit relativistic effects are included. The remaining overestimation of the isotropic and anisotropic coupling constants by the calculations can likely be attributed to deficiencies of the density functional. It has previously been noted that with standard GGA functionals, the PSO term tends to be overestimated in magnitude, and thus the coupling constants of systems in which the PSO term clearly dominates are often too large.[29−31,34,74] The missing treatment of the self-interaction correction (SIC) is an important factor here.[74]

REX calculations were carried out by Pyykkö and Wiesenfeld for Cl_2 and Br_2 in addition to iodine; however, they conclude their section on the dihalogens by stating that it is difficult to say whether the REX results are meaningful, and that they consider the issue of the sign and magnitude of dihalogen coupling constants unsettled.[71] In an effort to resolve the issues of the sign, magnitude, and periodic trends in the spin−spin coupling tensors of the dihalogen molecules, so-GGA ZORA calculations of the **J** tensors for all five homonuclear dihalogen molecules have been performed (Table 2). While relativistic effects are surely minor for a molecule as light as fluorine, the same computational methods have been applied to all of the molecules for consistency. The reduced spin−spin coupling constants, K_{iso}, as well as the reduced anisotropic coupling constants, ΔK, increase in magnitude for Cl_2 through At_2. Fluorine is an exception to this trend; K_{iso} for fluorine is larger than that for Cl_2, but smaller than that for Br_2. The earlier REX calculations[71] provide K_{iso} values of -17.0×10^{20} N A^{-2} m^{-3} for Cl_2 and $+24.1 \times 10^{20}$ N A^{-2} m^{-3} for Br_2. Buckingham and Love's[75] LCAO calculation of the **K** coupling tensor for F_2 gives $K_{\text{iso}} = -95.4 \times 10^{20}$ N A^{-2} m^{-3} and $\Delta K = 13.9 \times 10^{20}$ N A^{-2} m^{-3}; all of these early data are clearly in disagreement with the results presented in Table 2.

To confirm the result obtained using ZORA-DFT methods for fluorine, a MCSCF calculation using a RAS wave function was performed. The comparison of the two methods shown in Table 2 is very encouraging. Although, to our knowledge, there are no experimental data for comparison with the calculated coupling tensors in F_2, the DFT and MCSCF methods are in remarkable agreement both with respect to the isotropic and anisotropic portions of the coupling tensor, and also with respect to the relative importance of the coupling mechanisms to K_{iso}. For all of the diatomics except astatine, the relative importance of the PSO and FC + SD terms to K_{iso} is approximately constant, with the PSO term being the dominant contributor at ~70−80%. These results demonstrate that caution should be exercised when attempting to interpret spin−spin couplings solely in terms of the Fermi-contact mechanism. The dominance of the PSO term seems to increase slightly as the atomic number of the halogen is increased. Calculations for Cl_2, Br_2, I_2, and At_2 using the relativistic scalar-GGA and so-GGA methods indicate that the improvement in J_{iso} induced by adding the spin−orbit relativistic correction increases from 2% in Cl_2 to 11% in Br_2 to 21% in I_2 to 52% in At_2.[76]

To further examine the dependence of the reduced coupling tensor on the nature of the halogen atom in interhalogen compounds, results for heteronuclear diatomic halogens are presented in Table 3. Experimental data are available for comparison with ClF,[37,23] and BrF and IF.[38,23] MCSCF results using a CAS wave function for ClF were presented in ref 23, and ZORA-DFT results for ClF, BrF, and IF were presented in ref 34. Results for the other diatomics in Table 3 further confirm the relative importance of the PSO and FC + SD coupling mechanisms. In Ramsey's original formalism for spin−spin coupling tensors,[77] all of the coupling mechanisms except the Fermi-contact mechanism depend intimately on the expectation value of the inverse cube of the electron−nuclear distance, $\langle r^{-3}\rangle$. This quantity in turn varies periodically with the atomic number, $Z^{(N)}$, of the nucleus in question.[78,79] It should be noted that values

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(76) Spin−orbit (so) correction above and beyond the scalar correction is calculated as $|(J_{\text{iso}}(\text{so}) - J_{\text{iso}}(\text{scalar})/J_{\text{iso}}(\text{scalar})| \times 100\%$.
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Table 2. Summary of Calculated[a] Equilibrium Indirect Nuclear Spin−Spin Coupling Tensors for Homonuclear Dihalogens

molecule	J_{iso}/Hz	ΔJ/Hz	K_{iso}/ 10^{20} N A^{-2} m^{-3}	ΔK/ 10^{20} N A^{-2} m^{-3}	% PSO for K_{iso}	% FC + SD (+PSO cross term) for K_{iso}
$^{19}F_2$	13182	−13484	123.9	−126.7	67	33
$^{19}F_2$ (MCSCF/RAS)	12676	−11821	119.1	−111.1	63	37
$^{35}Cl_2$	119	−138	102.8	−118.8	78	22
$^{81}Br_2$	4109	−4461	466.1	−506.4	75	25
$^{127}I_2$	4263	−4941	877.0	−1017	79	21
At_2	-	-	2738	−2735	100	0

[a] so-GGA method, with the ZORA V basis set on all atoms, except where otherwise indicated.

Table 3. Summary of Calculated[a] Equilibrium Indirect Nuclear Spin−Spin Coupling Tensors for Heteronuclear Dihalogens. Experimental Values of J_{iso} and ΔJ Are Included for Comparison[b]

molecule	exptl J_{iso}/ Hz	J_{iso}/ Hz	exptl ΔJ/ Hz	ΔJ/ Hz	K_{iso}/ 10^{20} N A^{-2} m^{-3}	ΔK/ 10^{20} N A^{-2} m^{-3}	% PSO for K_{iso}	% FC + SD (+ PSO cross term) for K_{iso}
$^{35}Cl^{19}F$	840	969	−907	−1143	87.4	−103.1	78	22
$^{35}Cl^{19}F$ (MCSCF/RAS)	840	722	−907	−774	65.1	−69.8	79	21
$^{35}Cl^{81}Br$		711		−788	222.9	−246.9	75	25
$^{35}Cl^{127}I$		678		−801	286.1	−337.8	78	22
$^{81}Br^{19}F$	5240	5648	−6306	−6420	184.4	−209.6	75	25
$^{81}Br^{127}I$		3993		−4538	610.0	−693.4	76	24
$^{127}I^{19}F$	5730	4908	−5856	−6223	215.8	−273.6	80	20

[a] so-GGA method, with the ZORA V basis set on all atoms, except where otherwise indicated. [b] Experimental data are for the $v = 0$, $J = 1$ rovibrational state. References are given in the text.

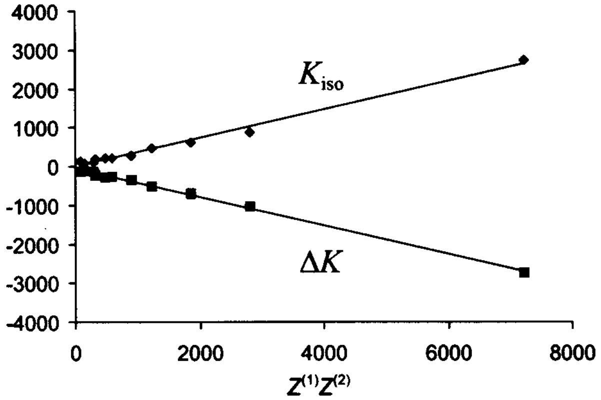

Figure 2. Calculated trends in the reduced isotropic (K_{iso}) and anisotropic (ΔK) portions of the indirect nuclear spin−spin coupling tensors for interhalogen diatomics. The so-GGA ZORA DFT data are plotted as a function of the product of the atomic numbers of the coupled nuclei, $Z^{(1)}Z^{(2)}$. The units for the coupling constants are 10^{20} N A^{-2} m^{-3}. The data, including those for F_2, were fit to the following linear equations: $K_{iso} = 0.3669(Z^{(1)}Z^{(2)}) + 6.552$, $R^2 = 0.9908$ and $\Delta K = -0.3674(Z^{(1)}Z^{(2)}) - 47.019$, $R^2 = 0.9972$. For convenience of the reader, the atomic numbers of the halogens are the following: 9 for fluorine, 17 for chlorine, 35 for bromine, 53 for iodine, and 85 for astatine.

of $\langle r^{-3}\rangle_{np}$ increase uniformly with $Z^{(N)}$ for the halogens Cl through to At. Attempts have been made to correlate known reduced coupling constants with the square of the atomic number in a series of molecules where one nucleus is fixed, e.g., fluorine.[80,81] In the present work, the atomic numbers of both coupled nuclei are varied. Shown in Figure 2 are the calculated values of K_{iso} and ΔK for all of the interhalogens plotted as a function of the product of the atomic numbers of the nuclei involved, $Z^{(1)}Z^{(2)}$. A good linear correlation is observed, with values of the correlation coefficient R^2 in excess of 0.99 for both K_{iso} and ΔK, including the data for F_2. As noted above, the values for F_2 are higher than one would predict based on a simple $Z^{(1)}Z^{(2)}$ dependence. This discrepancy may be rationalized by considering that the expectation value for the valence p electrons, $\langle r^{-3}\rangle_{np}$, is *greater* for fluorine, 7.544 au, than that for chlorine, 6.7905 au.[82] These values are the result of relativistic Dirac−Fock calculations carried out by Desclaux.[82b]

It is interesting to note that reliable experimental coupling tensors are available from Cederberg and co-workers for several alkali metal halides involving heavy nuclei,[23] e.g., LiI,[83] CsF,[84] and CsCl;[85] the values of both K_{iso} and ΔK for these molecules are generally significantly less than those for the interhalogen compounds discussed presently. This is in agreement with one of the periodic trends proposed in ref 23, i.e, that the absolute values of both K_{iso} and ΔK increase from left to right across the periodic table.

Jameson and Osten have presented a comprehensive analysis of isotope effects on spin−spin coupling, including the effects of bond extension on **K**.[86,87] In particular, the possible effects of lone pairs on the derivatives of the spin−spin coupling constant with respect to bond length, $(\partial K_{iso}/\partial r)_{r_e}$, are discussed. For a Se−H bond, for example, it is postulated that a possible negative Fermi-contact contribution to this derivative may arise as a result of lone pairs with s character. Since it is the PSO term that is dominant for the interhalogen couplings discussed here, it is of interest to determine the dependence of these couplings on bond length. Presented in Table 4 are the calculated derivatives of the isotropic and anisotropic reduced spin−spin coupling constants for all of the interhalogen diatomics. Shown in Figure 3 is an example of the plots which were generated to

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Table 4. Calculated[a] Derivatives of the Isotropic and Anisotropic Portions of the Indirect Nuclear Spin−Spin Coupling Tensors for Diatomic Halogens[b]

molecule	r_e/Å	$(\partial K_{iso}/\partial r)_{r_e}$ m = slope/ 10^{20} N A^{-2} m^{-3} per Å	$(\partial(\Delta K)/\partial r)_{r_e}$ m = slope/ 10^{20} N A^{-2} m^{-3} per Å
F_2	1.41193	492	−317
F_2 (MCSCF/RAS)	1.41193	536	−303
ClF	1.628332	338	−248
ClF (MCSCF/RAS)	1.628332	270	−185
BrF	1.75894	521	−401
IF	1.90975	475	−320
Cl_2	1.9885	317	−245
ClBr	2.13606	504	−420
Br_2	2.28105	816	−782
ClI	2.32087	475	−375
BrI	2.46898	810	−800
I_2	2.66614	982	−1097

[a] so-GGA method, with the ZORA V basis set on all atoms, unless otherwise indicated. [b] Results are fit to the linear equation $K = mr + b$, with correlation coefficient R^2. Values of R^2 are greater than 0.999 for all molecules.

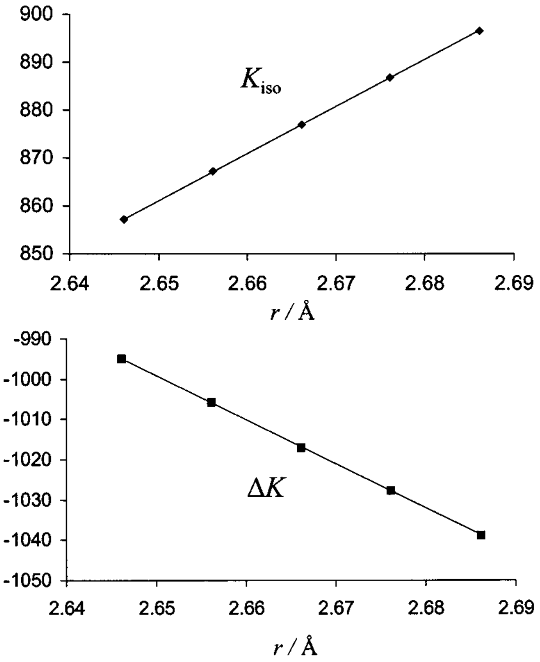

Figure 3. Plots of the reduced isotropic (top) and anisotropic (bottom) portions of the indirect nuclear spin−spin coupling tensors for iodine as a function of bond length. The equilibrium bond length for iodine is 2.66614 Å. The units for the coupling constants are 10^{20} N A^{-2} m^{-3}. The data were fit to a linear equation to yield the following relationships (see Table 4): $K_{iso} = 982(r/\text{Å}) - 1741$ and $\Delta K = -1097(r/\text{Å}) + 1908$.

determine the derivatives of the coupling constants near the equilibrium bond length. The data shown are for iodine, which has an equilibrium bond length of 2.66614 Å.[62] For comparison, we note that the derivatives $(\partial K_{iso}/\partial r)_{r_e}$ for the interhalogens are all 1 to 2 orders of magnitude larger than the corresponding values summarized by Jameson[87] for couplings involving hydrogen, e.g., for the phosphorus−hydrogen spin pair in phosphine, $(\partial K_{iso}/\partial r)_{r_e}$ is -42.2×10^{20} N A^{-2} m^{-3} per Å and for the tin−hydrogen spin pair in SnH_3^-, $(\partial K_{iso}/\partial r)_{r_e}$ is $-58.0 \pm 4.0 \times 10^{20}$ N A^{-2} m^{-3} per Å.

In addition to the small rotational dependence of the coupling tensor for I_2 shown in Table 1, the experimental vibrational dependence of the coupling tensor for BrF is also known.[38] Experimentally for BrF, K_{iso} increases from 171(9) × 10^{20} N A^{-2} m^{-3} for the $v = 0$ vibrational state to 228(30) × 10^{20} N A^{-2} m^{-3} for the $v = 1$ state. The data for the two states convincingly demonstrate that K_{iso} increases as the bond length is increased, which is the calculated trend for all of the diatomics in Table 4, i.e., $(\partial K_{iso}/\partial r)_{r_e}$ is positive. The experimental values of ΔK in BrF are $-206(25) \times 10^{20}$ N A^{-2} m^{-3} for $v = 0$ and $-183(27) \times 10^{20}$ N A^{-2} m^{-3} for $v = 1$. The apparent bond length dependence $((\partial(\Delta K)/\partial r)_{r_e} > 0)$ is in contradiction with the calculated derivative; however, we note that the error bars on the experimental values overlap. For iodine, the experimental data suggest that an increase in the iodine−iodine distance will lead to smaller values for both ΔK and K_{iso}. The calculated derivatives, $(\partial K_{iso}/\partial r)_{r_e} = 982 \times 10^{20}$ N A^{-2} m^{-3} per Å and $(\partial(\Delta K)/\partial r)_{r_e} = -1097 \times 10^{20}$ N A^{-2} m^{-3} per Å, are contrary to the experimental data. It is important to emphasize, however, that the experimental data for the two rotational states are identical within error and it may simply be incidental that the apparent experimental dependence on the rotational state is opposite to that calculated. Moreover, it is important to recognize that the ZORA-DFT derivatives for all of the compounds, $(\partial K_{iso}/\partial r)_{r_e} > 0$ and $(\partial(\Delta K)/\partial r)_{r_e} < 0$, are in agreement with the MCSCF derivatives determined for F_2 and ClF.

Conclusions

This study has elucidated trends in the isotropic and anisotropic portions of interhalogen indirect nuclear spin−spin coupling tensors. One of the general conclusions is that the magnitude of both the isotropic and anisotropic coupling constants increases linearly with the product of the atomic numbers of the nuclei involved, with the important exception of molecular fluorine. The notable agreement between the DFT and MCSCF methods for calculating the **K** tensor in fluorine is particularly gratifying. The paramagnetic spin−orbit mechanism is responsible for approximately 70−80% of the isotropic coupling constant for all of the interhalogen diatomics, with the exception of molecular astatine. This result clearly emphasizes the hazards of interpreting **J** couplings based solely on the Fermi-contact mechanism. Contrary to chemical intuition and common assumptions, this work has also demonstrated that for all of the interhalogen diatomics, the largest component of the **J** tensor lies *perpendicular* to the bond axis, rather than along it. All of the calculated derivatives of the isotropic coupling constant with respect to bond length are positive, and all of the derivatives for the anisotropic portion are negative. Additional precise experimental characterizations of the rotational−vibrational dependence of the coupling tensor for the interhalogen compounds discussed herein would be of great benefit.

The present work has also further demonstrated the accuracy and reliability of the ZORA-DFT method for the calculation of indirect nuclear spin−spin coupling tensors in molecules containing heavy nuclei, where relativistic effects are important. For example, the importance of the spin−orbit relativistic correction to **J** increases with atomic number, and improves the calculated value of J_{iso} in I_2 by 21% above and beyond the scalar relativistic result. The encouraging results presented herein suggest the general utility of the relativistic ZORA-DFT method for further investigations of periodic trends in spin−spin coupling tensors involving heavy nuclei and larger molecular systems.

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