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Indirect Nuclear Spin−Spin Coupling Tensors in Diatomic Molecules: A Comparison of Results Obtained by Experiment and First Principles Calculations

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Abstract: The importance of hyperfine structure observed in molecular beam or high-resolution microwave spectroscopy experiments has been almost completely overlooked by NMR spectroscopists and theoreticians. In the present work, we show for a series of diatomic molecules that the indirect spin−spin coupling tensor, of fundamental importance to magnetic resonance spectroscopy, is completely characterized by the hyperfine measurements. The hyperfine parameter c_4 is known to be equivalent to the isotropic spin−spin coupling constant, J_{iso}; what has not been exploited is the relationship between c_3 and the anisotropic portion of the spin−spin coupling tensor, $\Delta\mathbf{J}$. Through comparisons to highly precise experimental data available for LiH, LiF, KF, Na_2, and ClF, multiconfigurational SCF calculations using balanced complete active spaces and large correlation-consistent basis sets have been employed to establish the reliability of such calculations for determining the *complete tensor* rather than simply J_{iso}. The experimental data are for “isolated” molecules, making them ideal for comparison with ab initio results; agreement is generally within a few percent after accounting for rovibrational effects. These results, combined with further calculations on a larger set of diatomic molecules (HF, BF, AlF, KNa, HCl, NaF), provide new insights into the nature of indirect spin−spin coupling. Calculations indicate the importance of each of the various coupling mechanisms. The influence of the Fermi-contact mechanism, traditionally thought to be the dominant contribution to J_{iso}, is shown to vary considerably even for couplings between first-row elements. General conclusions about the relative importance of all mechanisms to both the isotropic and anisotropic portions of the coupling tensor are discussed, and periodic trends are proposed.

Introduction and Context

The indirect spin−spin coupling between nuclei is of fundamental importance in magnetic resonance spectroscopy.[1−3] Applications range from the identification of hydrogen bonding networks in nucleic acid base pairs[4] and in proteins[5−7] to probing binary semiconducting compounds[8,9] and high-temperature superconductors.[10] The indirect spin−spin coupling of two spins, $\mathbf{I}_1$ and $\mathbf{I}_2$, may be expressed as:

$$\hat{H}_{\mathrm{J}} = hJ_{\mathrm{iso}}\mathbf{I}_1\cdot\mathbf{I}_2 + h\mathbf{I}_1\cdot\mathbf{J}'\cdot\mathbf{I}_2 \qquad (1)$$

where J_{iso} is one-third the trace of the second-rank **J** tensor and $\mathbf{J}'$ is the traceless "$\Delta\mathbf{J}$" tensor which defines the anisotropy of the indirect spin−spin coupling tensor.[11,12] For a diatomic molecule, there are only two unique components of the **J** tensor,[13] $J_{\parallel}$ and $J_{\perp}$; thus, $J_{\mathrm{iso}} = (J_{\parallel} + 2J_{\perp})/3$ and the anisotropy, ΔJ, is simply $J_{\parallel} - J_{\perp}$.

Experimentally, it is difficult to measure reliable values of the anisotropy in **J** because the Hamiltonians describing the anisotropic $\mathbf{J}'$-interaction and the direct-dipolar interaction involve tensors of the same form.[12,14] As a result, one cannot independently measure the anisotropic $\mathbf{J}'$ tensor and the direct dipolar coupling tensor. In addition, the direct dipolar interaction

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is generally at least an order of magnitude larger than the anisotropic **J′**-interaction. Because of this close relationship between the direct dipolar interaction and Δ**J**, anisotropy in the **J** tensor has sometimes been termed the "pseudo-dipolar" interaction.[15]

Most NMR measurements are carried out on isotropic fluids where only J_{iso} is measured. Complete **J** tensors can be characterized by studying the NMR spectra of single crystals,[16] solid powder samples,[14,17] or samples oriented in liquid crystalline solvents.[18] Another less well-recognized source of spin−spin coupling tensor information is the hyperfine structure observed in molecular beam[19] or high-resolution microwave[20] spectroscopy experiments. The importance of experimental data from the latter experiments, with few exceptions, has been completely overlooked.

The theory of indirect spin−spin coupling was originally described by Ramsey.[11,19a,b,21] Qualitatively, the indirect nuclear spin−spin coupling may be pictured as a two-step process, in which one nucleus polarizes neighboring electrons, and this polarization is transferred via the electronic network to a second nucleus. There are three basic mechanisms by which the nucleus may interact with neighboring electrons. In the first of these, electronic currents are established by action of the magnetic field of one nuclear magnetic dipole on the *orbital* magnetic moments of the electrons. The induced currents then produce magnetic fields at the site of the second nucleus. This effect, termed the spin−orbit (SO) mechanism, is usually further subdivided into a diamagnetic (DSO) and paramagnetic (PSO) part. Second, the dipolar interaction between the magnetic moment of one nucleus and the electron spins produces an electron spin polarization so that there are nonvanishing magnetic fields which act on other nuclei; this is known as the spin-dipolar (SD) mechanism. Finally, and most important, there is the Fermi contact (FC) interaction between a nuclear magnetic moment and electrons which have finite probability of being at the nucleus. Again, electron spins are coupled by spin-polarization which in turn induces a field at the second nucleus. The different allowed spin states of the nuclei involved in the coupling lead to the spectral *J*-splittings commonly observed in NMR spectra of solutions and solids.

Pople and Santry[22] developed approximate formulas for each of the above interactions within the context of a simple valence electron molecular orbital theory. One of the main conclusions from this classic paper is that the Fermi contact term is generally the most important mechanism for spin−spin coupling, particularly if protons are involved. The orbital and spin-dipolar terms were found to be most important when there is multiple bonding between the two coupled nuclei. Buckingham and Love[23] extended the Pople−Santry work to investigate the full coupling tensor in terms of LCAO coefficients and singlet−triplet excitation energies. They were especially interested in determining the mechanisms which are responsible for anisotropy in the **J** tensor. There is one cross term, the spin-dipolar Fermi contact cross term (SD × FC), which contributes to the coupling tensor but not to its trace. According to molecular orbital theory as employed by Buckingham and Love, this term can make a significant contribution to the anisotropy of the electron-coupled nuclear spin−spin interactions. The Fermi contact mechanism itself is isotropic, while each of the other two mechanisms are, in principle, anisotropic. It should be noted that only a few molecules were investigated and used to draw general conclusions in this early study. Other than thallium fluoride, there were no reliable experimental data on isolated molecules in the gas-phase available in the mid- to late-1960s for comparison with the calculated results.

In 1967, Pople and co-workers developed a finite perturbation theory for calculating spin−spin coupling constants.[24] This technique was used with INDO semiempirical self-consistent molecular orbital methods to calculate indirect spin−spin coupling constants in numerous molecules. As implemented by Pople and co-workers, only the Fermi contact mechanism was considered. Others[25] incorporated the remaining mechanisms. Although these semiempirical methods often reproduced experimental trends, particularly for couplings involving protons, the results for pairs of heavier nuclei were often suspect. Early attempts to use the finite perturbation approach with nonempirical SCF calculations using minimal basis sets to calculate J_{iso} failed.[26]

Thus, reliable first-principles calculations of **J** tensors have been challenging and generally confined to relatively small molecules containing first-row elements.[27] A recent review summarizes the progress in the theory and calculation of nuclear spin−spin coupling constants.[28] Particularly promising results have recently been obtained using multiconfigurational self-

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consistent field (MCSCF) linear response methods with large correlation-consistent basis sets. With the exception of recent papers by Jokisaari and co-workers,[18b−d] judgments concerning the quality of the calculations have been based on a comparison of isotropic spin−spin coupling constants (calculated and observed). The role of medium effects is generally not considered, with some important exceptions.[29] The purpose of the present study is to compare the results of first principles calculations with highly precise experimental J_{iso} and ΔJ data deduced from molecular beam spectroscopy where isolated molecules are investigated. The discussion will first focus on LiH, LiF, KF, Na_2, and ClF since particularly reliable experimental data exist for these molecules. In addition, several other first- and second-row diatomic molecules will be examined in order to identify possible periodic trends. The relative importance of the various coupling mechanisms to J_{iso} and ΔJ will also be discussed. Results and conclusions obtained here will also be compared with earlier calculations. The present study further demonstrates the reliability of the MCSCF approach by predicting both J_{iso} and ΔJ in small molecules.

Experimental trends concerning J_{iso} have been recognized for some time;[30−34] however, periodic trends concerning ΔJ are less clear. There has been some evidence that ΔJ increases when one or more heavy nucleus is involved[9,15c,16,17,35−38] (e.g., ΔJ (^{199}Hg, ^{31}P) = 4.0 ± 0.5 kHz in $Hg(PPh_3)_2(NO_3)_2$[16b]), but there have also been indications that ΔJ could be important for light nuclei (e.g., ΔJ (^{19}F, ^{13}C) = 350 Hz in $^{13}CH_3F$[39]). Methyl fluoride in particular has attracted a great deal of attention. For example, although the currently accepted value for ΔJ (^{19}F, ^{13}C) is 350 Hz, previously reported values include 404 ± 31 Hz,[40] measured using liquid crystal techniques, and −1200 ± 1200 Hz, measured via ^{13}C NMR in a solid argon matrix at 15 K.[41] The present work endeavors to provide a combined experimental and theoretical foundation for periodic trends in indirect spin−spin coupling tensors.

Numerous NMR experiments, both solution- and solid-state, have been devised to measure direct dipolar coupling constants which depend on the inverse cube separation of the two nuclei.[42] What seems to be consistently ignored when these experiments are applied is the fact that anisotropy in the indirect spin−spin coupling will also contribute to the apparent dipolar coupling constant measured. It is essential to have a better understanding of the indirect spin−spin coupling, and in particular the magnitude of ΔJ, to have confidence in any internuclear separations derived from NMR measurements.

Extracting J_{iso} and ΔJ from Hyperfine Data. To illustrate the procedure for extracting J_{iso} and ΔJ from hyperfine data, the case of ^{35}Cl−^{19}F, which has been extensively investigated experimentally,[43] will be discussed. In the absence of any external fields, the hyperfine Hamiltonian for ^{35}Cl−^{19}F may be expressed as follows:

$$h^{-1}\hat{H}_{hf} = \mathbf{V}_{Cl}\cdot\mathbf{Q}_{Cl} + c_{Cl}\mathbf{I}_{Cl}\cdot\mathbf{J} + c_F\mathbf{I}_F\cdot\mathbf{J} + c_3\mathbf{I}_{Cl}\cdot\mathbf{d}_T\cdot\mathbf{I}_F + c_4\mathbf{I}_{Cl}\cdot\mathbf{I}_F \quad (2)$$

which describe the ^{35}Cl quadrupolar, ^{35}Cl spin-rotation, ^{19}F spin-rotation, tensor spin−spin, and scalar spin−spin interactions, respectively. It is well-known that the nuclear spin-rotation constants c_{Cl} and c_F are related to the nuclear magnetic shielding tensors,[19b,44] and it is understood in the literature that c_4 corresponds to J_{iso}. *What is not generally recognized is the significance of* c_3, *in particular the indirect spin−spin coupling contribution to* c_3. If the direct and indirect spin−spin coupling Hamiltonians are examined, it becomes apparent that the forms of the direct dipolar coupling tensor (**D**) and the $\Delta\mathbf{J}$ tensor are identical.[12] As a result of these similarities, it is impossible to separately observe the two contributions to the effective dipolar coupling constant, R_{eff}:[2,12−18]

$$R_{eff} = R_{DD} - \frac{\Delta J}{3} \quad (3)$$

$$R_{DD} = \left(\frac{\mu_0}{4\pi}\right)\frac{\hbar}{2\pi}\frac{\gamma_1\gamma_2}{\langle r^3\rangle} \quad (4)$$

Here, R_{DD} is the direct dipolar coupling constant. The hyperfine parameter c_3 is equivalent to R_{eff} (also sometimes denoted as d_T[45]). The direct contribution to c_3 can be determined if the rovibrationally averaged bond length is known. Thus, knowledge of the effective bond length and of c_3 (including its sign) also implies knowledge of ΔJ. Pyykkö and Wiesenfeld[46] recognized the validity of this separation. So far, this technique has been successfully applied to thallium fluoride, where ΔJ is actually larger than R_{DD}.[47] In this case, $c_4 = J(^{205}\mathrm{Tl},^{19}\mathrm{F})_{iso} = -13.3 \pm 0.7$ kHz and $c_3 = 3.50 \pm 0.15$ kHz. Since c_3(direct) can be calculated from the bond length to be 7.19 ± 0.07 kHz, the indirect contribution must be −3.69 ± 0.15 kHz. Associating c_3(indirect) with $-\Delta J/3$ yields $\Delta J(^{205}\mathrm{Tl},^{19}\mathrm{F}) = 11.1 \pm 0.5$ kHz for the $v = 0$ state (this number is also given by Buckingham and Love[23]).

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Table 1. Equilibrium Bond Lengths, Complete Active Spaces, Inactive Orbitals, Basis Sets, and Total Number of Orbitals Used for the Calculation of **J** Tensors

	r_e/Å	CAS/inactive	basis set	number of orbitals
HF	0.91682	6331/1000	cc-pV5Z	146
^{7}LiH	1.5957	6332/0000	cc-pV5Z	146
^{7}LiF	1.563864	6331/1000	cc-pV5Z	182
^{23}NaF	1.925947	7331/1000	20s12p4d/cc-pV5Z	167
^{39}KF	2.171457	6330/2000	26s17p1d/cc-pV5Z	173
^{35}ClF	1.6283323	7330/2000	aug-cc-pVQZ	164
^{23}Na$_2$	3.0788	41113111/ 20001000	20s12p4d	152
^{39}K^{23}Na	3.4990348	5331/6110	26s17p1d/20s12p4d	158
^{11}BF	1.26259	5331/1000	cc-pV5Z	182
^{27}AlF	1.654369	7331/1000	aug-cc-pVQZ	164
H^{35}Cl	1.27455	6331/1000	aug-cc-pVQZ	130

At first glance, the determination of the anisotropy of the **J** tensor seems trivial. However, unlike for TlF, in most cases the direct coupling contribution swamps the ΔJ contribution; additionally, the observed effect of ΔJ is reduced by a factor of 3 (see eq 3).[48] Thus, to extract reliable information from the experimentally determined c_3 values, rovibrational corrections to the direct contribution are essential. The procedure we have employed follows that of Bass et al.[49] and Tipping and Ogilvie;[50] a similar procedure was outlined by Schlier.[45] Since experimental c_3 values are determined for a particular rovibrational state (typically $v = 0$ and $J = 1$), and the direct dipolar coupling is calculated based on an equilibrium bond length, the rovibrationally averaged value of the direct dipolar coupling must be calculated, from which ΔJ can be determined:

$$\Delta J(v, J) = -3[c_3(v, J) - R_{DD}(v, J)] \tag{5}$$

Further details are given in Appendix 1.

Computational Details

All calculations of **J** tensors were carried out using the MCSCF approach and complete active space self-consistent field (CASSCF) wave functions[51] on an IBM RISC 6000 workstation running the DALTON[52] quantum chemistry program. In the MCSCF method, both the coefficients of the determinants and the orbitals are variationally optimized and a full-CI calculation is done within the chosen active space. As shown by Helgaker et al.[53] for hydrogen fluoride, very large basis sets and suitable CAS wave functions are required for convergence. For their calculations of the **J** tensor of HF, a very accurate result was obtained using the cc-pV6Z basis set. For our somewhat larger molecules, use of this sextuple-ζ basis set was not feasible. We have used the very large cc-pV5Z and aug-cc-pVQZ basis sets for most calculations,[52,54] and in cases where this was not possible (Na, K), the largest feasible uncontracted basis sets were used.[55] The largest possible balanced active spaces were chosen based on the MP2 natural orbital occupation numbers;[56] convergence limits were the DALTON defaults. Equilibrium bond lengths were obtained from the compilation of Huber and Herzberg,[57] except for KNa[58] and ClF.[59] The complete active spaces, basis sets, and equilibrium bond lengths employed in our calculations are summarized in Table 1.

Rovibrational corrections to the calculated coupling constants were carried out as originally suggested by Buckingham.[60] For any molecular property, P:

$$P(\mathrm{eq}) = P(v, J) - \left(v + \frac{1}{2}\right)\left(\frac{B_e}{\omega_e}\right)\left[\left(\frac{\partial^2 P}{\partial \xi^2}\right)_{\xi=0} - 3a\left(\frac{\partial P}{\partial \xi}\right)_{\xi=0}\right] - 4(J^2 + J)\left(\frac{B_e}{\omega_e}\right)^2\left(\frac{\partial P}{\partial \xi}\right)_{\xi=0} \tag{6}$$

Here, P(eq) is the property at the equilibrium bond length, r_e, and $P(v, J)$ is the property for a particular rovibrational state; note that J is the rotational quantum number and is not related to the indirect spin−spin coupling tensor. The rotational constant at the equilibrium bond length, B_e, is equal to $h/8\pi^2 I_e$ (in hertz), I_e is the moment of inertia at the equilibrium bond length, ω_e is the harmonic vibrational frequency, ξ is the reduced displacement from equilibrium, $(r - r_e)/r_e$, and a is the cubic force constant:

$$a = -1 - \frac{\alpha_e \omega_e}{6{B_e}^2} \tag{7}$$

First and second derivatives were estimated by carrying out additional MCSCF calculations in the region of the equilibrium bond length.

Results and Discussion

To demonstrate the utility of the approach described above for determining the anisotropy of indirect spin−spin coupling tensors, we have selected a series of diatomic molecules: HF, LiH, LiF, NaF, KF, KNa, Na$_2$, BF, AlF, HCl, and ClF. For some of these molecules, precise experimental hyperfine data are available: HF,[61] LiH,[62] LiF,[63] KF,[64] Na$_2$,[65] and ClF.[43a] For the calculation of J_{iso}, hydrogen fluoride has already been well-studied by Helgaker et al.,[53] although no discussion of the anisotropy of the **J** tensor was presented. Their MCSCF study of the basis-set dependence of nuclear spin−spin coupling constants for HF and H$_2$O indicates that the best results are obtained for basis sets of the cc-pVXZ type, supplemented with tight s functions. Our results for HF presented herein are for

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(48) Note that in general there is no a priori reason to conclude that the direct portion of the spin−spin coupling tensor should be greater than the indirect portion. See reference 45, section 3.3.9 and footnote 20.

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Table 2. Calculated and Experimental Hyperfine Data[a] for ^{7}LiH, ^{7}LiF, ^{39}KF, ^{23}Na$_2$, and ^{35}ClF

		calcd (v, J)[b]	expt (v, J)[b,c]
^{7}LiH	$c_3 = R_{\mathrm{eff}}$	−	11346 ± 7
	$c_3(\mathrm{dir}) = R_{\mathrm{DD}}$	11327	−
	$-3c_3(\mathrm{ind}) = \Delta J$	−13	−57 ± 21
	$c_4 = J_{\mathrm{iso}}$	151	135 ± 10
^{7}LiF	$c_3 = R_{\mathrm{eff}}$	−	11324 ± 9
	$c_3(\mathrm{dir}) = R_{\mathrm{DD}}$	11382	−
	$-3c_3(\mathrm{ind}) = \Delta J$	176.9	173.2 ± 27.7
	$c_4 = J_{\mathrm{iso}}$	199.0	172.3 ± 3.2
^{39}KF	$c_3 = R_{\mathrm{eff}}$	−	472 ± 4
	$c_3(\mathrm{dir}) = R_{\mathrm{DD}}$	514	−
	$-3c_3(\mathrm{ind}) = \Delta J$	109.5	125.7 ± 5.1
	$c_4 = J_{\mathrm{iso}}$	78.2	57.8 ± 1.3
^{23}Na$_2$	$c_3 = R_{\mathrm{eff}}$	−	302.6 ± 5.0
	$c_3(\mathrm{dir}) = R_{\mathrm{DD}}$	286.7	−
	$-3c_3(\mathrm{ind}) = \Delta J$	−30	−48 ± 15
	$c_4 = J_{\mathrm{iso}}$	1245	1067 ± 7
^{35}ClF	$c_3 = R_{\mathrm{eff}}$	−	2859 ± 9
	$c_3(\mathrm{dir}) = R_{\mathrm{DD}}$	2557	−
	$-3c_3(\mathrm{ind}) = \Delta J$	−800	−907 ± 27
	$c_4 = J_{\mathrm{iso}}$	829	840 ± 6

[a] All data in hertz. [b] For LiF and KF, $v = 0$, $J = 0$; for LiH and ClF, $v = 0$, $J = 1$; for Na$_2$, $v = 0$. [c] References are given in the text.

comparison purposes and to ensure the reproducibility of the previously reported results. To ensure the reliability of the MCSCF technique for calculating ΔJ as well as J_{iso} beyond HF, calculations of **J** tensors for LiH, LiF, KF, Na$_2$, and ClF were carried out and the results compared to the experimental data. The results in Table 2 indicate that the calculations perform very well; both the isotropic coupling constants and the anisotropies are in very good agreement with the experimental data. Given the history of the calculation of J_{iso} in small molecules,[27,66] the accuracy of our calculated results is encouraging. For a long time, difficulties were encountered even in reproducing the correct sign of J_{iso} in HF (see Table 16 of ref 66). It is also important to point out that in the past most comparisons between experiment and theory have been based solely on J_{iso}, when in fact **J** is a second-rank tensor. To our knowledge, this is the first time accurate **J** tensor data from molecular beam experiments have been compared with state-of-the-art first principles calculations.

The good agreement for both J_{iso} and ΔJ shown in Table 2 lends support to the notion that all contributions to **J** are calculated with reasonable accuracy. For example, the calculated ΔJ ($v = 0$, $J = 0$) of 176.9 Hz for ^{7}LiF is well within the experimental error (173.2 ± 27.7 Hz); the calculated J_{iso} for ^{35}ClF of 829 Hz is in notably good agreement with the experimental value of 840 ± 6 Hz. It is expected that the results for KF and Na$_2$ will be less accurate. Although the number of basis functions used is comparable to the number used for the other molecules, the basis sets for K and Na are not of the cc-pVXZ (correlation-consistent) type (Table 1). It is interesting to note that on moving across the periodic table, from left to right, the relative importance of the FC mechanism tends to decrease (vide infra); this is fortunate since it is the FC contribution which is the most difficult to calculate, in part due to the cusp problem associated with using Gaussian-type orbitals.[27,67] Rovibrational corrections to $R_{\mathrm{DD}}(r_e)$ were a few percent or less in all cases. It is important to make these corrections, however, to ensure that the experimental data are being compared to the appropriate calculated values.

Table 3. Calculated Equilibrium Contributions to the Isotropic Portion of the Indirect Spin−Spin Coupling Tensor for a Series of Diatomic Molecules

molecule	% DSO	% PSO	% SD	% FC	J_{iso}/Hz	K_{iso}/ 10^{20} N A^{-2} m^{-3}
HF	−0.05	38.83	−0.48	61.69	476.09	4.21
^{7}LiH	0.02	−0.06	0.07	99.98	152.47	3.27
^{7}LiF	−0.01	−4.23	0.12	104.11	193.10	4.39
^{23}NaF	0.00	−17.48	0.25	117.22	193.98	6.48
^{39}KF	0.00	−13.17	−0.16	113.34	76.59	14.5
^{23}Na$_2$	0.00	0.00	0.00	100.00	1243.6	148
^{39}K^{23}Na	0.00	0.00	0.00	100.00	479.89	323
^{11}BF	0.18	37.24	0.96	61.62	−222.58	−6.13
^{27}AlF	0.01	23.17	6.94	69.88	−627.13	−21.3
^{35}ClF	0.01	73.89	37.69	−11.60	832.24	75.0
H^{35}Cl	−0.01	21.86	0.01	78.15	58.87	5.00

Table 4. Calculated Equilibrium Contributions to the Anisotropy in the Indirect Spin−Spin Coupling Tensors for a Series of Diatomic Molecules

molecule	% DSO	% PSO	% SD	% SD × FC	ΔJ/Hz	ΔK/ 10^{20} N A^{-2} m^{-3}
HF	185.99	−262.75	−47.67	224.43	115.98	1.03
^{7}LiH	−34.54	−1.16	−0.55	136.14	−12.39	−0.27
^{7}LiF	11.23	18.28	−3.09	73.58	177.43	4.04
^{23}NaF	2.81	23.32	−2.06	75.93	494.19	16.51
^{39}KF	2.57	29.68	−2.99	70.74	109.22	20.68
^{23}Na$_2$	−3.64	0.10	0.02	103.53	−29.88	−3.55
^{39}K^{23}Na	−1.88	0.14	−0.08	101.82	−10.85	−7.31
^{11}BF	7.83	61.61	−6.97	37.53	469.38	12.94
^{27}AlF	4.45	76.42	−10.29	29.42	555.51	18.84
^{35}ClF	−1.53	109.99	−36.51	28.05	−805.68	−72.65
H^{35}Cl	32.41	−32.38	−5.97	105.94	61.18	5.19

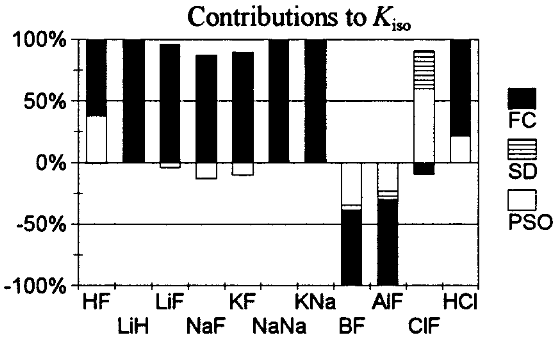

Figure 1. Graphical representation of the percentage contributions of each of the spin−spin coupling mechanisms to the total calculated reduced coupling constant, K_{iso}. Data are given in Table 3. In each case, the DSO contribution is too small to appear in the graph.

Having established the reliability of the MCSCF **J** calculations for molecules as large as ClF, the calculation of **J** tensors was carried out for the remaining molecules: NaF, KNa, BF, AlF, and HCl. The choice of molecules is of course limited by computational resources and the availability of suitably large basis sets. Results are summarized in Tables 3 and 4, and Figures 1 and 2. Unfortunately, reliable experimental hyperfine data are only available for comparison for a limited number of small

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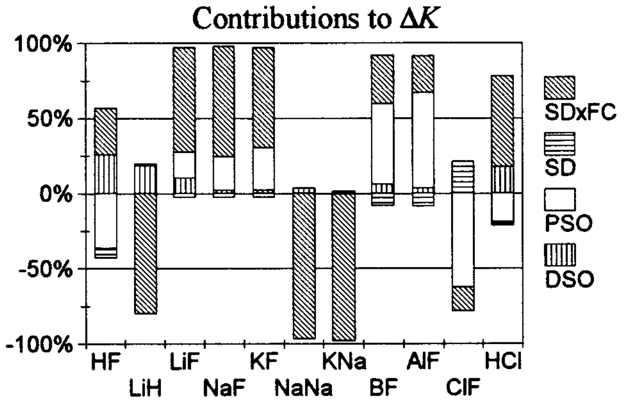

Figure 2. Graphical representation of the percentage contributions of each of the spin–spin coupling mechanisms to the total calculated anisotropy in the reduced coupling tensor, ΔK. Data are given in Table 4.

diatomics.[68] With this in mind, the chosen molecules should provide some insights into any periodic trends in indirect spin–spin coupling. Data are available for sodium fluoride;[69] however, the errors are quite large. Also, we note that a J_{iso} of 306 ± 30 Hz has been reported for KNa.[70] This value was obtained by an optical pumping technique, and a corresponding c_3 value was not reported.

Each term comprising the total **J** tensor is of the following form: $\gamma_N\gamma_{N'}h\boldsymbol{K}_{N,N'}/4\pi^2$, where $\boldsymbol{K}_{N,N'}$ is called the reduced indirect spin–spin coupling tensor involving nuclei N and N′. The reduced coupling tensor is independent of the magnitude of the nuclear magnetic moments; therefore, it is useful in comparing indirect spin–spin coupling tensors involving different spin-pairs. Note that $J_{N,N'}$ has units of Hz (s^{-1}) and $K_{N,N'}$ has units of N A^{-2} m^{-3} or equivalently, T^2 J^{-1}.[71] Shown in Table 3 are J_{iso}, K_{iso}, and a breakdown of these quantities into the various contributing mechanisms for the complete series of diatomics studied herein. The percentage contributions are also displayed graphically in Figure 1. The results for HF are in agreement with those reported by Helgaker et al.[53] For the alkali metal fluorides, MF (M = ^{7}Li, ^{23}Na, ^{39}K), there are several trends which are apparent. First, the reduced isotropic spin–spin coupling increases with the atomic number of the alkali metal atom, ranging from 4.4 N A^{-2} m^{-3} in LiF to 14.5 N A^{-2} m^{-3} in KF. The dominant contribution to the isotropic part of the coupling is from the Fermi contact mechanism, as expected from the arguments of Pople and Santry.[22] The only other notable contribution to K_{iso} for the alkali metal halides is due to the paramagnetic spin–orbit (PSO) mechanism; its effect is to oppose the FC contribution, and its relative importance seems to increase as the atomic number of the alkali metal increases. The DSO and SD contributions combined amount to less than 0.3% of the total isotropic coupling. In contrast, the early results of Buckingham and Love[23] indicate a significant negative spin-dipolar contribution to K_{iso} for the alkali metal fluorides.

No accurate experimental data (c_3 and c_4) are available for the lighter group 13 fluorides, BF, AlF, and GaF. Examination of the calculated results (Table 3) for K_{iso} once again reveals a trend as the atomic number of the group 13 element is increased. In contrast with the alkali metal halides, the K_{iso} values are negative; the magnitudes of K_{iso} for the two groups are fairly similar, with the group 13 fluorides exhibiting slightly larger values for a given row of the periodic table. Most interesting is the relative importance of the various coupling mechanisms to K_{iso}. The FC mechanism, while still the most significant, now only constitutes 60–70% of the total coupling, even in boron fluoride. The PSO and SD mechanisms are seen to play more prominent roles than in the alkali metal fluorides. The results for BF are of particular interest in the context of the work of Pople and Santry.[22] Their treatment included an average energy approximation, and as a result, the spin–orbital contribution was automatically zero for any molecule without π-bond character. Interpretation of the coupling constants only in terms of the FC mechanism is inappropriate, even for a molecule as small as BF, where our data reveal a PSO contribution to J_{iso} of 37%.

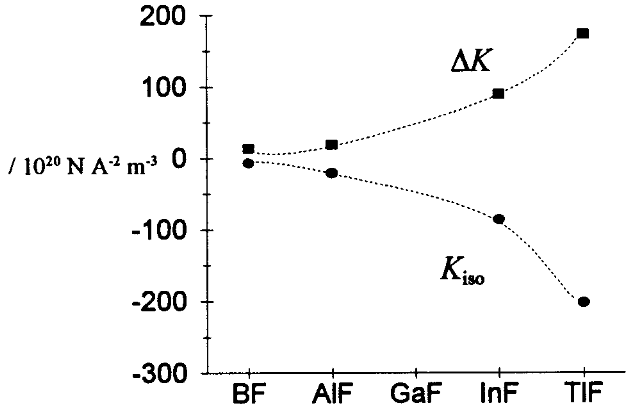

Figure 3. This plot demonstrates the variations in K_{iso} and ΔK for the group 13 fluorides. Calculated values (r_e) are given for ^{11}BF and ^{27}AlF. The data for ^{205}TlF ($v = 0$, $J = 1$) and ^{115}InF ($v = 0$, $J = 1$) are experimentally determined; see the text for further details. The dotted lines are not fits, but rather serve to accentuate the apparent trend.

Shown in Figure 3 is the dependence of both K_{iso} and ΔK on atomic number for the group 13 fluorides, with experimental data used for ^{205}TlF ($v = 0$, $J = 1$)[47] and for ^{115}InF ($v = 0$, $J = 1$).[72] Results for gallium fluoride can be easily interpolated. Anisotropy in the **K** tensor has also been extracted from existing data in the literature for ^{205}Tl^{35}Cl ($v = 0$, $J = 2$),[73] ^{205}Tl^{81}Br ($v = 0$, $J = 2$),[74] and ^{205}Tl^{127}I ($v = 0$, $J = 3$);[75] the results have been plotted along with those for ^{205}Tl^{19}F in Figure 4. These data clearly indicate increasing trends in the absolute values of K_{iso} and ΔK as the atomic number of the halide bonded to thallium increases.

Comparison of chlorine monofluoride and hydrogen chloride (Table 3) indicates the dramatic effect of replacing H with F on the **K** tensor and on the relative importance of the various contributing mechanisms. The isotropic coupling for liquid HCl has been measured as 38 Hz;[76] therefore, medium effects will play a role in any comparison with the calculated value of ~59 Hz. For HCl, the Fermi contact contribution is foremost, as it is in HF. For ClF, however, the FC mechanism becomes almost insignificant, making up only about 12% of the total coupling! Instead, it is the paramagnetic spin–orbit mechanism which

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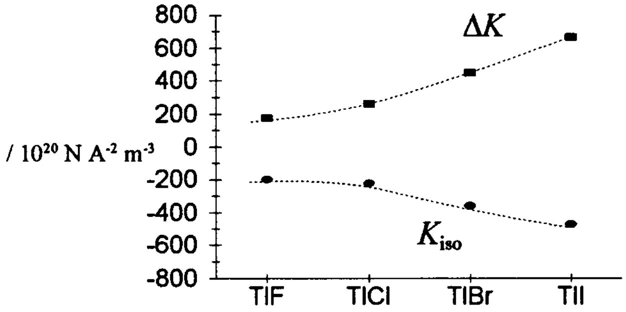

Figure 4. Experimental values for K_{iso} and ΔK for the thallium halides, deduced from the results of high-resolution rotational spectroscopy, are shown. The values are for the particular rovibrational states given in the text. The dotted lines serve as guides to the trends.

dominates (74%), and the spin-dipolar mechanism contributes 38% of the total coupling. These results suggest that the interpretation of any spin−spin coupling constant entirely on the basis of the Fermi contact mechanism is exceedingly dangerous, and reinforces what has been emphasized in the past: large ΔJ values imply significant non-FC contributions to **J**.[16a,b,18] The results for ClF are also useful for exploring trends in K_{iso} and the various contributions across a row of the periodic table. For example, inspection of the results for the second-row fluorides (NaF, AlF, and ClF) allows for the proposal of certain trends. The PSO contribution is seen to steadily increase, initially small and negative in NaF, and becoming positive and dominant in ClF. Similarly, the SD mechanism is negligible in NaF, but accounts for an increasing percentage of K_{iso} as the atomic number of the atom bonded to fluorine increases. The FC contribution steadily decreases across this row for the diatomic fluorides. The absolute value of K_{iso} itself increases across the row, beginning at roughly 6 N A^{-2} m^{-3} for NaF and increasing to ∼ 20 N A^{-2} m^{-3} for AlF and 75 N A^{-2} m^{-3} for ClF.

The trends and comparisons we have discussed thus far have been based primarily on the isotropic spin−spin coupling. Unfortunately, this is where most discussions of indirect spin−spin coupling terminate. As emphasized earlier, **J** is a second-rank tensor quantity and as such requires two independent components for its complete characterization in a linear molecule. Shown in Table 4 are the calculated results for the spin−spin coupling anisotropies, ΔJ, and the corresponding reduced values, ΔK, for HF, LiH, LiF, NaF, KF, Na_2, KNa, BF, AlF, HCl, and ClF. In addition, these values have been decomposed into their constituent contributions and summarized graphically in Figure 2. The first aspects of these results which are particularly striking are the relatively large anisotropies in **J** for HF and LiF since these are both small, light molecules for which one might intuitively expect a fairly isotropic coupling tensor. For HF, the anisotropy in **J** is about 25% of J_{iso}. For LiF, this relative anisotropy ratio[66] increases to 92%! This value is in good agreement with the rovibrationally averaged experimental ratio of 101%. Shown in Table 5 are the calculated relative anisotropy ratios for all of the molecules studied herein. Examination of the ΔK results (Table 4) for the alkali metal fluorides reveals that the anisotropy increases as the atomic number increases, and that the SD × FC mechanism is the most important in each case. All mechanisms (except FC) contribute significantly to ΔK, and the PSO mechanism becomes increasingly important for the heavier diatomics. The early calculations of Buckingham and Love[23] yielded a similar trend for the total ΔK; however, their results for LiF, NaF, KF, and RbF suggested that the spin−orbital mechanisms (DSO + PSO) were decidedly more important than the SD × FC cross term.

Table 5. Theoretical Relative Anisotropy Ratios, $\Delta J/J_{iso}$ and $\Delta J/R_{DD}$, As Determined from MCSCF Calculations at the Equilibrium Bond Length

	$\Delta J/J_{iso}$ (%)	$\Delta J/R_{DD}$ (%)
HF	24.4	0.08
^{7}LiH	−8.4	−0.12
^{7}LiF	91.9	1.55
^{23}NaF	255	11.8
^{39}KF	143	21.2
$^{23}Na_2$	−2.4	−10.4
^{39}K^{23}Na	−2.3	−31.4
^{11}BF	−211	2.61
^{27}AlF	−88.6	8.53
^{35}ClF	−96.8	−31.5
H^{35}Cl	104	1.08

Inspection of the ΔK data for the group 13 fluorides shows that, as for the LiF, NaF, KF series, the anisotropy becomes larger as the atomic number of the atom bonded to fluorine increases. In accord with the relative contributions to K_{iso}, the PSO mechanism is more important for the group 13 fluorides than for the alkali metal fluorides. The group 13 halides are of particular interest owing to the accurate experimental data available for thallium fluoride and indium fluoride. As mentioned above, ^{205}Tl^{19}F exhibits an extremely large spin−spin coupling anisotropy ($\Delta K = 173 \times 10^{20}$ N A^{-2} m^{-3}). Although accurate calculations of the **J** tensor for TlF are not currently feasible, the trend in ΔK illustrated by the results for BF and AlF in Table 4 indicates that the theoretical predictions are in line with the experimental anisotropy observed for InF and TlF (see Figure 3). Our results for BF are in contrast with one of the conclusions of Buckingham and Love,[23] who indicate that for molecules containing light atoms, the SD × FC term is the most important contribution to ΔK. Our results demonstrate that for BF, the paramagnetic spin−orbit mechanism is the origin of more than 60% of the total anisotropy.

The results for ClF are very important in the context of the present work. This is due to the fact that this molecule exhibits an exceptionally large indirect spin−spin coupling anisotropy for a compound composed of only first- and second-row elements (see expt data, Table 2) and is within the reach of high-level MCSCF calculations. Owing to the accuracy of the calculated results (Table 2), confidence can be placed in the overall accuracy of the method. This is very useful since the calculations provide the contributions from each individual mechanism, while experiments can only yield the two principal components of the total **J** tensor ($J_\perp$ and $J_\|$). Such a breakdown into the various contributions is indispensable in the interpretation of spin−spin couplings. In an attempt to update the results of Pople and Santry on the isotropic couplings and of Buckingham and Love on the anisotropic couplings, we present a summary of the trends observed in Figure 5. We note that only for the diatomics composed solely of *s*-block elements does the FC mechanism completely dominate, making the ΔJ values essentially negligible. Clearly, further experimental and theoretical research will be required to fully substantiate the generality of the trends depicted in Figure 5.

It is now common practice by many scientists to refer to indirect spin−spin coupling constants as *scalar* coupling constants.[3,77] This is clearly misleading. Also, the contribution that ΔJ makes to the dipole−dipole relaxation mechanism is either not recognized or ignored even though this was identified

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(77) See for example: Hore, P. J. *Nuclear Magnetic Resonance*; Oxford Chemistry Primers Volume 32; Oxford University Press: Oxford: 1995; p 43.

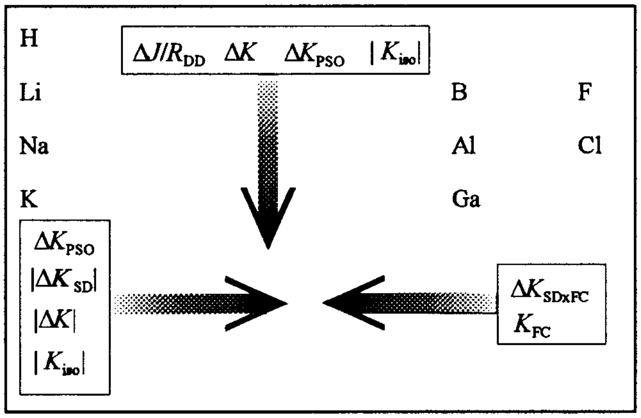

Figure 5. A summary of some of the observations made in the present work on diatomic fluorides, FX. A partial periodic table (indicating the nature of X) orients the reader. The large arrows indicate the direction of increasing magnitude of the properties listed at the base of the arrow. For example, ΔK_{SDxFC} and K_{FC} increase from right to left across the periodic table as X is changed.

by Blicharski in 1972.[78] In fact, relaxation via the indirect spin–spin coupling tensor is entirely analogous to relaxation by the direct dipolar interaction; the two cannot be separated.

As mentioned in the Introduction, one of the important applications of the understanding of spin–spin coupling mechanisms is the accurate measurement of internuclear distances. Since the contributions to R_{eff} from ΔJ and R_{DD} are inseparable, knowledge of periodic trends in the $\Delta J/R_{DD}$ ratio is essential if one wishes to determine reliable internuclear distances from any NMR experiment. Although the case of the thallium halides is extreme, it demonstrates the fact that dipolar recoupling experiments should be interpreted with caution. Shown in Table 5 are the $\Delta J/R_{DD}$ percentages for the molecules examined herein. Some nuclei which are commonly involved in heteronuclear recoupling experiments are represented in this table: ^{19}F,[79] ^{11}B,[80] and ^{27}Al,[81] for example. Buckingham and Love[23] concluded that for molecules containing light atoms (i.e., up to fluorine), the anisotropy in the indirect spin–spin coupling should be less than 1% of the anisotropy in the direct dipolar tensor, $-3R_{DD}$; our results confirm this conclusion. Although it could be argued that the ΔJ contribution is negligible compared to the direct dipolar contribution for HF, LiH, BF, LiF, and HCl, it is clear that its effect cannot be ignored for the other molecules presented. However, one must also bear in mind that the ΔJ term is always reduced by a factor of 3 when contributing to R_{eff}. In real systems, the combination of rovibrational averaging of R_{eff} and unknown ΔJ contributions should be given serious consideration in the interpretation of NMR data to yield internuclear distances. In the solid state, molecular librations in the lattice will also affect the observed dipolar coupling constant. As pointed out by Brouwer et al.,[79] the ΔJ contribution is generally negligible in cases where the dipolar coupling occurs between nuclei of two separate molecules.

Table 6. Reduced Spin–Spin Coupling Tensors and Relative Anisotropy Ratios Derived from Available Experimental Hyperfine Data[a]

	K_{iso}/ 10^{20} N A^{-2} m^{-3}	ΔK/ 10^{20} N A^{-2} m^{-3}	$\Delta J/J_{iso}$ (%)	$\Delta J/R_{DD}$ (%)	refs[b]
^{7}Li^{79}Br	5.15	18.1	351	19	82
^{23}Na^{79}Br	9.76	43.9	450	69	83
^{7}Li^{127}I	6.65	18.4	277	25	86
^{133}CsF	41.8	46.5	111	60	87
^{133}Cs^{35}Cl	39.4	67.9	172	167	85
^{115}InF	−86.4	89.9	−104	66	72
^{35}ClF	75.7	−81.8	−108	−35	43a
^{79}BrF	171	−206	−120	−113	84
^{127}IF	252	−257	−102	−179	84
^{205}TlF	−202	173	−85.6	156	47
^{205}Tl^{35}Cl	−224	262	−117	400	73
^{205}Tl^{81}Br	−361	448	−124	800	74
^{205}Tl^{127}I	−474	664	−140	1470	75

[a] Rovibrational states: $v = 0$, $J = 0$ (NaBr, BrF, IF, CsF, CsCl, LiI); $v = 0$, $J = 1$ (InF, TlF, TlCl, LiBr, ClF); $v = 0$, $J = 2$ (TlBr); $v = 0$, $J = 3$ (TlI). [b] For original hyperfine data.

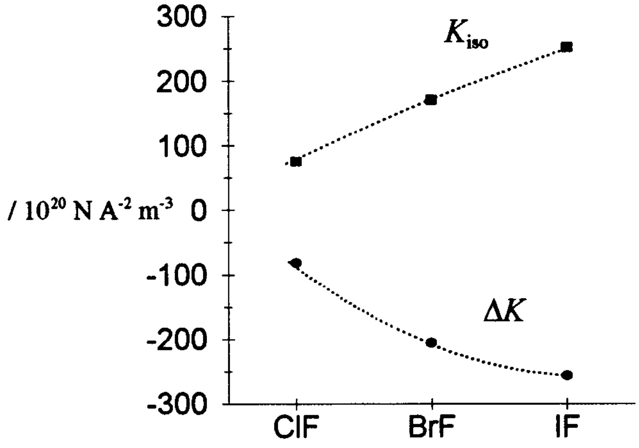

Figure 6. Experimental values for K_{iso} and ΔK for ClF, BrF, and IF, which have been calculated from experimental hyperfine data. The values are for the particular rovibrational states given in Table 6. The dotted lines serve as guides to the trends.

Shown in Table 6 are the reduced spin–spin coupling tensors and relative anisotropy ratios for another series of diatomics for which there are precise experimental data available, but for which accurate MCSCF calculations are not feasible at present due to computational limitations. Chlorine monofluoride is also included for comparison with BrF and IF. Using the technique described in this paper ΔJ was determined from the experimental c_3 values and from the rovibrationally averaged direct-dipolar coupling constants. ΔJ is significant compared to R_{DD} for all of these molecules. The results confirm some of the trends we have observed as a consequence of the MCSCF calculations on smaller molecules. For example, in addition to the series of thallium halides, the spin–spin couplings in the halofluorides (ClF, BrF, and IF) clearly demonstrate that as the atomic number of the halide bonded to fluorine increases, both components of the tensor increase in magnitude (see Figure 6), while $\Delta J/J_{iso}$ remains relatively constant, and $\Delta J/R_{DD}$ increases.

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Conclusions

The importance of hyperfine data obtained from high-resolution molecular beam and microwave spectroscopies has been demonstrated. In particular, the parameters c_3 and c_4 yield the complete experimental indirect spin−spin coupling tensor for an isolated molecule in the gas phase. These data are ideal for comparison with calculations, which are most easily and commonly carried out on isolated molecules. It has been demonstrated that if care is taken to account for rovibrational effects, then high-level MCSCF calculations of the **J** tensors accurately reproduce the experimental results for ^{7}LiH, ^{7}LiF, ^{39}KF, ^{23}Na$_2$, and ^{35}ClF. Calculations of the **J** tensors in these molecules and in HF, ^{11}BF, ^{23}NaF, ^{39}K^{23}Na, ^{27}AlF, and H^{35}Cl provide new insights into the relative importance of the various spin−spin coupling mechanisms and into the nature of the anisotropic portion of the coupling tensor. Clearly, further accurate experimental data on small diatomic molecules would be beneficial. Additionally, correlation-consistent basis sets of the cc-pVXZ type are much needed for sodium and potassium. The work of Jokisaari and co-workers, who have carried out both experimental and theoretical (MCSCF) determinations of the complete **J** tensor in a variety of small organic molecules,[18] is encouraging; we feel that the present study provides additional compelling evidence for the success of MCSCF calculations and in particular the unambiguous identification of large indirect spin−spin coupling anisotropies.

While experiments can yield the two components of the spin−spin coupling tensor in a linear molecule, only theory can designate which are the most important coupling mechanisms and how their relative influence changes throughout the periodic table (Figure 5). In general, the FC and PSO contributions are found to be the most important coupling mechanisms for the molecules studied herein. It is of foremost importance to stress the fact that **J** is a tensor property and, as such, the full tensor should be characterized whenever possible, both experimentally and theoretically.

It is hoped that the present study will encourage others to test their computational methods against the precise experimental data available from molecular beam experiments.[68] For example, calculations of the **J** tensors for the thallium halides would provide a stringent test of density functional methods since these tensors are available experimentally for isolated molecules in the gas phase.

Finally, we would like to underscore the relevance of this work to the profusion of dipolar recoupling experiments which have been and continue to be reported in the literature. Care must be taken to consider the significance of the contribution of the indirect spin−spin coupling anisotropy to the observed effective dipolar coupling, as well as rovibrational averaging of the direct dipolar coupling constant. Although there are many cases where both of these effects are indeed negligible, there are just as surely cases where they play an important role which cannot be ignored if accurate results are to be obtained.

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Appendix 1: Rovibrational Corrections to c_3(direct) (R_{DD})

Referring to eqs 3 and 5, the goal is to find the rovibrational average of R_{DD}, which is equivalent to c_3(direct). Following the work of Bass et al.,[49] this is accomplished as follows, where $\xi = (r - r_e)/r_e$. The quantity to be averaged is:

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{r_e^{\,3}} \frac{1}{(1 + \langle \xi \rangle)^3} \tag{8}$$

Expansion of $(1 + <\xi>)^{-3}$ using the MacLaurin series and substitution of the result into eq 4 gives, to fourth order,

$$R_{DD}(v, J) = \left(\frac{\gamma_1\gamma_2\hbar\mu_0}{2\pi\ \ 4\pi}\right)\frac{1}{r_e^{\,3}}(1 - 3\langle\xi\rangle + 6\langle\xi\rangle^2 - 10\langle\xi\rangle^3 + 15\langle\xi\rangle^4) \tag{9}$$

The rovibrationally averaged quantities, $<\xi>^n$ ($n = 1, 2, 3, 4$), depend on v and the rotational angular momentum quantum number, J, not to be confused with the indirect spin−spin coupling tensor, **J**. The lengthy expressions for $<\xi>^n$ are given by Tipping and Ogilvie.[50] These expressions depend on the Dunham coefficients a_0 through a_6,[88] which describe the shape of the potential energy well near the equilibrium bond length. These coefficients in turn depend on the spectroscopic constants of the diatomic molecule, including B_e and ω_e, for example. These values were obtained from the compilation of Huber and Herzberg, available online from the NIST Chemistry Webbook.[57] Analytical equations for the Dunham coefficients a_0, a_1, a_2, and a_3 are available;[20] unfortunately such equations are not readily available for the higher-order terms a_4, a_5, and a_6. Since most models adequately describe the potential well in the region of r_e, a recursive relationship applying to the Morse potential[50] was used to determine suitable values for a_4 through a_6. The results obtained by this method are in very close agreement with the $<\xi>^n$ values reported by Bass et al. for hydrogen fluoride.[49] Having found $R_{DD}(v, J)$ in this manner allows the application of eq 5 to determine ΔJ.

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