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Microwave Spectroscopy and Nuclear Magnetic Resonance Spectroscopy—What Is the Connection?

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ABSTRACT
The history and development of microwave spectroscopy and nuclear magnetic resonance (NMR) spectroscopy have much in common. In this Account, we discuss the less widely appreciated connections between the parameters measured using the two techniques. Selected examples from our laboratory and from the recent literature attest to the utility and importance of these connections. For example, how are nuclear spin−rotation tensors and NMR chemical shifts related? Why should chemists be interested in absolute magnetic shielding scales? What can chemists learn about trends in spin−spin coupling constants from the hyperfine parameters measured in microwave and molecular beam experiments? The increasingly important role of quantum-chemical calculations in the interpretation of the microwave and NMR data is also highlighted.

Introduction

Spectroscopy is the study of the interaction of electromagnetic radiation with matter. Different types of spectroscopy are distinguished by the frequency of the radiation and the eigenstates involved. The origins of rotational microwave spectroscopy, carried out in the microwave frequency region ($\nu \approx 1$ to 10^3 GHz), and nuclear magnetic resonance (NMR) spectroscopy, which utilizes lower energy radio frequency (rf) radiation ($\nu \approx 1$ to 10^3 MHz), have much in common. Both techniques were developed in the 1940s (certainly World War II influenced the desire to develop microwave oscillators and understand rf technology) and became important research tools in the decade that followed. "Microwave Spectroscopy" by Townes and Schawlow,[1] first published in 1955, became a classic text on the subject. The first NMR text, "Nuclear Moments" by N. F. Ramsey, was published in 1953.[2] Also among the first NMR texts were "Spectroscopy at Radio and Microwave Frequencies" by D. J. E. Ingram[3] and "Nuclear Magnetic Resonance" by E. R. Andrew.[4] Many of the experimental developments in the two fields parallel one another. Most important was the development of Fourier transform (FT) methods which revolutionized both fields. R. R. Ernst and W. A. Anderson published the first papers on FT NMR[5] in 1966. W. H. Flygare played an important role in the development of FT microwave techniques.[6] Microwave experiments are carried out on low-pressure gas samples (≤ 1 Torr), while NMR experiments are typically carried out on liquid or solid samples. Gas-phase NMR experiments are feasible; however, one typically requires pressures that exceed 1 Torr. In microwave spectroscopy, the focus is on the quantized rotational angular momentum of the molecule, $\mathcal{J}$, while in the case of NMR, the focus is on the quantized nuclear spin angular momentum, $\mathbf{I}$.

In addition to the similarities in their origins and developments as widely used techniques, the underlying theory and information which is available from microwave and NMR spectroscopies are intimately related. The purpose of this Account is to present the important, but widely overlooked, connections between these two seemingly disparate areas of spectroscopy, in the context of our recent experimental and computational investigations of their relationship. Specifically, we will discuss the information that one can extract from the hyperfine structure (hfs) present in high-resolution microwave experiments and molecular beam experiments[7−11] and contrast this information with the "observables" from NMR experiments. Due to the complicated nature of the interactions involved, the discussion will focus on small molecules, particularly on diatomic molecules. While much of the theory we discuss here was recognized and discussed by N. F. Ramsey in his classic text, "Molecular Beams", published in 1956, this information seems to have been largely forgotten by the general chemistry community.

Overview of Nuclear Spin Interactions: The Connections

The most important Hamiltonian operator in microwave spectroscopy is the rotational Hamiltonian, which leads to information about the molecular rotational constants and the molecular inertia tensor. Small perturbations to

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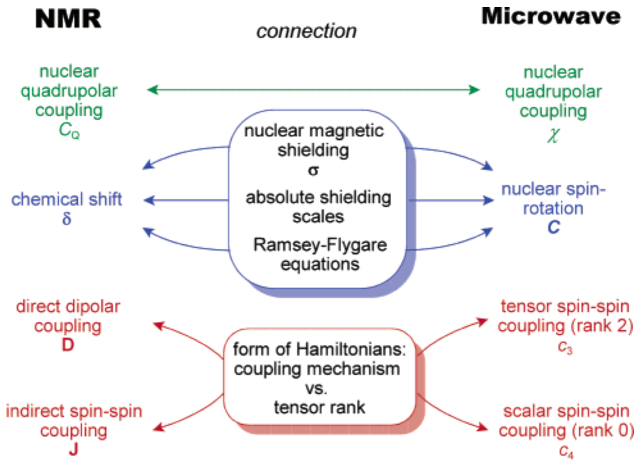

FIGURE 1. Schematic illustration of the connections between the hyperfine parameters of microwave and molecular beam spectroscopies, and the parameters of nuclear magnetic resonance spectroscopy.

this Hamiltonian are summarized in the relevant hyperfine Hamiltonian[7] for a $^1\Sigma$ diatomic molecule (e.g., for chlorine monofluoride, $^{35}Cl^{19}F$):

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

The nuclear spin quantum number, I, of ^{35}Cl is $^3/_2$, and that of ^{19}F is $^1/_2$. The four interactions of interest here are (i) the nuclear electric quadrupolar interaction for chlorine ($\mathbf{V}_{Cl}:\mathbf{Q}_{Cl}$), (ii) the nuclear spin–rotation interaction (for chlorine and for fluorine, $c_{Cl}\mathbf{I}_{Cl}\cdot\mathcal{J} + c_F\mathbf{I}_F\cdot\mathcal{J}$), (iii) the tensor spin–spin coupling interaction between chlorine and fluorine ($c_3\mathbf{I}_{Cl}\cdot\mathbf{d}_T\cdot\mathbf{I}_F$), and (iv) the scalar spin–spin coupling interaction between chlorine and fluorine ($c_4\mathbf{I}_{Cl}\cdot\mathbf{I}_F$). These interactions will be discussed in more detail below, and the connections between the microwave and NMR parameters will be elucidated (Figure 1).

A. Nuclear Quadrupolar Coupling and Electric Field Gradient Tensors. Most elements have at least one isotope with a quadrupolar nucleus, i.e., for which $I > {}^1/_2$. Nuclear quadrupolar coupling results from the interaction of a nonzero electric field gradient (EFG) ($\mathbf{V}_I$, cf. eq 1) at a nucleus with the nuclear electric quadrupole moment, Q. The product of Q and the largest component of the EFG tensor, V_{ZZ}, is known as the nuclear quadrupolar coupling constant (in frequency units):

$$\chi = C_Q = eQV_{ZZ}/h \quad (2)$$

The symbols χ, used in the microwave literature, and C_Q, used in the NMR literature, represent the same quantity. In NMR spectroscopy, one generally measures C_Q in solids,[12] while in microwave spectroscopy, one measures χ for essentially isolated molecules.

B. Nuclear Spin Rotation, Nuclear Magnetic Shielding, and Chemical Shift Tensors. Two connections must be made to associate the nuclear spin–rotation tensor (**C**) observed in microwave spectroscopy with the related NMR observable, the chemical shift tensor ($\boldsymbol{\delta}$). The nuclear spin–rotation interaction describes the magnetic coupling of the nuclear spin angular momentum with the rotational angular momentum of the molecule:

$$\mathcal{H}_{SR} = \mathbf{I}\cdot\mathbf{C}\cdot\mathcal{J} \quad (3)$$

The **C** tensor reduces to a coupling constant, c_I, for a linear molecule (cf. eq 1). This part of the coupling tensor represents the component which lies perpendicular to the bond axis.

The bridge between nuclear spin–rotation tensors and chemical shift tensors is the nuclear magnetic shielding tensor, $\boldsymbol{\sigma}$ (Figure 1). According to Ramsey's formalism,[13] σ may be decomposed into diamagnetic ($\boldsymbol{\sigma}^d$) and paramagnetic ($\boldsymbol{\sigma}^p$) contributions:

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}^d + \boldsymbol{\sigma}^p \quad (4)$$

The former depends on the ground state of the molecule and may be calculated accurately using standard quantum chemical methods. The paramagnetic shielding parallel to the bond axis, $\sigma_{\parallel}{}^p$, is zero for a linear molecule. Conversely, the paramagnetic shielding perpendicular to the bond axis, $\sigma_{\perp}{}^p$, is difficult to calculate accurately. Flygare[14] demonstrated that $\sigma_{\perp}{}^p$ could be determined from the experimental spin–rotation constant for a nucleus in a diatomic molecule as follows:

$$\sigma_{\perp}{}^p = \frac{3}{2}\sigma^p = -\left(\frac{m_p}{2m_e g_N}\right)\left(\frac{c_I}{B}\right) - \frac{3}{2}\left(\frac{\mu_0}{4\pi}\right)\left(\frac{e^2}{3m_e}\right)\left(\frac{Z}{r}\right) \quad (5)$$

Here, m_p is the mass of a proton, m_e is the mass of an electron, g_N is the nuclear g-factor for the nucleus of interest, B is the rotational constant of the molecule, μ_0 is the permeability of free space, e is the electronic charge, Z is the atomic number of the other nucleus in the molecule, and r is the internuclear distance.

Thus, there is a useful connection here between the nuclear spin–rotation constant for a nucleus, and its nuclear magnetic shielding constant. To make the leap from the nuclear magnetic shielding constant to the chemical shift, one simply appeals to the definition of the chemical shift

$$\delta = \frac{\nu - \nu_{ref}}{\nu_{ref}} = \frac{\sigma_{ref} - \sigma}{1 - \sigma_{ref}} \quad (6)$$

where ν_{ref} and σ_{ref} are the resonance frequency and shielding constant, respectively, of a reference compound, e.g., Cl^- (aq., ∞ dilute) for chlorine chemical shifts, tetramethylsilane for proton and carbon chemical shifts, and H_2O (l) for oxygen chemical shifts. The nuclear magnetic shielding interaction therefore represents a link between the spin–rotation interaction of microwave spectroscopy and the chemical shifts observed in NMR spectroscopy.

C. Spin–Spin Coupling Tensors. The direct dipolar coupling between two nuclei (**I** and **S**) is the classical magnetic interaction between two bar magnets:

$$\mathcal{H}_{DD} = \mathbf{I}\cdot\mathbf{D}\cdot\mathbf{S} \quad (7)$$

The direct dipolar coupling tensor, **D**, is fully described by the direct dipolar coupling constant, R_{DD}, which depends on the motionally averaged inverse cube of the distance separating the two spins involved:

$$R_{DD} = \frac{\mu_0}{4\pi}\frac{\gamma_I\gamma_S\hbar}{2\pi}\langle r_{IS}^{-3}\rangle \tag{8}$$

Nuclear spins are also coupled indirectly via the intervening electrons. This indirect nuclear spin–spin coupling, or **J**, interaction is represented by

$$\mathcal{H}_J = \mathbf{I}\cdot\mathbf{J}\cdot\mathbf{S} \tag{9}$$

For a diatomic molecule, the **J** coupling tensor contains contributions from isotropic and symmetric components. The isotropic part is widely known in NMR spectroscopy as the "scalar" coupling constant, J_{iso}, and is equal to one-third of the trace of the **J** tensor. The symmetric part of the **J** tensor may be completely described, in the case of a linear molecule, by J_{iso} and the anisotropy (ΔJ):

$$\Delta J = J_{\parallel} - J_{\perp} \tag{10}$$

To make the connection between the NMR parameters R_{DD}, J_{iso}, ΔJ, and the corresponding microwave parameters, it is instructive to consider the total spin–spin coupling tensor (direct dipolar and indirect). The sum NMR spin–spin coupling Hamiltonian in this simple case may be written as (cf. eqs 7 and 9)

$$\mathcal{H}_{DD} + \mathcal{H}_J = \mathbf{I}\cdot(\mathbf{D} + \mathbf{J})\cdot\mathbf{S} \tag{11}$$

Separating the isotropic and symmetric portions of the tensors gives

$$\mathcal{H}_{DD} + \mathcal{H}_J = J_{iso}\mathbf{I}\cdot\mathbf{S} + \mathbf{I}\cdot(\mathbf{D} + \mathbf{J}^{sym})\cdot\mathbf{S} \tag{12}$$

The effect of the sum $\mathbf{D} + \mathbf{J}^{sym}$ tensor is summarized in the effective dipolar coupling constant, R_{eff}:

$$R_{eff} = R_{DD} - \frac{\Delta J}{3} \tag{13}$$

The key result of this description (eqs 11–13) of the total symmetric spin–spin coupling tensor is that R_{DD} and ΔJ are inseparable in a real system.[15] Rather than separating the **D** and **J** interactions, the microwave Hamiltonian separates the total spin–spin coupling interaction based on tensor properties (Figure 1). The scalar terms are represented as $c_4\mathbf{I}_{Cl}\cdot\mathbf{I}_F$, while the symmetric tensor terms are represented in the $c_3\mathbf{I}_{Cl}\cdot\mathbf{d}_T\cdot\mathbf{I}_F$ term (eq 1). These expressions correspond to the NMR-based equations described above such that $c_4 = J_{iso}$ and $c_3 = R_{eff}$. These relationships have been alluded to;[7,9,16] however, they are not widely appreciated in the NMR community.

It is beneficial to define a reduced coupling tensor $\mathbf{K}(I, S)$ which is related to $\mathbf{J}(I,S)$ by the following equation:

$$\mathbf{K}(I,S) = \frac{4\pi^2\mathbf{J}(I,S)}{\gamma_I\gamma_S h} \tag{14}$$

The reduced coupling tensor is independent of the magnitude of the nuclear magnetic moments and is therefore useful in comparing indirect spin–spin coupling tensors involving different spin pairs. Note that $\mathbf{J}(I,S)$ has units of Hz ($\equiv s^{-1}$) and $\mathbf{K}(I,S)$ has units of N A^{-2} m^{-3}.

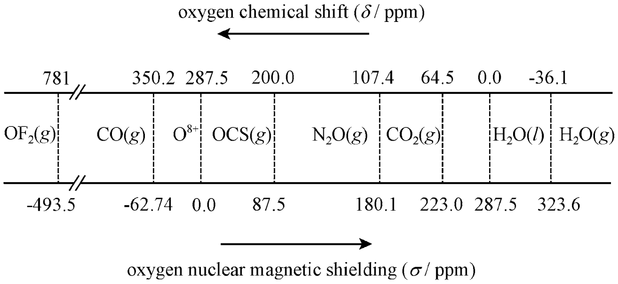

FIGURE 2. Comparison of the oxygen chemical shift and magnetic shielding scales. From ref 19.

In this Account, we will not attempt to treat in detail rotational–vibrational effects on the microwave and NMR parameters. We have found Buckingham's paper particularly useful in the case of diatomic molecules.[17] For the examples discussed here, we will indicate the approximate magnitude of these corrections; further details can be found in our original papers.[15,18,19]

Applications

A. Absolute Shielding Scales. One of the most important applications of the connection between nuclear spin–rotation constants and nuclear magnetic shielding constants is the establishment of absolute magnetic shielding scales.[20] In NMR spectroscopy, one measures the chemical shift of a particular peak in a spectrum with respect to a reference compound whose chemical shift is set to a particular arbitrary value for convenience. The arbitrary nature of the chemical shift is evidenced, for example, in the case of nitrogen chemical shifts where two scales with different origins are in common use. This arises from the fact that δ is not a fundamental quantity, but is a derived quantity defined in terms of the nuclear magnetic shielding (eq 6). Note that σ rather than δ is determined in quantum chemical calculations.[21] The origin of the nuclear magnetic shielding scale is the hypothetical "bare" nucleus, e.g., O^{8+} for oxygen (Figure 2).

To impart the chemical shift scales and chemical shift values used in NMR spectroscopy with a connection to fundamental molecular and electronic properties, one must establish an absolute shielding scale, whereby the absolute magnetic shielding constant for a particular compound (a reference compound) is measured. Once σ_{ref} is known for a compound whose chemical shift may also be measured with respect to a chemical shift reference, an absolute shielding scale is established. From that point forward, experimental chemical shifts may be directly converted to magnetic shielding constants (eq 6). Thus, an absolute shielding scale allows one to make use of quantum chemical calculations of shielding tensors, because a proper comparison between experimental and calculated chemical shifts (or magnetic shieldings) may be made.

If magnetic shielding constants cannot be directly measured in NMR, how does one go about determining the value of σ_{ref}? This is where the microwave connections become of paramount importance (Figure 1). The accepted absolute magnetic shielding scales for carbon[22] and oxygen[19] are based on ^{13}C and ^{17}O nuclear spin rotation constants measured for $^{13}C^{16}O$ and $^{12}C^{17}O$, respectively.

In 1984, we established an ^{17}O absolute magnetic shielding scale based on $c_{O-17} = -30.4 \pm 1.2$ kHz, which was determined from the $J = 1 \leftarrow 0$ rotational transition for $^{12}C^{17}O$ in interstellar space, namely, the Bok globule B335.[23] Using the Ramsey–Flygare equations, we employed this spin–rotation constant to calculate the isotropic value of the oxygen magnetic shielding tensor for $^{12}C^{17}O$, $\langle\sigma\rangle_{v=0} = -42.3 \pm 17.2$ ppm (this value corresponds to the ground vibrational state, $v = 0$). This value has served as a benchmark for quantum chemical calculations of oxygen magnetic shielding tensors over the past 18 years. Despite some discrepancies in the calculated results reported for various computational methods, it seemed that the calculations were generally indicating that the true value for the oxygen shielding constant in CO lay at the lower end of our experimental error range. In 2002, a particularly precise experimental value was reported for c_{O-17} in $^{12}C^{17}O$, -31.609 (41) kHz.[24] Such an improvement in the precision of the ^{17}O spin–rotation constant compared to the value used to setup the original 1984 scale prompted us to establish a revised, more precise scale.[19] The oxygen spin–rotation constant in the ground vibrational state was converted to the absolute shielding constant at 300 K, -62.7 ± 0.6 ppm. Obtaining reliable results requires incorporating corrections for rotational–vibrational averaging, as discussed in our original paper.[19] Given that the experimental oxygen chemical shift of carbon monoxide is known to be 350.2 ppm with respect to the primary reference, H_2O(*l*, 293 K) at 0.00 ppm, the absolute magnetic shielding constant for oxygen in any compound, whose chemical shift has been measured, may be determined (see Figure 2). For example, the absolute oxygen magnetic shielding constant for liquid water at 300 K is 287.5 ppm. The absolute shielding scale thus provides an abundance of absolute shielding values against which calculated results may be compared. We note that the oxygen magnetic shielding of liquid water decreases[25] by 0.047 ppm K^{-1}, while for CO(g) and H_2O(g)[26] the temperature dependence of the oxygen shielding will be negligible near 300 K.

Adaptations of Flygare's equations may be applied to molecules of lower symmetry for which there are three independent components of the interaction tensors. For example, the carbon and oxygen spin–rotation and $\boldsymbol{\sigma}$ tensors in formaldehyde have been discussed.[27] In this case, the $\boldsymbol{\sigma}$ tensors exhibit anisotropy and asymmetry; they are not isotropic and cannot be represented by a single scalar quantity.

B. Isotropic and Anisotropic J Coupling. "Scalar" *J* coupling constants are of ubiquitous importance in solution and solid-state NMR spectroscopy. Since *J* coupling is in fact represented by a second-rank tensor, the term "scalar" is not entirely fitting to describe the coupling. In the solid state and in liquid-crystal solutions, some information is available on the orientation-dependent nature of the *J* coupling, i.e., ΔJ.[28]

Interpretation of isotropic coupling constants in terms of empirical correlations may work well for couplings involving protons; however, a truly general interpretation of coupling constants which applies to all elements in all bonding environments is lacking. Phosphorus–phosphorus coupling constants are an interesting example.[29] The lack of a simple interpretation arises for two main reasons. First, routine NMR experiments do not measure the absolute sign of the coupling constant. Second, there are three independent mechanisms which contribute to J_{iso}: the spin–orbital (SO) mechanism, usually subdivided into diamagnetic (DSO) and paramagnetic (PSO) parts; the spin-dipolar (SD) mechanism; and the well-known Fermi-contact (FC) mechanism. The SD × FC cross term contributes to ΔJ but not to J_{iso}. These mechanisms are not required to follow a similar dependence on local structural variations. Nevertheless, there is an abundance of J_{iso} data available for interpretation. In contrast, the structural dependence of ΔJ is far less well-characterized.

Over the past few years, we have exploited the connection between NMR and microwave spectroscopy to extract numerous highly precise values of J_{iso} and ΔJ for a wide variety of spin pairs in diatomic molecules.[15,30] This has significantly increased the total number of precisely known values of ΔJ and also expanded appreciably the range of the periodic table for which values are known.[31]

As an example, we discuss the case of $^{35}Cl^{19}F$. Fabricant and Muenter reported in 1977 that $c_3 = 2859 \pm 9$ Hz and $c_4 = 840 \pm 6$ Hz for the $v = 0$, $J = 1$ state.[32] As for most molecular beam determinations of hyperfine constants, these parameters are the result of spectroscopic measurements *within* the indicated rotational–vibrational state. The value of c_4 may be immediately equated to J_{iso}. To determine ΔJ, we make use of independent knowledge of the bond length in ClF, $r_e = 1.628\,332\,3$ Å,[33] to obtain the direct dipolar contribution to c_3, $R_{DD} = 2571$ Hz. This value may then be converted from the hypothetical equilibrium state to the $v = 0$, $J = 1$ state to give $R_{DD} = 2557$ Hz. Identification of c_3 with R_{eff}, and application of eq 13, gives ΔJ as -907 ± 27 Hz. The precise data which we have been able to extract from microwave and molecular beam results are given in Table 1.

Around the same time we were attempting to propose periodic trends in **J** coupling on the basis of microwave data, we were fortunate to be visited by Kenneth Ruud, who introduced us to multiconfigurational self-consistent field (MCSCF) calculations of **J** tensors. **J** is the most challenging NMR parameter to calculate. During the past decade, however, remarkable advances in this area have been made. As the computational methods continue to improve, they offer the potential to systematically study trends in both the isotropic and anisotropic parts of **J**. One is limited to relatively small molecules, however, especially in the case of ab initio methods. The discovery of the abundant precise data for diatomic molecules was well-timed with the increasing feasibility of calculating **J** tensors for light molecules.

Table 1. Selection of Precise Reduced Indirect Nuclear Spin−Spin Coupling Data Available for Diatomic Molecules from Microwave-based Spectroscopies[a]

molecule	K_{iso} (10^{20} N A^{-2} m^{-3})	ΔK (10^{20} N A^{-2} m^{-3})
LiH	2.89	−1.22
LiF	3.92	3.94
LiBr	5.15	18.1
LiI	6.65	18.4
NaBr	9.76	43.9
KF	10.9	23.8
CsF	41.8	46.5
CsCl	39.4	67.9
Na_2	127	−5.71
ClF	75.7	−81.8
BrF	171	−206
IF	252	−257
InF	−86.4	89.9
TlF	−202	173
TlCl	−224	262
TlBr	−361	448
TlI	−474	664
I_2	763	−785

[a] References to original hyperfine data and rovibrational states are given in refs 15, 28, and 30.

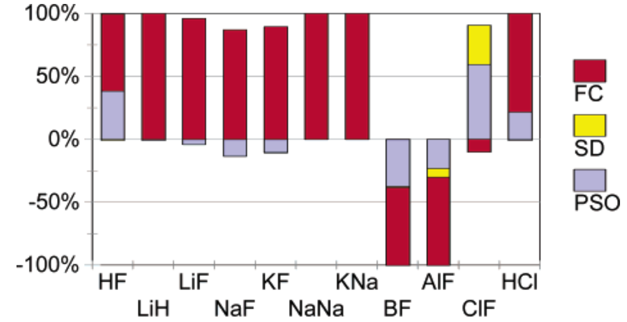

FIGURE 3. Graphical representation of the percentage contributions of each of the *J*-coupling mechanisms to the isotropic coupling constant for a series of diatomic molecules, as determined by MCSCF calculations. Adapted from ref 15.

MCSCF calculations on a series of first- and second-row diatomics helped to establish the reliability of the method for calculating the anisotropic part of the **J** tensor in addition to the isotropic part. The example of ClF turned out to be very important, exhibiting a particularly large value of ΔJ for a relatively light molecule which is accessible by the calculations. The combination of precise experimental data and accurate computational results allowed us to propose several periodic trends. While trends in J_{iso} had been proposed more than 30 years ago, trends in ΔJ were much less well-understood.[16,34] Furthermore, the calculations have allowed us to examine the contribution of each of the coupling mechanisms to the periodic trends (Figures 3 and 4). One of the important findings is that for ClF, the PSO contribution is the dominant contributor to both J_{iso} and ΔJ, while the FC mechanism (often assumed to be dominant) plays a relatively minor role.[15]

Some of the key periodic trends which have been elucidated are the following:

(i) the absolute value of K_{iso} and ΔK tend to increase as one moves down the periodic table;

(ii) the absolute value of K_{iso} and ΔK tend to increase as one moves from left to right across the periodic table;

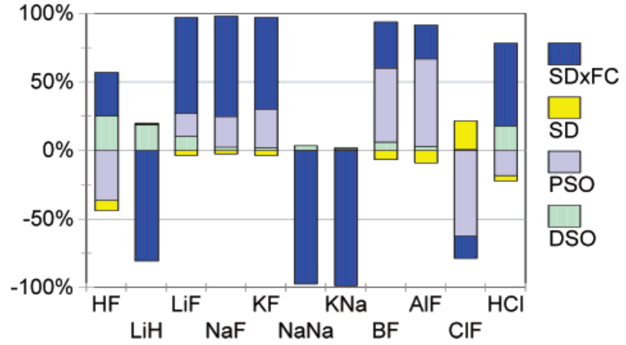

FIGURE 4. Graphical representation of the percentage contributions of each of the *J*-coupling mechanisms to the anisotropic coupling for a series of diatomic molecules, as determined by MCSCF calculations. Adapted from ref 15.

(iii) the dominance of the Fermi-contact term seems to be most important for spin pairs from the far left of the periodic table, and least important at the far right of the periodic table;

(iv) the ratio ΔJ:J_{iso} tends to increase as one moves to heavier nuclei, i.e., the anisotropy in **J** increases more rapidly with atomic number than does J_{iso};

(v) the contribution of ΔJ to R_{eff} tends to increase as one moves down the periodic table;

(vi) in general, all coupling mechanisms (SO, SD, FC) may contribute significantly to J_{iso};

(vii) in general, all coupling mechanisms (SO, SD, SD × FC) may contribute significantly to ΔJ.

Subsequently, in collaboration with Corey Evans and Michael Gerry, an experimental attempt was made to measure c_3 and c_4 for GaF using pulsed FT microwave spectroscopy[35] in order to expand the experimental data available for the group 13 fluorides. Unfortunately, the spectral resolution was not adequate to provide conclusively precise measurements in this case. However, precise nuclear quadrupolar coupling constants and spin−rotation constants were obtained. Later on, using relativistic zeroth-order relativistic approximation (ZORA) DFT calculations (vide infra), we calculated K_{iso}(Ga, F) as -47.9×10^{20} N A^{-2} m^{-3} and ΔK(Ga,F) $= -55.4 \times 10^{20}$ N A^{-2} m^{-3} (spin−orbit relativistic, ZORA V basis set, unpublished), values which are in good agreement with those proposed on the basis of an interpolation of the other group 13 fluoride data.[15,35]

In 2000, ZORA density functional code written by Jochen Autschbach in the research group of Tom Ziegler allowed them to carry out calculations on heavier diatomics such as TlX (X = F, Cl, Br, I), using the microwave data as benchmarks.[36,37] Their DFT methods were also shown to give results in good agreement with experiment[32,38] for the halogen fluorides (ClF, BrF, IF) and with our MCSCF results for ClF. In a collaboration with Autschbach and Ziegler, the accuracy of the ZORA-DFT method was further established for heavy diatomics where spin−orbit relativistic effects were found to play a very important role.[30] For example, in the case of molecular iodine, the spin−orbit relativistic contribution to $J_{iso}(^{127}I,^{127}I)$ was found to be 21%. This work also confirmed the dominance

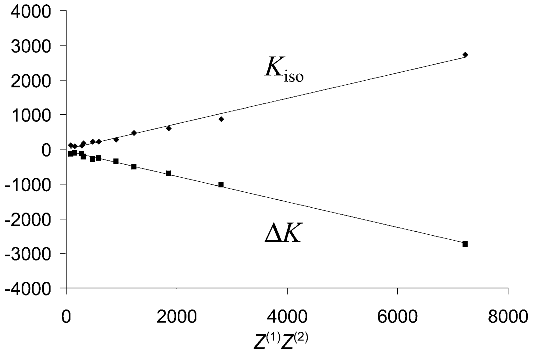

FIGURE 5. Plot of the reduced isotropic and anisotropic couplings for the interhalogen diatomics as a function of the product of the atomic numbers of the coupled nuclei. The units for the coupling constants are 10^{20} N $A^{-2}m^{-3}$. Results are from relativistic ZORA-DFT calculations presented in ref 30.

(~70−80%) of the PSO term and minor role of the FC term for interhalogen coupling constants. Calculations for the interhalogen diatomics provided data on both the isotropic and anisotropic portions of the coupling tensors such that their dependence on the atomic numbers of the nuclei involved could be examined (Figure 5). As shown, there is a linear dependence for both K_{iso} and ΔK.

More recently, Lantto et al. have used the microwave data which we have converted to J_{iso} and ΔJ as benchmarks for their new DFT implementation for the calculation of spin−spin coupling tensors.[39]

Some understanding of periodic trends in ΔJ is important to NMR spectroscopists who apply NMR experiments to determine internuclear distances.[40] In any NMR experiment designed to utilize direct dipolar coupling constants to measure internuclear distances or bond vector orientations, recognition that one can only measure R_{eff} which contains an a priori unknown contribution from ΔJ is important. Awareness of possible errors which could result from ignoring ΔJ is essential. To this end, we have recently investigated the influence of ΔJ on residual dipolar couplings (RDCs) for model peptides.[41] Over the past few years, the measurement of RDCs for peptides, proteins, oligosaccharides, and nucleic acids dissolved in weakly orienting media has become a popular technique for gaining structural information on these biopolymers.[42−44] Our DFT results indicate that very small corrections are required for one-bond carbon−carbon and carbon−nitrogen RDCs, while corrections to RDCs involving at least one proton are negligible.[41] In contrast, RDCs involving metals in metalloproteins could bear significant contributions from ΔJ.

Conclusions and Future Directions

We hope that this brief exposition is informative to active researchers in the areas of NMR and microwave spectroscopy, and to a wider audience who may frequently use NMR chemical shifts and J-coupling constants as a source of structural information in their research. The two areas where these NMR-microwave connections have had the most impact thus far are in (i) the establishment of absolute magnetic shielding scales and (ii) the increased availability of very precise complete spin−spin coupling tensors for a wide variety of spin pairs. Absolute shielding scales, in concert with ab initio and DFT calculations, are essential to provide a well-founded interpretation of chemical shifts which are routinely measured by scientists working in such diverse areas as structural biology, synthetic chemistry, geological sciences, and materials science. The spin−spin coupling data for isolated molecules have allowed for the proposal of new periodic trends, and provide accurate benchmarks for the testing of various computational methods. Of particular importance is the conclusion that the Fermi-contact mechanism is not necessarily dominant even for light molecules, and that in general *all* coupling mechanisms should be considered when calculating and interpreting spin−spin coupling tensors.

Further investigations of relativistic effects are expected to be very important, particularly in the case of nuclear spin−rotation tensors and magnetic shielding tensors.[45] For example, will Flygare's equations, which provide one of the bridges between microwave and NMR spectroscopies, still be valid if relativistic contributions dominate the spin−rotation tensor? Research in this area will help to determine the feasibility of establishing accurate, precise absolute magnetic shielding scales for heavy nuclei such as ^{199}Hg and ^{207}Pb.

Studies of the rotational−vibrational dependence of the spin−spin coupling tensor represent another important future research direction. For example, Cederberg et al. have reported $c_4(^{133}\text{Cs}, ^{19}\text{F}) = J_{\text{iso}}(^{133}\text{Cs}, ^{19}\text{F})$ in CsF to be $0.62745(30) - 0.00903(22) \times (v + 1/2)$ kHz, with 1 standard deviation of uncertainty reported in the last two digits shown in brackets.[46] How well do quantum chemical calculations reproduce this dependence? What is the situation for larger, more complicated molecules? Ruud and co-workers have begun to look into some of these questions.[47]

Finally, it is fitting to acknowledge the tremendous contributions that Norman Ramsey has made toward establishing the theoretical foundations for the "observables" of NMR spectroscopy, and his insights into how these parameters are related to those he measured by molecular beam techniques that he first carried out in the laboratory of I. I. Rabi.[48] Some of Ramsey's publications in these areas are among the most influential in 20th century quantum chemistry.[49]

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