

## Thermal averaging of the spin–rotation coupling in small molecules leads to an isotropic NMR shielding

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### ABSTRACT

It has been known for over 70 years that nuclear spins couple to molecular rotation via a Zeeman interaction. This spin–rotation coupling can be observed as a discrete splitting in molecular beam magnetic resonance experiments, but is quenched by molecular collisions at higher pressures. We show that because of differential thermal population of  $M_J$  levels at high magnetic fields, the spin rotation coupling retains a small isotropic component at high field. For all but the smallest molecules at very low temperature, the residual coupling is temperature independent and linear in the magnetic field; it therefore closely mimics the chemical shift. The ‘super spin rotation’ shift may in the future be a necessary correction to ultra – high precision computations of the NMR chemical shielding of small molecules in gases and liquids.

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The conventional nuclear magnetic resonance (NMR) spin- $\frac{1}{2}$  Hamiltonian for diamagnetic molecules in isotropic (liquid and gaseous) phases contains only three terms

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_\sigma + \mathcal{H}_J \quad (1)$$

where  $Z$ ,  $\sigma$  and  $J$  stand for the nuclear Zeeman, chemical shielding, and  $J$  (indirect spin–spin coupling) interactions respectively. There is in addition a direct dipole–dipole interaction, often the most significant source of spin relaxation, but it has no isotropic component. In addition, in gases at very low pressure, a spin–rotation coupling is observed. In molecular-beam magnetic resonance experiments [1] this coupling leads to discrete splittings of the NMR spectrum [2]. However, in liquids, and even in gases at pressures sufficient to allow direct inductive measurement of NMR spectra, the spin–rotation coupling is averaged the collisional quenching of angular momentum, and it has been observed only by its effect on the relaxation of gases [3] and of low molecular weight molecules in non-viscous liquid phases [4]. In this paper, we demonstrate that in gases, and probably in liquids, spin–rotation also leads to a small frequency shift which mimics the chemical shielding and which may have to be considered in computations that aim to match experimental NMR chemical shifts to a high degree of accuracy.

We consider the case of a single NMR-active nucleus in a linear molecule in the gas phase in a magnetic field  $B_z$ , and ignore the moment vibrational effects, centrifugal distortion terms and second-order effects due to the magnetic susceptibility. The Hamiltonian in frequency units is given by

$$\mathcal{H} = B_e J(J+1) - g\mu_N M_J B_z - \gamma(1-\sigma)M_I B_z - cM_J M_I \quad (2)$$

Here the first term is the conventional rigid-rotor kinetic energy with the rotational constant  $B_e = h/(8\pi^2 I_e)$ ,  $I_e$  being the moment of inertia at the classical equilibrium bond-length, and  $J$  being the rotational angular momentum quantum number. The second term is the molecular Zeeman interaction,  $g$  being the molecular  $g$  factor [5],  $\mu_N$  the nuclear magneton,  $M_J$  and  $M_I$  the  $z$ -axis molecular rotation and nuclear spin angular momentum quantum numbers respectively, and  $z$  the direction of the external magnetic field  $B_z$ . In the third term  $\gamma$  is the nuclear gyromagnetic ratio in Hz/T, and  $\sigma$  the isotropic chemical shielding. The final term describes the spin–rotation coupling, with  $c$  the spin–rotation coupling constant in Hz; the sign convention used in Ref. [6] is adopted. We have included only the secular part, which is valid as long as the difference between molecular and nuclear Zeeman frequencies is large compared with  $c$ . This Hamiltonian neglects susceptibility terms that are second order in the rotational quantum numbers, as well as averaging over the vibrational wavefunctions.

For any given value of  $J$ , the values of  $M_J$  vary between  $-J$  and  $J$ . The values of both  $J$  and  $M_J$  are scrambled by molecular collisions, and it has been conventional to assume the result is averaging to zero of terms linear in  $M_J$ , on the time scale of the rotational state lifetime, which is a fraction of a nanosecond for typical gases at ambient pressures and temperatures. This is assumption is not strictly correct. If values of the molecular  $g$  term enter the MHz regime, as they may do for high values of quantum number  $J$ , within any manifold of quantum number  $J$  the thermal average value of  $M_J$  will be non-zero, because of Boltzmann population differences between the states of different  $M_J$ . The effect is small

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enough that we can use the high temperature approximation truncated at the first term:

$$\exp(-\Delta E/kT) = 1 - \Delta E/kT + \dots \quad (3)$$

$\Delta E$  is the energy difference of the state of quantum number  $M_J$  relative to the corresponding  $M_J = 0$  state.

$$\Delta E = -hg\mu_N M_J B_z \quad (4)$$

Within a manifold of  $2J + 1$  states with the same quantum number  $J$ , and under the assumption the spin-rotation coupling is much smaller than the molecular  $g$  factor, the probability of being in the state  $M_J$  will be:

$$p_{M_J} = p_J \left( \frac{1 + hg\mu_N M_J B_z / kT}{2J + 1} \right) \quad (5)$$

Since the spin-rotation frequency of state  $M_J$  is  $-cM_J M_I$ , the ensemble average of the spin-rotation frequency within the manifold will be given by

$$\langle c_J \rangle = -\frac{cM_I}{p_J} \sum_{M_J=-J}^J p_{M_J} M_J = -cM_I \sum_{M_J=-J}^J \frac{M_J(1 + g\mu_N M_J B_z / kT)}{(2J + 1)} \quad (6)$$

Since

$$\sum_{M_J=-J}^J M_J(1 + aM_J) = a \sum_{M_J=-J}^J M_J^2 = \frac{a}{3} J(1 + J)(1 + 2J) \quad (7)$$

we can reduce (6) to

$$\langle c_J \rangle = \frac{J(1 + J)hcM_I B_z g\mu_N}{3kT} \quad (8)$$

We now perform a similar ensemble average over all manifolds  $J$ , to give the completely thermally averaged spin rotation coupling  $\langle c \rangle$

$$\langle c \rangle = \sum_{J=0}^{\infty} p_J \langle c_J \rangle \quad (9)$$

$p_J$  is the probability of a state being in manifold  $J$ , and is of course just given by the standard expression for the relative probability of rotational states.

$$p_J = \frac{(2J + 1) \exp[-J(1 + J)hB_0/kT]}{\sum_{j=0}^{\infty} (2j + 1) \exp[-j(1 + j)hB_0/kT]} \quad (10)$$

Inserting (10) and (8) in Eq. (9), making the usual high-temperature assumption that the sums over  $J$  can be replaced with integrals, we arrive at a remarkably simple expression:

$$\langle c \rangle = \frac{cB_z g\mu_N M_I}{3B_0} \quad (11)$$

This expression, which holds for most molecules of small to moderate size in the typical range of magnetic fields used for modern NMR, predicts a non-zero thermally-averaged spin-rotation shift that is linearly dependent on magnetic field, spin-rotation constant and molecular  $g$  factor, and inversely proportional to the rotational constant. In the limit  $hB_0/kT \ll 1$ , there is no temperature dependence. The shift therefore looks very similar to the chemical shielding, and in practice may be impossible to separate from it. We therefore take the frequency difference between the  $M_I = 1/2$  and  $M_I = -1/2$  states and divide by the field to obtain what we call the super spin rotation shielding or  $\sigma_{SSR}$ ; we also make it negative to concur with the sign convention for the chemical shielding.

$$\sigma_{SSR} = -\frac{(\langle c \rangle_{M_I=-1/2} - \langle c \rangle_{M_I=1/2})}{B_z} = \frac{cg\mu_N}{3B_0} \quad (12)$$

The shielding is named by analogy with the superhyperfine interaction, which arises from thermal averaging of hyperfine couplings. In another sense, it is analogous to the chemical shielding; just as rotation of the electrons about the magnetic field gives rise to the diamagnetic part of the chemical shielding, so rotation of the entire molecule gives rise to the super spin rotation.

In Table 1, we compute using Eq. (9),  $\sigma_{SSR}$  values, in parts per billion (ppb), of a set of diatomic linear molecules for which the molecular  $g$  factor has been measured experimentally. The computations are for the molecule at the classical equilibrium bond-distance, without considering rotational and vibrational effects. In a few cases, where spin-rotation constants were unavailable, they were computed using the program Gaussian-09 [7] using second order Møller-Plesset perturbation theory using the aug-cc-pV5Z basis set, at a bond-length optimized at the same level. Note that this program uses an earlier sign convention for  $c$ , opposite to that adopted here. Because Gaussian does not appear to use rotational London orbitals, which appreciably improve convergence of spin-rotation calculations [8], computations were also carried out at the double, triple and quadruple zeta levels, to check for basis set

**Table 1**  
super spin rotation contributions to chemical shieldings of diatomics, in parts per billion, computed using Eq. (11) from experimental values, except as noted.

| Mol.                          | Nucl.            | $B_e$ (GHz)         | Ref. | $g$                  | Ref. | $c$ (Hz)             | Ref.         | $\sigma_{SSR}$ (ppb) |
|-------------------------------|------------------|---------------------|------|----------------------|------|----------------------|--------------|----------------------|
| $^1\text{H}_2$                | $^1\text{H}$     | 1822.7              | [15] | 0.88291              | [5]  | 113904               | [5]          | 3.0                  |
| $^7\text{Li}^1\text{H}$       | $^1\text{H}$     | 225.24              | [15] | -0.65842             | [16] | 9345                 | [16]         | -1.6                 |
|                               | $^7\text{Li}$    |                     |      |                      |      | -10054               | [16]         | 4.5                  |
| $^{19}\text{F}^1\text{H}$     | $^1\text{H}$     | 627.74              | [15] | 0.74104              | [17] | 71500                | [18]         | 5.0                  |
|                               | $^{19}\text{F}$  |                     |      |                      |      | -283600              | [5]          | -21.2                |
| $^{35}\text{Cl}^1\text{H}$    | $^1\text{H}$     | 317.51              | [15] | 0.45935              | [5]  | 41000                | [19]         | 3.5                  |
|                               | $^{35}\text{Cl}$ |                     |      |                      |      | -47794               | <sup>a</sup> | -42.1                |
| $^{81}\text{Br}^1\text{H}$    | $^1\text{H}$     | 254.01              | [15] | 0.37122              | [20] | 41970 <sup>b</sup>   | [20]         | 3.7                  |
|                               | $^{81}\text{Br}$ |                     |      |                      |      | -313370 <sup>b</sup> | [20]         | -100.9               |
| $^{35}\text{Cl}^{19}\text{F}$ | $^{35}\text{Cl}$ | 15.485              | [15] | -0.1089              | [21] | -21596 <sup>b</sup>  | [22]         | 92.4                 |
|                               | $^{19}\text{F}$  |                     |      |                      |      | 22670                | [22]         | -10.1                |
| $^{81}\text{Br}^{19}\text{F}$ | $^{81}\text{Br}$ | 10.558              | [23] | -0.1004              | [21] | -95818 <sup>b</sup>  | [23]         | 200.7                |
|                               | $^{19}\text{F}$  |                     |      |                      |      | 24,170               | [23]         | -14.6                |
| $^{13}\text{C}^{16}\text{O}$  | $^{13}\text{C}$  | 55.354 <sup>c</sup> | [15] | -0.2689              | [6]  | -32,590              | [6]          | 37.6                 |
| $^{15}\text{N}_2$             | $^{15}\text{N}$  | 55.690              | [24] | -0.2593 <sup>b</sup> | [25] | 22000 <sup>b</sup>   | [26]         | 60.3                 |
| $^{13}\text{C}^{32}\text{S}$  | $^{13}\text{C}$  | 23.222 <sup>c</sup> | [15] | -0.2551 <sup>c</sup> | [27] | -23,650              | <sup>a</sup> | 61.6                 |
| $^{13}\text{C}^{77}\text{Se}$ | $^{13}\text{C}$  | 16.166 <sup>d</sup> | [27] | -0.2281 <sup>c</sup> | [27] | -17,084              | <sup>a</sup> | 57.2                 |
|                               | $^{77}\text{Se}$ |                     |      |                      |      | -62,138              | <sup>a</sup> | 273.1                |

<sup>a</sup> Computed as described in the text.

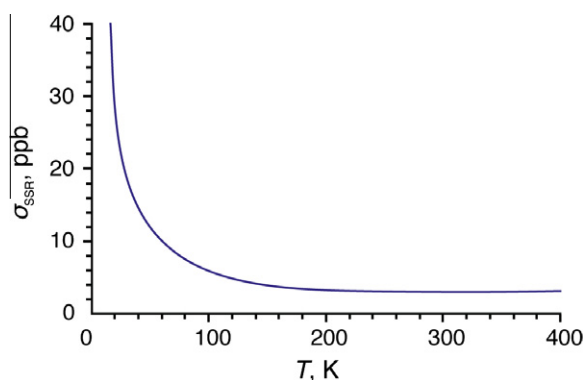
<sup>b</sup> Sign of published work reversed to conform with sign convention adopted in this paper, and verified by computation.

<sup>c</sup> Obtained from the value of the normal isotopomer using the ratio of reduced masses.

<sup>d</sup> Computed from  $r_e$  and the atomic masses.

convergence. The results of these computations are given in [Supplementary data](#). The maximum deviation from a complete basis set extrapolation was 3.3%, and in most cases it was much smaller. In almost all cases where experimental spin rotation constants were available, computed constants were in close agreement with them; corrections for rovibrational averaging, basis set incompleteness, and the approximate treatment of electron correlation were determined to be insignificant. The nuclear magneton  $\mu_N$  was assumed [9] to be 7.62259384 MHz/T; values for the nuclear gyromagnetic ratios are taken from the CRC handbook [10].

While in no case are the effects large – as can be seen from the compilation in [Table 1](#),  $\sigma_{SSR}$  can be a few tenths of a part per million (ppm) for third row diatomics – they are not negligible. In particular,  $^{13}\text{C}^{16}\text{O}$  and  $^{14}\text{N}_2/^{15}\text{N}_2$  are the respective primary benchmarks for computations of  $^{13}\text{C}$  and  $^{14}\text{N}/^{15}\text{N}$  chemical shielding. In state-of-the-art calculation of shieldings for both, incorporating coupled cluster computations of electron correlation, extensive basis sets, and correction for rovibrational effects [11], it will become increasingly important to include this correction. Second and particular third row corrections are even larger, although it is not clear that shielding of third row diatomics can be computed to a comparable degree of accuracy.



**Fig. 1.** The super spin rotation shift, in parts per billion, of molecular *ortho*-dihydrogen ( $\text{H}_2$ ), as a function of temperature.

Eq. (11) obviously breaks down outside the high-temperature approximation. At ambient temperatures this is a concern only for molecular hydrogen, and to a lesser extent diatomic hydrides. Molecular hydrogen (and, in principle, molecular fluorine and acetylene) also requires consideration of the quantum-mechanical coupling between nuclear spin and rotational states. Only the *ortho* form of hydrogen – where the hydrogen molecules occupy odd- $J$  states – gives an allowed NMR signal; collisional exchange between the odd- $J$  and even- $J$  manifolds is also very slow, and so the even- $J$  states must be excluded from the ensemble. The SSR shift of molecular hydrogen, calculated as an explicit average over only odd- $J$  states, is shown in [Fig. 1](#). The SSR shift is obviously temperature dependent, although it is still field-independent. As the temperature goes to zero, the  $J = 1$  level is the only *ortho* level populated,  $p_{J=1} \rightarrow 1$  and Eq. (8) reduces to

$$\langle C_{\text{H}_2, T \rightarrow 0} \rangle = \frac{2hcB_2g\mu_N M_l}{3kT} \quad (13)$$

giving

$$\sigma_{SSR, \text{H}_2, T} = \frac{2hcg\mu_N}{3kT} \quad (14)$$

As can be seen from [Fig. 1](#),  $\sigma_{SSR}$  is predicted to exceed 25 ppb near the normal boiling point of  $\text{H}_2$ . This could, in principle, be detected by NMR. At room temperature the shift is 3.0 ppb, quite close to its high temperature limit of 3.3 ppb. The NMR chemical shift of hydrogen gas has recently been measured at room temperature [12] to a claimed accuracy of 10 ppb, and so  $\sigma_{SSR}$  is a significant contribution. Similarly, room temperature SSR shifts of  $^1\text{H}^{19}\text{F}$  are computed to be about 3% below,  $^1\text{H}^{35}\text{Cl}$  about 2% below, and  $^1\text{H}^7\text{Li}$  1% below, their high- $T$  values given in [Table 1](#).

It should be noted, however, that *ortho*-hydrogen is only metastable, and given enough time will cool to the  $J = 0$  state.  $\sigma_{SSR}$  will therefore go to zero as  $T \rightarrow 0$ .

The temperature independence of the high-temperature limiting value of  $\sigma_{SSR}$  is a result of an interesting exact cancellation of two effects. As is seen from the computations for dihydrogen, an increase in temperature at constant non-zero  $J$  value leads to a reciprocal decrease in  $\sigma_{SSR}$ . However, increasing the temperature also increases the population of higher  $J$  levels. As  $J$  increases, so does

**Table 2**

super spin rotation contributions to chemical shieldings of linear triatomics, in parts per billion, computed using Eq. (11) from experimental values, except as noted.

| Mol.                                       | Nucl.             | $B_e$ (GHz)         | Ref.         | $g$                  | Ref. | $c$ (Hz)            | Ref.         | $\sigma_{SSR}$ (ppb) |
|--|-------------------|---------------------|--------------|----------------------|------|---------------------|--------------|----------------------|
| $^1\text{H}^{11}\text{B}^{33}\text{S}$     | $^1\text{H}$      | 18.932 <sup>b</sup> | [28]         | −0.0411 <sup>c</sup> | [29] | 1777                | <sup>a</sup> | −0.2                 |
|  | $^{11}\text{B}$   |                     |              |                      |      | −4600               | [30]         | 1.9                  |
|  | $^{33}\text{S}$   |                     |              |                      |      | −3700               | [30]         | 6.3                  |
| $^1\text{H}^{12}\text{C}^{15}\text{N}$     | $^1\text{H}$      | 43.028              | [31]         | −0.0904              | [32] | 4453                | <sup>a</sup> | −0.6                 |
|  | $^{15}\text{N}$   |                     |              |                      |      | −13,740             | [31]         | 17.0                 |
| $^1\text{H}^{12}\text{C}^{31}\text{P}$     | $^1\text{H}$      | 19.969              | [33]         | −0.0430              | [32] | 1869                | <sup>a</sup> | −2.4                 |
|  | $^{31}\text{P}$   |                     |              |                      |      | −43640 <sup>d</sup> | [34]         | 13.8                 |
| $^{19}\text{F}^{12}\text{C}^{15}\text{N}$  | $^{19}\text{F}$   | 10.539              | [35]         | −0.0504              | [36] | −7974               | <sup>a</sup> | 2.4                  |
|  | $^{15}\text{N}$   |                     |              |                      |      | 1817                | <sup>a</sup> | −5.1                 |
| $^{35}\text{Cl}^{12}\text{C}^{15}\text{N}$ | $^{35}\text{Cl}$  | 6.4843 <sup>b</sup> | [37]         | −0.0384              | [21] | −1695               | [38]         | 6.1                  |
|  | $^{15}\text{N}$   |                     |              |                      |      | 1744 <sup>e</sup>   | [37]         | −6.1                 |
| $^{81}\text{Br}^{12}\text{C}^{15}\text{N}$ | $^{81}\text{Br}$  | 4.0789              | [39]         | −0.03165             | [40] | −7344 <sup>f</sup>  | <sup>a</sup> | 12.5                 |
|  | $^{15}\text{N}$   |                     |              |                      |      | 1184                | <sup>a</sup> | −5.4                 |
| $^{15}\text{N}^{15}\text{N}^{16}\text{O}$  | $^{15}\text{N}_t$ | 12.214 <sup>b</sup> | [41]         | −0.07606             | [5]  | 2139                | <sup>a</sup> | −7.6                 |
|  | $^{15}\text{N}_m$ |                     |              |                      |      | 3229                | <sup>a</sup> | −11.5                |
| $^{16}\text{O}^{13}\text{C}^{32}\text{S}$  | $^{13}\text{C}$   | 6.0064              | <sup>a</sup> | −0.02871             | [42] | −3100 <sup>d</sup>  | [42]         | 3.5                  |
| $^{16}\text{O}^{13}\text{C}^{77}\text{Se}$ | $^{13}\text{C}$   | 4.0181              | [43]         | −0.01952             | [5]  | −2070 <sup>d</sup>  | [43]         | 2.4                  |
|  | $^{77}\text{Se}$  |                     |              |                      |      | −4610 <sup>d</sup>  | [43]         | 7.0                  |

<sup>a</sup> Computed as described in the text.

<sup>b</sup> Computed from the equilibrium bond lengths and atomic masses.

<sup>c</sup> Obtained from the value of the normal isotopomer using the ratio of rotational constants.

<sup>d</sup> Sign of published work reversed to conform with sign convention adopted in this paper, and verified by computation.

<sup>e</sup> Computed from the  $^{14}\text{N}$  constant by multiplying by the ratio  $\gamma_{^{15}\text{N}}/\gamma_{^{14}\text{N}}$ .

<sup>f</sup> Consistent with the imprecise experimental value [44] of  $\pm 8000 \pm 6000$  Hz.

**Table 3**  
Super spin rotation contributions to chemical shieldings of linear tetraatomics, in parts per billion, computed using Eq. (11) from experimental values, except as noted.

| Mol.   | Nucl.             | $B_e$ (GHz)         | Ref. | $g$      | Ref. | $c$ (Hz) | Ref.         | $\sigma_{SSR}$ (ppb) |
|--|-------------------|---------------------|------|----------|------|----------|--------------|----------------------|
| $^1\text{H}^{12}\text{C}^{12}\text{C}^1\text{H}$       | $^1\text{H}$      | 35.452              | [45] | -0.04903 | [46] | -3580    | [46]         | 0.3                  |
| $^{19}\text{F}^{12}\text{C}^{12}\text{C}^1\text{H}$    | $^{19}\text{F}$   | 9.7062 <sup>b</sup> | [12] | -0.0077  | [47] | -3483    | <sup>a</sup> | 0.2                  |
| $^{35}\text{Cl}^{12}\text{C}^{12}\text{C}^1\text{H}$   | $^1\text{H}$      | 6.2643 <sup>b</sup> | [48] | -0.0063  | [49] | 1066     | <sup>a</sup> | 0.0                  |
|  | $^{35}\text{Cl}$  |                     |      |          |      | -1290    | <sup>a</sup> | 0.8                  |
| $^{81}\text{Br}^{12}\text{C}^{12}\text{C}^1\text{H}$   | $^1\text{H}$      | 3.9784 <sup>b</sup> | [50] | -0.00388 | [32] | 615      | <sup>a</sup> | 0.0                  |
|  | $^{81}\text{Br}$  |                     |      |          |      | -6557    | <sup>a</sup> | 1.4                  |
| $^{12}\text{C}^{14}\text{N}^{12}\text{C}^{14}\text{N}$ | $^1\text{H}$      | 5.1740              | [51] | -0.05919 | [52] | 430      | <sup>a</sup> | 0.0                  |
|  | $^{14}\text{N}_t$ |                     |      |          |      | -889     | <sup>a</sup> | 8.8                  |
|  | $^{14}\text{N}_n$ |                     |      |          |      | -705     | <sup>a</sup> | 7.0                  |

<sup>a</sup> Computed as described in the text.

<sup>b</sup>  $B_0$  used instead of  $B_e$ .

the range of  $M_J$  values expand, resulting in a larger average  $\sigma_{SSR}$  within the level.

Second order corrections using a magnetic susceptibility term were evaluated for several of the diatomics, and were found to be insignificant. At this point, it is also pertinent to note that while, for consistency, we have used  $B_e$ , the equilibrium bond distance at the classical potential minimum, for most of the calculations in Tables 1–3, the experimental molecular  $g$  factors and spin-rotation constants were necessarily measured for excited rotational states, and are often a thermal average over such states. Fully rigorous work would require the conventional spectroscopic extrapolation of these data to the fictitious equilibrium state, and additional computation of corrections as a function of  $J$  and  $v$ . The sparseness of experimental data makes this procedure impossible in nearly all cases; moreover, the small size of the super spin rotation shifts hardly justifies it. If more rigor were deemed useful, high-level quantum calculations of  $g$  and  $c$  as a function of molecular geometry would be the best approach to follow.

Even higher accuracies are possible in experimental measurements of relative chemical shieldings in low pressure gases. In particular, because CO and N<sub>2</sub> are important reference compounds used to benchmark carbon and nitrogen chemical shieldings respectively,  $\sigma_{SSR}$  corrections may in the future need to be included in high-level calculations of chemical shieldings.

However, it is clear that  $\sigma_{SSR}$  values drop dramatically as the rotational constant decreases. Both the molecular  $g$  factor and spin rotation couplings decrease in concert with the rotational constant, and so  $\sigma_{SSR}$  decreases as the molecule becomes larger, notwithstanding its reciprocal relationship to  $B_e$ . Our use of linear mole-

cules (which are easier to calculate) probably exaggerates the molecular weight dependence of  $\sigma_{SSR}$ ; holding the density equal, the rotational constant for linear molecules scales as  $M^{-3}$ , whereas that of spherical molecules it scales as  $M^{-5/3}$ . Nonetheless, it is likely that these effects will be negligible for molecules of more than a few atoms.

In Fig. 2, we illustrate these trends by comparing  $\sigma_{SSR}$  values for several series of halogen compounds, from HX (X = H, F, Cl, Br) to HCCX. These calculations use the data given in Tables 1–3, except for difluorine (F<sub>2</sub>), where there is little experimental data available. In that case, equilibrium molecular  $g$  factors and spin rotation constants were computed for F<sub>2</sub> at the equilibrium MP2/aug-cc-pVTZ bond distance of 139.772 pm, using the program CFOUR [13]. The rotational constant used in the figure was derived from an  $r_e$  value of 141.268 pm [14]; the difference is insignificant in its effect on the final result.

Finally, it should not be assumed that the  $\sigma_{SSR}$  correction is confined to the gas phase. Spin-rotation effects on relaxation certainly are observable for small molecules in mobile liquids, and the drastic decrease in  $\tau_{SR}$  upon condensation to a liquid state, will have no effect on the thermal average of  $c$ . In the classical limit, of course, the SSR effect corresponds to a slight difference in energy between molecules undergoing right- and left-hand rotation about the magnetic field, as a result of charge distribution in the molecules. These effects do not disappear in the classical limit, albeit they decrease rapidly with molecular size.

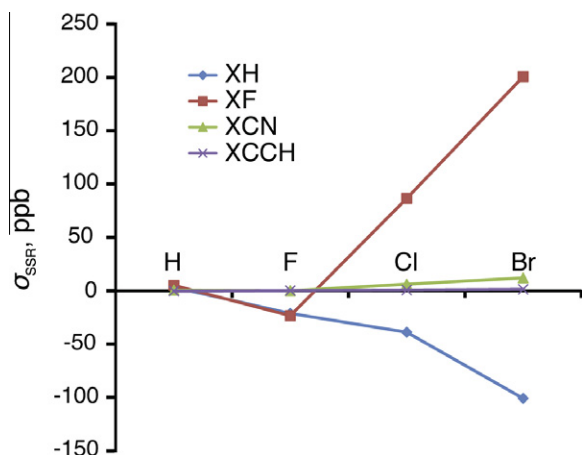
In this paper we have restricted ourselves to linear molecules for which molecular  $g$  factors can be experimentally measured. In fact, these factors are now computable, and so reasonable numbers for symmetric molecules such as (<sup>81</sup>Br)<sub>2</sub> should be quite accessible, even though conventional rotational spectroscopy is not possible. We have also not attempted to compute super spin rotation shieldings for less symmetric molecules. Certainly, the expressions for spherical and symmetric tops should be quite tractable, but given the rapid attenuation of these shieldings with molecular size, even non-linear triatomics would appear to be primarily of academic interest.

## Acknowledgments

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmr.2011.07.006.



**Fig. 2.** The super spin rotation shift, in parts per billion, of a series of halogen compounds, with X = (<sup>1</sup>H, <sup>19</sup>F, <sup>35</sup>Cl, <sup>81</sup>Br).



## References

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