Nuclear Magnetic Antishielding of Nuclei in Molecules. Magnetic Moments of F^{19}, N^{14}, and N^{15}

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The combination of molecular beam data on spin-rotational interactions in molecules with chemical shift data has been used to calculate the paramagnetic part of the nuclear magnetic shielding constant for F in HF and F_2. With the assumption of the sign of the spin-rotational constant in N_2^{15} as positive (i.e., a net *negative* rotational magnetic field at the nitrogen nucleus), the paramagnetic part of the nuclear magnetic shielding constant in N_2 has been calculated. The results, when combined with reliable calculations of the diamagnetic part of the shielding constant, yield the total shielding constants. These are found to be: F in HF: $\sigma=(414.9\pm1.4)\times10^{-6}$, F in F_2: $\sigma=(-210\pm8.0)\times10^{-6}$, N in N_2: $\sigma=(-101\pm25.0)\times10^{-6}$, and demonstrate the phenomenon of nuclear magnetic antishielding in F_2 and N_2, as well as in other compounds. Use of these shielding constants permits considerable improvement in the estimates of the bare nuclear magnetic moments of fluorine and nitrogen. The results are $\mu_N(\mathrm{F})=2.628353\pm0.000005$ nm, $\mu_N(N^{14})=0.403562\pm0.000010$ nm, $\mu_N(N^{15})=-0.283049\pm0.000007$ nm.

INTRODUCTION

IN the decade since the discovery of the shifts of nuclear magnetic resonances due to chemical environment, a very large amount of experimental data has been accumulated and correlated with chemical structure. Modern chemical analysis makes routine use of the high-resolution nuclear magnetic resonance spectrum of the proton and other nuclei to identify molecular subgroupings.[1] Comparison of nuclear resonance frequencies from one compound to another (in the same external magnetic field) have been made only on a relative basis, as the absolute value of the total magnetic shielding of the nucleus in any particular compound has been uncertain. This is largely because of poor estimates of the paramagnetic part σ_p of the magnetic shielding, the major cause of the different magnetic field seen by the nucleus in different electronic environments.

We will show that by combining data on the spin-rotation interaction constants in molecules, obtained from molecular beam experiments, with chemical shift data in the same molecules, one may obtain an unambiguous determination of the paramagnetic contribution to the nuclear shielding. The results may then be used with calculations of the diamagnetic contribution to the shielding to give a reliable value for the total shielding. This permits: (1) the establishment of an absolute reference scale in the theory of chemical shifts; (2) the evaluation of the bare nuclear magnetic moments. In particular, the method is applied to the fluorine nuclei in HF and F_2. The unshielded magnetic moment of F^{19} is calculated, and the existence of nuclear magnetic antishielding ($H_{\mathrm{nucleus}}>H_{\mathrm{external}}$) in F_2 and other fluorine compounds is demonstrated.

In case insufficient experimental data is available to permit this method to be applied, one must make an explicit assumption as to the sign of the spin-rotational interaction. In many cases, this may be done with a high degree of certainty. The result of such a choice in the case of N_2 is discussed, and the shielding constant for the N nucleus in N_2 is obtained. Antishielding in N_2 and other nitrogen compounds is demonstrated and the bare nitrogen nuclear magnetic moments obtained.

METHOD

The theory of magnetic shielding of nuclei in linear molecules,[2] with a particular choice of gauge, gives the effective field H at the nucleus in terms of the external field H as

$$H'=(1-\sigma)H, \tag{1}$$

where

$$\begin{aligned}\sigma&=\sigma_d+\sigma_p\\&=\frac{e^2}{3mc^2}\left(0\left|\sum_k\frac{1}{r_k}\right|0\right)-\tfrac{4}{3}\sum_{\substack{n\\i,k}}(E_n-E_0)^{-1}\\&\quad\times[(0|M_{zi}/r_i^3|n)(n|M_{zk}|0)\\&\qquad+(0|M_{zi}|n)(n|M_{zi}/r_i^3|0)].\end{aligned} \tag{2}$$

For simplicity, we have here averaged over all orientations of the molecule. The first term of Eq. (2), σ_d, is the nuclear shielding resulting from the diamagnetic circulation of the electrons, and is positive. It occurs for both atoms and molecules, and is sometimes referred to as the Lamb term, as it was first derived for atoms by Lamb.[3] The second term, which was first introduced by Ramsey,[2] is peculiar to molecular systems and is often referred to as the paramagnetic, second-order perturbation, or high-frequency term. Un-

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[1] J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High-Resolution Nuclear Magnetic Resonance* (McGraw-Hill Book Company, Inc., New York, 1959).

[2] N. F. Ramsey, Phys. Rev. **78**, 699 (1950); **83**, 540 (1951); **86**, 243 (1952).

[3] W. E. Lamb, Phys. Rev. **60**, 817 (1941).

like the Lamb term, which involves only the molecular ground-state wave function, the paramagnetic term in the above form requires summing over all excited molecular states of appropriate symmetry, including the continuum. Considerable progress has been made in calculating σ_p without recourse to the formidable summation by means of variational or gauge transformation techniques.[4] These calculations are not uniformly reliable from molecule to molecule. Hence, any method for obtaining σ_p directly or indirectly from experimental data is particularly useful at the present state of molecular theory.

It has been pointed out by one of the authors[2] that σ_p could be evaluated from measurement of the spin-rotational interaction constants in molecules by molecular beam experiments if both the sign and the magnitude of the spin-rotational constant were known. This may be done as follows. The spin-rotation interaction c (i.e., the interaction energy per unit rotational quantum number, of the net magnetic field H_r produced at the nucleus by molecular rotation with the nuclear magnetic moment) is composed of two contributions. The first is from the rotation of adjacent charged nuclei about the nucleus under consideration, the second from the circulating electron currents. The second contribution, whose form was derived by Wick,[5] is identical except for multiplicative constants and vibrational corrections, with the expression for σ_p. Thus, by subtracting out the magnetic field produced by the other rotating nuclei (a simple classical calculation), one can relate σ_p directly to experimental data. To do this unambiguously, however, requires a knowledge of the sign of the total rotational magnetic field, for if one knows only the magnitude of the rotational magnetic field, there are two possible resultant values of σ_p. In the case of H_2 the sign of the rotational magnetic field was known and σ_p directly obtained.

Recent progress in molecular beam techniques, notably in the field of beam detection, have enabled a wide variety of molecules to be studied.[6] Unfortunately, the nature of the data obtained on these molecules has in practice (although not in principle) yielded only the magnitude of the rotational magnetic fields, and not their sign, thus complicating the unambiguous evaluation of σ_p.

When the sign and magnitude of the chemical shift of a nuclear resonance from one molecule to another is known, it may be ascribed largely to σ_p. This assumption is equivalent to the statement that for a given atom, σ_d does not change appreciably from one molecule to another, i.e., is not affected by changes in chemical structure. The assumption is quite reasonable, as the form of σ_d, $\langle 1/r\rangle$, implies that the inner shell electrons make the largest contribution. Detailed calculations show, e.g., that the change in σ_d from F^{19} in HF to F^{19} in F_2 is less than 10%.[7] With the assumption of the constancy of σ_d, one may compare the approximate value of the quantity $[\sigma_p(\text{molecule 1}) - \sigma_p(\text{molecule 2})]$ obtained from chemical shift data with the four possible values for the same quantity derived from the experimentally known magnitudes of the spin-rotational interaction constants in the same molecules. Only one choice of signs for the spin-rotational constants will be consistent. With both the signs and magnitudes of the spin-rotational constants now known, one may obtain directly σ_p for both molecules. If a calculated value of σ_d is also known, the total shielding $\sigma=\sigma_d+\sigma_p$ is obtained. Alternatively, one may of course, use a calculated value of σ_d for each molecule from the start, obviating the assumption of the approximate constancy of σ_d.

CALCULATIONS

In the case of a nonvibrating diatomic molecule, one may write the following simplified equations for σ_p and the rotational magnetic fields[2]

$$\sigma_p = -0.9299\times10^{-6}\mu' a^2[H_r^{\text{nuc}} - H_r^{\text{tot}}] \quad (3)$$

and

$$H_r^{\text{nuc}} = 0.60355(ZB_0/a)\ \text{G}, \quad (4)$$

where μ' is the reduced mass of the molecule in nuclear units, a is the internuclear distance in A, H_r^{tot} is the rotational magnetic field per unit rotational quantum number at the nucleus under consideration. H_r^{nuc} is the magnetic field per unit rotational quantum number produced by the other nucleus rotating about the nucleus under consideration, Z is the charge of the other nucleus in units of e, and B is the molecular rotational constant in cm^{-1}.

Using the spectroscopic and molecular beam data shown in Table I in conjunction with the above equations, one can obtain values of σ_p in HF and F_2 for either alternative choice of sign of H_r^{tot}.

In HF,

$$\sigma_p = (46.86\pm0.4)\times10^{-6} \quad \text{for} \quad H^{\text{tot}} \text{ positive},$$

$$\sigma_p = (-67.19\pm0.4)\times10^{-6} \quad \text{for} \quad H_r^{\text{tot}} \text{ negative}.$$

In F_2,

$$\sigma_p = (681\pm90)\times10^{-6} \quad \text{for} \quad H_r^{\text{tot}} \text{ positive},$$

$$\sigma_p = (-799\pm90)\times10^{-6} \quad \text{for} \quad H_r^{\text{tot}} \text{ negative}.$$

These results can be combined with calculated values[7,8] for σ_p in HF of $(482.12\pm1.0)\times10^{-6}$ and σ_d

[4] C. W. Kern and W. N. Lipscomb, Phys. Rev. Letters **7**, 19 (1961); H. F. Hameka, Rev. Mod. Phys. **34**, 87 (1962); M. R. Baker, Bull. Am. Phys. Soc. **7**, 80 (1962); S. I. Chan and T. P. Das, J. Chem. Phys. **37**, 1527 (1962).
[5] G. C. Wick, Phys. Rev. **73**, 51 (1948).
[6] N. F. Ramsey, Am. Scientist **49**, 509 (1961).
[7] W. E. Kern and W. N. Lipscomb, J. Chem. Phys. **37**, 260 (1962).
[8] R. K. Nesbet, J. Chem. Phys. **36**, 1518 (1962).

TABLE I. HF and F_2 molecular data.

$$\begin{aligned} \text{HF:}\quad & a=0.9171\ \text{Å},\\ & \mu'=0.957347,\\ & B_0=20.554\ \text{cm}^{-1},^{a}\\ & |c_F|=305\pm2\ \text{kc/sec},^{b}\\ \text{or}\quad & |H_r^{\text{tot}}|=76.11\pm0.5\ \text{G}.\\ F_2:\quad & a=1.435\ \text{Å},\\ & \mu'=9.50227,^{a}\\ & B=0.8553\ \text{cm}^{-1},^{a}\\ & |c_F|=163\pm20\ \text{kc/sec},^{c}\\ \text{or}\quad & |H_r^{\text{tot}}|=40.67\pm5\ \text{G},\\ & \mu_N(F)=4.0072\ \text{(kc/sec)/G}. \end{aligned}$$

[a] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950).
[b] M. R. Baker, H. M. Nelson, J. A. Leavitt, and N. F. Ramsey, Phys. Rev. **121**, 807 (1961).
[c] C. H. Anderson, M. R. Baker, and N. F. Ramsey (unpublished data).

TABLE II. F^{19} chemical shifts in simple fluorides (Ref. 9).

Compound	Chemical shift ppm	Compound	Chemical shift ppm
F_2	−210.1	CF_4	280.9
IF_7	51.4	PF_3	281.0 (m)[c]
NF_3	74.9		226.2 (m)
BrF_5	80.4 (s)[c]	SbF_3	297.8
	−57.2	PF_5	310.2 (m)
ClF_3	133.3		273.8 (m)
SeF_6	162.6	SbF_5	327.2
SF_6	165.5	F−	338.1
IF_5	208.1 (s)[c]	BF_3	345.4
	158.8 (w)[c]	SiF_4	388.8
BrF_3	251.0	BeF_2	389.0
AsF_3	259.0	GeF_4	398.7
TeF_6	275.8	HF	414.9
UF_6[a]	−540.0		
FNO[b]	−269		

[a] J. N. Shoolery, Varian Tech. Inform. Bull. 1, 3 (1955).
[b] J. R. Holmes, B. B. Stewart, and J. S. MacKenzie, J. Chem. Phys. **37**, 2728 (1962).
[c] The letters s, m, and w after components of complex lines refer to relative intensities as strong, medium, and weak.

in F_2 of $(529.47\pm2.0)\times10^{-6}$ to give predicted values of $\sigma(\text{F in HF})-\sigma(\text{F in }F_2)$.

Thus,

$$\sigma(\text{F in HF})=(472.12\pm1.0)\times10^{-6}+\begin{Bmatrix}46.86\pm0.4\\-67.19\pm0.4\end{Bmatrix}\times10^{-6}$$

and

$$\sigma(\text{F in }F_2)=(529.47\pm2.0)\times10^{-6}+\begin{Bmatrix}681\pm90\\-799\pm90\end{Bmatrix}\times10^{-6}.$$

The corresponding predicted values for $\sigma(\text{F in HF})-\sigma(\text{F in }F_2)$ are (in units of 10^{-6}, i.e., parts per million, ppm):

$$\begin{aligned} -681.49\pm93.0 &\text{ for } H_r^{\text{tot}}(\text{F in HF})+,\ H_r^{\text{tot}}(\text{F in }F_2)+\\ 798.51\pm93.0 &\text{ for } H_r^{\text{tot}}(\text{F in HF})+,\ H_r^{\text{tot}}(\text{F in }F_2)-\\ 795.54\pm93.0 &\text{ for } H_r^{\text{tot}}(\text{F in HF})-,\ H_r^{\text{tot}}(\text{F in }F_2)-\\ 684.46\pm93.0 &\text{ for } H_r^{\text{tot}}(\text{F in HF})-,\ H_r^{\text{tot}}(\text{F in }F_2)-. \end{aligned}$$

Experimental chemical shift data reported in the literature[9] give

$$\sigma(\text{F in HF})-\sigma(\text{F in }F_2)=(+625\pm6)\times10^{-6}.$$

Comparison of the above information shows that the only consistent choice of signs is H_r^{tot} negative for both F in[10] HF and F in F_2. Combining the calculated value of σ_d with the now unambiguous experimental value for σ_p, we obtain

$$\sigma(\text{F in HF})=(414.9\pm1.4)\times10^{-6}.$$

$\sigma(\text{F in }F_2)$ can be obtained in a similar fashion. However, because of the large experimental uncertainty in the molecular beam data on F_2, greater precision for the value $\sigma(\text{F in }F_2)$ can be obtained by using the chemical shift data[9] to give

$$\sigma(\text{F in }F_2)=(-210\pm8)\times10^{-6}.$$

Thus, the magnetic field as seen at the fluorine nucleus in F_2 is larger than the applied external field by some 200 parts per million. This effect, which we call nuclear magnetic antishielding, has been previously suggested[9] and is now quantitatively established.

With the absolute shielding of the fluorine nucleus in HF known, use may be made of nuclear magnetic resonance measurements of $\nu(\text{F in HF})/\nu(\text{H})$ to determine the nuclear magnetic moment of the bare fluorine nucleus. Lindström[11] has obtained the result

$$\nu(\text{F in HF})/\nu(H^1)=0.9407714\pm0.000015.$$

Taking $\sigma(\text{F in HF})=(414.9\pm1.4)\times10^{-6}$ as obtained above, $\sigma(H^1)=26.8\times10^{-6}$ and $\mu(H^1)=2.792743$ nuclear magnetons, one obtains the result

$$\mu({}_9F^{19})=+2.628353\pm0.000005 \text{ nuclear magnetons}.$$

Table II shows the chemical shifts of the fluorine nucleus in a variety of compounds, recalculated so that the zero reference is the base fluorine nucleus. It will be noted that antishielding occurs in BrF_5, FNO, and UF_6 as well as in F_2.

SIGN OF THE SPIN-ROTATIONAL CONSTANT

Although one has no *a priori* preference for a choice of the sign of the spin-rotational constant, in many

[9] H. S. Gutowsky and C. J. Hoffman, J. Chem. Phys. **19**, 1259 (1951).
[10] This choice of sign for C_F in HF has recently been verified independently by molecular beam electric resonance experiments of R. Weiss, Phys. Rev. **131**, 659 (1963). An apparent difference is due to the use of a sign convention opposite to ours. Our convention makes H positive if rotating positive charge generates the magnetic field seen at the nucleus.
[11] G. Lindström, Arkiv Fysik **4**, 1 (1952).

TABLE III. Nitrogen molecule data.

$$a=1.094\ \text{Å} \quad \text{for} \quad N_2^{14},$$
$$\mu'=7.00377 \quad \text{for} \quad N_2^{14},$$
$$B_0=2.00065\ \text{cm}^{-1} \quad \text{for} \quad N_2^{14},^{a}$$
$$|c(N^{15})|=22.0\pm1.0\ \text{kc/sec} \quad \text{for} \quad N_2^{15},^{b}$$
or
$$|H_r^{\text{tot}}|=50.97\pm2\ \text{G},^{b}$$
$$\mu_N(N^{15})=-0.43166\ \text{kc/sec/G}.$$

[a] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950).
[b] S. I. Chan, M. R. Baker, and N. F. Ramsey (to be published).

cases, the sign may be guessed with considerable reliability. If the total spin-rotational constant is much larger than the contribution arising from the rotating nuclei ($H_r^{\text{tot}} \gg H_r^{\text{nuc}}$), then the sign of H_r^{tot} and c must be determined by the electronic contribution. This contribution, as was discussed above, is proportional to σ_p, the latter term in expression (2).

We have referred to this term as paramagnetic, because its sign has conventionally been assumed opposite to that of the first (diamagnetic) term. It should be pointed out that σ_p is the negative of a sum over products of matrix elements of mixed operators, i.e., products of M and M/r^3. In the absence of the $1/r^3$ term, the sum over products would clearly be positive definite and the total sum indeed opposite in sign to the diamagnetic term. The presence of the $1/r^3$ prevents such a simple proof. The "paramagnetic" term is indeed paramagnetic in the closure approximation as well as in several simplified but physical models.[12] No experimental observation to the contrary has yet been made. It would be desirable, however, to have as general a proof as possible for the paramagnetic character of the term, with a clear and realistic set of assumptions about the electronic structure of the molecule.

TABLE IV. Nitrogen chemical shifts in various compounds.

Compound	Chemical shift (ppm)
NH_4^+	233
$(C_3H_7)_2NH$, $(C_2H_5)_3N$	206
N_2H_4	197
$(CH_3)_4NBr$	183
NH_3	175
$(NH_2)_2CO$	167
$NH_2OH\cdot HCl$	151
$CH_3CO\ NH_2$	129
SCN^-	37
CH_3CN	16
CN^-	11
$C(NO_2)_4$, $C_2(NO_2)_6$	−69
Pyridine	−93
N_2	−101
NO_3^-	−115
$C_6H_5NO_2$	−117
n-$C_3H_7NO_2$	−141
NO_2^-	−369

[12] See, e.g., C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963), p. 78 ff.

NITROGEN SHIELDING

Molecular beam experiments have yielded the magnitude of the spin-rotation interaction for the nitrogen nucleus in N_2^{15}. This result and other data are shown in Table III. Using Eq. (4), one finds that H_r^{nuc} is 7 G, while H_r^{tot} is 51 G. Thus, the major contribution to H_r^{tot} is from the electrons. As discussed above, we explicitly assume this contribution to be negative (paramagnetic). Taking H_r^{tot} to be negative in Eqs. (3) and (4) yields

$$\sigma_p(\text{N in } N_2)=(-485.8\pm20)\times10^{-6}.$$

Combining this result with $\sigma_d=384.5\times10^{-6}$,[7] one obtains

$$\sigma=\sigma_d+\sigma_p=(-101.3\pm25)\times10^{-6}.$$

Using this value for the shielding constant in N_2, one may recalculate observed chemical shifts[13] relative to a bare nitrogen nucleus. The results for several nitrogen compounds are shown in Table IV. Antishielding may be seen to occur for a number of these compounds.

Baldeschwieler has recently measured the magnetogyric ratios for N^{14} and N^{15} relative to the protons in NH_4^+ ions.[14] His results are

$$\gamma(^{14}N)/\gamma(H)=(0.72236749\pm10)\times10^{-9}$$

and

$$\gamma(N^{15})/\gamma(H)=(-0.101330447\pm10)\times10^{-9}.$$

The proton resonance from the solvent water was observed at a field higher than the NH_4^+ protons by 2.38 ppm. Taking the shielding constant in water as 26.8×10^{-6}, gives the shielding of an NH_4^+ proton as 24.4×10^{-6}. With our result from Table IV [σ(N) in $NH_4^+=233$ ppm], and the proton magnetic moment as 2.792743 nuclear magnetons, one obtains from these magnetogyric ratios,

$$\mu_N(N^{14})=0.403562\pm0.000010\ \text{nm}$$

and

$$\mu_N(N^{15})=-0.283049\pm0.000007\ \text{nm}.$$

The principal source of uncertainty is from the spin-rotational constant measurement on N_2^{15}.

[13] B. E. Holder and M. P. Klein, J. Chem. Phys. **23**, 1956 (1955).
[14] J. D. Baldeschwieler, J. Chem. Phys. **36**, 152 (1962).