Geminal Isotope Effects on the Proton Magnetic Resonance of Some First-Row Molecules

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R. A. BERNHEIM AND H. BATIZ-HERNANDEZ†

Department of Chemistry, Whitmore Laboratory, The Pennsylvania State University, University Park, Pennsylvania

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Geminal substitution of H by D in first-row molecules generally causes upfield shifts in the proton magnetic resonance. These isotope shifts are sometimes explained in terms of intramolecular electrostatic effects. This work shows that they can also be considered as being due to the changes in bond rehybridization accompanying small changes in molecular geometry upon isotopic substitution. The diamagnetic part of the magnetic shielding at the protons in NH_3, CH_4, and CH_3D was evaluated as a function of HNH or HCH bond angle using localized equivalent orbitals constructed from Slater atomic orbitals. The treatment for CH_3D differed from that for CH_4 in that the shorter experimental CH bond distance was used. The results of the calculation showed that the magnetic shielding at the proton in a NH or CH bond increased with decreasing bond angle, and with a decrease in bond distance. For small changes in geometry, similar to what is experimentally found upon isotopic substitution, the calculated change in shielding was the same order of magnitude as that experimentally observed. Consideration of isotope shift data on first-row molecules reveals that the magnitude of the shift is also a function of the initial molecular geometry, being larger for molecules with smaller HXH bond angles (X=C, O, N) and H–H internuclear distances. Isotope shifts were measured for CH_2Cl_2, CH_2Br_2, and CH_2I_2. Upon monodeuteration the proton magnetic resonance shifted upfield by 0.0125 ± 0.0003, 0.0137 ± 0.0002, and 0.0135 ± 0.0002 ppm, respectively. The measured J_{HD} spin–spin coupling constants were also measured for these molecules and found to be in agreement with previous work.

I. INTRODUCTION

ISOTOPE chemical shifts have been known to exist in the high-resolution nuclear magnetic resonance of isotopically substituted molecules for some time.[1-3] Most of the observations of the effect have been in the proton or ^{19}F magnetic resonance spectra of compounds which contain mixtures of isotopes. With a few exceptions, the effect of substituting a heavy isotope for a light one is to increase the magnetic shielding σ of a nearby nucleus. Moreover, σ continues to increase with the number of heavy isotopes that are substituted into the molecule.[4,5]

The only species for which the isotope shift has received a detailed experimental and theoretical treatment is the hydrogen molecule. Two reasons are responsible for this interest: (a) the availability of good wavefunctions for H_2, with the prospect of a correct explanation of the effect, and (b) the importance of an accurate knowledge of the magnitude of the proton magnetic moment as obtained from a magnetic resonance experiment. Isotope chemical-shift experiments were first made on H_2 gas by Wimett[1] and starting with the early work of Ramsey[6] there have been several theoretical treatments of the phenomenon in hydrogen.[7,8] It is generally agreed that the change in σ is a result of the change of the average dynamic state of the molecule upon isotopic substitution. In hydrogen a theoretical value of σ has been found as a function of internuclear separation[9] and is also found to be different when averaged over the zero-point vibrational functions for the different isotopically substituted molecules.[7] Theory and experiment can be compared for the magnetic shielding at the proton in H_2 and HD where a recent experiment[10] yields $\sigma_{HD}-\sigma_{H_2}=0.04\pm0.01\times10^{-6}$ and theory[8] gives $\sigma_{HD}-\sigma_{H_2}=0.025\times10^{-6}$. The agreement is fair.

In polyatomic molecules the situation is, of course, more complicated, even though it is clear that the isotope shift must have its origin in a change of the average dynamic state of the molecule upon isotopic substitution. One approach is to consider it as being due to an intramolecular electrostatic effect.[3] In the presence of an electric field the magnetic shielding is reduced.[11-13] A proton in a CH_2 group, for example, will experience a shielding which is partially determined by an effective electric charge on the neighboring H atom. Substitution of H by D results in a smaller vibrational amplitude which gives rise to a smaller electric field at the proton and, hence, an effective increase in shielding.

In addition to the above paramagnetic effect of an intramolecular electric field, the possibility also exists for a contribution to σ which would arise from a slight change in hybridization accompanying a change in average bond distances and angles upon isotopic substi-

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tution. Such changes in the average geometry would be due to anharmonic terms in the vibrational potential. An indication of the magnitude of this effect can be obtained from a calculation of the change in σ that would accompany the corresponding change in the hybridization parameters of the bond to the atom under investigation. The aim of the present work is to investigate this aspect of the isotope chemical shift. The present results indicate that the change in the diamagnetic part of σ resulting from the expected changes in average dynamic molecular structure are of the same order of magnitude as the experimentally observed changes in σ. The molecules NH_3, CH_4, and CH_3D are chosen to illustrate this point because their molecular geometry has been fairly well investigated, and isotope-shift experiments are available.

The magnitude of the isotope shift will also reflect the initial molecular geometry before isotopic substitution regardless of whether it arises from intramolecular electric fields or from bond rehybridization. Additional experimental information reported here is consistent with the prediction that in the case of geminal protons the isotope chemical shift is larger for molecules that have a smaller initial HXH angle (X=C, N, O) and a smaller initial H–H internuclear separation.

II. ISOTOPE-SHIFT DATA

Most of the available data concerning the isotope shift of the proton magnetic resonance of molecules of the first-row elements are listed in Table I. The measurements are given in parts per million and a positive value of δ refers to a shift of the resonance upfield with respect to the unsubstituted molecule. Where possible the values for the average *geminal* bond angle $\angle$ HXH and average *geminal* proton–proton distance D_{HH} are listed for use in the discussion in subsequent sections.

The isotope chemical shifts for CH_2Cl_2, CH_2Br_2, and CH_2I_2 are reported here for the first time. The spectra of these compounds were observed at two resonance frequencies, 60 and 40 Mc/sec. The data reported in Table I for the methylene halides have an indicated precision which is the average deviation of at least 18 measurements for each compound.

The proton–deuterium spin–spin coupling constants were also measured and found to be $| J_{HD} | = 1.04 \pm 0.02$ cps for $CHDCl_2$, $| J_{HD} | = 0.85 \pm 0.02$ cps for $CHDBr_2$, and $| J_{HD} | = 0.83 \pm 0.02$ cps for $CHDI_2$. These values agree within about 10% with those reported in the literature.[14]

III. ISOTOPE EFFECTS ON MOLECULAR GEOMETRY

Changes in the average molecular geometry occur upon isotopic substitution if the various vibrational modes of the molecule possess anharmonic parts. The

changes can be somewhat arbitrarily broken down into primary and secondary isotope effects. The primary effect would refer to a change in internuclear separation in the bond holding the isotope and the secondary effect would refer to changes in the geometry of the remainder of the molecule. For example, the changes in bond distances in CH_4 and CH_3CH_3 upon full deuteration have been investigated in detail by electron-diffraction techniques.[15,16] In both cases a primary effect was found that resulted in the average C–D bond length being about 0.008 a.u. shorter than the average C–H bond length. A secondary effect was found in ethane which resulted in the C–C bond being about 0.0002 a.u. shorter in CD_3CD_3 than in CH_3CH_3. Full deuteration in CH_3Cl and CH_3Br results in a secondary isotope effect upon the carbon–halogen bond[17] (a shortening of about 0.002 a.u.). A general discussion by Laurie and Herschbach[18] concluded that substitution of H by D produces a primary reduction in bond length by 0.006 to 0.010 a.u. The effects for isotopic substitution of heavier atoms will, of course, be much smaller.

In Table I, data regarding the geometry of some molecules for which isotope chemical-shift measurements have been made are presented. In particular, data regarding NH_3 and CH_4 are available. From an analysis of the Raman spectra of CH_4, CH_3D, and CD_4 it was concluded[19] that the average C–H distance is shorter in CH_3D than in CH_4, and the average C–D distance is shorter in CD_4 than in CH_3D (secondary isotope effects). The average C–D distance in CH_3D is shorter than the average C–H distance in CH_4 (primary isotope effect). Although the analysis of the Raman data had to assume that CH_3D was tetrahedral, the magnitude of the primary and secondary isotope effects are about 0.006 and 0.0006 a.u., respectively. These measurements are in agreement with the electron-diffraction data of Bartell *et al.*,[15] although the actual magnitude of the bond distances differ slightly.

The effect of isotopic substitution on bond angles is not very well known. In phosphine the H–P–H angle decreases with deuteration in addition to a shortening of the P–H bond.[20] In ammonia one investigation gave evidence for a decrease of the H–N–H angle[21] while another indicated an increase[22] upon deuteration. However, recent results that compare NH_3 with ND_3 indi-

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TABLE I. Values of isotope chemical shifts δ, internuclear angles $\angle HXH$, and distances D_{HH} for some first-row compounds.[a]

Compounds	Solvent	δ(ppm)	Ref.	$\angle HXH$	D_{HH}(a.u.)	Ref.
H_2O	Aq. ac.	0	b	104°56′	2.8708	18
HDO		0.030±0.003				
CH_2O		0	34	123°26′	3.5644	d
CHDO	TMS	0.029				
	THF	0.023				
	CH_3CN	0.026				
$^{15}NH_3$	Neat	0	5	106°47′	3.0760	21, 22
$^{15}NH_2D$		0.029±0.002				
$^{15}NHD_2$		0.053±0.003				
CH_4	CCl_4	0	4	109°28′	3.3772	18, 19
CH_3D		0.019±0.001				
CH_2D_2		0.027±0.003				
CHD_3		0.045±0.004				
$^{14}NH_4^+$	H_2SO_4	0	35	109°28′	3.2020	e, f
$^{14}NH_3D^+$		−0.015				
$^{14}NH_2D_2^+$		−0.030				
$^{14}NHD_3^+$		−0.045				
CH_3COCH_3	Neat	0	3	108°30′	3.3310	g
CHD_2COCD_3		0.034±0.001				
CH_3CN	Neat	0	c	109°16′	3.4270	h
CH_2DCN		0.012±0.001				
CHD_2CN		0.023±0.001				
CH_3COOH	Neat	0	c			
CH_2DCOOH		0.012±0.001				
CHD_2COOH		0.025±0.001				
ϕCH_3	Neat	0	2			
ϕDCH_2		0.015±0.002				
CH_3NO_2	Neat	0	c			
CH_2DNO_2		0.015±0.001				
CHD_2NO_2		0.029±0.001				
$EtCH_2CN$	Neat	0	c			
EtCHDCN		0.014±0.001				
CH_2Cl_2	CCl_4	0	i	112°	3.3462	m
$CHDCl_2$		0.0125±0.0003				
CH_2Br_2	CCl_4	0	i	109°28′	3.3772	n, o
$CHDBr_2$		0.0137±0.0002				
CH_2I_2	CCl_4	0	i	109°28′	3.3772	n, o
$CHDI_2$		0.0135±0.0002				
$H_2C=CH_2$	TMS	0	j	116°	3.4422	p
$HDC=CH_2$		0.0085				
$\phi CH=CH_2$	Neat	0	k			
$\phi CD=CH_2$		{0.0090 − (*cis* proton) 0.0048 − (*trans* proton)				
cis-CHF=CHF	CCl_3F	0	l			
cis-CHF=CDF		−0.002				
trans-CHF=CHF	CCl_3F	0	l			
trans-CHF=CDF		0.005				
$1,1$-$CH_2=CF_2$	CCl_3F	0	l			
$1,1$-$CHD=CF_2$		0.010				

[a] Isotope shifts are reported in parts per million, a positive shift being upfield with respect to the unsubstituted compound. Internuclear distances are in atomic units.

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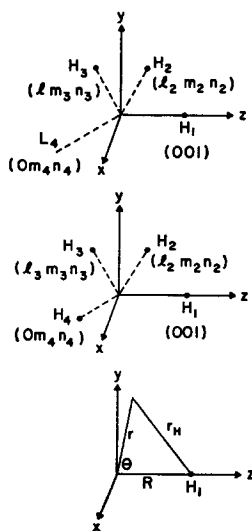[p] L. S. Bartell and R. A. Bonham, J. Chem. Phys. **27**, 1414 (1957).

FIG. 1. (a) Coordinate system for the evaluation of the proton magnetic shielding in NH_3. The nitrogen atom is at the origin, and the positions of the three protons, H_1, H_2, H_3, and the lone-pair orbital, L_4, are identified by the direction cosines in parentheses. (b) Coordinate system used for CH_4 and CH_3D with the carbon atom at the origin. The C–D bond distance is assumed equal to the C–H bond distance in CH_3D, but the C–H (D) distances in CH_3D are 0.0006 a.u. shorter than in CH_4. (c) Coordinate system defining the symbols in the magnetic shielding operator.

cate that the H–N–H angle decreases[23,24] with the N–H distance equal to[24] or slightly greater than[23] the N–D distance. As mentioned above, the investigation of CH_3D assumed a tetrahedral configuration of the molecule.[19]

IV. NUCLEAR MAGNETIC SHIELDING AS A FUNCTION OF BOND ANGLE

In the method of localized equivalent orbitals employed in this paper to describe NH_3, CH_4, and CH_3D the ground-state wavefunction, ψ_0, is written as an antisymmetrized product of one-electron wavefunctions, each of which is either (a) a linear combination of a (1s) hydrogen orbital and a (sp^n) hybrid bond orbital belonging to the heavy central nucleus, or (b) a lone-pair (sp^n) hybrid orbital. For NH_3 eight electrons may be assigned to the three doubly occupied bond equivalent orbitals and one doubly occupied lone-pair orbital. The NH_3 model is represented in Fig. 1(a), where the nitrogen atom is at the origin, one N–H bond is along the z axis, the lone-pair orbital is in the yz plane at $x=0$, and the remaining bonds are mirror images of each other in xyz directions. To describe CH_4 and CH_3D four bond equivalent orbitals are required to hold the eight electrons. The corresponding model in Fig. 1(b) is similar to that of NH_3 except for the substitution of the fourth bond orbital for the lone-pair orbital. Both the CH_4 and CH_3D models are initially assumed to be tetrahedral with the exception that the average C–H bond in CH_3D is about 0.0006 a.u. shorter[19] than in CH_4. In Figs. 1(a) and 1(b), l_j, m_j, and n_j are direction cosines of the equivalent orbitals that are obtained with a knowledge of the molecular geometry.

The wavefunction ψ_0 for NH_3 is of the form

$$\psi_0 = \det[1/(8!)^{\frac{1}{2}}]$$
$$\times \{\psi_1(1)\psi_1(2)\psi_2(3)\psi_2(4)\psi_3(5)\psi_3(6)\psi_4'(7)\psi_4'(8)\}. \quad (1)$$

For CH_4 and CH_3D it is

$$\psi_0 = \det[1/(8!)^{\frac{1}{2}}]$$
$$\times \{\psi_1(1)\psi_1(2)\psi_2(3)\psi_2(4)\psi_3(5)\psi_3(6)\psi_4(7)\psi_4(8)\}. \quad (2)$$

In Eqs. (1) and (2) ψ_j represents the localized bond orbital j:

$$\psi_j = \mu H_j(1s) + \lambda[a_j C_{2s} + b_j(l_j C_{2p_x} + m_j C_{2p_y} + n_j C_{2p_z})], \quad (3)$$

where

$$l_i l_j + m_i m_j + n_i n_j = \cos\theta, \qquad l_j^2 + m_j^2 + n_j^2 = 1,$$

and

$$j = 1, 2, \text{ and } 3 \text{ for } NH_3, \qquad j = 1, 2, 3, \text{ and } 4 \text{ for } CH_4.$$

The lone-pair orbital of NH_3 is

$$\psi_4' = a_4 C_{2s} + b_4(l_4 C_{2p_x} + m_4 C_{2p_y} + n_4 C_{2p_z}), \quad (4)$$

with

$$l_j l_4 + m_j m_4 + n_j n_4 = \cos\phi.$$

In these computations Slater-type[25] orbitals (C_{2s}, C_{2p_x}, C_{2p_y}, and C_{2p_z}) are employed throughout for carbon and nitrogen. The hybridization parameters a_j and b_j measure, respectively, the amount of s and p character of the orbitals; a given ratio (λ/μ) measures the polarity of a given bond orbital; θ is the angle between any two C–H or N–H bond orbitals; and ϕ is the angle between the lone-pair orbital of NH_3 and a N–H bond orbital. The bond angle θ is represented in the tables and figures by $\angle HXH$ (X=C or N). In addition, $a=a_1=a_2=a_3\neq a_4$ for NH_3, while $a=a_1=a_2=a_3=a_4$ for CH_4. Analogous relationships hold for the b_j parameters.

For molecules in $^1A_1$ states, Ramsey[26,27] has derived an expression for the diamagnetic shielding constant averaged over all possible molecular orientations. This is written in the form

$$\sigma^d = (e/3mc^2) \langle \psi_0 | \sum_k [r_k^{-1} - (\mathbf{R}_{kl} \cdot \mathbf{r}_k/r_k^3)] | \psi_0 \rangle, \quad (5)$$

where the summation is over the electrons k, and the origin must be taken at the nucleus where the shielding is to be evaluated. $\mathbf{R}_{kl}$ is an arbitrary constant arising from the arbitrariness of the gauge of the vector potential. In treating the shielding effects of electrons bound to an atom at a distance R from the shielded nucleus Eq. (5) can be transformed to

$$\sigma^d = \frac{2e^2}{3mc^2} \left\{ \sum_{j=1}^{N} \left\langle \psi_j \left| \frac{1}{r_H} - \frac{Rr \cos\theta}{r_H^3} \right| \psi_j \right\rangle \right\}, \quad (6)$$

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where ψ_0 has been written as an antisymmetrized product, given by Eqs. (1) and (2), for $2N$ electrons filling the N equivalent ψ_j orbitals. The coordinate system in Fig. 1(c) can be used for all molecules.

The substitution of Eqs. (3) and (4) into Eq. (6) is performed in the Appendix. Upon taking advantage of the molecular symmetry in each case the diamagnetic shielding at proton H_1 is given by

$$\sigma^d{}_{H_1}=2\sigma(1)+4\sigma(2)+2\sigma(4) \quad (7)$$

for NH_3, and by

$$\sigma^d{}_{H_1}=2\sigma(1)+6\sigma(2) \quad (8)$$

for CH_4 where $\sigma(j)$ is the shielding produced by one electron in the bond orbital ψ_j. The values of $\sigma(j)$ are, of course, sensitive to the orbital constants in Eqs. (3) and (4). The complete expressions for $\sigma(j)$ in terms of atomic orbital shielding integrals σ_j (defined in the Appendix) are

$$\sigma(1) = \{\mu^2\sigma_1+2a\lambda\mu\sigma_2+2b\lambda\mu\sigma_3$$
$$+\lambda^2[a^2\sigma_7+b^2\sigma_9+2ab\sigma_{10}]\}, \quad (9)$$

$$\sigma(2) = \{\mu^2\sigma_4+2a\lambda\mu\sigma_5+2bn_2\lambda\mu\sigma_6+\lambda^2[a^2\sigma_7$$
$$+b^2(m_2{}^2+l_2{}^2)\sigma_8+b^2n_2{}^2\sigma_9+2abn_2\sigma_{10}]\}, \quad (10)$$

$$\sigma(4) = \{a_4{}^2\sigma_7+b_4{}^2m_4{}^2\sigma_8+b_4n_4{}^2\sigma_9+2a_4b_4n_4\sigma_{10}\}. \quad (11)$$

In order to obtain σ^d, the different integrals $\sigma(j)$ must be evaluated using the numerical orbital constants. In addition, the atomic-type σ_j integrals, internuclear distances, and bond angles must be obtained numerically. The shielding constant as a function of bond angle, $\sigma^d(\theta)$, may also be evaluated if the variation of the orbital constants with bond angle θ can be found in each case.

The orbital constants in Eqs. (3) and (4) can be expressed in terms of the molecular dimensions. The problem of determining the hybridization parameters for different (λ/μ) ratios for NH_3 was analyzed in some detail by Duncan and Pople.[28] In their method the orthonormality condition was applied to the bond orbitals in Eq. (3) to obtain the following expressions:

$$\lambda^2(a^2+b^2\cos\theta)+2\lambda\mu(aS_s+bS_p\cos\theta)+\mu^2S_h=0, \quad (12)$$

$$\lambda^2+2\lambda\mu(aS_s+bS_p)+\mu^2=1. \quad (13)$$

The lone-pair orbital ψ_4' was orthogonalized with a given ψ_j bond orbital to obtain expressions of the form

$$\lambda(a_ja_4+b_jb_4\cos\theta)+\mu(a_4S_s+b_4S_p\cos\theta)=0;$$

$$\sin\phi= (2/\sqrt{3}) \sin(\theta/4). \quad (14)$$

[28] A. B. F. Duncan and J. A. Pople, Trans. Faraday Soc. **49**, 217 (1953).

TABLE II. Bond-orbital constants of NH_3: $(\lambda/\mu)=0.84$, $\mu=0.64000$, and $\lambda=0.53760$; $(\lambda/\mu)=1$, $\mu=\lambda=0.58110$.

∠HNH	(λ/μ)	a	b	a_4	b_4
100	0.84	−0.04362	1.14288	0.77939	0.62653
101	0.84	−0.02368	1.11584	0.75543	0.65524
102	0.84	−0.00541	1.09106	0.73126	0.68211
103	0.84	0.01146	1.06818	0.70678	0.70744
104	0.84	0.02709	1.04698	0.68204	0.73132
105	0.84	0.04167	1.02721	0.65689	0.75399
106	0.84	0.05529	1.00873	0.63129	0.77555
106°47′	0.84	0.06536	0.99508	0.61094	0.79169
107	0.84	0.06807	0.99140	0.60519	0.79609
108	0.84	0.08010	0.97508	0.57850	0.81569
109	0.84	0.09145	0.95969	0.55106	0.83446
110	0.84	0.10216	0.94516	0.52283	0.85243
100	1	0.04210	1.13226	0.77190	0.63575
101	1	0.06108	1.10653	0.74764	0.66411
102	1	0.07848	1.08292	0.72322	0.69062
103	1	0.09457	1.06110	0.69853	0.71558
104	1	0.10950	1.04085	0.67361	0.73909
105	1	0.12341	1.02198	0.64834	0.76136
106	1	0.13644	1.00431	0.62262	0.78252
106°47′	1	0.14607	0.99125	0.60222	0.79834
107	1	0.14866	0.98774	0.59647	0.80264
108	1	0.16018	0.97212	0.56977	0.82181
109	1	0.17104	0.95739	0.54238	0.84014
110	1	0.18131	0.94345	0.51423	0.85766

In these equations, S_h, S_s, and S_p are the overlap integrals

$$S_h=\int H_{1si}(1)H_{1sj}(1)d\tau,$$

$$S_s=\int H_{1s}(1)C_{2s}(1)d\tau,$$

$$S_p=\int H_{1s}(1)C_{2p_z}(1)d\tau; \quad (15)$$

θ is the H–N–H bond angle; and ϕ is the H–N–lone-pair angle.

Equations (12), (13), and (14) may be used to obtain λ, μ, and the hybridization parameters, provided the bond angle θ and a given ratio (λ/μ) can be estimated independently. Such a calculation was carried out by Duncan and Pople with different (λ/μ) ratios for the equilibrium configuration of NH_3. The variation of λ and μ with θ can not be obtained easily, and in the present case it was necessary to assume λ and μ constant and study the effect of varying θ in a given range for a constant N–H bond distance. This is equivalent to holding the bond dipole moment and C–H overlap constant. It is justified by the resulting relative insensitivity of the magnetic shielding to the (λ/μ) ratio, as is seen below. Equations (12), (13), and (14) were used to obtain a set of parameters a_j and b_j, using (λ/μ) values of 0.84 and 1. The value 0.84 was that found by Duncan and Pople in order to obtain agreement with the NH_3 electric dipole moment, and the value of 1 corresponds to the assumption of pure covalent character of the N–H bond. The angular variation examined was between 100° and 110°. The resulting bond parameters are listed in Table II. The

TABLE III. Bond-orbital constants of CH_4 and CH_3D with $(\lambda/\mu)=1$, and $\mu=\lambda=0.54443$.

∠HCH	(λ/μ)	a	b
105	1	0.25436	1.16659
106	1	0.26931	1.14833
107	1	0.28339	1.13112
108	1	0.29670	1.11486
109	1	0.30931	1.09944
109°28′	1	0.31577	1.09155
110	1	0.32127	1.08483
111	1	0.33265	1.07092
112	1	0.34347	1.05770
113	1	0.35380	1.04508
114	1	0.36368	1.03301
115	1	0.37310	1.02149

TABLE V. Evaluation of shielding constant $\sigma(\theta)$ of CH_4 (in parts per million).

∠HCH	(λ/μ)	$2\sigma(1)$	$6\sigma(2)$	$\sigma(\theta)$
105	1	24.224	6.551	30.775
106	1	24.151	6.494	30.645
107	1	24.084	6.446	30.530
108	1	24.020	6.404	30.424
109	1	23.962	6.369	30.331
109°28′	1	23.933	6.352	30.285
110	1	23.908	6.339	30.247
111	1	23.856	6.314	30.170
112	1	23.808	6.292	30.100
113	1	23.762	6.275	30.037
114	1	23.720	6.260	29.979
115	1	23.679	6.249	29.928

necessary overlap integrals are evaluated in the Appendix, according to the method of Coulson[29] utilizing the geometry given in Table II for NH_3.

In order to determine the hybridization parameters of CH_4 and CH_3D a value of $(\lambda/\mu)=1$ was assumed. Equations (12) and (13) then become

$$a^2+b^2\cos\theta+2(aS_s+bS_p\cos\theta)+S_h=0, \quad (16)$$

$$\mu^2=1/2(1+S)=1/2(1+aS_s+bS_p). \quad (17)$$

With μ again held constant, the parameters a_j and b_j could be computed as a function of θ. The results are given in Table III. The orbital constants for CH_3D were assumed to be identical to those of CH_4 because

the overlap integrals for the two molecules are very nearly the same. If the two molecules were considered separately, the value of μ would change from 0.54443 for CH_4 to 0.54442 for CH_3D.

The shielding constant as a function of θ, $\sigma(\theta)$, was obtained with the various $\sigma(j)$ integrals in Eqs. (9), (10), and (11). The atomic σ_j integrals were obtained from Refs. 30, 31, and 32 and are evaluated in the Appendix. Tables II and III were used to obtain values for $\sigma(j)$ as a function of θ, and the various $\sigma(j)$ integrals were added to obtain $\sigma^d(\theta)$ as in Eqs. (7) and (8) The results of these calculations are presented in Tables IV, V, and VI for NH_3, CH_4, and CH_3D, respectively.

V. ISOTOPE SHIFT AS A RESULT OF CHANGE IN BOND ANGLE

In Fig. 2 the calculated value of $\sigma(\theta)$ is plotted vs θ for NH_3 with $(\lambda/\mu)=0.84$. The results for NH_3, CH_4, and CH_3D with $(\lambda/\mu)=1$ are all shown in Fig. 3. For comparison the isotope chemical shift $\delta(\theta)$ in parts per million has been computed for NH_3 $[(\lambda/\mu)=1$ and

TABLE IV. Evaluation of shielding constant $\sigma(\theta)$ of NH_3 (in parts per million).

∠HNH	(λ/μ)	$2\sigma(1)$	$4\sigma(2)$	$2\sigma(4)$	$\sigma(\theta)$
100	0.84	26.344	3.706	3.818	33.868
101	0.84	26.214	3.630	3.840	33.684
102	0.84	26.097	3.567	3.853	33.517
103	0.84	25.990	3.513	3.863	33.366
104	0.84	25.893	3.468	3.865	33.226
105	0.84	25.803	3.430	3.864	33.097
106	0.84	25.720	3.398	3.859	32.977
106°47′	0.84	25.660	3.376	3.853	32.889
107	0.84	25.644	3.370	3.851	32.865
108	0.84	25.572	3.347	3.841	32.760
109	0.84	25.505	3.328	3.828	32.661
110	0.84	25.443	3.311	3.813	32.567
100	1	24.016	4.089	3.862	31.937
101	1	23.897	4.008	3.851	31.756
102	1	23.790	3.940	3.863	31.593
103	1	23.693	3.882	3.870	31.445
104	1	23.604	3.834	3.871	31.309
105	1	23.522	3.792	3.869	31.183
106	1	23.447	3.797	3.862	31.066
106°47′	1	23.392	3.734	3.855	30.981
107	1	23.377	3.728	3.853	30.958
108	1	23.312	3.702	3.842	30.856
109	1	23.252	3.681	3.828	30.761
110	1	23.196	3.663	3.812	30.671

TABLE VI. Evaluation of shielding constant $\sigma(\theta)$ of CH_3D (in parts per million).

∠HCH	(λ/u)	$2\sigma(1)$	$6\sigma(2)$	$\sigma(\theta)$
105	1	24.231	6.557	30.788
106	1	24.158	6.500	30.658
107	1	24.090	6.452	30.542
108	1	24.028	6.410	30.438
109	1	23.969	6.375	30.344
109°28′	1	23.939	6.359	30.298
110	1	23.914	6.345	30.259
111	1	23.863	6.320	30.183
112	1	23.814	6.299	30.113
113	1	23.769	6.281	30.050
114	1	23.726	6.267	29.993
115	1	23.685	6.255	29.940

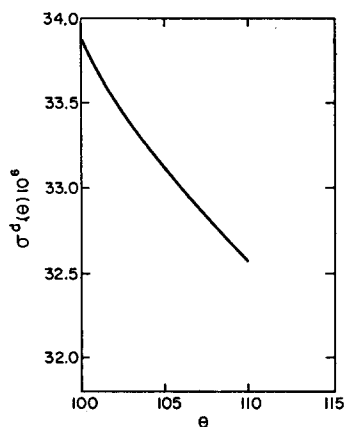[29] C. A. Coulson, Proc. Cambridge Phil. Soc. **38**, 210 (1942).

[30] J. I. Musher, J. Chem. Phys. **40**, 2399 (1964).
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[32] H. F. Hameka, Mol. Phys. **2**, 64 (1959).

FIG. 2. The diamagnetic part of the proton magnetic shielding in NH_3 as a function of HNH bond angle, θ, for $(\lambda/\mu) = 0.84$.

FIG. 4. Isotope chemical shift with respect to the unsubstituted species for (a) CH_4 with $(\lambda/\mu) = 1$, (b) NH_3 with $(\lambda/\mu) = 1$, and (c) NH_3 with $(\lambda/\mu) = 0.84$.

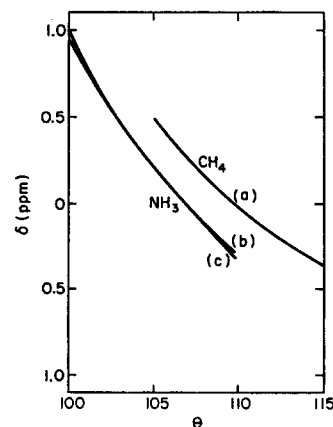0.84] and for CH_4 $[(\lambda/\mu) = 1]$ and are presented in Fig. 4. In this case $\delta(\theta)$ was defined by

$$\delta(\theta) = \sigma^d(\theta) - \sigma^d(\theta_e), \qquad (18)$$

where $\sigma^d(\theta_e)$ is the computed diamagnetic shielding constant for the equilibrium bond angle θ_e. For NH_3, $\theta_e = 106°47'$, and for CH_4, $\theta_e = 109°28'$.

From the curves in Figs. 2–4 it is apparent that the isotope shifts can be explained in terms of structural changes in the molecule. The salient features of Figs. 2, 3, and 4 are (a) the magnetic shielding increases as the bond angle decreases leading to upfield shifts, (b) the proton magnetic shielding increases if the C–H bond distance decreases, as shown by the comparison of CH_4 with CH_3D, and (c) the effect of a given bond angle change is greater for NH_3 than for CH_4 or CH_3D.

Experimentally, substitution produces upfield isotope shifts which increase with the number of deuterium substituents in the molecule. In addition, it has been found that substitution with a heavier isotope generally produces a reduction of the various average bond lengths in a molecule. This reduction becomes more pronounced with additional isotopic substitution. PH_3 is the only case where an unambiguous determination of the effect of isotopic substitution on bond

angle has been made. In this molecule the H–P–H average bond angle decreases upon deuteration. Although there is an indication that the same might be true for ammonia, there is not enough clear evidence to say that this is true in general. The proton magnetic resonance data with the above estimate of the influence of molecular geometry on the isotope shift indicates that either bond shortening or a decrease in bond angle or both are occurring upon isotopic substitution. The magnitude of the shifts are compatible with the small changes in the diamagnetic contribution to the magnetic shielding that would accompany reasonable small changes in geometry upon isotopic substitution. Shifts of the order of 0.02 ppm can be accounted for by changes in average bond angle as small as 10' or by bond length changes of about 0.0012 a.u. It must be emphasized that the foregoing should not be construed as the only source of the isotope shift. Changes in nonbonded electrostatic forces are present in addition to the dependence of the paramagnetic contribution to σ upon bond angle. The relative contribution of the latter can be estimated from the variational calculation of Stephen[33] to be 0.002 ppm/deg as opposed to 0.015 ppm/deg for the diamagnetic term.

If the experimental data are studied closely and

FIG. 3. The diamagnetic part of the proton magnetic shielding in NH_3, CH_4, and CH_3D as a function of HNH and HCH bond angle, θ, for $(\lambda/\mu) = 1$.
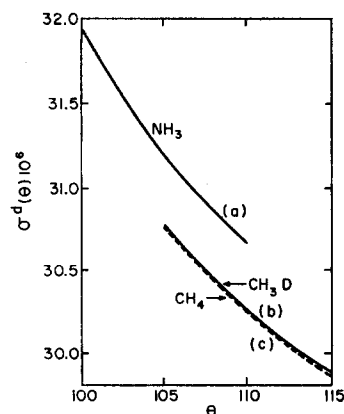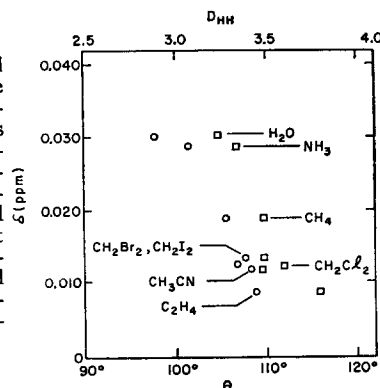

FIG. 5. Experimental values of the isotope chemical shift for monodeuterated compounds of some first-row compounds. Circles represent shift versus H–H internuclear distance, and squares represent shift versus HXH angle. Internuclear distances and angles are those measured for the unsubstituted species.

[33] M. J. Stephen, Proc. Roy. Soc. (London) **A243**, 264 (1957).

TABLE VII. Evaluation of the σ_j integrals for NH_3 expressed in parts per million for different values of (λ/μ).

	$(\lambda/\mu) = 1$	$(\lambda/\mu) = 0.84$
$\sigma_1 = 17.74920$	$\mu^2\sigma_1 = 5.99355$	$\mu^2\sigma_1 = 7.27007$
$\sigma_2 = 7.09450$	$2\lambda\mu\sigma_2 = 4.79134$	$2\lambda\mu\sigma_2 = 4.88187$
$\sigma_3 = 7.94774$	$2\lambda\mu\sigma_3 = 5.36759$	$2\lambda\mu\sigma_3 = 5.46900$
$\sigma_4 = 0.27029$	$\mu^2\sigma_4 = 0.09127$	$\mu^2\sigma_4 = 0.11071$
$\sigma_5 = 0.09956$	$2\lambda\mu\sigma_5 = 0.06724$	$2\lambda\mu\sigma_5 = 0.06851$
$\sigma_6 = -1.24924$	$2\lambda\mu\sigma_6 = -0.84369$	$2\lambda\mu\sigma_6 = -0.85963$
$\sigma_7 = 1.04199$	$\lambda^2\sigma_7 = 0.35186$	$\lambda^2\sigma_7 = 0.30115$
$\sigma_8 = 1.80705$	$\lambda^2\sigma_8 = 0.61020$	$\lambda^2\sigma_8 = 0.55226$
$\sigma_9 = -0.48812$	$\lambda^2\sigma_9 = -0.16483$	$\lambda^2\sigma_9 = -0.14107$
$\sigma_{10} = -1.67419$	$\lambda^2\sigma_{10} = -0.56534$	$\lambda^2\sigma_{10} = -0.48386$

compared with the theoretical calculations, certain additional observations can be made. For instance, one deuterium substituent causes a larger isotope chemical shift in NH_3 than in CH_4, or in the substituted methanes. A comparison of the slopes of the theoretical curves for NH_3 and CH_4 show clearly that for a given internuclear angular change the change in shielding is larger for NH_3 than for CH_4. In addition, the isotope chemical shifts of different molecules of the first row of the periodic table increase monotonically in the order of decreasing H–H distance and/or HXH angle. This can be seen in Fig. 5, where the isotope chemical shifts of some of the monodeutero molecules from Table I are plotted versus internuclear angle and distance. Of course, deuterium substitution will not produce an identical change in bond angles in all substances. Nevertheless, this dependence of isotope shift upon the initial geometry of the molecule is in accord with the curvature of the $\sigma^d(\theta)$-vs-θ plot for CH_4 in Fig. 3, being concave upwards.

If electronegative atoms or groups with π electrons are substituted onto methane the isotope shifts are slightly less than that found for methane itself. This is also true for the methylene halides where the isotope shifts are nearly all the same, indicating little or no dependence upon electronegativity of the substituents. If this is the case, the HCH angle in CH_2Br_2 and CH_2I_2

TABLE VIII. Evaluation of the σ_j integrals for CH_4 expressed in parts per million for $(\lambda/\mu) = 1$.

$\sigma_1 = 17.74920$	$\mu^2\sigma_1 = 5.26086$
$\sigma_2 = 7.12575$	$2\lambda\mu\sigma_2 = 4.22414$
$\sigma_3 = 8.42006$	$2\lambda\mu\sigma_3 = 4.99141$
$\sigma_4 = 0.16045$	$\mu^2\sigma_4 = 0.04756$
$\sigma_5 = 0.10592$	$2\lambda\mu\sigma_5 = 0.06279$
$\sigma_6 = -1.15588$	$2\lambda\mu\sigma_6 = -0.68521$
$\sigma_7 = 1.40827$	$\lambda^2\sigma_7 = 0.41714$
$\sigma_8 = 1.95977$	$\lambda^2\sigma_8 = 0.58088$
$\sigma_9 = 0.28787$	$\lambda^2\sigma_9 = 0.08532$
$\sigma_{10} = -1.07633$	$\lambda^2\sigma_{10} = -0.31902$

TABLE IX. Evaluation of the σ_j integrals for CH_3D expressed in parts per million with $(\lambda/\mu) = 1$.

$\sigma_1 = 17.74920$	$\mu^2\sigma_1 = 5.26086$
$\sigma_2 = 7.12861$	$2\lambda\mu\sigma_2 = 4.22584$
$\sigma_3 = 8.42258$	$2\lambda\mu\sigma_3 = 4.99291$
$\sigma_4 = 0.16112$	$\mu^2\sigma_4 = 0.04776$
$\sigma_5 = 0.10645$	$2\lambda\mu\sigma_5 = 0.06310$
$\sigma_6 = -1.15683$	$2\lambda\mu\sigma_6 = -0.68577$
$\sigma_7 = 1.04100$	$\lambda^2\sigma_7 = 0.41794$
$\sigma_8 = 1.96118$	$\lambda^2\sigma_8 = 0.58129$
$\sigma_9 = 0.29030$	$\lambda^2\sigma_9 = 0.08604$
$\sigma_{10} = -1.07606$	$\lambda^2\sigma_{10} = -0.31893$

should be similar to that in CH_2Cl_2, i.e., 112°, rather than the tetrahedral angle previously assumed.

Some of the data examined for this discussion do not follow the above general pattern. In particular, the isotope shifts for CH_2O–$CHDO$ are much larger than would be expected on the basis of Fig. 5. In this case the isotope shift is strongly solvent-dependent,[34] which may be the reason for the discrepancy. Another case which doesn't conform is that of the deuteroammonium ions, where the isotope shifts are in the opposite direction. Again, solvent effects (the solvent used was H_2SO_4) are thought to be responsible.[35]

In conclusion, we think that it is clear that small changes in molecular geometry, resulting from isotopic substitution, can be responsible for a large part of the observed isotope shift in the proton magnetic resonance of first-row compounds. Whether the isotope shift could actually be used as a tool for the investigation of molecular structure problems remains to be seen.

ACKNOWLEDGMENT

TABLE X. Bond angles, bond lengths, screening constants, and overlap integrals for NH_3, CH_4, and CH_3D used in the calculations.

	NH_3	CH_4	CH_3D
$\angle$HXH	106°47′	109°28′	109°28′
H–X	1.91610 a.u.	2.06733 a.u.	2.06670 a.u.
D–X	···	···	2.06500 a.u.
H–H	3.0762 a.u.	3.3772 a.u.	3.3762 a.u.
H–D	···	···	3.3748 a.u.
c	1.95	1.625	1.625
S_h	0.33361	0.27926	0.27955
S_s	0.54816	0.56815	0.56834
S_p	0.40416	0.46495	0.46506
S	···	0.68690	0.68710

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APPENDIX

The shielding constant Eq. (6) can be expressed in the convenient form

$$\sigma^d = 2[\sigma(1) + \sigma(2) + \sigma(3) + \sigma(4)], \tag{A1}$$

where a factor of 2 arises because there are two electrons in each equivalent orbital. From the geometry of NH_3, CH_4, and CH_3D in Figs. 1(a) and 1(b) it is evident that $\sigma(2) = \sigma(3) \neq \sigma(4)$, or $\sigma(1)$ for NH_3 while for CH_4 and CH_3D $\sigma(1) \neq \sigma(2) = \sigma(3) = \sigma(4)$. Now, by substituting Eqs. (3) and (4) into Eq. (6), σ^d is obtained as a function of $\sigma(j)$, as expressed by Eqs. (9), (10), and (11). These are

$$\sigma(1) = \frac{e^2}{3mc^2a_0} \left\{ \mu^2 \int H_1(r_H)^{-1} H_1 d\tau + 2\lambda\mu \left[a \int C_{2s}(r_H)^{-1} H_1 d\tau + b \int C_{2p_z}(r_H)^{-1} H_1 d\tau \right] \right.$$
$$\left. + \lambda^2 \left[a^2 \int C_{2s}(Q) C_{2s} d\tau + b^2 \int C_{2p_z}(Q) C_{2p_z} d\tau + 2ab \int C_{2s}(Q) C_{2p_z} d\tau \right] \right\}, \tag{A2}$$

$$\sigma(2) = \frac{e^2}{3mc^2a_0} \left\{ \mu^2 \int H_2(Q) H_2 d\tau + 2\lambda\mu \left[a \int C_{2s}(Q) H_2 d\tau + bn_2 \int C_{2p_z}(Q) H_2 d\tau \right] + \lambda^2 \left[a^2 \int C_{2s}(Q) C_{2s} d\tau \right. \right.$$
$$\left. \left. + b^2 n^2 \int C_{2p_z}(Q) C_{2p_z} d\tau + b^2(m_2^2 + l_2^2) \int C_{2p_x}(Q) C_{2p_x} d\tau + 2abn_2 \int C_{2s}(Q) C_{2p_z} d\tau \right] \right\}, \tag{A3}$$

$$\sigma(4) = \frac{e^2}{3mc^2a_0} \left\{ a_4^2 \int C_{2s}(Q) C_{2s} d\tau + b_4^2 n_4^2 \int C_{2p_z}(Q) C_{2p_z} d\tau + b_4^2 m_4^2 \int C_{2p_x}(Q) C_{2p_x} d\tau + 2a_4 b_4 n_4 \int C_{2s}(Q) C_{2p_z} d\tau \right\}, \tag{A4}$$

where $(Q) = (1/r_H) - (Rr/r_H^3) \cos\theta$ and Fig. 1(c) has been used to define the coordinates of the diamagnetic operator. The atomic orbitals are of the form

$$H_j = (1/\pi)^{\frac{1}{2}} \exp(-r),$$
$$C_{2s} = (c^5/3\pi)^{\frac{1}{2}} \exp(-cr),$$
$$C_{2p_z} = (c^5/\pi)^{\frac{1}{2}} r \cos\theta \exp(-cr),$$
$$C_{2p_x} = (c^5/\pi)^{\frac{1}{2}} r \sin\theta \cos\phi \exp(-cr),$$
$$C_{2p_y} = (c^5/\pi)^{\frac{1}{2}} r \sin\theta \sin\phi \exp(-cr). \tag{A5}$$

For convenience the following notation for the atomic orbitals is introduced in Eqs. (A2), (A3), and (A4):

$$\sigma_1 = (e^2/3mc^2a_0) \int H_1(1/r_H) H_1 dr, \qquad \sigma_6 = (e^2/3mc^2a_0) \int C_{2p_z}(Q) H_2 dr,$$

$$\sigma_2 = (e^2/3mc^2a_0) \int C_{2s}(1/r_H) H_1 dr, \qquad \sigma_7 = (e^2/3mc^2a_0) \int C_{2s}(Q) C_{2s} dr,$$

$$\sigma_3 = (e^2/3mc^2a_0) \int C_{2p_z}(1/r_H) H_1 dr, \qquad \sigma_8 = (e^2/3mc^2a_0) \int C_{2p_z}(Q) C_{2p_z} dr,$$

$$\sigma_4 = (e^2/3mc^2a_0) \int H_2(Q) H_2 dr, \qquad \sigma_9 = (e^2/3mc^2a_0) \int C_{2p_x}(Q) C_{2p_x} dr,$$

$$\sigma_5 = (e^2/3mc^2a_0) \int C_{2s}(Q) H_2 dr, \qquad \sigma_{10} = (e^2/3mc^2a_0) \int C_{2s}(Q) C_{2p_z} dr. \tag{A6}$$

These integrals were derived by methods similar to those of Musher[30] and Hameka,[31,32] and are given numerically in Tables VII, VIII, and IX for NH_3, CH_4, and CH_3D. In addition, the overlap integrals occurring in Eqs. (13) and (14) are listed in Table X.