The NMR isotope shift in polyatomic molecules. Estimation of the dynamic factors

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In a continuing study of the factors which determine the isotope shifts in NMR we consider here substitution of end atoms in molecular types in which the bond angle deformation does not play a significant role. We show that in molecules of the type AX_n the rovibrational correction to shielding of nucleus A can be obtained directly from the isotope shift without dynamical calculations. We propose a method for estimating $\langle \Delta r \rangle$, knowing only the equilibrium bond length, the masses, and the rows of the Periodic Table of the atoms in the bond. We test this on diatomic molecules for which we are able to calculate $\langle \Delta r \rangle$ directly from the spectroscopic constants and examine its dependence on bond order. We apply the estimation method to polyatomic molecules for which we have completed a full dynamical calculation using the best available force fields. We use the estimated $\langle \Delta r \rangle$ for other molecular systems and obtain estimates of the shielding derivatives from the observed isotope shifts. The results compare well with derivatives that are known for related electronic environments.

The large and growing number of observed NMR isotope shifts have the following general trends: (1) The sign is generally negative, heavy isotopic substitution leads to increased shielding. (2) The magnitude diminishes with remoteness of substitution from the observed nucleus, (3) reflects the chemical shift range of the observed nucleus, and (4) depends on the fractional change in mass of the substituted atom. (5) The magnitude is proportional to the number of substitutions at equivalent sites. In a series of earlier papers, we have explained these general trends.

In paper I[1] we presented a quantitative treatment of the isotope shifts in diatomic molecules. By invoking the Born–Oppenheimer separation and expanding the nuclear magnetic shielding in terms of the small displacements away from the equilibrium nuclear configuration, it is possible to express the isotope shift in a diatomic molecule as follows:

$$\sigma - \sigma' = (\partial\sigma/\partial\Delta r)_e[\langle\Delta r\rangle - \langle\Delta r\rangle'] + (\partial^2\sigma/\partial\Delta r^2)_e[\langle(\Delta r)^2\rangle - \langle(\Delta r)^2\rangle']. \tag{1}$$

This simplifies further to

$$\sigma - \sigma' \simeq \frac{(\mu' - \mu)}{2\mu'}\frac{3B_e r_e}{2\omega} \times (1 + \alpha\omega/6B_e^2)\coth\left(\frac{hc\omega}{2kT}\right)(\partial\sigma/\partial\Delta r)_e, \tag{2}$$

where μ is the reduced mass, and ω, B_e, and α are the usual spectroscopic constants. For polyatomic molecules the expression (1) would have to include several bond extensions Δr_i, bond angle deformations $\Delta\alpha_{ij}$ and cross terms between these. We presented the isotope shift in CO_2 explicitly in terms of the cubic force constants and other spectroscopic constants of this molecular type, and explained the general trends observed using the diatomic case and CO_2 type as a basis.

In paper II,[2] we established the quantitative basis for the observed additivity of isotope shifts in multiple substitutions at equivalent sites, using CH_4 and linear triatomics as examples. We established the general dependence of the one-bond isotope shifts on the fractional mass change $(m' - m)/m'$ upon substitution of m with m'. Furthermore we found that for substitution at an end atom the mass dependence of the one-bond isotope shift of nucleus A is approximately given by $[(m' - m)/m']\frac{1}{2}[m_A/(m_A + m)]$ in those molecular types where the mean bond angle deformation does not play a significant role. In addition we considered the factor of the remoteness of the substitution site from the observed nucleus in terms of derivatives $(\partial\sigma/\partial\Delta r)_e$ and $(\partial\sigma/\partial\Delta r')_e$. The primary one is the change in the nuclear shielding due to extension of the bond connected to the observed nucleus and the secondary one is the change in shielding due to extension of a remote bond. The relative magnitudes of these for ^1H in CH_4 and for ^{19}F in COF_2 have been determined.[3,4] Thus, the general trends noted by Batiz–Hernandez and Bernheim[5] have been explained at a quantitative level. Now we are ready to consider the other factors.

One-bond isotope shifts range over several orders of magnitude, from <0.001 to 7 ppm per substituted atom. Some correlations of these isotope shifts have been made with bond length, bond order, hybridization, chemical shifts, and the wavelength for the $n \rightarrow \pi^*$ transition.[6–9] However, these correlations are very limited, they are only predictive for a given observed nucleus, for a given atom substituted, and usually only for a given class of compounds for which many such isotope shifts have previously been reported. It would be very useful to be able to predict a previously unreported isotope shift, i.e., the isotope shift for a resonant nucleus-substituted atom combination, to within at least an order of magnitude.

It is not yet clear which part of any of the observed correlations is due to differences in the dynamic averaging and which part is due to differences in the shielding deriva-

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tives. Both the shielding surface and the potential energy surface are determined by electronic factors; therefore substitution with an electronegative atom, for example, will cause changes in both surfaces. The observed isotope shifts depend on derivatives on both surfaces at the coordinates corresponding to the minimum (the equilibrium configuration) of the potential energy surface. What we need is a quantitative global understanding of NMR isotope shifts. This will likely become possible after dynamic averaging calculations for a sufficient number of nuclei and molecular types have been carried out, fitting to the observed temperature dependence of the nuclear shielding at the zero-pressure limit. With these calculations empirical values of derivatives for nuclear shielding with bond extension and angle deformation can be obtained. An alternative source for shielding derivatives is *ab initio* calculations of nuclear shielding for molecular configurations infinitesimally displaced from the minimum energy one. There has been significant progress in both approaches. Some shielding calculations for ^1H up to ^{19}F nuclei in small molecules have given much improved agreement with experimental chemical shifts.[10–14] The IGLO method is sufficiently efficient that it is beginning to be applied to larger molecules containing ^1H to ^{19}F nuclei, although agreement with experiment still needs to be improved.[13] Very few *ab initio* calculations of shielding with bond displacements have been reported as yet.[15–18] On the other hand, several measurements of the temperature dependence of ^{13}C, ^{15}N, ^{31}P, and (mostly) ^{19}F nuclei in the zero-pressure limit have been reported, and a few dynamic averaging calculations have been made to fit those, yielding empirical derivatives of shielding with bond extention.[3,19–22] No derivatives of shielding with angle deformation have resulted from these measurements because the data in those cases where this is expected to be significant have not been sufficiently precise. This approach is also severely limited by the necessity for at least a well-known general harmonic force field for the molecule, and anharmonic corrections as well. Duncan has listed the cases in which this information is available.[23] Unfortunately the overlap between this set and the set of easily observable nuclei with large shifts in the zero-pressure limit is not particularly large.

All in all then, even with the combined information from both experimental and theoretical camps, we still do not have enough data to quantitatively relate the shielding derivatives with molecular structure in a global way, or to predict a semiquantitative value for this derivative, given a molecular structure. In this paper, we make use of existing isotope shift data to extract empirical estimates of shielding derivatives with respect to bond extension for several molecules, and provide a semiglobal equation which will allow us to do this for certain molecular types without having to perform a dynamic averaging calculation for each molecule. We consider only one-bond isotope shifts and only substitution at an end atom in molecular types in which bond angle deformation does not play a significant role.

THE ROVIBRATIONAL CORRECTION TO SHIELDING

Since the isotope shift and the temperature dependence of the nuclear shielding at the zero-pressure limit are intimately related (both involve averaging over the potential surface), the same information is available from isotope shifts as from the temperature dependence of the nuclear shielding. The difference in shielding between the rigid equilibrium configuration and the thermal average configuration is a correction which has to be applied to *ab initio* values of σ_e prior to comparison with experiment. We show here that it is possible to obtain such a correction directly from the isotope shift in some molecular types.

The temperature dependence of the nuclear shielding can be expressed as

$$\sigma_0(T) = \sigma_e + \sum_i (\partial\sigma^{\mathrm{A}}/\partial\Delta r_i)_e \langle\Delta r_i\rangle^T + \cdots . \tag{3}$$

For molecules of the type AX_n, in which all the bonds are identical and the equilibrium bond angle is determined by symmetry (for $n = 1,2,3,4,6$) the temperature dependence of the shielding can be written as

$$\sigma_0^{\mathrm{A}}(T) = \sigma_e^{\mathrm{A}} + (\partial\sigma^{\mathrm{A}}/\partial\Delta r)_e n\langle\Delta r\rangle^T + \cdots, \tag{4}$$

since all n bonds are equivalent and the terms in $\langle\Delta\alpha\rangle^T$ do not contribute in lowest order. On the other hand, the one-bond isotope shift is

$$^1\Delta\ \mathrm{A} = \sigma_0 - \sigma_0' = (\partial\sigma^{\mathrm{A}}/\partial\Delta r)_e \sum_i [\langle\Delta r_i\rangle - \langle\Delta r_i\rangle'] . \tag{5}$$

For a single substitution of m by m',

$$^1\Delta\ \mathrm{A}(^{m'/m}\mathrm{X}) = (\partial\sigma^{\mathrm{A}}/\partial\Delta r_{\mathrm{AX}})_e [\langle\Delta r_{\mathrm{A}m}\rangle - \langle\Delta r_{\mathrm{A}m'}\rangle], \tag{6}$$

where $\langle\Delta r_{\mathrm{A}m}\rangle$ and $\langle\Delta r_{\mathrm{A}m'}\rangle$ are the mean bond displacement of the A–^{m}X and A–$^{m'}$X bonds, respectively, if we neglect the secondary effects on other bonds by substitution on this bond.

We have shown previously[2] that for substitution at an end atom,

$$^1\Delta\ \mathrm{A}(^{m'/m}\mathrm{X}) \simeq (\partial\sigma^{\mathrm{A}}/\partial\Delta r_{\mathrm{AX}})_e \langle\Delta r_{\mathrm{A}m}\rangle \times [(m'-m)/m'](1/2)[m_{\mathrm{A}}/(m_{\mathrm{A}}+m)] . \tag{7}$$

Let us define a "reduced isotope shift" $^1\Delta^R(\mathrm{A,X})$ in which the fractional mass factor which gives the isotope shift its explicit dependence on the mass change is divided out:

$$^1\Delta^R(\mathrm{A,X}) = [^1\Delta\ \mathrm{A}(^{m'/m}\mathrm{X})] \left[\frac{m'-m}{m'}\frac{1}{2}\frac{m_{\mathrm{A}}}{m_{\mathrm{A}}+m}\right]^{-1} . \tag{8}$$

Equation (6) then becomes:

$$^1\Delta^R(\mathrm{A,X}) \simeq (\partial\sigma^{\mathrm{A}}/\partial\Delta r_{\mathrm{AX}})_e \langle\Delta r_{\mathrm{A}m}\rangle . \tag{9}$$

and Eq. (4) becomes, for $T = 300$ K,

$$[\sigma_0^A(300) - \sigma_e] = n\ {}^1\Delta^R(\mathrm{A,X}) . \tag{10}$$

Thus, if only linear terms are important and $\langle\Delta\alpha\rangle^T$ terms do not contribute significantly to either the temperature dependence or the isotope shift (and in these specific types these conditions are easily satisfied), then we can obtain directly from isotope shifts the same $[\sigma_0(300) - \sigma_e]$ that up to now have been obtained from fitting the experimental $[\sigma_0(T) - \sigma_0(300)]$ function to dynamical calculations of $[\langle\Delta r\rangle^T - \langle\Delta r\rangle^{300}]$. In Table I we present the reported isotope shifts and the derived rovibrational correction to the

TABLE I. The rovibrational correction to shielding, directly obtained from measured isotope shifts.[a]

Observed Nucleus	Molecule	m'/m	$-{}^1\Delta$, ppm	$-{}^1\Delta^R$	$[\sigma_0(300)-\sigma_e]$
^{1}H	H_2	$^{2/1}$H	0.0469	0.375	$-$ 0.375
^{11}B	BH_4^-	$^{2/1}$H	0.137–0.139	0.6	$-$ 2.4
^{13}C	CH_4	$^{2/1}$H	0.192	0.82	$-$ 3.3
	CN^-	$^{15/14}$N	0.03 ± 0.005	1.87	$-$ 1.87 ± 0.3
^{14}N	NH_4^+	$^{2/1}$H	0.307	1.32	$-$ 5.26
^{15}N	NO_3^-	$^{18/16}$O	0.056	2.16	$-$ 6.5
	CN^-	$^{13/12}$C	0.075 ± 0.005	3.51	$-$ 3.5 ± 0.2
^{19}F	HF	$^{2/1}$H	2.5 ± 0.5	10.5	-10.5 ± 2
^{31}P	$PO_4^{\equiv}$	$^{18/16}$O	0.019 ± 0.002	0.52	$-$ 2.1 ± 0.3
^{55}Mn	MnO_4^-	$^{18/16}$O	0.59 ± 0.02	13.7	-55 ± 2
^{95}Mo	$MoO_4^=$	$^{18/16}$O	0.25 ± 0.01	5.26	-21 ± 1
^{99}Tc	TcO_4^-	$^{18/16}$O	0.44 ± 0.06	9.2	-37 ± 5
^{195}Pt	$PtCl_6^=$	$^{37/35}$Cl	0.167	7.3	-43.8 ± 1.6
	$PtBr_6^=$	$^{81/79}$Br	0.028 ± 0.006	3.18	-19 ± 4

[a] References are in Table II.

shielding for molecules in which the specified conditions are met.

We can compare the numbers that we obtained using Eq. (10) with values obtained from full dynamical calculations. For H_2, Raynes and Panteli[24] obtained $[\sigma_0^H(296)-\sigma_e^H] = -0.326$ ppm, compared to our -0.375 ppm. For CH_4, our own calculations including secondary vibrational effects on mean bond displacements,[4] yield $[\sigma_0^C(300)-\sigma_e^C] = -2.985$ ppm, to be compared to -3.3 here. For HF, Hindermann and Cornwell found $[\sigma_0^F(300)-\sigma_e^F] = -9.75$ ppm,[25] and Ditchfield calculated -11.23 ppm,[17] to be compared with -10.5 ppm from Eq. (10).

There are practical implications of Eq. (7) for measurements of isotope shifts. Quite apart from the advantage of a large chemical shift range for heavier nuclei, the mass dependence alone favors the observation of the chemical shift of a heavy nucleus upon substitution of a light neighboring atom with an isotope. The most favorable case is the $^{2/1}$H-induced shift of a heavy nucleus. In addition to the favorable fractional mass change, the factor $m_A/(m_A+m)$ is close to 1.0. It would be wise to calculate the mass factors prior to attempting an isotope shift measurement. For example, in the Se–C bond the $^{13/12}$C-induced ^{77}Se shift is easily observable, whereas the $^{80/77}$Se-induced ^{13}C shift is not. In $NCSe^-$ we observed a 26.4 Hz (-0.683 ppm) $^{13/12}$C-induced Se shift, but could not observe any shifts due to the Se isotopes in the ^{13}C spectrum. The mass factor $[(m'-m)/m'] \times [m_A/(m_A+m)] = 0.067$ in the first case and 0.005 in the second.

ESTIMATION OF $\langle \Delta r \rangle$

In order to implement Eq. (7) for the determination of $(\partial\sigma/\partial\Delta r)_e$ we need to know $\langle\Delta r\rangle$, the calculation of which requires an adequate force field for the molecule. Since the number of such polyatomic molecules which also have magnetically interesting central nuclei is small, we present here an empirical method of estimating $\langle\Delta r\rangle$ for bonds involving end atoms without carrying out any dynamic calculations, without even a harmonic force field.

Bartell has pointed out that the leading term in an expression for the mean bond displacement is[26]

$$\langle \Delta r_i \rangle_{\rm vib} \simeq \frac{3}{2}\frac{F_{iii}}{F_{ii}} \langle (\Delta r_i)^2 \rangle, \tag{11}$$

where $F_{ii} \equiv (1/2)(\partial^2 V/\partial r^2)_e$ and $F_{iii} \equiv -(1/6)(\partial^3 V/\partial r^3)_e$. This approximation is equivalent to considering only the Morse anharmonicity connected with the stretching of this particular bond and neglecting all other cross terms. Since we are considering only $\langle\Delta r\rangle$ for a bond to an end atom in this paper, it is natural to express $\langle(\Delta r)^2\rangle$ in the same way as for diatomic molecules:

$$\langle (\Delta r)^2 \rangle = \langle Q^2\rangle/\mu = (h/\mu 8\pi^2 c\omega)\coth(hc\omega/2kT). \tag{12}$$

The temperature dependence can be suppressed for our purposes since for most bond stretches, coth $(hc\omega/2kT)$ is very close to 1.0 at room temperature for stable bonds. For a harmonic oscillator

$$2\pi c\omega = (2F_{ii}/\mu)^{1/2}, \tag{13}$$

so that

$$\langle (\Delta r)^2 \rangle \simeq (h/4\pi)(2\mu F_{ii})^{-1/2}. \tag{14}$$

Substituting this into Eq. (11),

$$\langle \Delta r \rangle_{\rm vib} \simeq (3h/8\pi) F_{iii} F_{ii}^{-3/2} (2\mu)^{-1/2}$$

or

$$\simeq (3h/8\pi)(-F_3 F_2^{-3/2})\mu^{-1/2}, \tag{15}$$

if we use Herschbach and Laurie's [27] notation for the force constants $[F_3 \equiv (1/3)(\partial^3 V/\partial r^3)_e$ and $F_2 \equiv (\partial^2 V/\partial r^2)_e]$.

Herschbach and Laurie found that quadratic, cubic, and quartic vibrational force constants for diatomic molecules are approximately exponential functions of internuclear distance, described by a family of curves which are determined by the location of the bonded atoms in rows of the periodic table. In other words, F_3 and F_2 can be written in the form

$$(-1)^n F_n = 10^{-(r_e - a_n)/b_n}, \tag{16}$$

where the force constants are expressed in the usual units, mdyn Å^{-1}, mdyn Å^{-2}, etc.; a_n and b_n are parameters given by their tables. Using these we can write Eq. (15) as follows:

$$\langle\Delta r\rangle_{\rm vib}/\text{Å}\simeq(3h/8\pi)\mu^{-1/2}10^{-D} = 19.35\times10^{-3}\mu^{-1/2}10^{-D}, \qquad (17)$$

where $D\equiv[(r_e-a_3)/b_3-3(r_e-a_2)/2b_2]$, and μ is in amu.

In Fig. 1 we plot $\mu^{-1/2}\,10^{-D}$ vs the values of the mean bond displacement $\langle\Delta r\rangle_{\rm vib}$ calculated for diatomic molecules using

$$\langle\Delta r\rangle_{\rm vib}=(3/2)(B_e r_e/\omega)(1+\alpha\omega/6B_e^2)\coth(hc\omega/2kT). \qquad (18)$$

Spectroscopic constants and r_e were taken from the compilation by Mills[28] and T was chosen to be 300 K. The straight line is drawn with the slope 19.35×10^{-3}. We see that for diatomic molecules, Eq. (17) gives reasonably good predictions of mean bond displacements. The total mean bond displacement requires the additional term $\langle\Delta r\rangle_{\rm rot}=(4B_e r_e/\omega^2)\,(kT/hc)$ for diatomics.

The Herschbach and Laurie parameters are found to describe F_3 for polyatomic molecules as well. It appears that stretching cubic constants for polyatomic molecules can be predicted from diatomic data simply by allowing for the change in the bond length. Therefore, we expect Eq. (17) to predict mean bond displacements in polyatomic molecules if the Morse anharmonic stretching accounts for most of the mean bond displacement. In Fig. 2 we plot $\mu^{-1/2}\,10^{-D}$ vs $\langle\Delta r\rangle_{\rm vib}$ which we have calculated for selected polyatomic molecules. A least squares fit gives a slope of 22×10^{-3} rather than 19.35×10^{-3}. We did expect the slope for the polyatomic molecules to be somewhat larger. Bartell has shown that for molecules of the AX_n type, the other contributions due to bending and nonbonded interactions can be significant (the Morse stretching contribution to $\langle\Delta r\rangle$ is only 64% in CH_4,[29] only about 40% in SF_6[30]) and only a full dynamical calculation can give the entire $\langle\Delta r\rangle$. However, Eq. (17) with a modified factor of 22×10^{-3} for polyatomics gives a satisfactory estimate of $\langle\Delta r\rangle$ from r_e. Therefore, we shall use

$$\langle\Delta r\rangle_{\rm vib}/\text{Å}\simeq22\times10^{-3}\mu^{-1/2}10^{-D}. \qquad (19)$$

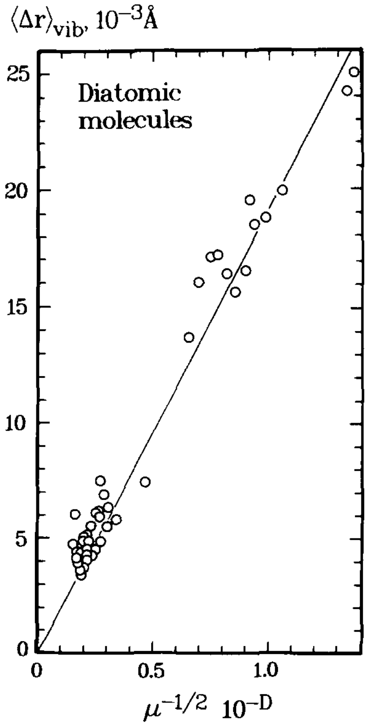

FIG. 1. Test of Eq. (17) for diatomic molecules. $D=\{(r_e)-a_3/b_3-[3(r_e-a_2)]/(2b_2)\}$ with r_e from the compilation by Mills (Ref. 28) a and b parameters from Herschbach and Laurie. (Ref. 27). $\langle\Delta r\rangle_{\rm vib}$ were calculated using spectroscopic constants from Mills.

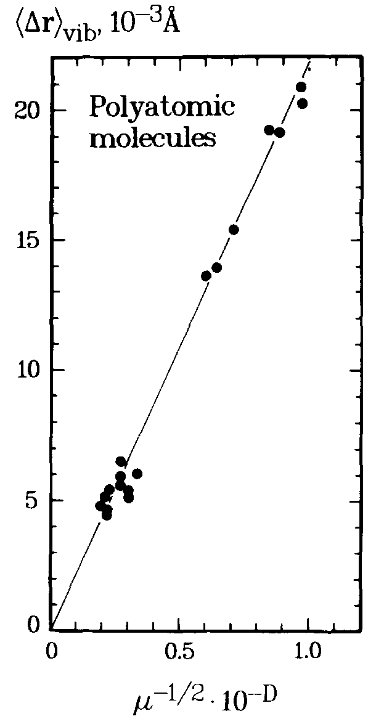

FIG. 2. Estimate of $\langle\Delta r\rangle_{\rm vib}$ using the same method as for diatomics, applied to polyatomic molecules. The line is a least squares fit to the data. We used $\langle\Delta r\rangle_{\rm vib}$ for the following molecules: OCS, NNO, C_2F_4, OCF_2, CH_4, CD_4, CF_3Cl, H_2O, D_2O, H_2Se, D_2Se, CH_3F, CF_4, and SiF_4, all calculated using the best available force fields. (References 3, 4, 21, and unpublished calculations.)

The rotational contribution to $\langle\Delta r\rangle$ is likewise easily estimated from r_e alone for an AX_n molecule[29]:

$$\langle\Delta r\rangle_{\rm rot}=2\bar{E}_{\rm rot}/(nF_2r_e), \qquad (20)$$

where $\bar{E}_{\rm rot}$ is the classical average, kT for linear molecules, and $(3/2)kT$ for nonlinear ones. Equation (20) gives the same centrifugal stretching equations for the symmetric cases as does Toyama, Oka, and Morino.[31] For the symmetrical and diatomic molecules, $\langle\Delta r\rangle_{\rm rot}$ is invariant to isotopic substitution. We have already shown[4] that for the unsymmetrical methanes $\Sigma_i\,\langle\Delta r_i\rangle_{\rm rot}=$ constant, although each $\langle\Delta r_i\rangle$ is affected by isotopic substitution. Therefore, although there is centrifugal stretching contribution to $\langle\Delta r\rangle$, as long as we limit the discussion to substitution at an end atom, and molecular types in which $\langle\Delta\alpha\rangle$ does not play a significant role, $\langle\Delta r\rangle_{\rm rot}$ need not be included in the calculation of the $\langle\Delta r\rangle$ that goes into Eq. (8).

ESTIMATION OF $(\partial\sigma/\partial\Delta r)_e$ FROM ISOTOPE SHIFTS

We have previously obtained $(\partial\sigma^{\rm F}/\partial\Delta r_{\rm CO})_e$ for $O=CF_2$,[3] $(\partial\sigma^{\rm C}/\partial\Delta r_{\rm CH})_e$ and $(\partial\sigma^{\rm H}/\partial\Delta r_{\rm CH})_e$ in CH_4[4] from isotope shifts. These involved dynamic calculations using the best available force fields for these molecules. Now we have an empirical method of estimating $\langle\Delta r\rangle_{\rm vib}$ which we can apply to the estimation of the shielding derivatives from reported one-bond isotope shifts using Eqs. (7) and (19) or

$$(\partial\sigma^{A}/\partial\Delta r)_e \simeq {}^1\Delta\,{}^R(\mathrm{A,X})/\langle\Delta r_{\mathrm{AX}}\rangle_{\mathrm{vib}}. \tag{9}$$

Only the measured isotope shift and r_e for the bond are needed to estimate the shielding derivative. This cannot be applied when the contribution of $\langle\Delta\alpha\rangle$ terms to the isotope shift are significant, or for substitution at other than an end atom. The results of applying this equation to polyatomic molecules are shown in Table II. We have also included the diatomic molecules for which we used Eq. (18) to calculate $\langle\Delta r\rangle_{\mathrm{vib}}$. For the transition metal complexes the actual F_2 values were calculated from the vibrational frequencies observed in solution[32,33]; since Herschbach and Laurie's tables do not provide a and b values for these, a_3 and b_3 were assumed to be the same as for the main group atoms of the same rows. Error estimates shown for the shielding derivatives are those associated with the isotope shift measurements, they do not include the uncertainties associated with the estimation of $\langle\Delta r\rangle_{\mathrm{vib}}$.

In a few cases, we have compared our estimated derivatives with other reported values. Some are from *ab initio* calculations (H_2, HF), others are from isotope shifts, using calculated $\langle\Delta r\rangle$ values (H_2, CN^-, CH_4). We see that our estimates agree quite well with these other values.

We note that these derivatives are on the small side when compared with the ones which we have obtained for ^{19}F in molecules such as F_2, ClF, CF_4, SF_6, $O=CF_2$, for example. This is not unexpected. Most of the nuclei in Table

TABLE II. Nuclear shielding derivatives obtained from isotope shifts.

Observed nucleus	molecule	m'/m	$-{}^1\Delta$, ppm	Ref.	r_e, Å	Ref.	$\langle\Delta r\rangle_{\mathrm{vib}}\cdot 10^3$ Å	$(\partial\sigma/\partial\Delta r)_e$, ppm/Å this work	$(\partial\sigma/\partial\Delta r)_{e'}$ other	Ref.
^1H	H_2	$^{2/1}H$	0.0469	a	0.7413	r	24.67	$-$ 15.2	$-$ 20.7, $-$ 21.8, $-$ 12.1	u,v,w
^{11}B	BH_4^-	$^{2/1}H$	0.138 ± 0.0002	b	1.19	r	22.57	$-$ 26.7		
^{13}C	CH_4	$^{2/1}H$	0.192 ± 0.0003	c	1.094	r	21.12	$-$ 39	$-\ 35 \pm 3$	x
	$CHCl_3$	$^{2/1}H$	0.203 ± 0.0005	d	1.073	r	20.90	$-$ 42		
	CH_2Cl_2	$^{2/1}H$	0.199 ± 0.0003	d	1.068	r	20.84	$-$ 41		
	CH_3I	$^{2/1}H$	0.049	d	1.1	r	21.24	$-$ 10.9		
	CH_3OD	$^{2/1}H$	0.283	d	1.096	r	21.19	$-$ 57		
	CH_3CN	$^{2/1}H$	0.148	d	1.112	r	21.40	$-$ 30		
	CN^-	$^{15/14}N$	0.03 ± 0.005	e	1.157	r	4.97	$-\ 380 \pm 60$	-473 ± 90	j
	$C=O$	$^{18,16}O$	0.028 to 0.052	f	1.215	r	5.24	$-$ 215 to $-$ 400		
	$M\cdots C\equiv O$	$^{18/16}O$	0.040	g	1.145	r	4.74	$-$ 340	$-$226, 414	y,z
^{14}N	NH_4^+	$^{2/1}H$	0.307	h	1.032	r	20.34	$-$ 65		
	NO_3^-	$^{18/16}O$	0.056	i	1.220	r	5.08	$-$ 425		
^{15}N	CN^-	$^{13/12}C$	0.075 ± 0.005	j	1.157	r	5.00	$-\ 700 \pm 50$	-872 ± 160	j
^{19}F	HF	$^{2/1}H$	2.5 ± 0.5	k	0.9175	r	15.60	$-\ 675 \pm 135$	$-$411	u
^{31}P	$PO_4^{\equiv}$	$^{18/16}O$	0.019 ± 0.002	l	1.537	r	4.33	$-\ 120 \pm 13$		
	$P=O$	$^{18,16}O$	0.0354	m	1.52	r	4.21	$-$ 230		
^{55}Mn	MnO_4^-	$^{18/16}O$	0.59 ± 0.02	n	1.61	s	5.51	-2485 ± 85		
^{95}Mo	$MoO_4^=$	$^{18/16}O$	0.25 ± 0.01	n	1.77	s	3.76	-1400 ± 55		
^{99}Tc	TcO_4^-	$^{18/16}O$	0.44 ± 0.06	0	1.711	s	4.53	-2030 ± 280		
^{119}Sn	Bu_3SnH	$^{2/1}H$	1.62	p	1.70	r	17.80	$-$ 367		
^{195}Pt	$PtCl_6^=$	$^{37/35}Cl$	0.167	q	2.334	t	2.89	$-$2530		
	$PtBr_6^=$	$^{81/79}Br$	0.028 ± 0.006	q	2.484	t	2.17	-1470 ± 310		

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II are in highly symmetric electronic environments (T_d,O_h,D_{3h}), for which a smaller paramagnetic contribution to shielding and therefore a smaller derivative of shielding with bond extension may be expected. There is however, a noticeable trend of increasing shielding derivative with the range of chemical shifts for the nucleus, although the data is too sparse to show this explicitly.

CONCLUSIONS

In calculating values for Fig. 1, we noted that $\langle \Delta r \rangle_{\text{vib}}$ has a bond order dependence. Although the ranges of values overlap, $\langle \Delta r \rangle_{\text{vib}}\, \mu^{1/2}/r_e$ tends to decrease with increasing bond order. A bond order dependence has been noted[7,9] in ^{13}C and ^{31}P one-bond isotope shifts: $(-{}^1\Delta)$ tends to increase with increasing bond order. Since the dynamic factor tends in the opposite direction, we conclude that this must be due to purely electronic factors, i.e., $-(\partial\sigma/\partial\Delta r)_e$ tends to increase with bond order. The observed dependence of $(-{}^1\Delta)$ on bond length[6] must then also be due to electronic factors.

We have proposed a method of obtaining estimates of $(\partial\sigma/\partial\Delta r)_e$ (without use of a force field) from one-bond isotope shifts due to substitution at an end atom only for molecular types in which the $\langle \Delta\alpha \rangle$ contributions are not significant. Isotope shifts are much easier to measure than the temperature dependence in the gas at the zero-pressure limit, and are not very sensitive to intermolecular effects (except in cases such as hydrogen bonding). Equations (7) and (19) provide us with a means of obtaining empirical estimates of shielding derivatives for a much larger class of molecular systems than either the limited list of molecules with well-known force fields or the comparably limited list of molecules with few electrons for *ab initio* shielding calculations. For isotopic substitution not at an end atom, the situation becomes less amenable to simple treatment and the isotope shift will probably not be easily predicted. Although the $(m'-m)/m'$ factor is still good, the $m_A/(m_A+m)$ factor is no longer adequate. For these cases it appears that a full dynamic calculation is required. The molecular types in which $\langle \Delta\alpha \rangle$ makes a substantial contribution will be considered in another paper.

The temperature dependence of the shielding at the zero-pressure limit $(d\sigma_0/dT)$ and the isotope shifts are complementary measures of the shielding derivatives. $(d\sigma_0/dT)$ are usually smaller for central nuclei and they are larger for end nuclei. On the other hand, the convenient isotope shift formula applies to central nuclei upon substitution of a neighboring end atom, whereas for end nuclei, substitution of neighboring nonend atoms lead to a mass dependence for which we have no general formula. Thus, both measurements will continue to be useful. Once we have collected a sufficient number of empirical shielding derivatives from these two techniques it may be possible to correlate them with the local electronic structure around the observed nucleus in a semiquantitative way. Then, armed with such values for the derivatives, Eqs. (7) and (19) will provide estimates of one-bond isotope shifts for resonant nucleus-substituted atom combinations not previously reported, or for bonding situations different from those previously reported.

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use large metal atom clusters which give a realistic treatment of molecular chemisorption.[3(b),7,8]

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ERRATA

Erratum: Observation of thelowest triplet transitions $^3\Sigma_g^+ - ^3\Sigma_u^+$ in Na_2 and K_2 [J. Chem. Phys. 80, 4794 (1984)]

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The factor $3hc$ was inadvertently deleted from the denominator of the right-hand side of Eq. (1). The correct expression is

$$k_\nu(T) = \frac{4\pi^4 \nu D^2 g^* n^2 [R(\nu)]^2}{3hc|d\nu/dR|} e^{-V/kT}. \qquad (1)$$

The calculations described in the paper were carried out using this correct expression so that the results shown in the figures are valid.

Erratum: The NMR isotope shift in polyatomic molecules. Estimation of the dynamic factors [J. Chem. Phys. 81, 4300 (1984)]

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In Table I the first line should read ^{2}H HD $^{2/1}$H 0.0469 0.2814 -0.2814. In Table II the first line should read ^{2}H HD $^{2/1}$H 0.0469 0.7413 21.37 -11.5 and for ^{19}F in HF the theoretical derivative should read -441 (Ditchfield's value)[1] instead of -411 (Stevens and Lipscomb's value).[2] The error arose in attributing the -0.0469 ppm isotope shift to ^{1}H in the H_2–HD system rather than to ^{2}H in the HD–D_2 system. With the above correction, our estimate of $(2\sigma^D/\partial\Delta r_{HD})_e = -11.5$ ppm Å^{-1} comes closer to the more accurate value calculated by Raynes and Panteli (-12.5 ppm Å^{-1})[3] which included the term in the second derivative $(\partial^2\sigma/\partial\Delta r^2)_e$ in the interpretation of the isotope shift measured by Beckett and Carr.[4] It is worth noting that if we use $(\partial\sigma^D/\partial\Delta r_{HD})_e = -11.5$ ppm $= (\partial\sigma^H/\partial\Delta r_{HH})_e$ to calculate the ^{1}H isotope shift in the H_2–HD system using $(\partial\sigma^H/\partial\Delta r_{HH})_e [\langle r_{HH}\rangle - \langle r_{HD}\rangle]$, we get -0.038 ppm which is completely consistent with the value -0.036 ± 0.002 ppm reported by Evans[5] for H_2 and HD dissolved in organic solvents. The difference between Beckett and Carr's -0.0469 ± 0.0005 ppm and the earlier value of -0.036 ± 0.002 ppm is not due to the lower accuracy of the latter experiment, or the intermolecular effects of the organic solvent. It is a real difference which is to be expected from the different dynamic factors involved in the two sets of isotopomers.

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