the larger hyperfine coupling constant.

The comparatively weak enhancement of the tertiary protons can be explained if the tertiary cyclopropane carbons adopt a pyramidal structure. Although pyramidal radicals are reasonably rare, they have been established for several strained ring systems.[25] For the radical cation **16**, the change in the angle, ϕ, and the adoption of a pyramidal structure apparently relieve some of the strain in the system, yet maintain a reasonable degree of overlap between the tertiary carbon orbitals and the benzene ring.

Conclusion

The results observed for the spiro[cyclopropane-1,9′-fluorene] and the benzocyclopropanorbornene systems demonstrate the importance of molecular orbital effects for the structures of strained ring radical cations and underscore the value of the FMO/PMO approach. The structure assumed by the radical cation of **4** is dictated by the favorable interaction between the S orbital of benzene and the S orbital of cyclopropane. The radical cations of the spiro compounds **3** are derived in most cases from the S orbital. However, the radical cation **12** of the parent species is derived from the A orbital of cyclopropane and owes its relative stability to the interaction with the second HOMO of biphenyl. The degree of structural detail derived for these radical cations illustrates the fact that CIDNP patterns reflect subtle structural details. These results underscore the value of the CIDNP method in the study of electron transfer generated intermediates.

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Registry No. **3a**, 167-02-2; **3b**, 87319-62-8; **9b**$^{+\cdot}$, 96612-27-0; **3c**, 87319-59-3; **3d**, 87319-58-2; **3e**, 87319-57-1; **3f**, 87319-61-7; **4**, 15577-76-1; **4**$^{+\cdot}$, 96612-28-1; chloranil, 118-75-2.

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Applications of the Reduced Isotope Shift to General Estimation of One-Bond Isotope Shifts in NMR

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Abstract: We discuss general magnitudes of isotope shifts in NMR in terms of an electronic and a dynamic factor. The electronic factor is shown to be related to other measures of shielding sensitivity such as ranges of chemical shifts and $\langle a_0{}^3/r^3\rangle$ values for free atom of the observed nucleus. The dynamic factors can essentially be separated out by defining a reduced isotope shift. A table of values of reduced isotope shifts for a major part of the periodic table is provided, from which it is possible to estimate the order of magnitude of a one-bond isotope shift for these nuclei in any bond. Estimates for specific $^{2/1}$H- and $^{18/16}$O-induced isotope shifts are also given for nuclei in groups 4–7 in the periodic table.

NMR isotope shifts are differences in nuclear magnetic shielding between isotopically related species which are observed in high-resolution NMR spectra. Comprehensive reviews by Batiz-Hernandez and Bernheim[2] and by Hansen[3] include most of the reported data. The general trends noted by Batiz-Hernandez and Bernheim have been explained in a series of papers.[4,5] The feasibility of observing a one-bond isotope shift, e.g., $^{80/77}$Se-induced ^{13}C shift, depends on the mass factors and on the shielding sensitivity. In this paper we discuss the general magnitudes of observed isotope shifts and provide estimates of others. We also provide a periodic table of relative sensitivities of nuclei to isotopic substitution at a nearest neighbor. The feasibility of observing the isotope shift for a nucleus upon isotopic replacement of an atom bonded to it can be estimated from this table by simply multiplying by appropriate mass factors.

The Dynamic Factor for End Atom Substitution

It has been shown that one-bond isotope shifts of nucleus A due to substitution of ^{m}X by $^{m'}$X in a symmetrical AX$_n$ molecule in which the mean bond angle distortions do not contribute significantly to the isotope shift can be interpreted by the following equation:[5]

$$^1\Delta A(^{m'/m}\mathrm{X}) = \sigma_0 - \sigma_0' = (\partial\sigma^{\mathrm{A}}/\partial\Delta r_{\mathrm{AX}})_e \sum_n (\langle\Delta r\rangle - \langle\Delta r\rangle') + \ldots \qquad (1)$$

We found that secondary isotope effects on $\langle\Delta r\rangle$ and isotope effects on centrifugal stretching can be neglected so that the sum of isotope effects on the mean bond displacements $\sum_n(\langle\Delta r\rangle - \langle\Delta r\rangle')$ by a single substitution can be replaced by the isotope effect on the bond in question, $\langle\Delta r_{\mathrm{A}m}\rangle - \langle\Delta r_{\mathrm{A}m'}\rangle$, and the latter, the mass dependence of the vibrational contribution, can be quantitatively estimated by $\langle\Delta r_{\mathrm{A}m}\rangle\cdot(m'-m)/m'\cdot(1/2)m_{\mathrm{A}}/(m_{\mathrm{A}}+m)$.[5] Under these conditions, the one-bond isotope shift can be expressed as

$$^1\Delta A(m'/m_{\mathrm{X}}) \simeq (\partial\sigma^{\mathrm{A}}/\partial\Delta r_{\mathrm{AX}})_e \langle\Delta r\rangle \frac{m'-m}{m'}\frac{1}{2}\frac{m_{\mathrm{A}}}{m_{\mathrm{A}}+m} \qquad (2)$$

where $\langle\Delta r\rangle$ is the mean bond displacement in the unsubstituted molecule A^{m}X$_n$. The observed additivity of multiple isotopic substitutions of equivalent atoms has been interpreted quantitatively.[5] In this paper we will consider only single isotopic replacement.

Calculations of the mean bond displacement $\langle\Delta r\rangle$ and mean bond angle deformations $\langle\Delta\alpha\rangle$ in bent triatomic molecules using anharmonic force fields showed that the mass dependence of $\langle\Delta r\rangle$ is 6 to 80 times as large as that of $r\langle\Delta\alpha\rangle$, so that in these molecules $\langle\Delta\alpha\rangle$ does not contribute significantly to the isotope shift of the

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central atom.[6] In NH_3 the mass effect on $r\langle\Delta\alpha\rangle$ is about half that on $\langle\Delta r\rangle$.

We introduced the reduced one-bond isotope shift[5]

$$^1\Delta^R \equiv {}^1\Delta\left[\frac{m'-m}{m'}\frac{1}{2}\frac{m_A}{m_A+m}\right]^{-1} \tag{3}$$

as a means of removing the dependence of the measured isotope shifts on the masses of the observed nucleus and the isotopes involved in end atom substitution. Thus, $^1\Delta^R$ for ^{31}P in PH_3 can be directly compared to ^{31}P in $PO_4{}^{3-}$ or to ^{15}N in NH_3. For molecular types in which $\langle\Delta\alpha\rangle$ terms do not contribute significantly to the isotope shift $^1\Delta^R$ can be approximately identified with $(\partial\sigma/\partial\Delta r)_e\langle\Delta r\rangle + {}^1/_2(\partial^2\sigma/\partial\Delta r^2)_e\langle(\Delta r)^2\rangle$. The range of values of $^1\Delta^R$ for a given observed nucleus therefore reflects the variation of $(\partial\sigma/\partial\Delta r)_e\langle\Delta r\rangle$ with nuclear environment. We have already shown that $\langle\Delta r\rangle$ is (15–24) × 10^{-3} Å for hydrides and (4–8) × 10^{-3} Å for most other bonds and that it is possible to estimate $\langle\Delta r\rangle$ involving an end atom by knowing only the equilibrium bond length r_e, the masses, and the rows of the periodic table of the bonded atoms.[5]

Equation 2 is an approximation based on results of full dynamical calculations on a large number of diatomic molecules and polyatomic molecules with isotopic substitution at an end atom. With isotopic end atom substitution the difference $\langle\Delta r_{Am}\rangle - \langle\Delta r_{Am'}\rangle$ can be obtained with a diatomic-like formula, i.e., the two factors reduce to the mass factor derived earlier for diatomic molecules, $(\mu'-\mu)/2\mu'$.[4] Although the mass factor $(m'-m)/m'$ is more general (as has been shown experimentally for the ^{77}Se shifts with Se substitution in R_1SeSeR_2 molecules with R_1, R_2 = CH_3, CF_3), the factor $(1/2)m_A/(m_A+m)$ only works well for end atom substitution.[5]

Isotopic Substitution of Other Than End Atoms

With substitution of ^{12}C by ^{13}C, dymamic calculations on fluoromethane derivatives ranging from CH_3F to CF_3I and $CFCl_3$[7] give $\langle\Delta r_{mX}\rangle - \langle\Delta r_{m'X}\rangle$ values which are smaller than what would be obtained with the factor $\langle\Delta r\rangle\cdot(m'-m)/m'\cdot(1/2)m_X/(m_X+m)$. Calculated $\langle\Delta r\rangle - \langle\Delta r'\rangle$ values for $^{13/12}C$ replacement in a C–F bond in various substituted fluoromethanes and in $O{=}CF_2$ are (7.03–11.51) × 10^{-5} Å, for a C–Cl bond in halomethanes (5.19–6.31) × 10^{-5} Å, and for a C=O bond in $O{=}CF_2$, CO_2, and OCS (11.68–14.63) × 10^{-5} Å. No general formula to replace $(1/2)m_X/(m_X+m)$ could be found. In every case dynamic calculations resulted in somewhat smaller numbers, with the best case being that for the effect of ^{13}C substitution on $\langle\Delta r_{CH}\rangle$. This is understandable in terms of the normal modes which contribute to a change in $\langle\Delta r\rangle$ when the mass of a centrally located nucleus is changed. The modes which involve displacement of the central atom are asymmetric stretches, bends, wags, etc., motions which are more characteristic of the rest of the molecule than a diatomic-like stretch of the bond in question. Although the factors replacing $(1/2)m_X/(m_X+m)$ cannot be characterized by a single form for all bonds, they nevertheless differ from this by no more than a factor of 2 or 3 in the case of $^{13/12}C$ substitution in a variety of methane derivatives even as masses of end atoms m_X vary from 1 to 127 and electronegativities from 2 to 4. Therefore, if only an *order of magnitude* estimate is required, the reduced isotope shift formula given in eq 3 can be used, even *for non-end atom substitution.*

Estimation of the Electronic Factor

The value of $(\partial\sigma/\partial\Delta r)_e$ for a given nucleus reflects the range of chemical shifts for that nucleus, since both are a measure of nuclear shielding sensitivity, the former to bond extension and the latter to changes in electronic structure. For example, the ratio of the ab initio theoretical ^{19}F shielding derivative $(\partial\sigma^F/\partial\Delta r_{HF})_e$ in HF to the empirical ^1H shielding derivative $(\partial\sigma^H/\partial\Delta r_{HH})_e$ in H_2 (−441 ppm Å^{-1}/−12.1 ppm Å^{-1})[8,9] is approximately the same as the ratio of the chemical shift ranges of ^{19}F and ^1H, about 800 ppm/20 ppm. Since the periodicity of $\langle a_0{}^3/r^3\rangle$ of the valence p or d orbitals of the observed nucleus has been found to be generally reflected in the ranges of chemical shifts,[10] we may also use $\langle a_0{}^3/r^3\rangle$ in the same fashion (where a_0 = 0.529 Å). Values of $(\partial\sigma^X/\partial\Delta r_{XH})_e$ estimated from $^{2/1}H$-induced isotope shifts in ^{119}Sn and ^{13}C in Bu_3SnH and CH_4 are −367 and −35 ppm Å^{-1}, respectively.[5,11] These are in the ratio 10.5, which may be compared with the ratio of $\langle a_0{}^3/r^3\rangle_{np}$ for Sn and C atoms, which is 7.[12] Similarly, the derivatives $(\partial\sigma^X/\partial\Delta r_{XH})_e$ for ^{11}B, ^{13}C, and ^{14}N in $BH_4{}^-$, CH_4, and $NH_4{}^+$ have been estimated; these are −26.7, −35, and −65 ppm Å^{-1}, respectively,[5] or 0.76:1:1.85. These may be compared with the values of $\langle a_0{}^3/r^3\rangle_{2p}$ for the free atoms which are in the ratio 0.5:1:2.0, roughly the same ratios as the observed ranges of chemical shifts for these nuclei. In CN^- the ratio of $(\partial\sigma^N/\partial\Delta r)_e$ to $(\partial\sigma^C/\partial\Delta r)_e$ is −872 ppm Å^{-1}/−473 ppm Å^{-1},[13] the same as for the derivatives in $NH_4{}^+$ and CH_4.

When the values of $\langle\Delta r\rangle$ are comparable, the reduced isotope shifts will appear to be related to one another in the same way as chemical shifts in general. In the above example, the $\langle\Delta r\rangle$ values for $BH_4{}^-$, CH_4, and $NH_4{}^+$ are similar, 2.257 × 10^{-2}, 2.134 × 10^{-2}, and 2.034 × 10^{-2} Å, respectively,[5,11] so that the reduced isotope shifts are related in very nearly the same way as the respective $(\partial\sigma/\partial\Delta r)_e$. The mean bond displacements in H_2O and H_2Se are nearly equal, $\langle\Delta r\rangle$ = 2.003 × 10^{-2} and 2.049 × 10^{-2} Å, respectively,[6] so that the ratio of the reduced isotope shifts[15,16] is the ratio of the respective derivatives, if we can assume that $\langle\Delta\alpha\rangle$ terms are not important in isotope shifts for these molecules.

$$\frac{^1\Delta^R(^{77}Se^{2/1}H),\ H_2Se}{^1\Delta^R(^{17}O^{2/1}H),\ H_2O} \simeq \frac{(\partial\sigma^{Se}/\partial\Delta r_{SeH})_e,\ H_2Se}{(\partial\sigma^{O}/\partial\Delta r_{OH})_e,\ H_2O} = 4.34$$

This number is about the same magnitude (1.9 times as large) as the ratio (2.24) of $\langle a_0{}^3/r^3\rangle$ factors for Se and O atoms.[12] Although the $\langle\Delta\alpha\rangle$ contributions to the isotope shifts in NH_3 and PH_3 may not be negligible compared to the $\langle\Delta r\rangle$ terms it is nevertheless found that the ratio[17,18]

$$\frac{^1\Delta^R(^{31}P^{2/1}H),\ PH_3}{^1\Delta^R(^{15}N^{2/1}H),\ NH_3} = 1.26$$

is comparable to the ratio of $\langle a_0{}^3/r^3\rangle_p$ for the P and N atoms, which is 1.4.[12] Thus, the trends relating $(\partial\sigma/\partial r)_e$ magnitudes to shielding sensitivity and the similarities of $\langle\Delta r\rangle$ for the bonds being compared lead to *relationships between reduced isotope shifts* which make it possible to obtain an estimate of isotope shifts from chemical shift ranges (or from $\langle a_0{}^3/r^3\rangle$) if the isotope shift of one chemical analogue is known. From the $^{18/16}O$-induced ^{95}Mo isotope shift of $MoO_4{}^{2-}$ (−0.25 ppm),[19] by using the ratio of $\langle a_0{}^3/r^3\rangle$ for the $3d_{3/2}$ and $4d_{3/2}$ states of the atoms,[12] we can estimate the $^{18/16}O$-induced ^{99}Tc isotope shift in $TcO_4{}^-$, −0.34 ppm, to be compared with the experimental value of −0.44 ± 0.06 ppm.[20] Also, the $^{34/32}S$-induced ^{95}Mo isotope shift in $MoS_4{}^{2-}$, which should

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Table I. Observed and Estimated (in Parentheses) $^{2/1}H$-Induced One-Bond Isotope Shifts in Hydrides (in ppm per D)

H_2	BH_4^-	CH_4	NH_4^+	/	NH_3	H_2O	HF
-0.0402^a	-0.138^b	-0.192^c	-0.307^d		-0.65^e	-1.54^f	-2.5^g
		SiH_4	PH_3^h			H_2S	HCl
		(−0.4)	−0.843			(−2.2)	(−2.8)
		GeH_4	AsH_3			H_2Se^i	HBr
		(−1.1)	(−2.0)			−7.02	(−5.6)
		SnH_4	SbH_3			H_2Te	HI
		(−1.6)	(−3.0)			(−10.6)	(−7.9)
		PbH_4					
		(−2.9)					

[a] Calculated from the measured isotope shift, −0.0469 ppm between HD and D_2: Beckett, J. R.; Carr, H. Y. *Phys. Rev. A* **1981**, *24*, 144–148. [b] Smith, B. E.; James, B. D.; Peachey, R. M., *Inorg. Chem.* **1977**, *16*, 2057–2062. [c] Alei, M.; Wageman, W. E. *J. Chem. Phys.* **1978**, *68*, 783–784. [d] Wasylishen, R. E.; Friedrich, J. O. *J. Chem. Phys.* **1984**, *80*, 585–587. [e] Litchman, W. M.; Alei, M.; Florin, A. E. *J. Chem. Phys.* **1969**, *50*, 1897–1898. [f] Lutz, O.; Oehler, H. *Z. Naturforsch. A* **1977**, *32*, 131–133. [g] Hindermann, D. K.; Cornwell, C. D. *J. Chem. Phys.* **1968**, *48*, 2017–2024. [h] Jameson, A. K.; Jameson, C. J. *J. Magn. Reson.* **1978**, *32*, 455–457. [i] Jakobsen, H. J.; Zozulin, A. J.; Ellis, P. D.; Odom, J. D. *J. Magn. Reson.* **1980**, *38*, 219–227.

have roughly the same value of $^1\Delta^R$ as MoO_4^{2-} (−5.26 ppm), can be predicted to be $-5.26 \times (34 - 32)/34 \times (1/2) \times 95/(95 + 32) = -0.11$ ppm if electronic factors are about the same, and $\langle \Delta r_{MoO} \rangle$ is comparable to $\langle \Delta r_{MoS} \rangle$. The measured value is −0.090 ppm.[21]

The relationship between chemical shift ranges or $\langle a_0^3/r^3 \rangle np$ and magnitudes of isotope shifts due to non-end atom replacement is not clearly observed as in examples noted above. In part this is due to lack of data on analogous compounds. It is interesting, however, that the relationship holds even in the case of $^{13/12}C$-induced ^{199}Hg and ^{111}Cd shifts in Me_2Hg and Me_2Cd. Here the isotope shifts are of *unusual* sign (same sign as that predicted for Li in LiH[8]): +0.4 ppm and +0.14 ppm, respectively.[22,23] Nevertheless, the reduced isotope shifts, 11 and 4.0 ppm, are in the same ratio as $\langle a_0^3/r^3 \rangle_{np}$ of Hg and Cd.[12]

Prediction of Isotope Shifts

The above examples indicate that predictions to within a factor of 2 are possible when chemically analogous compounds are compared. In Table I we show $^{2/1}H$-induced one-bond isotope shifts for various nuclei where they have been observed, and our predictions of the magnitudes of $^1\Delta$ for yet unknown shifts are in parentheses. We present similar values and predictions for $^{18/16}O$-induced one-bond isotope shifts in Table II. The predicted values in Tables I and II are based on calculations of $\langle \Delta r \rangle$ using methods described earlier,[5] and estimates of $(\partial \sigma/\partial \Delta r)_e$ are based on correlations of the type described in this paper.

It would be useful to have a way of making an order of magnitude estimate of the isotope shift that may be expected for a nucleus in *any* bond, at least as a prediction of the feasibility of the observation. Our previous work on the interpretation of the temperature dependence of the nuclear shielding in the gas phase at the zero-pressure limit and the data on electronic structural factors affecting isotope shifts indicate that derivatives $(\partial\sigma/\partial\Delta r)_e$ vary with these structural factors by as much as 2-fold even for the same bond (^{19}F in CF bond, for example).[14] There are other variations in electronic factors for a given nucleus which imply that the derivatives $(\partial \sigma/\partial \Delta r)_e$ should have a spread of about a factor of 2 to 10.

In table III we show the known ranges of $^1\Delta^R$ for various observed nuclei and in parentheses our predictions of $^1\Delta^R$ for other nuclei in any electronic environment. These predictions are based on two measured isotope shifts and the $\langle a_0^3/r^3 \rangle$ for the observed nucleus. From this table an estimate of $^1\Delta$ can be made for nucleus A due to substitution of an end atom ^mX by $^{m'}X$ by multiplying the number in Table III by $(m' - m)/m' \cdot (1/2) m_A/(m_A + m)$. Given no further information these estimates predict the feasibility of observation of any given one-bond isotope shfit. Equation 3 indicates that the least feasible observations are those of the shifts in light nuclei A upon isotopic substitution of heavy ligands X. In these cases the mass factor $(m' - m)/m'$ is unfavorable, $m_A/(m_A + m)$ is also unfavorable, and the derivative is expected to be small for the smaller chemical shift ranges typical of light nuclei.

Table II. Observed and Estimated (in Parentheses) $^{18/16}O$-Induced One-Bond Isotope Shifts (in ppm per ^{18}O)

CO_2	NO_2^-	/	NO_3^-	O_3			
-0.019^a	-0.138^b		-0.056^b	(−0.26)			
	PO_4^{3-}			SO_2	/	SO_4^{2-}	ClO_4^-
	-0.019^c			(−0.27)		(−0.026)	(−0.03)
	AsO_4^{3-}			SeO_2	/	SeO_4^{2-}	BrO_4^-
	(−0.06)			(−0.72)		(−0.06)	(−0.09)
				TeO_2	/	TeO_4^{2-}	IO_4^-
				(−1.6)		(−0.14)	(−0.16)

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More Refined Estimation of Isotope Shifts

While Table III is useful for an order of magnitude estimate when no previous information is available, more accurate estimates can be obtained with ratios involving analogous compounds as we have shown here, and such estimates may be further refined by taking into consideration the following empirical trends concerning the electronic factor.

(1) The derivative $(\partial \sigma^A/\partial \Delta r_{AX})_e$ depends on the absolute shielding of the nucleus.[24] The more shielded nucleus has a smaller paramagnetic term. The magnitude of $(\partial\sigma/\partial\Delta r)_e$ depends largely on the paramagnetic term, so it is generally smaller for the more shielded nucleus (i.e., the one with the lower resonance frequency). The example, ^{13}C in the carbonyl group in a large number of compounds shows a linear plot of $^{18/16}O$-induced isotope shifts vs. ^{13}C chemical shifts, with the ^{13}C at higher frequencies having the larger isotope shifts.[25] We have found a similar relationship for ^{19}F fluoromethanes.[24] Of the elements of the shielding tensor, the components perpendicular to the bond are the important ones since they are expected to be more sensitive to bond extension than the component parallel to the bond. However, when perpendicular components are not known, the isotropic average serves as a useful guide.

(2) For a given nucleus A, $(\partial \sigma^A/\partial \Delta r_{AX})_e$ depends on the AX bond properties. In general its magnitude is greater for the stronger bond. Thus, it is expected to correlate with bond order, bond length, and spin–spin coupling J_{AX}. The shorter bond (which accompanies higher bond order, higher s character, greater *J* coupling, and more electronegative substituents) is associated with larger isotope shifts.[26] Correlations of isotope shifts with one-bond coupling have been shown for $^{13/12}C$-induced F shifts[2] as well as $^{18/16}O$-induced ^{31}P shifts.[27] In the latter case a 1.9-fold increase in the magnitude of isotope shifts is associated with a 1.8-fold increase in the magnitude of the coupling constant. In doubly and triply linked PO_4 tetrahedra (e.g., $P_2O_7^{4-}$, $P_3O_{10}^{5-}$) the shorter bond is to terminal oxygen atoms (1.471 Å) and the P–O bridging bond is longer (1.625 Å).[28] In similar biological phosphate

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Table III. Magnitudes of Reduced Isotope Shifts Observed for Various Nuclei (in ppm) and Predicted Values for Other Nuclei in Parentheses[a,b]

	H 0.375–0.81								
	Li (0.006–0.1)	Be (0.02–0.36)	B 0.6 (0.09–1.26)	C 0.2–1.87	N 1.3–5.1	O 6.5 (0.6–9)	F 0.6–10.5		
	Na (0.036–0.5)	Mg (0.1–1.6)	Al (0.2–2.6)	Si (0.3–4.8)	P 0.4–5.4	S (0.7–10.4)	Cl (1.1–14.8)		
	K (0.065–0.91)	Ca (0.2–2.3)	Ga (0.5–7.2)	Ge (0.9–11.9)	As (1.1–15.6)	Se 0.4–30	Br (2.0–28.1)		
	Rb (0.13–1.75)	Sr (0.3–4.1)	In (0.8–11.8)	Sn 6.5 (1.3–17.9)	Sb (1.8–24.4)	Te 1.6–9.7 (up to 31)	I (2.7–37.3)		
	Cs (0.2–2.7)	Ba (0.4–5.9)	Tl (1.8–24.5)	Pb (2.4–33.2)	Bi (3.7–51)				
Sc (2.1–5.2)	Ti (2.8–7)	V 4.5 (3.6–9)	Cr 10.3 (4–9.9)	Mn 13.7 (5.5–13.7)	Fe (6.7–16.6)	Co 28.6 (8–19.8)	Ni (9.4–23.3)	Cu (0.2–2.5)	Zn (0.4–5)
Y (2.7–6.7)	Zr (3.8–9.3)	Nb (4.1–10.2)	Mo 4.1–5.3 (5.3–13.1)	Tc 9.2 (7.1–17.5)	Ru (7.5–18.7)	Rh (8.8–21.9)	Pd 9.7–23.9	Ag (0.4–5.2)	Cd 4 (0.7–9.5)
La (3.9–9.6)	Hf (7.5–18.7)	Ta (9.3–23)	W (11.1–27.4)	Re (13.1–32.4)	Os (15.1–37.3)	Ir (17.4–43.1)	Pt 3.2–7.3 (18.6–46)	Au (0.9–12.4)	Hg 4–11 (1.5–20.7)

[a] The predictions are based on P in PO_4^{3-} for the lower limit and N in NO_2^- for the upper limit for the main groups. [b] For the transition elements the predictions are based on MoO_4^{2-} and MnO_4^-, respectively, i.e., for highly symmetric environments only. Furthermore, the factor ΔE^{-1} in the chemical shift depends on the ligands, so the given ranges should be multiplied by the factor by which ΔE^{-1} varies for a given transition element in its complexes compared to ions of the type MO_4^{n-} For example, the observed values for Pt in $PtCl_6^{2-}$ and $PtBr_6^{2-}$ are smaller, whereas that for Co in $Co(CN)_6^{3-}$ is greater.

systems the $^{18/16}O$-induced ^{31}P isotope shifts are −0.0281 to −0.0285 ppm and −0.0163 to −0.0172 ppm for a middle phosphate group, for terminal and bridging oxygens.[29] The bond orders (nominally 1.5 and 1.0) are also consistent with these magnitudes. The shorter equatorial bonds compared to axial ones also are associated with larger isotope shifts (e.g., $^{15/14}N$-induced P shifts in phosphoranes,[30] $^{34/32}S$-induced F shifts in SF_4[31]) and generally correlate with greater magnitudes of one-bond couplings to equatorial atoms compared to axial ones in trigonal-bipyramidal systems. The $^{34/32}S$-induced ^{31}P isotope shift in P=S can be estimated to be −0.015 ppm from a typical $^{18/16}O$ isotope shift (−0.0354 ppm) in P=O, neglecting differences in the derivatives. We should observe values smaller than this because $(\partial\sigma^P/\partial\Delta r_{P=S})_e$ is expected to be somewhat smaller for a P=S bond length of 1.86 Å than $(\partial\sigma^P/\partial\Delta r_{P=O})_e$ for a P=O bond length of 1.52 Å. Similarly, $(\partial\sigma^{Pt}/\partial\Delta r_{PtBr})_e$ should be smaller than $(\partial\sigma^{Pt}/\partial\Delta r_{PtCl})_e$ in PtX_6^{2-} where bond lengths are 2.484 and 2.334 Å, respectively.[32] Gombler has shown that $^{13/12}C$-induced ^{77}Se isotope shifts depend on bond length; the values range from −0.012 ppm for a 2.03 Å single bond, to −0.438 ppm for a 1.854 Å single bond, and −0.6 to −1.1 ppm for 1.7 Å double bonds.[33]

(3) $(\partial\sigma/\partial\Delta r)_e$ is expected to be strongly affected by the presence of low-lying electronic excited states (such as n → π^* or $d_\pi \rightarrow d_{\sigma^*}$) which have magnetic-dipole-allowed transitions to the ground state. These are precisely the states which contribute greatly (in Ramsey's perturbation theory) to the paramagnetic shielding, and therefore to $(\partial\sigma/\partial\Delta r)_e$. For this reason, the estimates of transition metal reduced isotope shifts in Table III should be used with caution. They are based on environments of the type MO_4^{n-}. It is well-known that the oxidation state and coordination number and the nature of the ligands greatly affect the energies of d–d transitions (roughly ordered in the spectrochemical series).

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