JOURNAL

OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 108, NUMBER 10 MAY 14, 1986

Isotope Effects on Spin–Spin Coupling

Cynthia J. Jameson*[1a] **and H.-Jörg Osten**[1b]

Contribution from the Department of Chemistry, University of Illinois at Chicago, Box 4348, Chicago, Illinois 60680, and Academy of Sciences of the GDR, Central Institute of Physical Chemistry, 1199 Berlin, Rudower Chaussee 6, German Democratic Republic.

Received October 3, 1985

Abstract: The change in the spin–spin coupling in high-resolution NMR spectra brought about by isotopic substitution is examined. A review of available experimental values shows some general trends which can be explained by changes in the dynamical averaging upon isotopic substitution. The theoretical basis for the signs of observed primary isotope effects on one-bond coupling is proposed. With use of a simple physical model for one- and two-bond coupling, and dynamic calculations on H—C≡C—H as an example, the relative magnitudes and signs of the primary and secondary isotope effects on these couplings are interpreted. With an MO calculation of $^1J(\mathrm{PH})$ in PH_3 and $H_2P(O)OH$ as a function of PH bond length, the opposite signs and the magnitudes of the primary isotope effects on $^1J(\mathrm{PH})$ in these molecules are reproduced. The negative contribution of the lone pair to the derivative $(\partial J(\mathrm{PH})/\partial \Delta r)_e$ in PH_3, which does not occur in $H_2P(O)OH$, is found to be responsible for the positive sign of the primary isotope effect on PH coupling in PH_3 (and by extension, also for the other $\mathrm{P^{III}H}$ couplings and the SeH coupling in H_2Se).

I. Introduction

The effect of isotopic substitution on nuclear magnetic shielding has been widely observed in high-resolution NMR spectroscopy. These effects are sometimes fairly large (0.001–7 ppm per substituted atom) and the general trends were summarized in 1967 by Batiz-Hernandez and Bernheim.[2] These trends have been successfully interpreted by a theoretical model based on the effects of isotopic substitution on mean bond displacements and the derivatives of nuclear magnetic shielding with respect to bond extension and angle deformation.[3] On the other hand, isotope effects on spin–spin couplings observed in high-resolution NMR spectroscopy have only been sparsely reported. One of the reasons for this is their small magnitudes—so small that some of the earliest reported values were within the quoted experimental errors for the coupling constants. In addition, there have not been any obvious practical diagnostic applications as in the case of the isotope effects on shielding, a natural consequence of their very small magnitudes. Nevertheless, there are some trends which can be found in the scattered experimental reports and in some theoretical calculations of coupling constants as a function of bond length. It is the purpose of this paper to summarize the general trends that we have found and to present a theoretical interpretation which is consistent with what is known about isotope effects on nuclear shielding and on hyperfine interactions so as to view the isotope effects on coupling constants not as an isolated phenomenon but as a natural part of a unified theoretical interpretation of isotopic effects on molecular electronic properties in general.

II. Experimental Measurements of Isotope Effects on Spin–Spin Coupling

The primary isotope effect on spin–spin coupling, the difference in the coupling constants from observations on different isotopes of the coupled nuclei, may be expressed as follows for the effect of deuterium substitution on the coupling between nucleus A and H,

$$\Delta_p{}^nJ(\mathrm{A}^{2/1}\mathrm{H}) \equiv |{}^nJ(\mathrm{AD})|(\gamma_\mathrm{H}/\gamma_\mathrm{D}) - |{}^nJ(\mathrm{AH})| \qquad (1)$$

where $\gamma_\mathrm{H}/\gamma_\mathrm{D} = 6.514\,398\,04\ (120)$,[4] or in terms of the reduced coupling constant,

$$\Delta_p{}^nK(\mathrm{A}^{2/1}\mathrm{H}) \equiv |{}^nK(\mathrm{AD})| - |{}^nK(\mathrm{AH})| \qquad (2)$$

where

$$K(\mathrm{NN'}) \equiv 4\pi^2 J(\mathrm{NN'})/h\gamma_\mathrm{N}\gamma_\mathrm{N'} \qquad (3)$$

Although eq 1 has been used more commonly, eq 2 is more appropriate for comparisons between *different* nuclei since the reduced coupling constant is a purely electronic property (the nuclear γ factors have been removed). The secondary isotope effect, the change in the coupling constant between A and B due to isotopic substitution of a neighboring nucleus C, can be defined as

$$\Delta_s{}^nJ(\mathrm{AB})[{}^{m'/m}X] \equiv |{}^nJ(\mathrm{AB})_{{}^{m'}\mathrm{X}}| - |{}^nJ(\mathrm{AB})_{{}^{m}\mathrm{X}}| \qquad (4)$$

where the mass is $m' > m$ for the neighbor X.

Magnitudes and signs of the observed primary and secondary isotope effects on coupling constants are shown in Tables I and II, respectively. Most of the available data are on one-bond

---

[1] (a) University of Illinois. (b) Academy of Sciences of GDR.

[2] Batiz-Hernandez, H.; Bernheim, R. A. *Prog. NMR Spectrosc.* **1967**, *3*, 63.

[3] Jameson, C. J. *J. Chem. Phys.* **1977**, *66*, 4983. Jameson, C. J.; Osten, H. J. *J. Chem. Phys.* **1984**, *81*, 4293, 4300. Osten, H. J.; Jameson, C. J. *J. Chem. Phys.* **1985**, *82*, 4595.

[4] Smaller, B.; Yasaitis, E.; Anderson, H. L. *Phys. Rev.* **1951**, *81*, 896.

0002-7863/86/1508-2497$01.50/0

Table I. Primary Isotope Effects on Spin–Spin Coupling Constants[a]

molecule		coupling	J/hz	$\Delta_p{}^nJ$/Hz	ref	$K/10^{20}$ cm^{-3}	$\Delta_p{}^nK/10^{20}$ cm^{-3}
HC≡CD	HC≡CH	^1J(CH)	248.29	−0.64 ± 0.10	9	82.19	−0.21 ± 0.03
CHD_3	CH_4		125.3	−0.8 ± 0.2	27	41.5	−0.26 ± 0.07
$CDCl_3$	$CHCl_3$		209.16	−0.96 ± 0.13	28	69.24	−0.32 ± 0.04
CD_2Cl_2	CH_2Cl_2		178.18	−0.88 ± 0.38[b]	28	58.98	−0.29 ± 0.12
CD_3I	CH_3I		151.07	−0.833 ± 0.03[b]	28	50.01	−0.276 ± 0.002
CD_3OD	CH_3OD		140.50	−0.946 ± 0.040[b]	28	46.51	−0.313 ± 0.013
$(CD_3)_2SO$	$(CH_3)_2SO$		137.57	−0.43 ± 0.40[b]	28	45.54	−0.14 ± 0.13
CD_3CN	CH_3CN		136.32	−0.955 ± 0.035[b]	28	45.27	−0.32 ± 0.01
$(CD_3)_2CO$	$(CH_3)_2CO$		126.77	−0.668 ± 0.060[b]	28	41.96	−0.22 ± 0.02
$PhCH_2D$	$PhCH_3$		126.0	−0.60 ± 0.2	29	41.71	−0.20 ± 0.07
NH_3D^+	NH_4^+	$^1J(^{14}NH)$	52.52	(+0.18 ± 0.2)[c]	8	60.49	(+0.21 ± 0.23)[c]
HDSe	H_2Se	^1J(SeH)	60.75	+2.55 ± 0.8	5	26.45	+1.11 ± 0.34
D_2Se	HDSe		61.65	+2.30 ± 0.8	5	26.84	+1.00 ± 0.34
PH_2D	PH_3	^1J(PH)	185.6	+12.19	6	38.13	+2.5
PD_3	PHD_2		183.1	+11.05	6	37.62	+2.27
PhPHD	$PhPH_2$		199.3	+2.0 ± 0.8	7	40.94	+0.41 ± 0.16
$(i\text{-}BuO)_2PD$	$(i\text{-}BuO)_2PH$		200.5	+4.7 ± 0.8	7	41.19	+0.96 ± 0.16
Ph_2PD	Ph_2PH		216.8	+2.1 ± 0.8	7	44.54	+0.43 ± 0.16
$Ph_2P(O)D$	$Ph_2P(O)H$		493.3	−0.8 ± 0.8	7	101.34	−0.16 ± 0.16
HDP(O)OH	$H_2P(O)OH$		569.6	−4.8 ± 0.8	7	117.02	−0.97 ± 0.16
$(HO)_2P(O)D$	$(HO)_2P(O)H$		687.3	−3.9 ± 0.8	7	141.20	−0.80 ± 0.16
$(MeO)_2P(O)D$	$(MeO)_2P(O)H$		704.8	−3.9 ± 0.8	7	144.8	−0.80 ± 0.16
$(PhO)_2P(O)D$	$(PhO)_2P(O)H$		732.7	−5.0 ± 0.8	7	150.5	−1.03 ± 0.16
$(MeO)_2P(O)D$	$(MeO)_2P(O)H$		690.25	−3.7 ± 1.3	30	141.81	−0.76 ± 0.27
SiH_2DI	SiH_3I	^1J(SiH)	−239.5	−0.9 ± 0.7	31	100.18	−0.38 ± 0.29
HC≡CD	HC≡CH	^2J(CH)	49.74	+0.09 ± 0.13	9	16.46	+0.03 ± 0.04
CDF_3	CHF_3	^2J(FH)	79.339	−0.078 ± 0.048	32	7.017	−0.007 ± 0.005
SiD_3F	SiH_3F		45.764	−0.153 ± 0.052	32	4.047 ± 0.001	−0.014 ± 0.004
Me(PhCHD)SO	$Me(PhCH_2)SO$	^2J(HH)	12.97	−0.46 ± 0.2	33	1.080	−0.038 ± 0.017

[a] $\Delta_p{}^nJ(X^2/^1H) \equiv |^nJ(XD)|(\gamma_H/\gamma_D) - |^nJ(XH)|$. [b] Includes secondary isotope effect. [c] Although the primary isotope effect appears to be positive in NH_4^+, this number is within the experimental error. [d] Primary isotope effects have also been reported in $^{69,71}GaH_nD_{4-n}^-$ (Tarasov, V. P.; Privalov, V. I.; Buslaev, Yu. A.; Eichhoff, U. *Z. Naturforsch. Teil B* **1984**, *39* 1230). However, we have not included these in this table. If the quoted errors in the ^{71}GaH couplings are taken as reported, they would be ±1 Hz. A comparable error in the measurements of ^{71}GaD couplings would lead to primary isotope effects on $J(^{71}GaH)$ of 2.3 ± 7 Hz for GaD_4^-–GaD_3H^-. We believe this error estimate to be more realistic than their quoted errors for $J(^{71}GaD)$. The ^{69}Ga couplings have even larger errors.

Table II. Secondary Isotope Effects on Spin–Spin Coupling Constants

molecule		coupling	^nJ/Hz	$\Delta_s{}^nJ$/Hz	ref	$K/10^{20}$ cm^{-3}	$\Delta_s{}^nK/10^{20}$ cm^{-3}
HC≡CD	HC≡CH	^1J(CH)	248.29	+0.10 ± 0.05	9	82.19	+0.033 ± 0.016
CHD_3	CH_4		125.3	−0.8 ± 0.2	27	41.48	−0.26 ± 0.07
NHD_3^+	NH_4^+	$^1J(^{14}NH)$	52.52	−0.15 ± 0.03	8	60.49	−0.17 ± 0.03
ND_4^+	NH_3D^+	$^1J(^{14}ND)$	8.09	−0.03 ± 0.03	8	60.67	−0.22 ± 0.22
DCN	HCN	$^1J(^{15}N^{13}C)$	−18.5	+0.3 ± 0.1	34	60.41	+0.98 ± 0.33
BH_3D^-	BH_4^-	$^1J(^{11}B\text{–}H)$	81.5	−0.4	35	21.1	−0.1
BHD_3^-	BH_4^-		81.00	−1.09 ± 0.04	36	21.01	−0.28 ± 0.01
BHT_3^-	BH_4^-		80.57	−1.53	37	20.86	−0.40
BT_4^-	BTH_3^-	$^1J(^{11}BT)$	86.43	−1.90	37	21.02	−0.46
HDSe	H_2Se	^1J(SeH)	60.75	+0.9 ± 0.2	5	26.45	+0.39 ± 0.09
D_2Se	HDSe	^1J(SeD)	9.7	+0.11 ± 0.3	5	26.46	+0.30 ± 0.82
PHD_2	PH_3	^1J(PH)	185.60	−2.44	6	38.13	−0.51
PD_3	PH_2D	^1J(PD)	30.36	−0.57	6	40.63	−0.76
$PhPH_2$	PhPHD	^1J(PH)	199.3	+0.12 ± 0.04	7	40.94	+0.25 ± 0.01
$H_2P(O)OH$	HDP(O)OH		569.6	−0.58 ± 0.04	7	117.0	−0.12 ± 0.01
$HDPO_2$	H_2PO_2		718.5	−0.54 ± 0.07	37	147.6	−0.11 ± 0.01
D_2PO_2	$HDPO_2$	^1J(PD)	110.5	−0.12 ± 0.03	37	147.9	−0.16 ± 0.04
SiH_2DI	SiH_3I	^1J(SiH)	−239.5	−0.3 ± 0.1	31	100.3	−0.12 ± 0.04
$DSiF_3$	$HSiF_3$	^1J(SiF)	276.6	−2.0 ± 0.2	29	123.0	−0.89 ± 0.09
D_2PO_2F	H_2PO_2F	^1J(PF)	1033.5	−3.5 ± 0.2	29	225.6	−0.76 ± 0.04
HC≡CD	HC≡CH	^2J(CH)	49.74	+0.25 ± 0.05	9	16.46	+0.08 ± 0.02
$SiHD_3$	SiH_3D	^2J(HD)	0.412	−0.15 ± 0.004	38	0.223	−0.081 ± 0.002

couplings. The reduced coupling constants and isotope effects in terms of the reduced couplings are also in the tables, to allow direct comparison of magnitudes and signs of couplings involving *different* pairs of nuclei. This is specially useful in bringing into a common discussion the couplings involving nuclei with negative magnetogyric factors (e.g., ^{29}Si and ^{15}N). The general trends in these measurements can be summarized as follows:

(1) The sign of the primary or secondary isotope effect on the coupling constant is not directly related to the absolute sign of the coupling constant.

(2) Primary isotope effects are negative usually and positive in some cases, the positive signs being found only in molecules involving one or more lone pairs on one of the coupled nuclei. For example, primary isotope effects are positive in H_2Se,[5] in PH_3,[6] and in other 3-coordinate phosphorus but negative in 4- and 5-coordinate phosphorus.[7]

---

(5) Jakobsen, H. J.; Zozulin, A. J.; Ellis, P. D.; Odom, J. D. *J. Magn. Reson.* **1980**, *38*, 219.

(6) Jameson, A. K.; Jameson, C. J. *J. Magn. Reson.* **1978**, *32*, 455.

(3) Secondary isotope effects can have either sign.

(4) Secondary isotope effects are roughly additive upon substitution of several equivalent sites neighboring the coupled nuclei. For example, in NH_4^+ ion, each D substitution decreases ${}^1J({}^{14}NH)$ by 0.05 ± 0.02 Hz,[8] and in PH_3, each D substitution decreases ${}^1J(PH)$ by 2.5 Hz.[6]

(5) The magnitudes of isotope effects are small, the largest primary effect being about 6% of the coupling constant in PH_3 and the largest secondary effects being about 1.5% in H_2Se, so that only the effects of deuterium (and tritium) substitution, where the largest fractional changes in mass are involved, have been observed.

(6) The magnitudes of the isotope effects are roughly proportional to the fractional change in mass, in the very few instances where effects of isotopic substitution of ${}^1H$ by ${}^2H$ and ${}^3H$ have been reported.

III. Theoretical Interpretation

Some interesting questions which need to be answered are the following: Why are both + and − signs of the primary isotope effect on J observed whereas the (secondary) isotope effects on nuclear shielding are nearly always the same sign (negative)? What is the mechanism for the isotope effect on two-bond coupling, such that the secondary isotope effect can become larger than the primary isotope effect on two-bond coupling (e.g., in HC≡CH the primary and secondary effects on ${}^2J(HC)$ are +0.09 ± 0.13 and +0.25 ± 0.05 Hz, respectively[9])? A positive primary isotope effect on ${}^1J$ seems to be associated with a lone pair on one of the coupled nuclei; what is the theoretical basis of this?

There are three general mechanisms for spin–spin coupling, the orbital, spin-dipolar, and Fermi contact mechanisms. Although the noncontact mechanisms can sometimes be significant, the contact term has been shown to be dominant in the general case.[10] Furthermore, as we shall see later, the noncontact mechanisms are less sensitive to bond extension. Therefore, we need to look for the answers to our questions in the Fermi contact mechanism.

A. A Simple Physical Model. It is well-known that when no lone pairs are involved, the mean energy approximation works fairly well for one-bond coupling constants.[10] A simple physical model can then be used for the contact mechanism.[11] The Fermi contact term in ${}^1K(AB)$ may be viewed as a correlation in the spin orientations of nucleus B and A resulting from three interactions: (i) the Fermi contact interaction of nucleus B with electron 1 in the AB bond, (ii) the spin correlation of electron 1 with electron 2 in the bond, and (iii) the Fermi contact interaction of electron 2 with nucleus A. Of these, (ii) the electron spin correlation in the bond is a very strong interaction so that the one-bond coupling ${}^1K(AB)$ is determined by the magnitudes and signs of the two nuclear spin–electron spin interactions i and iii. Here one treats the nuclear spin–electron spin interactions in the molecule in a fashion similar to that for the nuclear spin–electron spin interactions in the radical or the radical fragments (or the atom or ion A and B having unpaired spins, if no other information is available). Although there is no unpaired electron in the molecule, the interaction between the nuclear spin and an electron in the atomic orbital of atom B participating in the bond with atom A is of the same nature. Thus, one could estimate the coupling constant as

$$h\,{}^1J(AB) \simeq A_A A_B/4(\overline{{}^3\Delta E}) \text{ or } {}^1K(AB) \simeq \mathcal{A}_A \mathcal{A}_B/4(\overline{{}^3\Delta E}) \quad (5)$$

where the reduced hyperfine interaction is

$$\mathcal{A}_B = A_B/\gamma_B \hbar = (8\pi g_e \beta_e/3)[\rho_s(B)] \quad (6)$$

in which $[\rho_s(B)]$ is the net electron spin density on nucleus B. $\overline{{}^3\Delta E}$ is an average energy of excitation to triplet states mixed with the ground state by the Fermi contact interaction.

For heavy nuclei the relativistic theory of spin–spin coupling constants which was developed by Pyykkö[12] is the appropriate vehicle for this discussion. However, Pyykkö has shown that the K_{ss} term in this theory, which corresponds to the Fermi contact term in the nonrelativistic limit, dominates the isotropic coupling constant. That is, in relativistic theory a "contact" part can be separated out as the contribution from the relativistic radial hyperfine integrals involving the s AOs on both nuclei.[13] A positive contribution to the A–H coupling constant arises from a single $a_1 \rightarrow a_1^*$ excitation. Thus, the simple model discussed above can be preserved even when heavy nuclei are involved. Although the appropriate quantities in Pyykkö's relativistic theory are the integrals

$$a_{\kappa\kappa'} = \int_0^\infty (g_\kappa^* f_{\kappa'} + g_{\kappa'} f_\kappa^*)\, \mathrm{d}r$$

where g_κ and f_κ are the radial parts of the large and small components of the 4-component relativistic wave functions, we will use the more familiar language of nonrelativistic theory. In the nonrelativistic limit the integral a_{-1-1} becomes $-(2c)^{-1}|g_{-1}(0)|^2$. Thus, we will use nonrelativistic language such as spin densities at the nucleus, or $|\psi(0)|^2$, with the understanding that the empirical values are relativistic values.

In the context of the above model, the isotope effects on spin–spin coupling constants should be interpretable in a manner consistent with the isotope effects and the temperature dependence of hyperfine interaction constants in the corresponding radical fragments. A suitable illustration of this is the comparison of the isotope effects on the spin–spin coupling ${}^1J(AB)$ between directly bonded nuclei A and B with the isotope effects on A and B hyperfine coupling constants in the AB radical. The changes in the rovibrationally-averaged spin densities upon mass changes are large enough to be observable in one such system, the HgH radical. The HgH radical trapped in solid argon at 4 K has been studied by Knight and Weltner,[14] and the hyperfine splittings in HgD relative to HgH have been observed. The ${}^1H$ hyperfine data and the Hg hyperfine data reveal the following:

(a) The electron spin density on ${}^1H$ is greater than on D. The empirical value of $|\psi(0)|_H^2$ is 0.159 (1) au at the ${}^1H$ nucleus in HgH. This empirical value corresponds to a thermal average over rotational and vibrational motion and is weighted according to the fractional contributions of various isotopic masses of Hg in natural abundance. The decrease of 14 MHz out of 719 MHz in going from HgH to HgD corresponds to a change of −0.003 au in the spin density, i.e., 0.159 au for H in HgH and 0.156 au for D in HgD.

(b) The shift in electron spin density is shown by the 0.8% increase in ${}^{199}Hg$ hyperfine constant when deuterium substitutes H. In ${}^{199}Hg{}^1H$ and in ${}^{199}HgD$, $|\psi(0)|_{Hg}^2 = 8.88$ and 8.95 au, respectively.[14]

In our simple physical model, ${}^1J(HgH) \propto A_{Hg}A_H$ and is proportional to $|\psi(0)|_{Hg}^2 \cdot |\psi(0)|_H^2$. It is acceptable to use the spin densities in the HgH radical since the MO which is responsible for the spin densities at the nuclei is the same type of localized σ bonding MO describing the Hg–H bond in the CH_3HgH molecule, for example. The products 8.88 × 0.159 = 1.412 in ${}^{199}HgH$ and 8.95 × 0.156 = 1.396 in ${}^{199}HgD$ would predict that

$$|{}^1J(HgD)|(\gamma_H/\gamma_D)| - |{}^1J(HgH)| < 0$$

In other words, a negative primary isotope effect on the one-bond HgH spin–spin coupling is consistent with the experimental isotope effects on the ${}^{199}Hg$ and H hyperfine constants in the HgH and HgD radicals.

The bond length in HgD is shorter by 0.0026 Å than that in HgH.[14] The isotope effect has then indirectly probed the change of the spin distribution upon a change of interatomic distance in

---

(7) Borisenko, A. A.; Sergeyev, N. M.; Ustynyuk, Y. A. *Mol. Phys.* **1971**, *22*, 715.

(8) Wasylishen, R. E.; Friedrich, J. O. *J. Chem. Phys.* **1984**, *80*, 585.

(9) Luzikov, Y. N.; Sergeyev, N. M. *J. Magn. Reson.* **1984**, *60*, 177.

(10) Kowalewski, J. "Annual Reports on NMR Spectroscopy"; G. A. Webb, Ed.; Academic Press: London, 1982; Vol. 12, p 81.

(11) Jameson, C. J.; Gutowsky, H. S. *J. Chem. Phys.* **1969**, *51*, 2790.

(12) Pyykkö, P. *Chem. Phys.* **1977**, *22*, 289–296.

(13) Pyykkö, P.; Wiesenfeld, L. *Mol. Phys.* **1981**, *43*, 557–580.

(14) Knight, L. B.; Weltner, W. *J. Chem. Phys.* **1971**, *55*, 2061.

the molecule. An additional observation is that the hyperfine constant A_{Hg} observed in the optical spectra of HgH, HgD, and HgT[15] shows a decrease with increasing vibrational quantum number in the first five or six vibrational levels of the ground state of these molecules. That is, $|\psi(0)|_{\mathrm{Hg}}{}^2$ decreases with increasing vibrational quantum number. Both pieces of empirical evidence, the vibrational dependence and the isotope effect on the hyperfine constants, indicate that we must consider a rovibrational averaging model for the coupling constant just as we have done for the nuclear shielding.

B. Rovibrational Averaging of *J*. The usual model for rovibrational averaging of any molecular electronic property will be used here. We expand the spin–spin coupling (or the hyperfine constant, or any other molecular electronic property) in terms of the dimensionless normal coordinates around the equilibrium configuration.

$$J = J_e + \sum_s (\partial J/\partial q_s)_e q_s - \tfrac{1}{2}\sum_s \sum_{s'} (\partial^2 J/\partial q_s \partial q_{s'})_e\, q_s q_{s'} + \ldots \quad (7)$$

The vibrational average is then given by

$$\langle J\rangle^v = J_e + \sum_s (\partial J/\partial q_s)_e \langle q_s\rangle^v + \ldots \quad (8)$$

where the nonvanishing average of the normal coordinate is given by the anharmonic vibration and centrifugal stretching (rotation) contributions:

$$\langle q_s\rangle^v = -[3k_{sss}(v_s + \tfrac{1}{2}) + \sum_{s'} k_{ss's'}\,(v_{s'} + g_{s'}/2)]/\omega_s + (1/4\pi c\omega_s)(1/hc\omega_s)^{1/2}\sum_\alpha a_s{}^{(\alpha\alpha)}\langle v^*,R|(P_\alpha - p_\alpha{}^*)^2|v^*,R\rangle \quad (9)$$

The molecular constants involved in eq 9 are the harmonic frequencies ω_s, the cubic force constants $k_{ss's'}$, the degeneracy of the s′ vibrational mode $g_{s'}$, and the coefficients $a_s{}^{(\alpha\alpha)}$ ($\alpha = x, y, z$) which appear in the expansion of the molecular moment of inertia $I_{\alpha\alpha}$ in terms of the coordinates q_s. The thermal average of J can be evaluated by replacing $\langle v_s + {}^1/_2\rangle$ by its thermal average which is approximately ${}^1/_2$ coth $(hc\omega_s/2kT)$. The integral which appears in the second term in eq 9 has a thermal average which is $kT/I_{\alpha\alpha}$ when the spacings between the rotational energy levels are assumed to be small enough for the classical limit to hold. In a diatomic molecule

$$\langle J\rangle^{\mathrm{T}} = J_e + (\partial J/\partial \Delta r)_e\langle \Delta r\rangle^{\mathrm{T}} + \tfrac{1}{2}(\partial^2 J/\partial \Delta r^2)_e\langle(\Delta r)^2\rangle^{\mathrm{T}} + \ldots \quad (10)$$

The derivatives $(\partial J/\partial \Delta r)_e$ and $(\partial^2 J/\partial \Delta r^2)_e$ are electronic properties which describe the spin–spin coupling surface and (in the Born–Oppenheimer approximation) are independent of mass. The mass dependence lies entirely in the dynamic factors $\langle \Delta r\rangle$ and $\langle(\Delta r)^2\rangle$. The isotope effect on J would then be given by

$$|\langle J\rangle^{\mathrm{T}}|_{\mathrm{heavy}} - |\langle J\rangle^{\mathrm{T}}|_{\mathrm{light}} = (\partial J/\partial \Delta r)_e\{\langle \Delta r\rangle^{\mathrm{T}}_{\mathrm{heavy}} - \langle \Delta r\rangle^{\mathrm{T}}_{\mathrm{light}}\} + \tfrac{1}{2}(\partial^2 J/\partial \Delta r^2)_e\{\langle(\Delta r)^2\rangle^{\mathrm{T}}_{\mathrm{heavy}} - \langle(\Delta r)^2\rangle^{\mathrm{T}}_{\mathrm{light}}\} + \ldots \quad (11)$$

It is generally found that the quantity $\{\langle \Delta r\rangle^{\mathrm{T}}_{\mathrm{heavy}} - \langle \Delta r\rangle^{\mathrm{T}}_{\mathrm{light}}\}$ is negative, that is, the mean bond length in the heavy isotopomer of the diatomic molecule is shorter than that in the light isotopomer.[3] The same is true for the mean square amplitudes, $\{\langle(\Delta r)^2\rangle^{\mathrm{T}}_{\mathrm{heavy}} - \langle(\Delta r)^2\rangle^{\mathrm{T}}_{\mathrm{light}}\} < 0$. The magnitudes of the isotope effects on mean bond displacements and mean square amplitudes are dependent on the masses and the potential function in a known way for a diatomic molecule and can be approximated for end atom substitution even for a polyatomic molecule by[3]

$$\Delta\langle \Delta r\rangle \equiv \{\langle \Delta r\rangle^{\mathrm{T}}_{\mathrm{A}m'} - \langle \Delta r\rangle^{\mathrm{T}}_{\mathrm{A}m}\} \simeq \langle \Delta r\rangle_{\mathrm{A}m}[(m' - m)/m'][m_{\mathrm{A}}/(m_{\mathrm{A}} + m)]^{1/2} \quad (12)$$

for the bond between A and an end atom X upon substitution of ${}^{m}X$ by its isotope ${}^{m'}$X. In addition, there are secondary effects on all other bonds away from the substitution site which we may denote as $\delta\langle \Delta r\rangle$. The typical magnitude of $\Delta\langle \Delta r\rangle$ for CH bonds is 5×10^{-3} Å, i.e., a CO bond is shorter than a CH bond by 5×10^{-3} Å.[16] The typical magnitude of $\delta\langle \Delta r\rangle$ for a CH bond, due to D substitution one bond away, is an order of magnitude smaller.[16] For other types of bonds many examples of $\Delta\langle \Delta r\rangle$ are given in ref 3. Since the dynamic factors are reasonably well-understood and their calculation or estimation is relatively straightforward, the interpretation of the isotope effect on the spin–spin coupling constant then becomes a problem of characterization of the derivatives $(\partial J/\partial \Delta r)_e$, $(\partial^2 J/\partial \Delta r^2)_e$, ...

Table III. Calculated Primary Derivatives of One-Bond Spin–Spin Coupling[a]

molecule	coupling	$(\partial J/\partial \Delta r)_e$/ Hz Å^{-1}	$(\partial^2 J/\partial \Delta r^2)_e$/ Hz Å^{-2}	ref
HD	^1J(HD)	+71	−690	39
		+97	−150	40
		+106	−40	41
		+192	+1200	42
		+102	−43	43
HF	^1J(HF)	−583	$+2.1 \times 10^3$	24
CH_4	^1J(CH)	+189.8	+972	18
$CH_2{=}CH_2$[b]	^1J(CH)	+(290 est.)	+(1770 est.)	44
$HC{\equiv}CH$[b]	^1J(CH)	+(430 est.)	+(2800 est.)	44
cyclopropane	^1J(CH)	+295	+1400	22
trans-butadiene	^1J(CH)	+305	+1100	22

[a] These derivatives are electronic quantities which describe the sensitivity of the spin–spin coupling to changes in the distance between the coupled nuclei. They are independent of mass, in the Born–Oppenheimer approximation. For these particular nuclei the signs of derivatives of the *reduced* coupling $(\partial K/\partial \Delta r)_e$ (and $(\partial^2 K/\partial \Delta r^2)_e$) are *the same* as shown. [b] No values given, only plots of J(CH) vs. r from which these derivatives have been estimated.

C. The Change of Spin–Spin Coupling with Bond Extension. There have been several calculations of ^1J(HD) in HD molecule. The derivatives resulting from these are shown in Table III, together with the calculations on ^1J(HF) in HF and ^1J(CH) in CH_4, $CH_2{=}CH_2$, $HC{\equiv}CH$, cyclopropane, and *trans*-butadiene. These are all primary derivatives, that is, they are a measure of the change in J with respect to a change in the distance between the coupled nuclei. Except for HF, the first derivatives $(\partial K/\partial \Delta r)_e$ are all positive, that is, the shift in electron spin densities at the nuclei as the bond is lengthened increases the magnitude of the reduced coupling constant. Furthermore, in HD and HF the noncontact terms which involve quantities other than spin density have also been calculated and have been shown to be less sensitive to bond extension than the contact mechanism.

^{199}Hg hyperfine coupling data indicate that the average Hg spin density decreases with increasing vibrational quantum number (longer average bond length) in HgH, HgD, and HgT. This is consistent with an electron spin density surface which shifts the unpaired electron density from Hg to H as the bond lengthens, since one expects the unpaired spin to be entirely on H in the limit of dissociation (Hg + H). For a triplet state of a diatomic molecule mixed with the ground state by the Fermi contact interaction the electron spin density ends up on *each* of the separated atoms in the limit of dissociation. Therefore, the model discussed in section A, illustrated by the HgH example, is consistent with $(\partial K/\partial \Delta r)_e > 0$. The HgH coupling constant increases with increasing vibrational quantum number, consistent with an increasing average bond length due to anharmonicity and centrifugal distortion, as shown in eq 9.

With the first derivatives shown in Table III, it becomes possible to explain the usual negative sign of the primary isotope effect on the one-bond coupling constant.

$$\Delta_p{}^1K(\mathrm{A}^{2/1}\mathrm{H}) = (\partial K/\partial \Delta r_{\mathrm{AH}})_e[\langle \Delta r_{\mathrm{AD}}\rangle - \langle(\Delta r_{\mathrm{AH}})\rangle] + \tfrac{1}{2}(\partial^2 K/\partial \Delta r_{\mathrm{AH}}{}^2)_e[\langle(\Delta r_{\mathrm{AD}})^2\rangle - \langle(\Delta r_{\mathrm{AH}})^2\rangle] + \ldots \quad (13)$$

For the isotopomers of HD, Raynes and Riley find that the term in the first derivative is mostly responsible for the isotope effect on one-bond spin–spin coupling, with the oppositely signed term in the second derivative making a small contribution.[17] If the

---

(15) Eakin, D. M.; Davis, S. P. *J. Mol. Spectrosc.* **1970**, *35*, 27.

(16) Osten, H. J.; Jameson, C. J. *J. Chem. Phys.* **1984**, *81*, 4288.

Table IV. Isotope Effects on the Mean Bond Displacements in Acetylene (Å)[a]

	$H—C{\equiv}^{13}C—D$		$H—C{\equiv}^{13}C—H$		$D—C{\equiv}^{13}C—H$
$\langle \Delta r_1 \rangle$	1.7911×10^{-2}		1.8071×10^{-2}		1.3902×10^{-2}
$\langle \Delta r_2 \rangle$	1.3844×10^{-2}		1.8025×10^{-2}		1.7864×10^{-2}
$\langle \Delta r_C \rangle$	5.5125×10^{-3}		5.6700×10^{-3}		5.5111×10^{-3}
$\delta\langle \Delta r_1 \rangle$		1.601×10^{-4}			
$\Delta\langle \Delta r_2 \rangle$		4.1817×10^{-3}			
$\delta\langle \Delta r_C \rangle$		1.575×10^{-4}			
$\Delta\langle \Delta r_1 \rangle$				4.1694×10^{-3}	
$\delta\langle \Delta r_2 \rangle$				1.602×10^{-4}	
$\delta\langle \Delta r_C \rangle$				1.589×10^{-4}	

[a] $\langle \Delta r_1 \rangle$, $\langle \Delta r_2 \rangle$, and $\langle \Delta r_C \rangle$ are the mean bond displacements of the $H—^{12}C$, the $H—^{13}C$, and the $^{12}C{\equiv}^{13}C$ bonds, respectively, calculated by using the anharmonic force field of Strey and Mills.[20]

first term dominates, then the positive derivative with the negative dynamic term gives a negative isotope effect. Thus, the uniformly positive values of $(\partial^1 J(\mathrm{CH})/\partial \Delta r_{\mathrm{CH}})_e$ which have been calculated for CH_4, $CH_2{=}CH_2$, cyclopropane, and *trans*-butadiene in Table III are consistent with the observed uniformly negative primary isotope effects on $^1J(\mathrm{CH})$ in Table I.

The secondary isotope effect involves the following terms:

$$\Delta_s{}^1K(\mathrm{AB})[^{2/1}\mathrm{H}] = (\partial K(\mathrm{AB})/\partial \Delta r_{\mathrm{XH}})_e\{\langle \Delta r_{\mathrm{XD}} \rangle - \langle \Delta r_{\mathrm{XH}} \rangle\} + (\partial K(\mathrm{AB})/\partial \Delta r_{\mathrm{AB}})_e\{\langle \Delta r_{\mathrm{AB}} \rangle_{\mathrm{XD}} - \langle \Delta r_{\mathrm{AB}} \rangle_{\mathrm{XH}}\} + \ldots \quad (14)$$

The derivatives shown in eq 14 are the change in the spin–spin coupling between A and B due to the extension of the XH bond and the change in the AB coupling due to the extension of the AB bond. Here we have the secondary derivative $(\partial K(\mathrm{AB})/\partial \Delta r_{\mathrm{XH}})_e$ multiplied by the primary change in bond length (given by eq 12, for example) as an important contribution (as the first term in eq 14). The second term is the primary derivative $(\partial K(\mathrm{AB})/\partial \Delta r_{\mathrm{AB}})_e$ multiplied by the secondary change in bond length due to substitution at a remote site. Terms involving intermediate bonds have not been included in eq 14 since they involve products of smaller terms, secondary derivatives with secondary bond length changes. Of the two terms in eq 14 it is not immediately obvious which is more important. That a negative sign of the secondary isotope effect can occur even when the primary isotope effect is positive (as when one of the coupled nuclei has lone-pair electrons) seems to indicate the dominance of the first term (involving the secondary derivative) in eq 14 and implies a positive sign for this secondary derivative. The reasoning behind this is the following. In eq 13 and 14 both the primary and secondary isotope effects on the coupling contain the primary derivative, but in $\Delta_p{}^1K$ it is multiplied by the relatively large primary isotope effect on the mean bond length, whereas in $\Delta_s{}^1K$ it is multiplied by the smaller secondary isotope effect on the mean bond length due to remote substitution. Thus, the sign of $\Delta_s{}^1K$, if it is to be different from the sign of $\Delta_p{}^1K$, cannot be dominated by the primary derivative and is more likely to be dominated by the secondary derivative. The theoretical positive sign for the secondary derivative $[\partial J(\mathrm{CH})/\partial \Delta r_{\mathrm{CH'}}]$ in CH_4[18] is consistent with the observed negative secondary isotope effect on $^1J(\mathrm{CH})$ in CH_4 in Table II.

In these discussions we have left out the bond angle deformation term which should be important in PH_3 or H_2Se. However, to both $\Delta_p{}^1J(\mathrm{PH})$ and $\Delta_s{}^1J(\mathrm{PH})[\mathrm{D}]$ this contribution is the same. That is, $[\partial J(\mathrm{PH})/\partial \Delta\alpha]_e[\langle \Delta\alpha \rangle_{\mathrm{HPD}} - \langle \Delta\alpha \rangle_{\mathrm{HPH}}]$, whatever its sign, cannot account for the sign difference between $\Delta_p{}^1J(\mathrm{PH})$ and $\Delta_s{}^1J(\mathrm{PH})$ in PH_3. We discuss in section E the basis for the unusual sign of $\Delta_p{}^1J(\mathrm{PH})$ in PH_3 and other 3-coordinate phosphorus.

D. Two-Bond Coupling. For two-bond couplings in which a mean energy approximation may be used, the mechanism of the coupling can be discussed in terms of three factors,[19]

$$^2K(\mathrm{AMB}) \sim \mathcal{A}_{\mathrm{A}}\gamma_{\mathrm{AMB}}\mathcal{A}_{\mathrm{B}}/4(\overline{^3\Delta E}) \quad (15)$$

where $\mathcal{A}_{\mathrm{A}}$ and $\mathcal{A}_{\mathrm{B}}$ are the terms for spin information transfer from nucleus A to an electron in the bond from A to M and from nucleus B to an electron in the bond from B to M, respectively. These are of the same nature as the terms which appear in our model for ^1K. γ_{AMB} is a measure of the transfer of spin information from bond AM to bond MB, dependent on the angle between the bonds.

We use the $^2K(\mathrm{CCH})$ in acetylene to illustrate the primary and secondary isotope effects on two-bond coupling. The primary isotope effect on ^2K can be denoted as follows

$$\mathrm{D/H_1—C_1{\equiv}C_2—H_2} \qquad \Delta_p{}^1K(\mathrm{H_1C_1C_2})$$

and the secondary isotope effect on ^2K as

$$\mathrm{H_1—C_1{\equiv}C_2—H_2/D} \qquad \Delta_s{}^2K(\mathrm{H_1C_1C_2})$$

We have carried out dynamic calculations on $HC{\equiv}^{13}CH$, $DC{\equiv}^{13}CH$, and $HC{\equiv}^{13}CD$ using the anharmonic force field of Strey and Mills.[20] The method of calculation of the mean bond displacements has been described previously.[3] The results are shown in Table IV.

The mechanism for $\Delta_p{}^2K$ may be described as follows. Deuterium substitution at H_1 shortens the C_1H_1 bond and affects the rovibrationally-averaged electron spin densities on both H_1 and C_1. At the same time there is a minor effect on the lengths of the H_2C_2 bond and the C_1C_2 bond, which slightly affects the electron spin density at the C_2 nucleus. On the other hand, the mechanism for $\Delta_s{}^2K$ may be described as the following: deuterium substitution at H_2 shortens the C_2H_2 bond and affects the average spin densities on both H_2 and C_2 nuclei. At the same time there is a minor effect on the H_1C_1 bond length which slightly affects the electron spin density at the H_1 nucleus. The electron spin densities at H_1 and C_2 determine $^2K(\mathrm{H_1C_1C_2})$. In our simple model we write (as in eq 15)

$$^2K(\mathrm{H_1C_1C_2}) \simeq \mathcal{A}_{\mathrm{H_1}}\gamma_{\mathrm{HCC}}\mathcal{A}_{\mathrm{C_2}}/4(\overline{^3\Delta E})$$

Let us suppose that the effect of shortening the CH bond is similar to that observed upon shortening the HgH bond, i.e., shortening the CH bond increases $\mathcal{A}_{\mathrm{C}}$ and decreases $\mathcal{A}_{\mathrm{H}}$. Upon substitution of H_1 by deuterium, $\mathcal{A}_{\mathrm{H_1}}$ decreases due to the shortening of the C_1H_1 bond by 4.17×10^{-3} Å. At the same time $\mathcal{A}_{\mathrm{C_2}}$ changes only slightly due to the secondary change of about 10^{-4} Å in the C_2H_2 and C_1C_2 bonds. If we assume that the transmission of spin information (γ_{HCC}) from the H_1C_1 bond to the C_1C_2 bond is unchanged, this predicts a decrease in the product $\mathcal{A}_{\mathrm{H_1}}\gamma_{\mathrm{HCC}}\mathcal{A}_{\mathrm{C_2}}$ and therefore a decrease in $^2K(\mathrm{H_1C_1C_2})$, i.e., a negative primary isotope effect. However, γ_{HCC} is expected to increase when the H_1C_1 bond gets shorter, since the mechanism of spin information transfer depends on the exchange interaction between the electron pairs in the H_1C_1 bond and the C_1C_2 bonds. Therefore, we find that the primary isotope effect on the two-bond coupling is due to two opposing changes, a decrease in $\mathcal{A}_{\mathrm{H_1}}$ and an increase in γ_{HCC}. Depending on which one dominates, either sign of $\Delta_p{}^2K$ may be observed, but in any case, the opposing effects lead to a smaller magnitude than might otherwise be expected.

---

(17) Raynes, W. T.; Riley, J. P. *Mol. Phys.* **1974**, *27*, 337.

(18) Sergeyev, N. M.; Solkan, V. N. *J. Chem. Soc., Chem. Commun.* **1975**, 12.

(19) Jameson, C. J. *J. Am. Chem. Soc.* **1969**, *91*, 6232. Jameson, C. J.; Damasco, M. C. *Mol. Phys.* **1970**, *18*, 491.

(20) Strey, G.; Mills, I. M. *J. Mol. Spectrosc.* **1976**, *59*, 103.

On the other hand, substitution of H_2 by D leads to an increase in $\mathcal{A}_{C_2}$ due to the shortening of the C_2H_2 bond by 4.19 × 10^{-3} Å while $\mathcal{A}_{H_1}$ changes only slightly due to the minor change of about 10^{-4} Å in the C_1H_1 bond length. In this case, γ_{HCC} should remain essentially unchanged since the C_1C_2 and C_1H_1 bonds suffer only very minor changes upon D substitution at the other end of the molecule. Thus, our model predicts an increase in the product $\mathcal{A}_{H_1}\gamma_{HCC}\mathcal{A}_{C_2}$ and therefore a positive secondary isotope effect, $\Delta_s\,{}^2K(H_1C_1C_2) > 0$. The actual observed isotope effects in acetylene are +0.09 ± 0.13 and +0.25 ± 0.05 Hz for the primary and secondary isotope effects, respectively.[9] It is encouraging that our simple model works so well.

A calculation of the derivative of ${}^2J$(HCC) with respect to bond displacement would be very helpful. However, this would require a very good ab initio calculation. UHF (unrestricted Hartree–Fock) instabilities show up in the ground state wave function of acetylene so that it is necessary to describe the ground state in terms of multiconfigurational SCF wave functions. This was accomplished only recently, recovering 97% of the experimental value of +49.3 Hz.[21] Previous best calculations had given values of −2.91 up to +7.42 Hz. Furthermore, even a calculation at this level may not be able to reproduce the very small primary isotope effect (+0.09 ± 0.13 Hz)[9] which comes from cancelling opposite-signed terms, as our simple model indicates.

The calculated derivatives of two-bond couplings with bond extension have both signs.[22,23] However, these must be considered less reliable than the derivatives of one-bond couplings. It is well-known that calculations of ${}^2J$(CCH) have been disappointing, with the FPT method at the CNDO/2, INDO, and MINDO/3 levels of approximation giving results bearing no relationship to the experimental data.[10] The calculations reported for cyclopropane and *trans*-butadiene have been done at this level (FP-T-PNDO),[22] so the derivatives of ${}^2J$(CCH) so obtained are probably not as reliable as the derivatives of ${}^1J$(CH). A large configuration interaction calculation of the ${}^2J$(HH) coupling in NH_3 shows a strong dependence on molecular geometry. However, the vibrational effects on the coupling are small.[23]

E. Decrease in |*J*| with Bond Extension for Coupled Nuclei with Lone Pairs. The only cases in which the primary isotope effect has been observed to be positive are in SeH_2, PH_3, and tricoordinate phosphorus (4- and 5-coordinate phosphorus have negative isotope effects on ${}^1J$(PH)). A calculation predicts a positive sign for HF as well. A possible explanation for the negative primary derivative of ${}^1J$(HF), and possibly also in SeH_2 and PH_3, is as follows:

Whenever lone pairs with some s character are centered on one or both of the coupled nuclei there is a negative contribution to the reduced coupling constant. In the Pople–Santry picture, there is a nonbonding MO describing the lone pair with some s character on the central atom A (Se or P^{III} or F); because this MO is A–H antibonding, it will give a negative contribution to ${}^1K$(AH).[13] On the other hand, the AH bonding MO which has also some s_A character gives a positive contribution. In a molecule with no lone pairs such as CH_4, a single $a_1 \rightarrow a_1^*$ excitation gives a positive contribution to the CH coupling constant. Pyykkö has shown that a relativistic treatment preserves the signs of these contributions.[13] Thus, while the derivative of the coupling constant with respect to bond extension is positive in the case of CH_4, it could easily be dominated by the lone pair contribution in the HF, HSe (in H_2Se), and P^{III}H couplings, conceivably giving rise to a net derivative $(\partial K/\partial\Delta r)_e$ which is negative. We consider a mechanism by which a negative $(\partial K/\partial\Delta r)_e$ might arise: When the SeH bond (for example) is extended, the Se atom tends to use more p character in the SeH bond, leaving more s character for the lone pair MO. The more s character in the lone pair MO (which gives a negative Fermi contact contribution to ${}^1K$) the larger negative is the lone pair contribution to ${}^1K$. Thus, the lone pair contribution to $(\partial K/\partial\Delta r)$ would be negative. In HF, the lone pair contribution to $(\partial K/\partial\Delta r)_e$ apparently dominates, giving $(\partial J/\partial\Delta r)_e = -583$ Hz Å^{-1}.[24]

Table V. Isotope Effects on the PH Bond Length and the PH Spin–Spin Coupling and Its Derivatives with *Respect* to Bond Extension in 3- and 4-Coordinate Phosphorus Compounds

	PH_3	$H_2P(O)OH$
${}^1J$(PH)(obsd)	+185.6 Hz	+569.6 Hz
$\Delta_p{}^1J$(PH)(obsd)	+12.2 Hz	−4.8 ± 0.8 Hz
$[\langle\Delta r_{PD}\rangle - \langle\Delta r_{PH}\rangle]^a$	5.494 × 10^{-3} Å	5.494 × 10^{-3} Å
$(\partial J(PH)/\partial\Delta r_{PH})_e$(calcd)	−1115 Hz Å^{-1}	+245 Hz Å^{-1}
$\Delta_p{}^1J$(PH)(calcd)	+6.1 Hz	−1.4 Hz

[a] For PH_3 this value was obtained with an anharmonic force field calculation.[3] We use the same value for $H_2P(O)OH$, for which no force field is available. The equilibrium geometries of PH_3 and $H_2P(O)OH$ were obtained from the following: Duncan, J. L.; McKean, D. C. *J. Mol. Spectrosc.* **1984**, *107*, 301. Ewig, C. S.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 1965.

It has been shown[10] that the basis set sensitivity of coupling constants is weak in hydrides of groups 4 and 5 of the periodic table and strong for the hydrides of groups 6 and 7, so we choose to calculate the derivatives of PH couplings rather than calculating the derivative of ${}^1J$(SeH) in H_2Se. In addition, we wish to compare the P^{III} with P^{V} behavior, which are known experimentally to be of opposite sign. We see in the above qualitative discussions that it might be expected that the primary isotope effect on P^{III}H one-bond couplings can show the opposite sign compared to the isotope effect on $P^{IV,V}$H one-bond couplings, provided only that the negative terms involving the lone pair dominate the derivative of ${}^1J$(PH) with respect to bond extension in the 3-coordinate phosphorus environments. We have carried out calculations of ${}^1J$(PH) in two representative compounds, PH_3 and $H_2P(O)OH$, in order to illustrate this.

The contributions from the orbital and spin-dipolar terms to PH coupling in PH_3 have been calculated[25,26] and are found to be 2% and −0.9% of the Fermi contact term, so we are justified in excluding these mechanisms. Using the SOS method we are able to assign separate contributions to the derivative of the Fermi contact term in the PH coupling from individual occupied molecular orbitals. We find that the a_1 MO which is essentially a lone pair with s character on the phosphorus atom in PH_3 does indeed make negative contributions to ${}^1J$(PH) and also to the derivative $(\partial J(PH)/\partial\Delta r_{PH})_e$. On the other hand, there are no corresponding negative contributions in $H_2P(O)OH$. We estimate the isotope effect on ${}^1J$(PH) in these molecules using SOS–INDO calculations and the mean PH bond displacements from previous work.[3] In the calculation of the isotope effect on ${}^1J$(PH) we scaled our calculated derivative by the ratio of the experimental and calculated values of ${}^1J$(PH). Results are shown in Table V, in which we see that at this level of approximation our calculated isotope effects on ${}^1J$(PH) are of the right order of magnitude and the correct signs in PH_3 and $H_2P(O)OH$. Therefore, we propose that the basis for the signs of the experimental primary isotopic effects in H_2Se, PH_3, and other P^{III}H couplings (as opposed to the other molecular systems in Table I) is the opposite-signed contribution of the lone pair to the derivative $(\partial J/\partial\Delta r)$.

---

(21) Laaksonen, A.; Kowalewski, J.; Saunders, V. R. *Chem. Phys.* **1983**, *80*, 221.

(22) Mamaev, V. M.; Orazberdiev, Kh. A. *Theor. Exp. Chem.* **1977**, *13*, 170.

(23) Kowalewski, J.; Roos, B. *Chem. Phys.* **1975**, *11*, 123. Solomon, P.; Schulman, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 7776.

(24) Murrell, J. N.; Turpin, M. A.; Ditchfield, R. *Mol. Phys.* **1970**, *18*, 271.

(25) Guest, M. F.; Overill, R. E. *Chem. Phys. Lett.* **1980**, *73*, 612.

(26) Kowalewski, J.; Laaksonen, A.; Saunders, V. R. *J. Chem. Phys.* **1981**, *74*, 2412.

(27) Alei, M.; Wageman, W. E. *J. Chem. Phys.* **1978**, *68*, 783.

(28) Everett, J. R. *Org. Magn. Reson.* **1982**, *19*, 169.

(29) Murray, M. *J. Magn. Reson.* **1973**, *9*, 326.

(30) McFarlane, W.; Rycroft, D. S. *Mol. Phys.* **1972**, *24*, 893.

(31) Schumann, C.; Dreeskamp, H. *J. Magn. Reson.* **1970**, *3*, 204.

(32) Banwell, C. N.; Murrell, J. N.; Turpin, M. A. *J. Chem. Soc., Chem. Commun.* **1968**, 1466.

(33) Fraser, R. R.; Petit, M. A.; Miskow, M. *J. Am. Chem. Soc.* **1972**, *94*, 3253.

(34) Friesen, K. J.; Wasylishen, R. E. *J. Magn. Reson.* **1980**, *41*, 189.

IV. Conclusions

We examined the signs and magnitudes of the primary and secondary isotope effects on one- and two-bond spin–spin coupling constants observed in high-resolution NMR spectra. The usual negative sign of the primary isotope effect on one-bond couplings and the primary and secondary isotope effects on the two-bond coupling in $HC{\equiv}CH$ are interpreted by a simple model and a dynamical calculation on $HC{\equiv}CH$ isotopomers. The interpretation involves mass-independent electronic factors (derivatives of spin–spin coupling) and mass-dependent dynamic factors (mean bond displacements $\langle \Delta r \rangle$, etc.). The positive sign of the primary isotope effect on ^{1}J(PH) in 3-coordinate phosphorus compounds and its negative sign in 4-coordinate phosphorus are reproduced by calculations of ^{1}J(PH) as a function of bond length in PH_3 and $H_2P(O)OH$. With these theoretical calculations and physical models, the observed general trends in primary and secondary isotope effects on one- and two-bond couplings can be understood.

Acknowledgment. This research has been supported in part by the National Science Foundation (Grant CHE81-16193). This paper was written while CJJ was a guest of the Central Institute of Physical Chemistry of the Academy of Sciences of the GDR as a participant in the National Academy of Sciences Interacademy Exchange Program. The support of the Academy of Sciences of the GDR is gratefully acknowledged.

Registry No. C, 7440-44-0; H_2, 1333-74-0; P, 7723-14-0; Se, 7782-49-2.

(35) James, B. D.; Smith, B. E.; Newman, R. H. *J. Chem. Soc., Chem. Commun.* **1974**, 294.
(36) Smith, B. E.; James, B. D.; Peachey, R. M. *Inorg. Chem.* **1977**, *16*, 205.
(37) Altman, L. J., private communications. Diehl, P.; Leipert, Th. *Helv. Chim. Acta* **1964**, *47*, 545.
(38) Ebsworth, E. A. V.; Turner, J. J. *J. Chem. Phys.* **1962**, *36*, 2628.
(39) Ishiguro, E. *Phys. Rev.* **1958**, *111*, 203.
(40) Schulman, J. M.; Kaufman, D. N. *J. Chem. Phys.* **1972**, *57*, 2328.
(41) Kowalewski, J.; Roos, B.; Siegbahn, P.; Vestin, R. *Chem. Phys.* **1974**, *3*, 70.
(42) Facelli, J. C.; Contreras, R. H.; Scuseria, G. E.; Engelmann, A. R. *J. Mol. Struct.* **1979**, *57*, 299.
(43) Schulman, J. M.; Lee, W. S. *J. Chem. Phys.* **1980**, *73*, 1350.
(44) Orazberdiev, Kh.; Mamayev, V. M.; Sergeyev, N. M. In "Magnetic Resonance and Related Phenomena", Proceedings of the XXth Congress Ampere, Tallinn, 1979, p 495.

Studies of Cyclodextrin Inclusion Complexes in the Solid State by the ^{13}C CP/MAS and ^{2}H Solid Echo NMR Methods[1]

Laurance D. Hall* and T. K. Lim†

Contribution from the Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6.

Received September 30, 1985

Abstract: Solid complexes have been formed from a variety of organic molecules encaged in the α- and β-cyclodextrins, in heptakis(2,6-di-*O*-methyl)-β-cyclodextrin, and in β-cyclodextrin peracetate. The ^{13}C cross polarization magic angle spinning spectra of these inclusion complexes in the solid state have been assigned by comparison with the corresponding solution spectra and suggest that the guest molecules undergo anisotropic motion, which can be detected by use of the dipolar dephasing technique. The deuterium quadrupole echo method has been used to study the molecular reorientation of the guest molecules, and it is shown that the motion of the smaller guests is least affected by the cavity size of the host.

Cyclodextrins (CDs) were first isolated as degradation products of starch in the last century by Villiers[2] and were subsequently characterized as cyclic oligosaccharides in 1904 by Schardinger.[3,4] They are cyclic, nonreducing sugars containing between 6 and 12 α(1 -- > 4)-linked glucopyranose units in the form of torus-like macrorings with a 6–10-Å diameter cavity which is capable of forming inclusion complexes with small "guest" molecules. Selective chemical modification[5] of the CDs provides an array of opportunities to tailor both the equilibrium thermodynamics and the molecular motion of these complexes. Thus, methylated CDs have been shown[6] to be versatile complexing agents, in both aqueous and organic solvents; the stability of their crystalline complexes depends on the shape and size of the encaged molecule.[7] Fully O-acetylated β-CD may also serve as host for smaller size organic molecules.

Although ^{1}H and ^{13}C NMR methods have been used extensively to study soluble complexes of unsubstituted CDs in solution, equivalent studies in the solid state have only been reported recently.[8,9] A preliminary report[9] gave an evaluation of the ^{13}C CP/MAS[10] and ^{2}H quadrupole echo[11] methods for studying inclusion complexes of both unsubstituted- and substituted-CD inclusion complexes, and we now describe a more detailed analysis of the relationships between motion, structure, and mobility for several related series of guest molecules.[12]

As will be seen, the resonances observed by the ^{13}C CP/MAS method reflect not only chemical distinctions and stoichiometry but also magnetic inequivalences present in those complexes,[13]

---

† Present address: Division of Biochemistry and Biophysics, Food and Drug Administration, 8800 Rockville Pike, Bethesda, MD 20205.

(1) This work has been presented in part at the Gordon Research Conference on Carbohydrate Chemistry, Tilton, NH, June 1983.
(2) Villiers, A. *C. R. Hebd. Seances Acad. Sci.* **1891**, *112*, 536.
(3) Schardinger, F. *Wien. Klin. Wochenschr.* **1904**, *17*, 207.
(4) Schardinger, F. *Zentralbl. Bakteriol., Parasitenkd., Infektionskrankh. Hyg., Abt. 2, Naturwiss: Allg., Landwirtsch. Tech. Mikrobiol.* **1911**, *29*, 188.
(5) Boger, J.; Corcoran, R. J.; Lehn, J. M. *Helv. Chim. Acta* **1978**, *61*, 2190.
(6) Casu, B.; Reggiani, M.; Gallo, G. G.; Vigevani, A. *Tetrahedron* **1968**, *24*, 803.
(7) (a) Saenger, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 344. (b) Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*; Springer: Berlin, 1978.
(8) (a) Inoue, Y.; Okadu, T.; Kuan, F. H.; Chûjô, R. *Carbohydr. Res.* **1984**, *129*, 9. (b) Inoue, Y.; Kuan, F. H.; Takahashi, Y.; Chûjô, R. *Ibid.* **1985**, *135*, C12.
(9) Hall, L. D.; Lim, T. K. *J. Am. Chem. Soc.* **1984**, *106*, 1858.
(10) Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976**, *98*, 1031 and references therein.
(11) Davis, J.; Jeffrey, K.; Bloom, M.; Valic, M.; Higgs, T. *Chem. Phys. Lett.* **1976**, *42*, 390.
(12) Lim, T. K., Ph.D. Thesis, University of British Columbia, Vancouver, 1985.
(13) Lippmaa, E. T.; Alla, M. A.; Pehk, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 1929.