Isotope Effect on the Coupling Constant $^1J(^{13}C–H)$

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Summary The negative isotope effect on the coupling constant $^1J(^{13}C–H)$ $\{\Delta J = (\gamma_H/\gamma_D)[^1J(^{13}C–D)] - {}^1J(^{13}C–H)\}$ has been confirmed by INDO FP calculations of the $^1J(^{13}C–H)$ coupling constant in methane by varying one of the C–H distances.

THE effect of isotopic substitution on spin–spin coupling constants has attracted considerable attention. Gutowsky *et al.*[1] considered the bond-bending vibration effects on the geminal coupling constant ^2J(HD) compared with ^2J(HH) in an H–C–D (relative to H–C–H) fragment. Earlier experimental attempts to observe isotope effects on coupling constants included both secondary[2,3] and primary effects.[3] More recently primary isotope effects have been discovered for $^1J(^{31}P–H)$ in both three-[4a] and four-co-ordinate phosphorus compounds.[4] The difference, ΔJ $\{\Delta J = (\gamma_H/\gamma_D)[^1J(^{13}C–D)] - {}^1J(^{13}C–H)\}$ for the different isotopomers has been measured, but no isotope effect was found within the reported accuracy. Recently Colli *et al.*[6] found ΔJ values of *ca.* -1 to $-1{\cdot}5$ Hz though the root mean square deviations were of a comparable magnitude (*ca.* $\pm$ 1 Hz). We now report the results of theoretical calculations on $^1J(^{13}C–H)$ at various C–H distances, which confirm the existence of the isotope effect. The calculations were made for methane by using the finite perturbation approach with INDO-functions.[7] Standard geometry was used ($r_{C–H}$ = 1·093 Å) and the parameters used in the INDO formulation were as reported.[8] The calculations were performed by varying only one C–H distance, from 1·013 to 1·173 Å. The values of coupling constants $^1J(^{13}C–H)$ are in Table 1 where H_x is the proton with variable position. The values of $^1J(^{13}C–H)$ constants are also included in Table 1 for

TABLE 1

Calculated values of the coupling constant $J(^{13}C–H_x)$ (in Hz) (INDO FP) in CH_4 *vs.* $r(C–H_x)$[a]

$r(C–H_x)/(Å)$	$J(^{13}C–H_x)$	$J(^{13}C–{}^1H)$
1·013	109·7	120·7
1·023	111·1	120·8
1·033	112·5	b
1·063	117·2	b
1·083	120·8	b
1·093	122·7	b
1·098	123·7	122·8
1·101	124·3	122·9
1·113	126·8	b
1·143	133·7	b
1·153	136·2	124·1
1·163	138·9	124·2
1·173	141·7	b

[a] $C–H_x$ distance is varied; [b] Not calculated.

selected distances. We consider the isotope effect to be due to changes in molecular geometry, according to the approach given in a recent review.[9]

From the data given in Table 1 it is obvious that $^1J(^{13}C\text{–}H_x)$ increases with $r(C\text{–}H_x)$, the changes being *ca.* 2 Hz per 0·01 Å, while substantial nonlinear deviations are observed for the *J vs. r* dependence. The dependence can be approximated by a quadratic equation: the mean deviation does not exceed 0·1 Hz for the entire range studied. For other types of C–H bonds (*e.g.*, in ethylene or acetylene where the carbon hybrid orbitals are sp^2 or sp, respectively) the $J(r)$ dependence is expected to be similar to that in equation (1). However, greater *s*-character should result in substantially higher J values.

$$^1J(CH) = 487{\cdot}4 - 864{\cdot}8\, r(CH) + 486{\cdot}0 r^2(CH) \qquad (1)$$

The geometrical isotope effect consists of the changes of the average internuclear distance and the average amplitude of vibration. The coupling constant can be represented by the function $\Delta r = r - r_e$, where r_e is the effective internuclear distance. According to Bartell, *et al.*,[10] the values of r_e coincide for the isotopomeric CH_4 and CD_4 and are equal to 1·085 Å, thus giving equation (2).

$$^1J(^{13}C\text{–}H) = 121{\cdot}2 + 189{\cdot}8\, \Delta r + 486\, (\Delta r)^2 \qquad (2)$$

For the present problem diffraction data for CH_4 and CD_4 can be used.† Under thermal equilibrium conditions $<r(CH)> =$ 1·101 Å and $<r(CD)> =$ 1·098 Å while the amplitudes of vibrations, l, are 0·076 and 0·068 Å, for C–H and C–D bonds, respectively.

Equation (1) can be used to estimate the vibration-averaged value of the coupling constant $^1J\,(^{13}C\text{–}H)$ using the relationships $\Delta r(CH) = <r(CH)> - r_e$, $\Delta r(CD) = <r(CD)> - r_e$, $(\Delta r)^2 = l^2$ and the approach previously proposed by Buckingham.[11] The corresponding data are given in Table 2.

TABLE 2

Contributions (in Hz) in $^1J(^{13}C\text{–}H)$ for C–H and C–D bonds in methane

Bond	Standard value[a]	Contribution[b] Linear	Quadratic	Total
C–D	121·2	2·5	2·2	125·9
C–H	121·2	3·0	2·7	126·9
Isotope effect	—	−0·5	−0·5	−1·0

[a] At $r(CH)$ $[r(CD)] = r_e$ (1·085 Å); [b] Calculated from equation (2) by using Δr and l values determined as in the text.

The data in Table 2 prove that an isotope effect on ^1J-(C–H) does exist and is negative in accord with the experimental data.[6] The contributions due to linear and quadratic terms are almost equal.

It is also evident from the data available that the secondary isotope effect is substantially lower and is not likely to be detectable at the normal accuracy of 0·1 Hz. This is confirmed by reported attempts[5] to find a secondary isotope effect for $^1J(^{13}C\text{–}H)$.

Usually H–D replacement results in shortening of X–D (X–H) bonds; thus the sign of the isotope effect is determined by the signs of the derivative $\delta J/\delta r$. For positive values of $\delta J/\delta r$, negative isotope effects should be expected and *vice versa*. A positive sign for $\delta J/\delta r$ has also been calculated by Raynes and Riley[12] for H_2, based on data by Shulman and Kaufman.[13]

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† Structural data for CH_3D are not available from the literature, so we consider the geometrical C–D bond parameters in CH_3D to be equal to those in CD_4. This assumption is valid if one neglects the secondary isotope effect.

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