MAGNETIC RESONANCE IN CHEMISTRY, VOL. 36, 255–260 (1998)

Deuterium-Induced Primary and Secondary Isotope Effects on ^{13}C,H Coupling Constants in Halomethanes

N. D. Sergeyeva,[1] N. M. Sergeyev[2]* and W. T. Raynes[3]*

[1] Department of Natural Sciences, Russian University of Peoples' Friendship, 117198, Moscow, Russia
[2] Department of Chemistry, Moscow State University, 119899, Moscow, Russia
[3] Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK

Received 23 July 1997; Revised 5 November 1997; Accepted 5 November 1997

ABSTRACT: Primary $^{p}\Delta J(^{13}C,H)$ and secondary $^{s}\Delta J(^{13}C,H)$ isotope effects on carbon–proton coupling constants were measured in studies of proton- and deuteron-coupled ^{13}C NMR spectra of the halomethanes $CH_nD_mX_{4-n-m}$, where X is Cl, Br or I. Both effects are always negative. The magnitudes of $^{p}\Delta J(^{13}C,H)$ increase with the number of halogen atoms whereas those of $^{s}\Delta J(^{13}C,H)$ decrease. $^{p}\Delta J(^{13}C,H)$ is almost linearly dependent on the number of halogen atoms whereas for $^{s}\Delta J(^{13}C,H)$ the dependence is non-linear. New results for the isotope effect on the ^{13}C,H coupling constant in fluoroform are in accord with data for the other members of the haloform series. For CH_3Br and CH_3I estimates of the main features of the surfaces for the ^{13}C,H coupling constants were made using known molecular force fields. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: ^{13}C NMR; halomethanes; carbon–proton spin–spin coupling constants; deuterium isotope effects

INTRODUCTION

Isotope effects on ^{13}C,H coupling constants have been the subject of many experimental and theoretical investigations. A thorough review of papers published before 1993 has already appeared.[1] In particular, detailed studies of the methane molecule have been performed both experimentally[2] and theoretically.[3] The most intriguing result of these methane studies is that, while the primary isotope effect on the ^{13}C,H coupling constant defined as

$$^{p}\Delta J(^{13}C,H) = (\gamma_H/\gamma_D)J(^{13}C,D)(CH_3D) - J(^{13}C,H)(CH_4) \quad (1)$$

is found to be very small (-0.07 Hz), the secondary isotope effect defined as

$$^{s}\Delta J(^{13}C,H) = J(^{13}C,H)(CH_3D) - J(^{13}C,H)(CH_4) \quad (2)$$

is significant and equals -0.35 Hz.

This experimental finding was supported by *ab initio* calculations[3b] of ^{13}C,H coupling constants in methane at the CCSDPPA level, which include electron correlation to high order. Similar experimental results were found in the case of toluene.[4] Many experimental data are known for compounds containing perdeutero groups,[5,6] but the observed isotope effects are usually combinations of primary and secondary effects. Thus a series with a varying number of deuteriums is needed. In a recent paper,[7] we reported our studies of the series CH_2Cl_2, $CHDCl_2$ and CD_2Cl_2 which allowed us to determine both primary and secondary isotope effects on the ^{13}C,H coupling constants. They are -0.60 ± 0.05 and -0.25 ± 0.01 Hz, respectively. This showed that at least primary effects are subject to some influence from the substituent.

In this paper, we present the results of a study of several halomethanes, namely CH_2Cl_2, $CHCl_3$, CH_3Br, CH_2Br_2, $CHBr_3$, CH_3I, CH_2I_2 CHI_3 and CHF_3. The results of our study of the H/D-induced ^{13}C isotope shifts in these compounds have already been published.[8] The non-additivity of successive H/D-induced ^{13}C isotope shifts in some halomethanes[9] has also been discussed.

EXPERIMENTAL

The samples studied are listed in the first and last columns of Table 1, which give the solvent, lock substance and isotopomeric ratios of the deuterated species labelled d_0–d_3. In most cases pure liquids were used (with 5–10% of perdeuterotetramethylsilane added as the lock substance) to create the best conditions for the recording of ^{13}C,H coupled spectra and to minimize the time of experiment. In the case of CH_2I_2 we were forced to add methyl iodide owing to the low solubility of tetramethylsilane in this halomethane. Difficulties that we encountered in studying the isotope shift in iodoform[8] were substantially greater in studying the isotope effect on the coupling constant. We were not able to measure the ^{13}C,H and ^{13}C,D constants of this compound in acetone solution as used previously[8] (maximum concentration 2 mol%) with sufficient accuracy to estimate the isotope effect. Using methyl iodide as a solvent we achieved a CHI_3 concentration of 10

---

* *Correspondence to*: W. T. Raynes, Department of Chemistry, University of Sheffield, Sheffield, 53 7HF, UK or N. M. Sergeyev, Dept. of Chemistry, Moscow State University, 119899 Moscow, Russia.

† *Contract/grant sponsor*: Russian Foundation for Fundamental Research; *Contract/grant number*: 97-03-33574.

CCC 0749-1581/98/040255–06 $17.50

Table 1. Spin–spin coupling constants $J(^{13}C,H)$ in halomethanes and the composition of the isotopomeric mixtures studied

Sample	n^{a}	$J(^{13}C,H)$ (Hz)	$J^{*}(^{13}C,H)$ (Hz)	Sample; lock substance; isotopomeric composition[b]
CH_3I	0	150.984 ± 0.004	—	10 mol.% TMS-d_{12};
	1	150.706 ± 0.004	150.74 ± 0.02	TMS-d_{12};
	2	150.420 ± 0.01	150.44 ± 0.02	$d_0:d_1:d_2:d_3 = 0.7:1:1.3:1.5$
	3	—	150.13 ± 0.01	
CH_3Br	0	151.484 ± 0.002	—	10 mol.% TMS-d_{12};
	1	151.175 ± 0.001	151.193 ± 0.01	TMS-d_{12};
	2	150.872 ± 0.001	150.86 ± 0.01	$d_0:d_1:d_2:d_3 = 1:1.5:2:2$
	3	—	150.540 ± 0.007	
CH_2I_2	0	172.653 ± 0.005	—	25 mol.% CH_3I, 5 mol.%;
	1	172.509 ± 0.002	172.27 ± 0.03	TMS-d_{12};
				$d_0:d_1 = 1:1$
CH_2Br_2	0	178.927 ± 0.001	—	7 mol.% TMS-d_{12};
	1	178.735 ± 0.001	178.423 ± 0.007	$d_0:d_1:d_2 = 1:2:2$
	2	—	178.23 ± 0.03	
CH_2Cl_2 [c]	0	177.507 ± 0.007	—	30 mol.% C_6D_{12};
	1	177.258 ± 0.010	176.91 ± 0.04	$d_0:d_1 = 1:2.5$
CHI_3	0	186.37 ± 0.01	—	10 mol.% in CH_3I/CD_3I;
	1	—	185.92 ± 0.06	TMS-d_{12};
				$d_0:d_1 = 1:2.5$
$CHBr_3$	0	204.85 ± 0.005	—	10 mol.% TMS-d_{12};
	1	—	204.15 ± 0.10	$d_0:d_1 = 1:2.5$
$CHCl_3$	0	209.10 ± 0.01		$CDCl_3$;
	1		208.18 ± 0.13	$d_0:d_1 = 1:2.5$

[a] Number of deuterium atoms.
[b] For synthesis, sample preparation and experimental details see Refs 7–9.
[c] From Ref. 7.

mol%, which allowed us to record a spectrum in a reasonable time interval without strong broadening of lines due to the very high temperature coefficient of the chemical shift for this compound (of the order of 10 Hz K^{-1} for a ^{13}C NMR resonance frequency of 100 MHz, by our estimation). It should be noted, however, that in these circumstances possible self-association could occur. To test this we carried out two runs using two concentrations, 5 and 10 mol.%, with the results being close to each other. Hence self-association can be ignored. The synthesis and preparation of the samples have been described.[7–9]

The proton-coupled ^{13}C NMR measurements were made on the AM 250 and WH 400 Bruker spectrometers at the University of Sheffield with an instrumental resolution of about 0.1 and 0.2 Hz, respectively. In all cases the ^{2}H NMR signal of tetramethylsilane-d_{12} was used for locking.

Typical conditions for recording ^{13}C NMR spectra were as follows: sweep width 500–1000 Hz, pulse width about 40°, acquisition time about 10 s, FT size 32–64K with digital resolution of about 0.03 Hz. Good resolution is essential for measurements of isotope effects on coupling constants. That is why in some cases we had to take into account some additional broadening of the ^{13}C NMR lines. For CH_2Cl_2 and $CHCl_3$ we encountered the $^{37}Cl/^{35}Cl$-induced ^{13}C isotope shifts first observed in the spectra published in 1994[7] and reported in detail later.[10] The ^{13}C NMR lines of chlorinated compounds are additionally broadened owing to the residual ^{13}C–$^{35}Cl(^{37}Cl)$ spin–spin coupling of about 1 and 2 Hz for CH_2Cl_2 and $CHCl_3$, respectively. Similar broadening was observed previously,[5,11] thus preventing accurate measurements of the isotope effects. In several cases $^{13}C,H$ coupling constants were measured using ^{13}C satellites in the ^{1}H NMR spectra.

We now consider fluoroform, which was first studied many years ago.[12] In that work a mixture of CHF_3 and CDF_3 was studied in solutions of tetrahydrofuran and cyclohexane by ^{19}F NMR. It was found that the ^{19}F isotope shifts due to D/H substitution were in the range 750–790 ppb, depending on the concentration and temperature of the solutions. However, in interpreting the experimental results, the authors[12] suggested that the isotope effect is mainly due to the shifts of the equilibrium between free fluoroform and the fluoroform–tetrahydrofuran complex and neglected the intrinsic isotope effect completely.

In a more recent study,[13] a mixture of liquid CDF_3 and liquid CHF_3 was prepared in a sample tube which also contained 5 vol.% $Si(CD_3)_4$ in order to provide a ^{2}H NMR signal for the locking system. ^{13}C NMR spectra were taken on a Bruker AC 200 spectrometer with a resonance frequency of 50.3221 MHz in both proton decoupled and coupled modes. Typical accuracies were ±0.001 ppm for isotope shifts and *ca.* ±0.1

Table 2. ^{13}C chemical shifts (δ^{13}C) and ^{13}C,H and ^{13}C,^{19}F coupling constants in fluoroform

Compound	δ^{13}C^a ($\pm$0.001) (ppm)	$J(^{13}$C,H) ($\pm$0.1) (Hz)	$J(^{13}$C,^{19}F) ($\pm$0.01) (Hz)
CHF_3	119.116	239.10	−274.26
CDF_3	118.880	237.45^b	−272.70
Isotope effect	0.236	−1.65	+1.56

[a] Relative to tetramethylsilane-d_{12}.
[b] $J^*(^{13}\mathrm{C,H}) = (\gamma_H/\gamma_D)J(^{13}\mathrm{C,D})$.

Hz for the isotope effects on coupling constants. The final data are summarized in Table 2.

RESULTS

Isotope Effects on ^{13}C,H Coupling Constants

The ^{13}C,H and ^{13}C,D coupling constants measured in this work are presented in Table 1; ^{13}C,D coupling constants were converted to the ^{13}C,H basis in terms of $J^*(^{13}\mathrm{C,H}) = (\gamma_H/\gamma_D)J(^{13}\mathrm{C,D})$. The absolute values of the ^{13}C,H coupling constants of the undeuterated compounds, of course, have been reported previously.[1,14] However, they can be subject to solvent effects to an extent exceeding the possible effects of isotopic substitution. Thus only the differences between J(C,H) and J^*(C,H) values from a given mixture of isotopomers in the same solvent will be considered. For methyl derivatives, CH_3X, primary isotope effects can be measured in several ways, namely as the differences of the following coupling constants:

$$^{p}\Delta J(^{13}\mathrm{C,H}) = J^*(^{13}\mathrm{C,H})(\mathrm{CH_2DX}) - J(^{13}\mathrm{C,H})(\mathrm{CH_3X}) \tag{3a}$$

$$^{p}\Delta J(^{13}\mathrm{C,H}) = J^*(^{13}\mathrm{C,H})(\mathrm{CHD_2X}) - J(^{13}\mathrm{C,H})(\mathrm{CH_2DX}) \tag{3b}$$

$$^{p}\Delta J(^{13}\mathrm{C,H}) = J^*(^{13}\mathrm{C,H})(\mathrm{CD_3X}) - J(^{13}\mathrm{C,H})(\mathrm{CHD_2X}) \tag{3c}$$

Assuming the additivity of successive H/D replacements, one should obtain equal values for all three types of difference. However, we found very small but significant variations in the values of $^{p}\Delta J(^{13}$C,H) as defined in Eqns (3a)–(3c). For example, for CH_3I and its isotopomers these three values are −0.244, −0.266, −0.290(±0.024) Hz, respectively; for CH_3Br they are −0.291, −0.315 and −0.333(±0.011) Hz, respectively. As can be seen, the differences are nearly constant and are equal to about −0.02 Hz for each successive replacement of a proton by a deuterium. Although of interest, we ignore for the moment these non-additivity effects and limit ourselves to the differences of coupling constants due the substitution of the first deuterium atom in the molecule [i.e. from Eqn (3a)].

The final data on the primary and secondary isotope effects are represented in Fig. 1 and summarized in Table 3. It can be seen that the primary effects depend almost linearly on the number of halogens. We can represent the dependence of $^{p}\Delta J(^{13}$C,H) on the number of deuteriums n by the linear equation

$$^{p}\Delta J(^{13}\mathrm{C,H}) = a + bn \tag{4}$$

where the values of the a/b pairs are −0.061/−0.294, −0.075/−0.21 and −0.087/−0.142 for Cl, Br and I, respectively, with correlation coefficients not worse than 0.995, with all values in Hz. Hence the a coefficients are close to the value of the primary isotope effect (−0.07 Hz) measured for methane[2] whereas the b coefficients demonstrate an decreasing effect in the series Cl, Br, I. For secondary effects the dependence on the number of halogen atoms seems to be non-linear. It is interesting that the magnitudes of primary isotope effects increase with increase in the number of halogens whereas the secondary effects decrease, falling to −0.144 Hz for CH_2I_2. The dependence of the primary isotope effect on the nature of the substituents can be followed by the series of haloforms. The magnitude of $^{p}\Delta J(^{13}$C,H) reaches its maximum (−1.65 Hz) for fluorine and falls to −0.45 Hz for iodine. This is in good correspondence with the electronegativity of halogen atoms. For secondary effects the influence of the substituent increases in the series Cl, Br, I and seems to be controlled mostly by steric factors.

The secondary isotope effect on the ^{13}C,^{19}F coupling constant in CHF_3 has been measured for the first time. It is defined as

$$\Delta J = J(^{13}\mathrm{C},^{19}\mathrm{F})(\mathrm{CDF_3}) - J(^{13}\mathrm{C},^{19}\mathrm{F})(\mathrm{CHF_3}) \tag{5}$$

and, assuming that the direct ^{13}C,^{19}F coupling constant is negative, it will be positive and equal to 1.56 Hz. This

Table 3. Primary and secondary isotope effects on ^{13}C,H coupling constants due to the substitution by a single deuterium atom in halomethanes $CH_{4-n}X_n$

No. of halogens (n)	$^{p}\Delta J(^{13}$C,H) (Hz)			$^{s}\Delta J(^{13}$C,H) (Hz)	
	1	2	3	1	2
Cl	Not measured	−0.60 ± 0.02	−0.92 ± 0.13	Not measured	−0.25 ± 0.01
Br	−0.29 ± 0.01	−0.504 ± 0.007	−0.70 ± 0.07	−0.306 ± 0.003	−0.192 ± 0.002
I	−0.25 ± 0.02	−0.38 ± 0.02	−0.45 ± 0.15	−0.285 ± 0.006	−0.144 ± 0.006

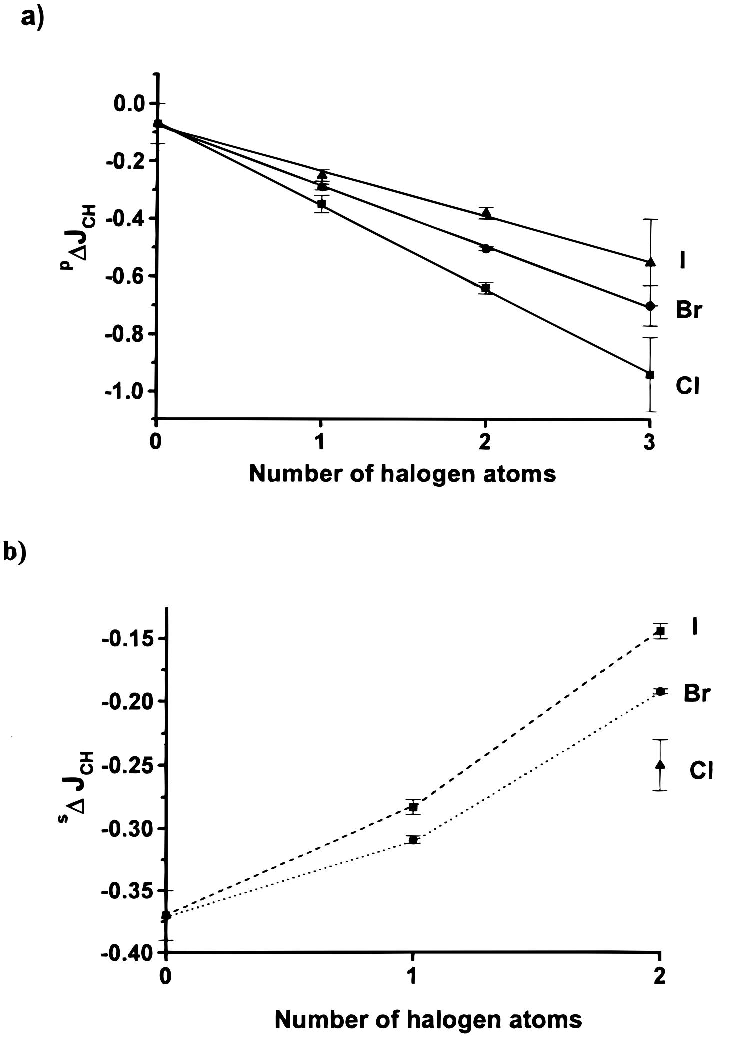

Figure 1. Dependences of (a) primary and (b) secondary deuterium isotope effects on $J(^{13}C,H)$ in the halomethanes on the number of halogen atoms. The single point on the ordinate in each case refers to methane.[2]

contrasts with secondary isotope effects on $J(^{13}C,H)$, which are usually negative.

The ^{13}C (D/H) isotope shift in fluoroform is 236 ppb. This value can be compared with that for the value for methane, for which the corresponding isotope shift is 200.3 ppb.[15] Assuming an additive influence of fluorine atoms on isotope shifts (as was suggested previously[8]), one can estimate the incremental parameter for one fluorine atom to be *ca.* −13 ppb, which is intermediate between those of the nitro group (*ca.* −30 ppb) and the chlorine atom (*ca.* 0 ppb) as substituents.

Calculations

Isotope effects on coupling constants can be regarded as arising from the very slight changes in molecular geometry which occur upon isotopic substitution.[1,16] To calculate these changes one requires a knowledge of the molecular force field including both harmonic and cubic anharmonic coefficients. Of the molecules listed in Table 1 it is only CH_3Br and CH_3I for which the required data are available, the relevant constants having been calculated *ab initio* at the SCF level by Schneider and Thiel.[17] We shall use their results to deduce molecular constants for these two molecules.

For a methyl halide molecule, CH_3X, we expand the coupling constant $J(^{13}C,H)$ as a power series in internal displacement coordinates. Thus for small displacements

$$\begin{aligned} J(^{13}\mathrm{C,H}) = {} & J_e + J_r r_1 + J_s(r_2 + r_3) + J_R R \\ & + J_\alpha(\alpha_{12} + \alpha_{13} + \alpha_{23}) \\ & + J_\beta(\beta_{12} + \beta_{13} + \beta_{23}) + (\tfrac{1}{2})J_{\alpha\alpha}(\alpha_{12}^2 + \alpha_{13}^2 + \alpha_{14}^2) \end{aligned} \quad (6)$$

where all first-order terms and only one of the second-order terms are shown and the angle terms have been simplified. J_e is the value of $J(^{13}C,H)$ at equilibrium geometry, r_1 is the displacement from equilibrium of the C—H_1 bond which contains the coupled nuclei of interest, r_2, r_3 and R are the displacements of the other two C—H bonds and the C—X bond, respectively, α_{12}, α_{13} and α_{23} are the displacements of the H—C—H angles from equilibrium and β_{12}, β_{13} and β_{23} are those of the H—C—X angles. The coefficients J_r, J_s, J_R, $J_\beta(= -J_\alpha)$, $J_{\alpha\alpha}$, etc., are molecular constants which are independent of molecular geometry and isotopic substitution assuming the Born–Oppenheimer approximation, which we adopt here.

Table 4. Thermal averages at 300 K of the bond extensions in methyl bromide and methyl iodide and their deuterated isotopomers[a]

Isotopomer	$\langle r_H \rangle$	$\langle r_D \rangle$	$\langle R \rangle$
$^{13}CH_3{}^{79}Br$	0.019 045	—	0.009 232
$^{13}CH_2D^{79}Br$	0.019 123	0.013 851	0.009 107
$^{13}CHD_2{}^{79}Br$	0.019 181	0.013 926	0.008 921
$^{13}CD_3{}^{79}Br$	—	0.013 982	0.008 776
$^{13}CH_3{}^{129}I$	0.018 925	—	0.009 537
$^{13}CH_2D^{129}I$	0.018 986	0.013 781	0.009 422
$^{13}CHD_2{}^{129}I$	0.019 038	0.013 850	0.009 235
$^{13}CD_3{}^{129}I$	—	0.013 899	0.009 099

[a] All results are in Å and were calculated from the force field of Schneider and Thiel.[17]

A recent *ab initio* study of the methane molecule[3b] has shown that the dominant terms contributing to $J(^{13}C,H)$, in addition to J_e, are those involving $J_s(= J_R)$ and $J_{\alpha\alpha}$. All other terms including, surprisingly, those involving J_r, made very small contributions. For methane it was found that $J_r = 12.84$ Hz Å^{-1}, J_s $(= J_R) = 58.23$ Hz Å^{-1} and $J_{\alpha\alpha} = 46.10$ Hz, with angles in radians. We find that the present data for CH_3Br and CH_3I cannot be fitted to Eqn (6) if the parameters J_e, J_s, J_r and $J_{\alpha\alpha}$ are used. Indeed, we cannot fit the data at all if $J_{\alpha\alpha}$ is included. A reasonable fit, however, can be obtained using the parameters J_e, J_r and $J_s = J_R$. Accordingly, we have the following three equations for $J(^{13}C,H)$:

$$CH_3X: \quad \langle J(^{13}C,H) \rangle = J_e + J_r \langle r_H \rangle + J_s(2\langle r_H \rangle + \langle R \rangle) \qquad (7)$$

$$CH_2DX: \quad \langle J(^{13}C,H) \rangle = J_e + J_r \langle r_H \rangle + J_s(\langle r_H \rangle + \langle r_D \rangle + \langle R \rangle) \qquad (8)$$

$$CHD_2X: \quad \langle J(^{13}C,H) \rangle = J_e + J_r \langle r_H \rangle + J_s(\langle 2r_D \rangle + \langle R \rangle) \qquad (9)$$

and the following three equations for $J^*(C,H)$:

$$CH_2DX: \quad \langle J^*(^{13}C,H) \rangle = J_e + J_r \langle r_D \rangle + J_s(2\langle r_H \rangle + \langle R \rangle) \qquad (10)$$

$$CHD_2X: \quad \langle J^*(^{13}C,H) \rangle = J_e + J_r \langle r_D \rangle + J_s(\langle r_H \rangle + \langle r_D \rangle + \langle R \rangle) \qquad (11)$$

$$CD_3X: \quad \langle J^*(^{13}C,H) \rangle = J_e + J_r \langle r_D \rangle + J_s(2\langle r_D \rangle + \langle R \rangle) \qquad (12)$$

The angular brackets in Eqns (7)–(12) denote a thermal average of the appropriate quantity in the corresponding isotopomer.

Values of the required thermal averages at 300 K calculated from the force field of Schneider and Thiel[17] are given in Table 4. Fitting the data leads to the following results:

$$CH_3Br: \quad J_e = 147.56 \text{ Hz}, \quad J_r = 64.9 \text{ Hz Å}^{-1} \text{ and } J_s = 56.4 \text{ Hz Å}^{-1}$$

$$CH_3I: \quad J_e = 147.36 \text{ Hz}, \quad J_r = 56.4 \text{ Hz Å}^{-1} \text{ and } J_s = 53.8 \text{ Hz Å}^{-1}$$

The fitting was done by calculating J_e, J_r and J_s from the three most accurately measured coupling constants —CH_2DBr, CHD_2Br and CD_3Br for methyl bromide and CH_3I, CH_2DI and CD_3I for methyl iodide with one value of J(C,D) used in each case. The recalculated values of the coupling constants are compared with the original experimental values in Table 5.

The values of J_e given above show that the effect of nuclear motion is to increase the coupling by about 3–4 Hz. The J_s values are very similar to the values for methane, as one might expect. However, it is puzzling that J_r appears to be important for the methyl halides but not for methane whereas the $J_{\alpha\alpha}$ terms are important for methane but not for the methyl halides. One factor to bear in mind in the present work is that the force field was calculated at the SCF level and it is well established that electron correlation affects force constants. We also ignored solvent effects, although one expects isotope effects to be very little affected by solvents, especially for spin–spin coupling.

Acknowledgements

The authors thank N. S. Golubev and S. N. Smirnov (St Petersburg University) for the measurements on fluoroform. N.M.S. is grateful to the Royal Society for a Visiting Fellowship. N.M.S. and N.D.S thank the Russian Foundation for Fundamental Research for support under grant No. 97-03-33574.

Table 5. Comparison of observed and calculated values of J(^{13}C,H) and J*(^{13}C,H)[a] in isotopomers of methyl bromide and methyl iodide

Isotopomer	J_{obs} (Hz)	J_{calc} (Hz)	Isotopomer	J_{obs} (Hz)	J_{calc} (Hz)
CH_3Br	151.484	151.46	CH_3I	150.984	150.97
CH_2DBr	151.175	151.17	CH_2DI	150.706	150.70
CHD_2Br	150.872	150.88	CHD_2I	150.420	150.42
CH_2DBr	151.193[a]	151.13	CH_2DI	150.74[a]	150.69
CHD_2Br	150.86[a]	150.83	CHD_2I	150.44[a]	150.41
CD_3Br	150.54[a]	150.54	CD_3I	150.13[a]	150.13

[a] $J^*(^{13}C,H) = (\gamma_H/\gamma_D)J(^{13}C,D)$.

REFERENCES

1. N. M. Sergeyev, in *NMR—Basic Principles and Progress*, edited by P. Diehl, E. Fluck, H. Günther, R. Kosfeld and J. Seelig, Vol. 22, p. 31. Springer, Berlin (1990).
2. B. Bennett, W. T. Raynes and C. W. Anderson, *Spectrochim. Acta, Part A* **45**, 821 (1989).
3. (a) W. T. Raynes, J. Geertsen and J. Oddershede, *Chem. Phys. Lett.* **197**, 516 (1992); (b) R. D. Wigglesworth, W. T. Raynes, S. P. A. Sauer and J. Oddershede, *Mol. Phys.* **92**, 77 (1997).
4. I. F. Leshcheva, V. N. Torocheshnikov, N. M. Sergeyev, V. A. Chertkov and V. N. Khlopkov, *J. Magn. Reson.* **94**, 9 (1991).
5. J. R. Everett, *Org. Magn. Reson.* **19**, 169 (1982).
6. Yu. A. Strelenko, V. N. Torocheshnikov and N. M. Sergeyev, *J. Magn. Reson.* **89**, 123 (1991).
7. N. M. Sergeyev, N. D. Sergeyeva and W. T. Raynes, *Magn. Reson. Chem.* **32**, 381 (1994).
8. N. M. Sergeyev, N. D. Sergeyeva and W. T. Raynes, *J. Chem. Soc., Chem. Commun.* 485 (1994).
9. N. M. Sergeyev, N. D. Sergeyeva and W. T. Raynes, *Chem. Phys. Lett.* **221**, 385 (1994).
10. N. M. Sergeyev, P. Sandor, N. D. Sergeyeva and W. T. Raynes, *J. Magn. Reson., Ser. A* **115**, 174 (1995).
11. R. Aydin and H. Günther, *Magn. Reson. Chem.* **28**, 448 (1990).
12. C. J. Creswell and A. L. Allred, *J. Am. Chem. Soc.* **84**, 3966 (1962).
13. N. S. Golubev, S. N. Smirnov and N. M. Sergeyev, in *Abstracts of the 1995 NMR Meeting*, p. 33. Institute of Bioorganic Chemistry, Moscow (1995).
14. P. E. Hansen, in *Progress of NMR Spectroscopy*, edited by J. W. Emsley, J. Feeney and L. H. Sutcliffe, Vol. 14, p. 175. Pergamon Press, Oxford (1981).
15. B. Bennett and W. T. Raynes, *Spectrochim. Acta, Part A* **45**, 1267 (1991).
16. C. J. Jameson and H. J. Osten, *J. Am. Chem. Soc.* **108**, 2497 (1986).
17. W. Schneider and W. Thiel, *Chem. Phys.* **159**, 49 (1992).