Nuclear magnetic shielding in the acetylene isotopomers calculated from correlated shielding surfaces

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Ab initio, symmetry-coordinate and internal valence coordinate carbon and hydrogen nuclear shielding surfaces for the acetylene molecule are presented. Calculations were performed at the correlated level of theory using gauge-including atomic orbitals and a large basis set. The shielding was calculated at equilibrium and at 34 distinct geometries corresponding to 53 distinct sites for each nucleus. The results were fitted to fourth order in Taylor series expansions and are presented to second order in the coordinates. The carbon-13 shielding is sensitive to all geometrical parameters and displays some unexpected features; most significantly, the shielding at a carbon nucleus (C_1, say) is six times more sensitive to change of the $C_1C_2H_2$ angle than it is to change of the $H_1C_1C_2$ angle. In addition, for small changes, $\sigma(C_1)$ is more sensitive to the C_2H_2 bond length than it is to the C_1H_1 bond length. These, and other, examples of ''unexpected differential sensitivity'' are discussed. The proton shielding surface is much more as expected with $\sigma(H_1)$ being most sensitive to the C_1H_1 bond length, less so to the CC bond length and hardly at all to the C_2H_2 bond length. The surfaces have been averaged over a very accurate force field to give values of $\sigma(C)$, $\sigma(H)$, and $\sigma(D)$ for the ten isotopomers containing all possible combinations of ^{12}C, ^{13}C, ^1H, and ^2H nuclei at 0 K and at a number of selected temperatures in the range accessible to experiment. For the carbon shielding the dominant nuclear motion contribution comes from the bending at ''the other'' carbon atom with the combined stretching contributions being only 20% of those from bending. For the proton shielding it is the stretching of the CH bond containing the proton of interest which provides the major nuclear motion contribution. For $\sigma(C)$ in $H^{13}C^{13}CH$ at 300 K our best result is 117.59 ppm which is very close to the experimental value of 116.9 (±0.9) ppm. For $\sigma(H)$ in $H^{13}C^{13}CH$ at 300 K we obtain 29.511 ppm which is also in very close agreement with the experimental value of 29.277 (±0.001) ppm. Calculated values are also very close to recent, highly accurate carbon and proton isotope shifts in the ten isotopomers; carbon isotope shifts differ by no more than 10% from the measured values and proton isotope shifts are generally in even better agreement than this. The observed anomaly whereby the ^{13}C isotope shift in $H^{13}C^{12}CD$ is greater than that in $D^{13}C^{12}CH$ both with respect to $H^{13}C^{12}CH$ is explained in terms of the bending contribution at ''the other'' carbon. The observed nonadditivity of deuterium isotope effects on the carbon shielding can be traced to a cross term involving second order bending. © *2000 American Institute of Physics.* [S0021-9606(00)30401-9]

I. INTRODUCTION

The accuracy of present-day *ab initio* calculations of the magnetic shielding of nuclei in small polyatomic molecules and the long-standing accuracy in their measurement requires that to achieve close agreement between the two it is insufficient merely to calculate the shielding at equilibrium geometry. Instead, one must perform calculations over a range of geometries near to equilibrium and from the results construct a nuclear shielding surface. Averaging jointly over this surface and the molecular force field then leads to a thermal average which can be compared with the experimental result obtained by measurements in the low density gas at the temperature of interest followed by extrapolation to zero density. Since the different isotopomers of a molecule produce different thermal averages at any temperature, nuclear shielding surfaces can also be used to explain (and predict) the signs and magnitudes of isotope shifts—quantities often measurable to high precision in NMR experiments.

Early calculations on polyatomic shielding surfaces produced results for both nuclei in water,[1] the carbon nucleus in methane,[2] and the nitrogen and phosphorus nuclei in

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ammonia[3] and phosphine,[4] respectively. It is now a routine procedure to include the effects of electron correlation and correlated shielding surfaces fully to second order are presently available for the nuclei in water,[5–7] ammonia,[5,8] phosphine,[5] and the carbon nucleus of methane.[5] Recently, noncorrelated shielding surface coefficients have been obtained for the nuclei in OCS,[9] CSe$_2$,[10] and the methyl halide molecules CH$_3$X(X=F, Cl, Br).[11]

In the current paper we present the first nuclear shielding surfaces for the acetylene molecule. These correlated surfaces are then averaged over an *ab initio* force field to give nuclear shielding constants and isotope shifts for the carbon-13 nuclei, protons and deuterons in the ten acetylene isotopomers containing these nuclei. The results are compared with experimental values determined recently. In particular, the carbon-13 and proton isotope shifts have been determined to great accuracy and precision in experimental work carried out by Chertkov[12] as part of a project (see Acknowledgment) of which the present work forms part. As will be seen excellent agreement is obtained between experimental and calculated results. In a later paper we shall present results for the four spin–spin coupling surfaces of acetylene and compare the calculated effects of isotopic substitution with those observed experimentally.

II. FORM OF THE SURFACES

Assuming the Born–Oppenheimer approximation the nuclear shielding surfaces for both species of nuclei in acetylene can be written

$$\sigma = \sigma_e + \sigma_r r_1 + \sigma_s r_2 + \sigma_R R + \sigma_{rr} r_1^2 + \sigma_{ss} r_2^2 + \sigma_{RR} R^2$$
$$+ \sigma_{rs} r_1 r_2 + \sigma_{rR} r_1 R + \sigma_{sR} r_2 R + \sigma_{\alpha\alpha}(\alpha_{1a}^2 + \alpha_{1b}^2)$$
$$+ \sigma_{\beta\beta}(\alpha_{2a}^2 + \alpha_{2b}^2) + \sigma_{\alpha\beta}(\alpha_{1a}\alpha_{2a} + \alpha_{1b}\alpha_{2b}) \quad (1)$$

to second order in the displacement coordinates. These are, r_1, an extension/contraction of the C$_1$–H$_1$ bond which contains the proton and carbon nucleus of interest, r_2 an extension/contraction of the C$_2$–H$_2$ bond, R an extension/contraction of the C≡C bond, α_{1a} and α_{2a} the changes in the interbond angles H$_1$C$_1$C$_2$ and C$_1$C$_2$H$_2$, respectively, in a vertical plane containing the acetylene molecule, which is imagined to lie along a horizontal line, and α_{1b} and α_{2b}, the changes in these same angles, respectively, in the horizontal plane containing the molecule.

The coefficients in the above equation are independent of geometry and are either derivatives with respect to the displacement coordinates, or are simply related to such derivatives.

III. COMPUTATIONAL ASPECTS

All shielding calculations were carried out with gauge-including atomic orbitals at the multiconfiguration self-consistent field (MCSCF) level using the DALTON program.[13,14] The full theory involved has been given previously[7,14] and, therefore, will not be repeated here. The chosen equilibrium geometry was that of Bramley *et al.*,[15] viz., r_e(CC)=1.20241 Å and r_e(CH)=1.0625 Å. The basis set was developed in the process of carrying out the present

TABLE I. Calculation of the carbon-13 shielding at equilibrium geometry in the acetylene molecule with different types of RAS-MCSCF wave functions. It is estimated that the true value of σ_e(C) is close to 121 ppm (see text).

Active space[a]	Allowed excitations from RAS I to RAS III			
Orbitals in RAS III	SD	SDT	SDTQ	All CAS[b]
4–$5\ \sigma_g^+, 3$–$4\ \sigma_u^+,$ $2\ \pi_u, 1\ \pi_g$	126.266	126.315	128.728	128.885[c]
4–$5\ \sigma_g^+, 3$–$4\ \sigma_u^+,$ $2\ \pi_u, 1\ \pi_g, 1\ \delta_g$	124.236	123.999	126.365	126.476[d]
4–$6\ \sigma_g^+, 3$–$5\ \sigma_u^+,$ 2–$3\ \pi_u, 1$–$2\ \pi_g,$ $1\ \delta_g, 1\ \delta_u$	123.134	123.609	126.093	
4–$8\ \sigma_g^+, 3$–$7\ \sigma_u^+,$ 2–$5\ \pi_u, 1$–$3\ \pi_g,$ 1–$2\ \delta_g, 1\ \delta_u$	121.834			
4–$11\ \sigma_g^+, 3$–$9\ \sigma_u^+,$ 2–$8\ \pi_u, 1$–$6\ \pi_g, 1$–$3\ \delta_g,$ 1–$3\ \delta_u$	121.633			

[a]RAS I: 2–$3\ \sigma_g^+, 2\ \sigma_u^+, 1\pi_u$.
[b]Allowing all possible excitations from RAS I to RAS III gives a CAS wave function with all orbitals in RAS I and RAS III included in the active space.
[c]Subsequently referred to as CAS A.
[d]Subsequently referred to as CAS B.

calculations and the concurrent calculations on the four spin–spin coupling surfaces. The final basis set started from the $13s7p$ carbon and the $7s$ hydrogen basis set of van Duijneveldt,[16] from which the most diffuse s-type function on carbon ($\zeta_s = 0.099090$) was removed. The carbon basis set was augmented with three s-type functions ($\zeta_s = 339685, 2282300, 15334100$), three sets of d-type functions ($\zeta_d = 1.848, 0.649, 0.228$) and one set of f-type functions ($\zeta_f = 0.761$), whereas the hydrogen basis set was augmented with four s-type functions ($\zeta_s = 1258.122088, 8392.099358, 55978.13782, 373393.090348$), two sets of p-type functions ($\zeta_p = 1.407, 0.388$) and one set of d-type functions ($\zeta_d = 1.057$). The final basis set therefore consists of $15s7p3d1f$ Gaussian functions on carbon and $11s2p1d$ Gaussian functions on hydrogen.

At the time when our surfaces were being calculated there existed no accepted literature values of the carbon and proton shielding of acetylene at equilibrium geometry. In our calculation of the surfaces a MCSCF wave function of the complete active space (CAS) type was employed. The 2–$5\sigma_g^+$, 2–$4\sigma_u^+$, 1–$2\pi_u$, and $1\pi_g$ molecular orbitals were included in the active space, whereas the $1\sigma_g^+$ and $1\sigma_u^+$ molecular orbitals (the two carbon $1s$ core orbitals) were kept doubly occupied. This will be subsequently referred to as CAS A; it gave at equilibrium σ_e(C)=128.885 ppm.

It subsequently emerged from a combination of our nuclear motion correction of 4.1 ppm and experimental data, that the correct σ_e(C) is near to 121 ppm (see below). To approach this more closely we have performed several restricted active space (RAS) calculations with larger active spaces. In all RAS calculations the RAS I space contained the occupied valence orbitals of the Hartree–Fock wave function (2–$3\sigma_g^+$, $2\sigma_u^+$, and $1\pi_u$), the RAS II space was kept empty and the RAS III space consisted of the virtual orbitals given in Table I. All single and doubles (SD), or

single doubles and triples (SDT) or single, doubles, triples, and quadruples (SDTQ) excitations from RAS I to RAS III were then allowed. This corresponds to a restricted SD/SDT/SDTQ-CI with optimization of the orbitals. Allowing for all possible excitations gives the CAS wave function with the same active orbitals. One can therefore consider the different RAS wave functions as approximations to the corresponding CAS wave function. We found a rather slow convergence towards the correct $\sigma_e(C)$ value (see Table I). It is also noticeable that quadruple excitations have to be included in the RAS calculations in order to reproduce the corresponding CAS results and that the CAS results are ~2.5 ppm higher and thus further away from the correct value than the SD-RAS results for a given active space. This implies that although the result of our largest SD-RAS calculation (121.633 ppm) is within 1 ppm from the correct value (121.0 ppm), the corresponding CAS result can be estimated to be about 124 ppm which is thus in worse agreement. Our best CAS result is 126.476 ppm at equilibrium; the active space used for this is referred to as CAS B.

Our experience from the previous study of the shielding surfaces in water[7] is that contrary to the absolute value, the derivatives of the shielding constants are only slightly influenced by the size of the active space. We expect therefore that for acetylene the derivatives of the shielding constants are also more accurate than the absolute values.

IV. CALCULATIONS AT EQUILIBRIUM GEOMETRY

Calculated values of $\sigma_e(C)$ and $\sigma_e(H)$ obtained by a variety of authors[17-35] are listed in Table II. Noncorrelated results (Refs. 17–27) are given in the upper part of the table; correlated results are given in the lower part of the table. The twenty-three citations in the table cover the period from 1980 with 15 of them referring to work of the last 5 years. There is fairly good agreement for $\sigma_e(H)$ with values ranging by ±3% around a value near to 30.0 ppm, whereas for $\sigma_e(C)$ there is a much wider spread of ±10% around a value near to 122 ppm.

It is first desirable to acquire equilibrium values obtained as independently as possible of any of the calculated values. For the carbon shielding there is a published[36] experimental value of 117.2 (±1.2) ppm from the zero pressure limit at 300 K. This can be adjusted by using an improved carbon-13 scale[37] to 116.8 (±0.9) ppm. However, we shall start with a more recent experimental value[38] of 116.88 (±0.9) ppm obtained for the low density (0.9 atm) isotopomer $H^{13}C^{13}CH$ at 300 K based on the shielding scale of Ref. 37. The error of (±0.9) ppm arises almost wholly from the error in the absolute ^{13}C-shielding of carbon monoxide. The nuclear motion correction for this isotopomer at 300 K calculated from the shielding derivatives of the present work is 4.083 ppm. If we make a generous allowance of ±0.4 ppm for the error in this quantity than $\sigma_e(C)$ is estimated to be 121.0 (±1.0) ppm.

The proton shielding in $H^{13}C^{13}CH$ has been found from experimental measurement[38] to be 29.277 (±0.001) ppm at the zero pressure limit at 300 K. Our nuclear motion correction for this isotopomer at 300 K is 0.843 ppm. Making a generous allowance of ±0.08 for the error in this quantity we estimate $\sigma_e(H)$ to be 30.12 (±0.08) ppm. It is a curious fact

TABLE II. Calculated values of the carbon and proton shielding in the acetylene molecule at equilibrium geometry. In the upper part of the table (Refs. 17–27) are given noncorrelated results in order of the date of publication. In the lower part of the table (Refs. 28 to the end) are given correlated results in order of the date of publication. All results are in ppm. The best current values of these quantities estimated from a combination of experimental and theoretical data are $\sigma_e(C)=121.0$ ppm and $\sigma_e(H)=30.12$ ppm (see text).

	$\sigma(C)$	$\sigma(H)$	Method
Höller and Lischka (Ref. 17)	119.1	29.07	CHF
Schindler and Kutzelnigg (Ref. 18)	117.4	29.02	IGLO
McMichael Rohlfing *et al.* (Ref. 19)	128.6[a]	29.4[b]	CHF
Lazzeretti *et al.* (Ref. 20)	116.552	29.86	CHF
Hansen and Bouman (Ref. 21)	122		LORG
Chestnut and Foley (Ref. 22)	118.3	30.89	CHF
Craw and Nascimento (Ref. 23)	112.66		CHF
Grayson and Raynes (Ref. 24 and 25)	119.77	30.76	CHF
Bohmann and Farrar (Ref. 26)	120.3		CHF
Jackowski *et al.* (Ref. 27)	122.2[c]		CHF
Sauer *et al.* (Refs. 28 and 29)	116.09	30.04	SOPPA
Rizzo *et al.* (Ref. 30)	129.1	30.5	MCSCF
Gauss and Stanton (Ref. 31)	121.8		CCSD
Cybulski and Bishop (Ref. 32)	122.682	30.623	L-CCD
Chestnut (Ref. 33)		29.87	MP2
Kaski *et al.* (Ref. 34)	126.1	30.28	MCSCF
Pecul and Sadlej (Ref. 35)	132.12	30.68	MCSCF
This work	128.885	30.448	CAS-MCSCF (CAS A)
This work	126.476	30.346	CAS-MCSCF (CAS B)
This work	121.633	30.235	RAS-MCSCF

[a]Obtained using $\sigma(C)$ in $CH_4=195.1$ ppm from A. K. Jameson and C. J. Jameson, J. Chem. Phys. **134**, 461 (1987).
[b]Obtained using $\sigma(H)$ in $CH_4=30.611$ ppm from W. T. Raynes, in *Specialist Periodical Report: NMR* (The Chemical Society, London) 1978, Vol. 7, p. 1.
[c]Obtained using $\sigma(C)$ in $Si(CH_3)_4=188.1$ ppm from A. K. Jameson and C. J. Jameson, *loc.cit.*

that the proton shielding in such very different molecules as water and methane are both so very similar to this, viz., 30.052(15) and 30.611(24), respectively.[39]

Comparing the above results for $\sigma_e(C)$ with those calculated (see Table II) it is seen that, on the whole, the noncorrelated results are too low whilst the correlated results are, with one exception, all higher than the estimated $\sigma_e(C)$. On the other hand for $\sigma_e(H)$ the correlated results are much closer to the estimated value unlike the noncorrelated results which are somewhat more widespread. The principal correlated calculations—ours and Refs. 30–32, 34—differ little in the choice of basis set (approximately 60 basis orbitals on each C and 15 on each H) and in the chosen equilibrium geometry [varying from 1.0598 to 1.0625 Å for $r_e(CH)$ and from 1.20241 to 1.2092 Å for $r_e(CC)$].

We have used our largest SD-RAS function to calculate the components of the shielding tensors at equilibrium geometry; they are $\sigma_\parallel(C)=279.194$ ppm, $\sigma_\perp(C)=42.8553$ ppm, $\sigma_\parallel(H)=40.723$ ppm, and $\sigma_\perp(H)=24.991$ ppm giving a carbon shielding anisotropy of 236.340 ppm and a proton anisotropy of 15.732 ppm. These values are very close to the

calculated values 229.7 ppm and 15.86 ppm, respectively, obtained by Kaski et al.[34] and compare well with four experimental values for the carbon shielding anisotropy: 240 (± 6) ppm,[40] 245 (± 20) ppm,[41] 253 (± 17) ppm,[42] and 269 (± 11) ppm.[43]

V. THE SHIELDING SURFACES

All calculations were carried out using the set of seven symmetry coordinates defined by Strey and Mills[44] (see also Martin et al.[45]). These coordinates are

$$S_1 = \frac{1}{\sqrt{2}}(r_1 + r_2), \tag{2}$$

$$S_2 = R, \tag{3}$$

$$S_3 = \frac{1}{\sqrt{2}}(r_1 - r_2), \tag{4}$$

$$S_{4a} = \frac{1}{\sqrt{2}}(\alpha_{1a} - \alpha_{2a}), \tag{5}$$

$$S_{4b} = \frac{1}{\sqrt{2}}(\alpha_{1b} - \alpha_{2b}), \tag{6}$$

$$S_{5a} = \frac{1}{\sqrt{2}}(\alpha_{1a} + \alpha_{2a}), \tag{7}$$

$$S_{5b} = \frac{1}{\sqrt{2}}(\alpha_{1b} + \alpha_{2b}). \tag{8}$$

In terms of these coordinates each of the two shielding surfaces can be written

$$\sigma = \sigma_e + \sigma_1 S_1 + \sigma_2 S_2 + \sigma_3 S_3 + \tfrac{1}{2}\sigma_{11} S_1^2 + \tfrac{1}{2}\sigma_{22} S_2^2 + \tfrac{1}{2}\sigma_{33} S_3^2$$
$$+ \sigma_{12} S_1 S_2 + \sigma_{13} S_1 S_3 + \sigma_{23} S_2 S_3 + \sigma_{44}(S_{4a}^2 + S_{4b}^2)$$
$$+ \sigma_{55}(S_{5a}^2 + S_{5b}^2) + \sigma_{45}(S_{4a} S_{5a} + S_{4b} S_{5b}). \tag{9}$$

Nuclear shielding was calculated at equilibrium and at 34 distinct geometries corresponding in total to 53 distinct sites for each nucleus. Four geometries were chosen for each of the variations of S_1 and S_2. Two geometries were chosen for each of the variations of S_3, S_{4a}, and S_{5a} since for S_3 each geometry yields two distinct shielding constants for each nucleus whilst for S_{4a} and S_{5a} there are only second-order terms to consider. For the joint S_1/S_2 variation eight geometries were chosen and, since each variation yields two values of each constant, only four distinct geometries were chosen when varying each of the pairs S_1/S_3, S_2/S_3, and S_{4a}/S_{5a}. Displacements from equilibrium covered the ranges ± 0.17 Å for the C–H bond lengths, ± 0.04 Å for the C≡C bond length and ± 0.283 rad ($\pm 16°$) for the bond angles.

The resulting set of shielding constants was fitted to Eq. (9) to obtain the symmetry coordinate shielding coefficients and these were then converted to the internal coordinate symmetry coordinates listed in Table III. In the fitting, the surface coefficients were obtained to fourth order in each

TABLE III. Coefficients of the carbon and proton internal valence coordinate shielding surfaces of the acetylene molecule as defined in Eq. (1). Angle derivatives are in terms of radians.

	$\sigma(C)$	$\sigma(H)$
σ_r/ppm Å^{-1}	-10.569	-32.638
σ_R/ppm Å^{-1}	-57.893	-4.519
σ_s/ppm Å^{-1}	12.008	-0.192
σ_{rr}/ppm Å^{-2}	-48.030	36.146
σ_{RR}/ppm Å^{-2}	-97.073	1.500
σ_{ss}/ppm Å^{-2}	20.718	0.067
σ_{rR}/ppm Å^{-2}	54.067	4.248
σ_{sR}/ppm Å^{-2}	-25.601	-0.223
σ_{rs}/ppm Å^{-2}	-0.252	0.082
$\sigma_{\alpha\alpha}$/ppm	-8.449	-4.052
$\sigma_{\beta\beta}$/ppm	-51.040	-1.170
$\sigma_{\alpha\beta}$/ppm	-26.801	-4.632

single variable so as to determine the correct coefficients to second order for that variable. Cross-coefficients were obtained by methods used in previous work.[7] Sections through the shielding surfaces are shown in Figs. 1–3. Figure 1 shows the change in $\sigma(C_1)$ with respect to equilibrium for variations of (a) the C_1H_1 bond length, (b) the CC bond length, and (c) the C_2H_2 bond length. It is not, perhaps, surprising that the carbon shielding is far more sensitive to the
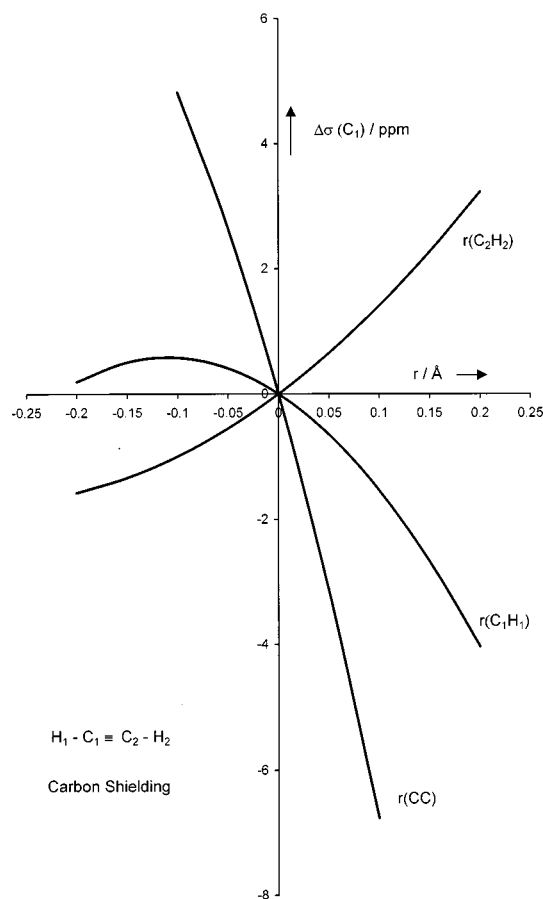

FIG. 1. Bond length dependencies of the carbon shielding in acetylene. The three curves show how the shielding of C_1 changes with separate variations of the C_1H_1 bond length, the CC bond length, and the C_2H_2 bond length.
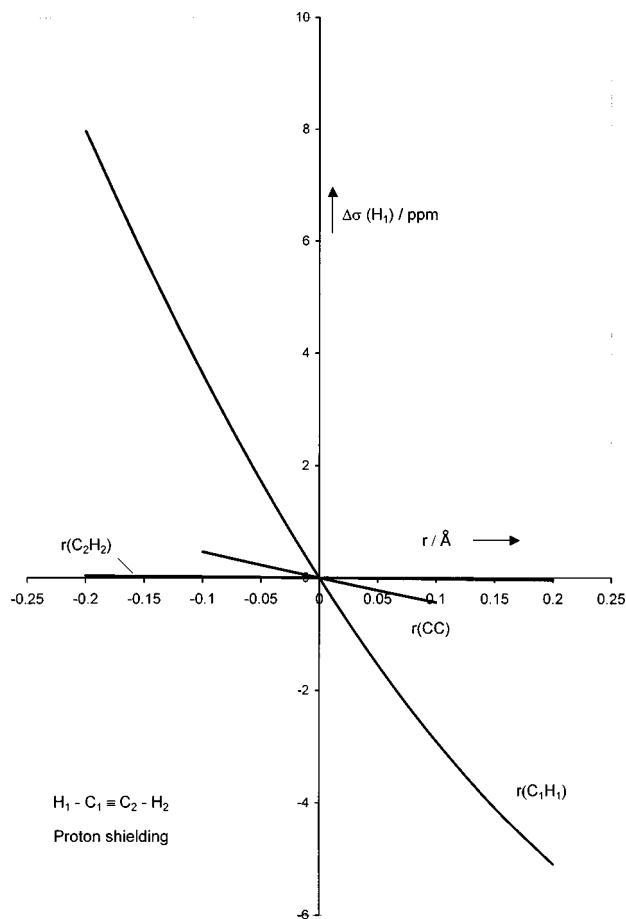
FIG. 2. Bond length dependencies of the proton shielding in acetylene. The three curves show how the shielding of proton 1 changes with separate variations of the C_1H_1 bond length, the CC bond length and the C_2H_2 bond length. In the last case the curve straddles the horizontal axis.
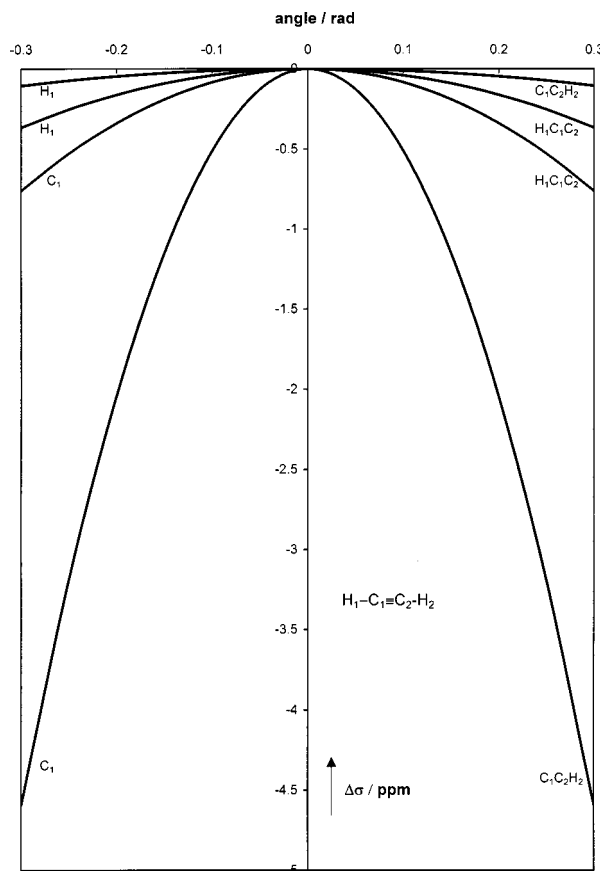

FIG. 3. Bond angle dependences of the carbon and proton shielding in acetylene. The four curves show how the shielding of C_1 and H_1 change with separate variations of the $H_1C_1C_2$ bond angle and the C_1C_2H bond angle.

stretching of the C≡C bond than to the stretching of either of the other bonds. However, it is certainly surprising that the shielding at C_1 is more sensitive to the C_2H_2 bond length than to the C_1H_1 bond length, at least for small displacements (compare σ_r and σ_s in Table III). It is also noticeable that the stretching of the C_1H_1 bond and the C_2H_2 bond have quite opposite effects on the C_1 shielding with the former leading to a brisk reduction with stretching and the latter to a sharp increase. When the C_1H_1 bond is compressed $\sigma(C_1)$ reaches a maximum at $r(C_1H_1) = -0.10$ Å and, on further compression, falls back towards the equilibrium value. This change of direction is not at all surprising when one considers that the shielding of nitrogen (the ''united atom'') in the HCN molecule is negative; Jameson[46] quotes a value for this of -20.4 ppm.

The proton shielding behaves very differently and much more as expected with $\sigma(H_1)$ being changed to a decreasing extent by a given change in the C_1H_1 bond length, the CC bond length, and the C_2H_2 bond length, respectively (see Fig. 2 and Table III). Indeed $\sigma(H_1)$ is hardly affected by r_2. Comparing the dependencies of $\sigma(C)$ and $\sigma(H)$ (see Table III) we see, again surprisingly, that $\sigma(H_1)$ is more than three times more sensitive than $\sigma(C_1)$ to an initial stretch of the C_1H_1 bond; it is the value of σ_r for the carbon shielding which is anomalously low here whilst that for the proton

shielding is in the vicinity of the expected value. This is discussed further below. The second derivatives with respect to bond length are all very much smaller for the proton shielding than for the carbon shielding with the sole exception of σ_{rr}.

Another quite unexpected result is found for the dependence of $\sigma(C)$ on angle. $\sigma(C_1)$ is more than six times more sensitive to the variation of the $C_1C_2H_2$ angle than to the $H_1C_1C_2$ angle. This can be seen by comparing the value of $\sigma_{\alpha\alpha}$ and $\sigma_{\beta\beta}$ in the second column of Table III and it is illustrated in Fig. 3. On the other hand $\sigma(H_1)$ behaves as expected being nearly four times more sensitive to the $H_1C_1C_2$ angle than to the $C_1C_2H_2$ angle. It is also worth noting that although $\sigma(C_1)$ is more sensitive than $\sigma(H_1)$ to the $H_1C_1C_2$ angle, the orders of magnitude of their derivatives are the same.

VI. THE FORCE FIELD

The force field chosen for this work is the $C(R2)$ force field of Bramley *et al.*[15] It is the result of a variational refinement of the quartic force field of Strey and Mills.[44] The equilibrium geometrical parameters for this force field are given early in Sec. III. The expectation values at 300 K of the required geometrical parameters are listed in Tables IV and V for each of the ten isotopomers of interest in this

TABLE IV. Mean geometrical parameters at 300 K for the isotopomers of acetylene which possess identical isotopes of carbon. r_1 denotes the left-hand bond (HC or DC), R denotes the CC bond, and r_2 denotes the right-hand bond (CH or CD). Angular averages are denoted similarly. Bond lengths are in Å and bond angles in rad.

	$H^{12}C^{12}CH$	$D^{12}C^{12}CH$	$D^{12}C^{12}CD$	$H^{13}C^{13}CH$	$D^{13}C^{13}CH$	$D^{13}C^{13}CD$
$\langle r_1 \rangle$	0.023 019	0.018 028	0.017 981	0.022 913	0.017 903	0.017 858
$\langle R \rangle$	0.007 824	0.007 520	0.007 222	0.007 651	0.007 347	0.007 049
$\langle r_2 \rangle$	0.023 019	0.022 982	0.017 981	0.022 913	0.022 878	0.017 858
$\langle r_1^2 \rangle$	0.005 300	0.003 871	0.003 871	0.005 286	0.003 853	0.003 853
$\langle R^2 \rangle$	0.001 283	0.001 278	0.001 273	0.001 233	0.001 229	0.001 225
$\langle r_2^2 \rangle$	0.005 300	0.005 300	0.003 871	0.005 286	0.005 286	0.003 853
$\langle r_1 R \rangle$	$-0.000\,240$	$-0.000\,293$	$-0.000\,294$	$-0.000\,224$	$-0.000\,275$	$-0.000\,276$
$\langle r_2 R \rangle$	$-0.000\,240$	$-0.000\,241$	$-0.000\,294$	$-0.000\,224$	$-0.000\,225$	$-0.000\,276$
$\langle r_1 r_2 \rangle$	0.000 001	$-0.000\,008$	$-0.000\,020$	0.000 003	$-0.000\,006$	$-0.000\,016$
$\langle \alpha_1^2 \rangle$	0.033 018	0.028 396	0.028 395	0.032 762	0.028 119	0.028 119
$\langle \alpha_2^2 \rangle$	0.033 018	0.033 014	0.028 395	0.032 762	0.032 758	0.028 119
$\langle \alpha_1 \alpha_2 \rangle$	$-0.010\,253$	$-0.010\,147$	$-0.010\,126$	$-0.010\,052$	$-0.009\,939$	$-0.009\,912$

work. They were computed by standard methods using the quadratic and cubic force constants of Bramley et al.[15]

The changes in these geometrical parameters on passing from one isotopomer to another, very small though they are, produce the isotope shifts observed at 300 K (and, of course, contribute to the changes of all other molecular properties upon isotope substitution at this temperature). As Tables IV and V show heavy isotopic substitution leads to a reduction in mean bond lengths. Thus on passing from $H^{12}C^{12}CH$ to $D^{12}C^{12}CH$ the $D^{12}C$ bond is shorter by 0.004 991 Å than the original $H^{12}C$ bond, the CC bond is shorter by 0.000 304 Å and the ^{12}CH bond by 0.000 037 Å. (There is some contrast here with results for methane; on passing from $^{12}CH_4$ to $^{12}CH_3D$ the CD bond is shorter by 0.005 76 Å than the original CH bond, but the remaining CH bonds are longer by 0.000 10 Å. These results are for the zero point levels.) The root mean square displacements for the CH and CC bonds in $H^{12}C^{12}CH$ at 300 K are 0.072 80 Å and 0.003 58 Å, respectively. The root mean square displacement for the HCC angle in $H^{12}C^{12}CH$ at 300 K is 10.4°, but this falls to 8.4° for the DCC angle in $D^{12}C^{12}CH$. The negative sign of $\langle \alpha_1 \alpha_2 \rangle$ for all isotopomers indicates that the ''trans'' form is very slightly favoured over the ''cis'' form during molecular vibrations.

The formulas developed by Toyama et al.[47] were used to obtain the thermally averaged shielding values given in tables in the remaining sections of the paper. They are given in several of our previous publications[48–50] and will not be repeated here.

VII. NUCLEAR MOTION EFFECTS FOR $\sigma(C)$

Carbon-13 chemical shifts for an assembly of noninteracting acetylene molecules at 0 K and at several selected temperatures in the range 220–380 K are given in Table VI for the seven isotopomers containing one or two ^{13}C-nuclei. For reasons of economy and to bring out the effects of temperature variation and isotopic substitution more clearly, the results are reported as shielding differences with respect to the $H^{13}C^{12}CH$ isotopomer at 300 K for which the shielding is 122.415 ppm. This last result was obtained by combining the CAS B value of $\sigma_e(C)$ with the nuclear motion correction of

-4.061 ppm at this temperature calculated from the CAS A surface. The general trends in Table VI are for the shielding to decrease with increasing temperature for any one isotopomer and to increase with heavier isotopic substitution (either D for H or ^{13}C for ^{12}C). These are the usual trends for these variations. The predicted variation of 0.466 ppm for $H^{13}C^{12}CH$ over the range 220–380 K should be detectable experimentally.

For $H^{13}C^{13}CH$ our value of 122.437 ppm at 300 K compares well with the experimental value of 116.88 (± 0.9) ppm given earlier. Almost all of this difference comes from the error in the calculation of $\sigma_e(C)$. Taking the best value we have obtained for $\sigma_e(C)$, viz., 121.633 ppm, leads to a predicted experimental value of 117.59 ppm which is only 1 ppm above the measured one. The experimental ^{13}C-shifts (in parts per billion) of other isotopomers with respect to $H^{13}C^{12}CH$ obtained by Chertkov[12] are listed in the third column of Table VII. They have been obtained to great accuracy and display a particularly interesting feature; substitution of D for H affects the remote carbon nuclear shielding more than that of the near one. Thus on passing from $H^{13}C^{12}CH$ to $D^{13}C^{12}CH$ the carbon shielding increases by 226.67 ppb whilst on passing from $H^{13}C^{12}CH$ to $H^{13}C^{12}CD$

TABLE V. Mean geometrical parameters at 300 K for the isotopomers of acetylene which contain differing isotopes of carbon. r_1 denotes the left-hand bond (HC or DC), R denotes the CC bond, and r_2 denotes the right-hand bond (CH or CD). Angular averages are denoted similarly. Bond lengths are in Å and bond angles in rad.

	$H^{13}C^{12}CH$	$D^{13}C^{12}CH$	$H^{13}C^{12}CD$	$D^{13}C^{12}CD$
$\langle r_1 \rangle$	0.023 007	0.018 013	0.022 970	0.017 967
$\langle R \rangle$	0.007 738	0.007 434	0.007 434	0.007 136
$\langle r_2 \rangle$	0.022 926	0.022 890	0.017 918	0.017 871
$\langle r_1^2 \rangle$	0.005 300	0.003 871	0.005 300	0.003 870
$\langle R^2 \rangle$	0.001 258	0.001 253	0.001 254	0.001 249
$\langle r_2^2 \rangle$	0.005 287	0.005 287	0.003 854	0.003 853
$\langle r_1 R \rangle$	$-0.000\,242$	$-0.000\,296$	$-0.000\,243$	$-0.000\,297$
$\langle r_2 R \rangle$	$-0.000\,223$	$-0.000\,223$	$-0.000\,273$	$-0.000\,274$
$\langle r_1 r_2 \rangle$	0.000 002	$-0.000\,007$	$-0.000\,007$	$-0.000\,018$
$\langle \alpha_1^2 \rangle$	0.032 969	0.028 345	0.032 969	0.028 345
$\langle \alpha_2^2 \rangle$	0.032 811	0.032 807	0.028 170	0.028 170
$\langle \alpha_1 \alpha_2 \rangle$	$-0.010\,153$	$-0.010\,145$	$-0.010\,041$	$-0.010\,020$

TABLE VI. Carbon-13 chemical shifts of acetylene isotopomers in ppm at selected temperatures. All results are relative to the shielding in H^{13}C^{12}CH at 300 K for which the shielding is 122.415 ppm.

T/K	H^{13}C^{12}CH	D^{13}C^{12}CH	H^{13}C^{12}CD	D^{13}C^{12}CD	H^{13}C^{13}CH	D^{13}C^{13}CH	H^{13}C^{13}CD	D^{13}C^{13}CD
0	0.278	0.512	0.812	1.056	0.305	0.539	0.844	1.088
220	0.186	0.409	0.654	0.883	0.211	0.434	0.681	0.910
260	0.107	0.323	0.538	0.760	0.130	0.346	0.564	0.785
300	0	0.209	0.396	0.610	0.022	0.232	0.420	0.633
340	−0.130	0.073	0.233	0.439	−0.109	0.094	0.255	0.461
380	−0.280	−0.083	0.053	0.252	−0.260	−0.063	0.073	0.272

the increase is 438.17 ppb. When the remaining proton is substituted the corresponding relative changes occur to bring both shifts to 668.39 ppb in D^{13}C^{12}CD. An exactly parallel series of changes occurs in passing along the doubly ^{13}C-substitution series from H^{13}C^{13}CH to D^{13}C^{13}CD. Similar changes were noted in an earlier study of acetylene by Luzikov and Sergeyev.[51] Our calculated ^{13}C shifts are given in the second column of Table VII. We only give them to ±1 ppb since this is already the sixth significant figure in the shielding and we regard our results as not reliable beyond this figure. As can be seen the agreement with experiment is very good and the unexpected trends referred to above are reproduced. There is a small discrepancy ranging from 5 to 50 ppb between the calculated and experimental values, but it is not clear at this time to what extent this is due to limitations in the surface, or to the effects of the acetone-d_6 solvent.

The excellent agreement here justifies the analysis of the nuclear motion effects into individual contributions. This is done for the H^{13}C^{12}CH istopomer at 300 K in the second column of Table VIII. It is seen that by far the largest contribution to $\Delta\sigma$(C) comes from the $\sigma_{\beta\beta}$ term, i.e., from the bending at the ''other'' carbon atom. Even all the stretching terms combined amount to only 20% of the $\sigma_{\beta\beta}$ term. Other noticeable features are the almost exact cancellation of the $\sigma_{\alpha\alpha}$ and $\sigma_{\alpha\beta}$ terms, the near cancellation of the σ_r and σ_s terms, but with the latter being slightly greater numerically, and the numerically greater magnitude of the σ_{rr} than the σ_r

term. In previous work on water[7] we found all cross terms to be negligibly small; this is true here for all cross terms (σ_{rR}, σ_{rs}, and σ_{sR}) with the exception of the $\sigma_{\alpha\beta}$ term which makes an individual contribution which is larger than any one of the stretching terms. Most of the total nuclear motion correction of −4.061 ppm comes from the zero-point nuclear motion viz., −3.783 ppm with −0.278 ppm being due to rotational-vibrational excitation (see the second column of Table VI).

Further analysis makes clear the source of the unexpected ^{13}C-isotope shifts presented in Table VII and discussed above. This is given in Table IX. Substitution of D adjacent to the ^{13}C in H^{13}C^{12}CH produces no change in the $\sigma_{\beta\beta}$ term (second column), but relatively small changes of the σ_r, σ_R, σ_{rr}, and $\sigma_{\alpha\alpha}$ terms—all of the same sign. On the other hand substitution of D at the ^{12}C atom (third column) produces a very large shielding increase of 472 ppb from the $\sigma_{\beta\beta}$ term which far outweighs the deshielding of the σ_s and σ_{ss} terms. On passing from H^{13}C^{12}CD (third column) to D^{13}C^{12}CD (fourth column) the changes are almost identical with those occurring on passing from H^{13}C^{12}CH to D^{13}C^{12}CH.

VIII. NUCLEAR MOTION EFFECTS FOR σ(H)

Proton chemical shifts for an assembly of noninteracting acetylene molecules at 0 K and at selected temperatures in the range 220–380 K are given in Table X for the seven

TABLE VII. Comparison of calculated and observed isotope shifts on the carbon-13 and proton shielding in acetylene isotopomers at 300 K. All values are in parts per billion. Results for $\Delta\sigma$(C) are relative to H^{13}C^{12}CH; those for $\Delta\sigma$(H) are relative to H^{12}C^{12}CH. Experimental (Ref. 12) values refer to acetylene dissolved in acetone-d_6. Also shown are calculated values of deuterium isotope shifts at 300 K relative to H^{12}C^{12}CD.

	$\Delta\sigma$(C)		$\Delta\sigma$(H)		$\Delta\sigma$(D)
	CALC	OBS	CALC	OBS	CALC
H^{12}C^{12}CH	⋯	⋯	0	0	⋯
H^{12}C^{12}CD	⋯	⋯	13	14.64(4)	0
D^{12}C^{12}CD	⋯	⋯	⋯	⋯	15
H̲^{13}C^{12}CH	0	0	3	2.24(4)	⋯
H^{13}C^{12}CH̲	0	0	1	0.72(3)	⋯
D^{13}C^{12}CH	209	226.67(14)	14	15.40(1)	5
H^{13}C^{12}CD	396	438.17(6)	17	16.90(2)	1
D̲^{13}C^{12}CD	610	668.67(12)	⋯	⋯	16
D^{13}C^{12}CD̲	610	668.67(12)	⋯	⋯	19
H^{13}C^{13}CH	22	27.65(6)	4	2.92(1)	⋯
D^{13}C^{13}CH	232	253.58(8)	17	17.55(1)	6
D^{13}C^{13}CH̲	420	467.32(7)	17	17.55(1)	6
D^{13}C^{13}CD	633	697.21(12)	⋯	⋯	20

TABLE VIII. Contributions to the nuclear motion corrections to the carbon and proton shielding in H^{13}C^{12}CH at 300 K of terms containing the coefficients defined in Eq. (1). Results are in ppb.

	$\Delta\sigma(C)$	$\Delta\sigma(H)$
σ_r	−242	−748
σ_R	−448	−35
σ_s	276	−4
Total first order stretch	−414	−787
σ_{rr}	−254	191
σ_{RR}	−122	2
σ_{ss}	110	0
σ_{rR}	−12	1
σ_{rs}	0	0
σ_{sR}	6	0
Total second order stretch	−272	194
$\sigma_{\alpha\alpha}$	−554	−266
$\sigma_{\beta\beta}$	−3365	−77
$\sigma_{\alpha\beta}$	544	94
Total second order bend	−3375	−249
Total nuclear motion contribution	−4061	−842

TABLE IX. Contributions to the carbon isotope shifts in acetylene isotopomers of terms containing the coefficients defined in Eq. (1). All results are relative to H^{13}C^{12}CH at 300 K and are in ppb.

	D^{13}C^{12}CH	H^{13}C^{12}CD	D^{13}C^{12}CD
σ_r	53	0	53
σ_R	18	18	35
σ_s	0	−60	−60
Total first order stretch	71	−42	28
σ_{rr}	69	0	69
σ_{RR}	0	0	1
σ_{ss}	0	−30	−30
σ_{rR}	−3	0	−3
σ_{rs}	0	0	0
σ_{sR}	0	2	2
Total second order stretch	66	−28	39
$\sigma_{\alpha\alpha}$	78	0	78
$\sigma_{\beta\beta}$	0	472	472
$\sigma_{\alpha\beta}$	−6	−6	−7
Second order bend	72	466	543
Total nuclear motion correction	209	396	610

isotopomers which contain one or two protons. As in the ^{13}C case results are presented as shielding differences—this time with respect to the H^{12}C^{12}CH isotopomer at 300 K for which the calculated shielding is 29.504 ppm. This result was obtained by combining the CAS B value of 30.346 ppm (see Table II) with the nuclear motion contribution of −0.839 (see Tables VIII and X) calculated from the CAS A surface; [the value of σ_e(H) obtained from the CAS A surface was 30.448 ppm]. Again the general trends show decreased shielding with increased temperature for one isotopomer and increased shielding with heavy isotopic substitution at a single temperature. Here, however, the changes are, as expected, much smaller than for the carbon-13 shielding. Over the range 220–380 K the change is only 0.072 ppm for H^{12}C^{12}CH, but this could be detected in careful measurements.

From Tables VIII and X and the CAS B value of 30.346 ppm in Table II we predict a value of 29.511 ppm for the proton shielding in the H^{13}C^{13}CH isotopomer at 300 K. This is in very good agreement with the measured value[39] given earlier of 29.277 (±0.001) ppm at this temperature. Chertkov's measurements[12] of the proton isotope shifts are given in the fifth column of Table VII in parts per billion relative to H^{12}C^{12}CH. It will be noticed that this time there are no unexpected effects. For example, substitution of ^{13}C

for ^{12}C changes the proton shielding much more when this substitution occurs at the adjacent carbon atom than at the other carbon atom. The agreement between our calculations and the observed isotope shifts is excellent with differences being often within 1 ppb and being never more than 2 ppb.

The excellent agreement again justifies analysis into contributions. These are given in the third column of Table VIII. Here the dominant contribution to the deshielding comes from the σ_r term, i.e., the stretching of the C$_1$–H$_1$ bond involving the proton of interest. There is a fairly substantial contribution from the $\sigma_{\alpha\alpha}$ term involving bending at the C$_1$ atom, but the other bending contributions are quite small and largely cancel one another. The second order stretching term (σ_{rr}) is also significant and cancels part of the σ_r term. In total the contribution of stretching terms to $\Delta\sigma$(H) of −593 ppb is only slightly smaller than that of −686 ppb for $\Delta\sigma$(C).

Finally in the last column of Table VII we give calculated values of the deuterium shielding differences relative to H^{12}C^{12}CD. They are seen to be slightly larger than the corresponding calculated proton isotope shifts given in the fourth column of Table VIII. At present there are no experimental deuterium resonance data for the deuterated acetylenes.

TABLE X. Proton chemical shifts of acetylene isotopomers in ppm at selected temperatures. All results are relative to the shielding in H^{12}C^{12}CH at 300 K for which the shielding is 29.507 ppm.

T/K	H^{12}C^{12}CH	H^{12}C^{12}CD	$\underline{H}$^{13}C^{12}CH	$\underline{H}$^{13}C^{12}CH	D^{13}C^{13}CH	H^{13}C^{12}CD	H^{13}C^{13}CH	D^{13}C^{13}CH
0	0.045	0.060	0.049	0.045	0.061	0.064	0.050	0.065
220	0.028	0.043	0.032	0.029	0.044	0.047	0.033	0.048
260	0.016	0.030	0.020	0.017	0.031	0.034	0.021	0.035
300	0	0.013	0.003	0.000	0.014	0.017	0.004	0.017
340	−0.020	−0.008	−0.017	−0.020	−0.007	−0.004	−0.016	−0.004
380	−0.044	−0.032	−0.040	−0.043	−0.031	−0.028	−0.039	−0.027

TABLE XI. Nonadditivity in deuterium isotope effects on the ^{13}C-shielding in acetylene isotopomers. Results are given in parts per billion for isotopomers containing one and two ^{13}C-nuclei.

	One ^{13}C nucleus			Two ^{13}C nuclei	
	Luzikov and Sergeyev[a]	Chertkov[b]	Calc[c]	Chertkov[b]	Calc[c]
Primary	223	226.67(14)	209	225.93(10)	210
Secondary	438	438.17(6)	396	439.67(9)	398
Sum	661	664.84(15)	605	665.60(14)	608
Obs/Combined	668	668.67(10)	610	669.56(13)	611
Nonadditivity	−7	−3.83	−5	−3.96	−3

[a]Reference 51.
[b]Reference 12.
[c]This work.

IX. NONADDITIVITY

It was noticed[52] very early in the study of isotope effects on chemical shifts that they appeared to be additive, i.e., they were to a very high degree linearly dependent on the number of identical isotopes substituted in equivalent positions. This phenomenon has been periodically reviewed.[53–56] As more accurate experiments were carried out deviations from this additivity were observed—*inter alia* for the ^{14}N-shifts in the $[NH_{4-n}D_n]^+$ ions,[57] the ^{119}Sn-shifts in the $[SnH_{3-n}D_n]^-$ ions,[58] the ^{13}C-shifts in the halomethanes[59,60] and the ^{17}O shift in water.[61] There has also been some discussion[56,59,62] of this topic of ''nonadditivity.''

For acetylene a slight nonadditivity was noticed in the early work of Luzikov and Sergeyev.[51] This is confirmed by Chertkov's results as shown in Table XI. In this case additivity occurs if the sum of the ^{13}C-isotope shifts on passing from (a) $H^{13}C^{12}CH$ to $D^{13}C^{12}CH$ and (b) $H^{13}C^{12}CH$ to $H^{13}C^{12}CD$ is equal to the observed shift on passing directly from $H^{13}C^{12}CH$ to $D^{13}C^{12}CD$. As shown in Table XI the sum of the primary effect (a) and the secondary effect (b) falls short of the observed change giving a ''nonadditivity'' of −3.83 ppb. This is also the case for the doubly ^{13}C-substituted isotopomer where the ''nonadditivity'' is −3.96 ppb.

Although our calculated primary and secondary effects are somewhat less than the measured ones of Chertkov, their sums also fall short of the combined value by −5 ppb and −3 ppb, respectively. The origin of this nonadditivity can be attributed to the $\sigma_{\alpha\beta}$ term (see Table IX), where the primary and secondary values sum to −12 ppb whilst the combined value is −7 ppb. For all the other terms the sum of the primary and secondary effects (second and third columns of Table IX) is equal to the combined result (fourth column of Table IX) apart from deviations of only 1 ppb for each of the σ_R and σ_{RR} terms. We note here that it was also a second order bending term which produced the nonadditivity on the ^{17}O shielding in water with successive deuterium substitution.[7]

The experimental results in Table VII also suggest a possible nonadditivity for the proton shielding changes upon ^{13}C-isotopic substitution. Thus, the primary effect of 2.24 ppb on passing from $\underline{H}^{12}C^{12}CH$ to $\underline{H}^{13}C^{12}CH$ and the secondary effect of 0.72 ppb on passing from $\underline{H}^{12}C^{12}CH$ to $\underline{H}^{12}C^{13}CH$ sum to 2.96 ppb which is larger than the 2.92 ppb

observed on passing directly to $H^{13}C^{13}CH$. However, the difference is just within experimental error and, is in any case, too small to be accessible to present-day calculation. Further possible nonadditivity in the proton shielding could arise from several combinations of deuterium and carbon-13 substitution. However, they are all additive within experimental error.

X. UNEXPECTED DIFFERENTIAL SENSITIVITY

In calculations of the geometry dependence of nuclear spin–spin coupling in polyatomic molecules a phenomenon was encountered[63,64] to which was given the name ''unexpected differential sensitivity,'' or UDS for short. Its essential feature is that the change of a bond length or interbond angle by a small amount from its equilibrium value produces a greater change in the coupling of a more remote pair of nuclei than in that of a less remote pair. Most strikingly in methane it was found from a correlated calculation[63] that $J(C,H)$ is changed less by a small extension of the C–H bond involving the coupled nuclei than by an extension of the same amount of one of the other C–H bonds. The phenomenon manifests itself experimentally through isotopic substitution—in passing from $^{13}CH_4$ to $^{13}CH_3D$ the secondary isotope shift [the change in $J(C,H)$] is greater than the primary one [the change in $J(C,D)$ from the original $J(C,H)$ after making allowance for differing manetogyric ratios].

Subsequent studies on spin–spin coupling have found the UDS effect to occur in silane,[65] ethane,[66] and from our own work, in acetylene.[67] It appears to be a correlation effect since it does not occur when calculations at the noncorrelated level are carried out on these molecules. It also appears to be present only when lone pairs are absent since it is not found in the ammonia[65] and water molecules[68] even in correlated calculations.

There is no obvious reason why UDS should not occur for nuclear shielding or any other property which is essentially localized within a molecule (e.g., nuclear quadrupole coupling, hyperfine coupling, etc.). Indeed, it is already clear from Table III that it occurs in two distinct instances in acetylene; the much greater numerical value of $\sigma_{\beta\beta}$ than $\sigma_{\alpha\alpha}$ for $\sigma(C)$ is a good example, as is the larger value of σ_s than $|\sigma_r|$. Electron correlation also appears to be significant here, whereas we obtain $\sigma_r = -10.57$ and $\sigma_s = 12.01$ ppm Å^{-1}, at

the MCSCF level, Chesnut and Foley[22] obtained -15.0 and 12.5 ppm Å^{-1}, respectively, at the SCF level. There is no corresponding UDS effect for the proton shielding in acetylene but for angle variations it can be seen that $|\sigma_{\alpha\beta}| > |\sigma_{\alpha\alpha}|$ so that values of equal amounts, say 0.1 rad, for both α_{1a} and α_{2a}, will mean that the cross term produces a larger change in $\sigma(H_1)$—0.046 ppm—than produced by the $\sigma_{\alpha\alpha}$ term, 0.041 ppm.

HCN, CH_3F, and H_2CO are other molecules studied in the SCF work of Chesnut and Foley[22] which produce UDS effects to fit our formal definition. Using units of ppm Å^{-1} throughout, they give for HCN, $\partial\sigma(C)/\partial r_{CH} = 10.3$ and $\partial\sigma(N)/\partial r_{CH} = 24.5$; for CH_3F, $\partial\sigma(C)/\partial r_{CH} = -42.0$ and $\partial\sigma(F)/\partial r_{CH} = -84.3$; and for H_2CO, $\partial\sigma(C)/\partial r_{CH} = 22.6$ and $\partial\sigma(O)/\partial r_{CH} = 94.0$. However, it should be remembered that in each of these three example comparisons are being made of the shielding dependences of pairs of nuclei which have different ranges of shielding.

Finally, we note a parallel with the effects of certain substituents in acetylenic compounds where the shielding of the β-carbon nucleus of the $C\equiv C$ bond is affected more than that of the α-carbon nucleus such as in fluoroacetylene,[26] for other examples, see Table 3.3.4 (p. 92) in Levy et al.,[69] or Table 3.24 (p. 148) in Kalinowski et al.[70] A more recent review of substituent effects on ^{13}C-shielding in acetylenes is that of Proidakov et al.[71] who give yet more examples. However, it is only a parallel since these substituent effects are essentially electronic whilst the phenomena studied here are largely vibrational.

XI. DISCUSSION

It was stated in Sec. V that of the two nuclei involved in the stretching of a C–H bond in acetylene, it was $\partial\sigma(C)/\partial r_{CH} = -10.57$ ppm Å^{-1} which was anomalously low numerically, whereas $\partial\sigma(H)/\partial r_{CH} = -32.64$ ppm Å^{-1} was of the usual magnitude for a C–H bond. This is confirmed by comparison with literature values which, except where indicated, come from the SCF calculations of Chesnut and Foley.[22] Throughout the following all results are in units of ppm Å^{-1}. For $\partial\sigma(H)/\partial r_{CH}$ there are values for methane of -25.47 and, from experiment,[72] of -38 (± 3), for ethane of -23.37, for acetonitrile of -35.02 and for methyl fluoride of -20.00. Somewhat smaller numerical values of -15.66 and -11.48 were obtained for ethylene and formaldehyde respectively. Even for water $\partial\sigma(H)/\partial r_{OH}$ has a very similar value of -36.14.[7]

Our numerically low value of $\partial\sigma(C)/\partial r_{CH} = -10.57$ for acetylene is to be compared with calculated values of -51.0 and -52.62 (Ref. 73) for methane, -59.2 for ethane, -34.4 in ethylene, and -42.0 in methyl fluoride. However, reversal of sign occurs for HCN and H_2CO for which there are values of $+10.3$ and $+22.6$, respectively. Thus it appears that the anomalous values are to be associated with CH bonds involving sp-hybridized carbon or sp^2-hybridized carbon together with a highly electronegative neighbor atom.

There has been considerable interest in the effects of torsion on nuclear shielding including carbon shielding; see Ref. 46 and other volumes in the series for references to specific studies. Acetylene is the simplest molecule for

which such effects can be defined in relation to carbon shielding. However, the relevant coefficients appear at much higher orders of distortion than considered in this work. Thus to produce torsional effects in acetylene one must alter at least three angular coordinates but, because of the high symmetry, it is at fourth order when they will first appear. The required coefficients are those of the factors $(\alpha_{1a}\alpha_{2a}\alpha_{2b}^2 + \alpha_{1b}\alpha_{2a}^2\alpha_{2b} + \alpha_{1a}\alpha_{1b}^2\alpha_{2a} + \alpha_{1a}^2\alpha_{1b}\alpha_{2b})$ and $\alpha_{1a}\alpha_{1b}\alpha_{2a}\alpha_{2b}$. As stated above we have never varied more than two angular coordinates in this work.

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