# The dependence of the $^{13}C$ and the $^{1}H$ nuclear magnetic shielding on bond extension in methane

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The mean bond displacements $\langle \Delta r \rangle$ in the methane isotopic homologous series $^{13/12}CX_{4-n}Y_n$ (X, Y = H, D, T) at 300 K, and the temperature dependence of $\langle \Delta r_{CH} \rangle$ in $^{13}CH_4$ from 250 to 350 K were calculated. With the assumption that the linear terms are sufficient to account for the isotope shifts, we determine from the $^{2/1}H$-induced $^{13}C$ isotope shift an empirical value of $(\partial\sigma^C/\partial\Delta r_{CH})_e = -35 \pm 3$ ppm/Å. This predicts a temperature dependence in the $^{13}C$ resonance in $CH_4$ gas in the zero-pressure limit of $2.7 \times 10^{-2}$ ppm over 100 °, which explains why it could not be observed. We observed the $^{13/12}C$-induced $^{1}H$ isotope shift in $CH_4$, $-0.0024$ ppm. With the same mean bond displacements, this isotope shift gives an estimate of $(\partial\sigma^{H_i}/\partial\Delta r_{CH_i})_e = -38 \pm 3$ ppm/Å. From the reported $^{2/1}H$-induced two-bond $^{1}H$ isotope shift in $CH_4$, $-0.016$ ppm, using the mean bond displacements and the derivative obtained from the $^{13/12}C$-induced one-bond isotope shift, we get an estimate of $(\partial\sigma^{H_i}/\partial\Delta r_{CH_j})_e = -1.3 \pm 0.2$ ppm/Å.

Measurements of the nuclear resonance frequencies in the gas phase as a function of temperature yield information about the nuclear magnetic shielding.[1] When the intermolecular interaction terms are removed, the temperature dependence of the resonance frequencies in the zero-pressure limit gives the rovibrationally averaged shielding in the "isolated molecule" $\sigma_0(T)$. This function is determined by two factors: the magnitude and sign of the change in the shielding upon variation of molecular configuration, such as bond extension, $(\partial\sigma/\partial\xi)_e$; and the magnitude of the average displacement from equilibrium molecular configuration (combinations of bond extensions and/or bond angle distortions) $\langle \Delta\xi \rangle^T$. For example, for $^{17}O$ in $H_2O$,

$$\sigma_0(T) = \sigma_e + 2(\partial\sigma/\partial\Delta r)_e \langle \Delta r \rangle^T + (\partial\sigma/\partial\Delta\alpha)_e \langle \Delta\alpha \rangle^T + \cdots . \tag{1}$$

$(\partial\sigma/\partial\Delta\xi)_e$ is an intensity factor which is expected to reflect the inherent sensitivity of a nucleus to changes in its electronic environment, as well as the nature of the changes in the electronic distribution with nuclear displacement as the electrons follow the nuclear motion in an adiabatic or Born–Oppenheimer sense. $\langle \Delta\xi \rangle^T$, on the other hand, is purely dynamic in nature, and is observed as thermal average bond displacement (as in electron diffraction measurements). This has a temperature dependence and an isotopic mass dependence and is calculable from the same anharmonic force fields that are used to interpret infrared and Raman fundamentals, overtones and combination bands, and electron diffraction intensities. The mass dependence of $\langle \Delta\xi \rangle$ gives rise to isotope shifts in nuclear magnetic resonance spectra, changes in the rovibrationally averaged nuclear shielding upon isotopic substitution of a neighboring atom.

Isotope shifts of nuclei in highly symmetric nuclear sites are considerably smaller than those in less symmetric environments. For example, the $^{18/16}O$-induced isotope shift of $^{14}N$ in $NO_3^-$ $(D_{3h})$ is 0.056 ppm per $^{18}O$,[2] compared with $-0.138$ ppm per $^{18}O$ in $NO_2^-$ $(C_{2v})$,[3] and the $^{2/1}H$-induced shift in $NH_4^+$ $(T_d)$ is $-0.293$ ppm per D,[4] compared with $-0.68$ ppm per D in $NH_3(C_{3v})$.[5] The $^{18/16}O$-induced isotope shift of $^{31}P$ in $PO_4^{3-}$ $(T_d)$ is likewise small, $-0.02$ ppm per $^{18}O$.[6] If we convert this to the equivalent isotope shift appropriate to the fractional mass change of $^{2/1}H$ substitution, it is still only $-0.16$ ppm compared to $-0.843$ ppm per D for $PH_3$.

One important difference between the $T_d$ molecules and their less symmetric counterparts is that in the former, the equilibrium bond angles are determined by the point group symmetry, so that the sum of the mean bond angle changes vanish, whereas in $NH_3$ or $NO_2^-$ there are important contributions of bond angle deformations to the shielding change. Thus, the latter contributions may account for the larger isotope shifts. On the other hand, the difference may be purely electronic, the more symmetrical nuclear sites having smaller changes in the shielding upon bond extension. We have attempted to determine $(\partial\sigma^C/\partial\Delta r)_e$ in $CH_4$ and $(\partial\sigma^B/\partial\Delta r)_e$ in $BF_3$.[7] In both cases, the limited precision of our measurements together with the uncertainty in the lock solvent temperature dependence precluded the empirical determination of this derivative in the usual manner. This indicates that the derivatives we are seeking may be much smaller than the others which we have previously measured. If this is the case, then the $^{13}C$ temperature dependence in the zero-pressure limit must be measured in a spectrometer operating at much higher fields than 21.1 kG. Alternatively, we can obtain the derivative $(\partial\sigma^C/\partial\Delta r_{CH})_e$ from the isotope shift, which has been reported[8]: $-0.192 \pm 0.003$ ppm per D. In order to do this, and for a systematic study of the additivity of isotope shifts in general (see accompanying paper)[9] we need to calculate mean bond displacements in all the members of the isotopic series $^{13/12}CX_{4-n}Y_n$ (X,Y = H, D, T).

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## CALCULATION OF THE MEAN BOND DISPLACEMENTS IN $^{13/12}CX_{4-n}Y_n$ (X, Y = H, DT)

The anharmonic force field of methane has recently been refined to fit spectroscopic data from the isotopic species $^{12}CH_4$, $^{13}CH_4$, $^{12}CD_4$, $^{12}CH_3D$, $^{12}CHD_3$, and $^{12}CH_2D_2$ by Gray and Robiette.[10] They determined six of the 13 cubic force constants experimentally and the remaining cubic force constants were fixed at values derived from *ab initio* calculations.[11] Another recent force field by Hirota is refined with data on only one isotopic species, $CH_2D_2$.[12] Although he checks his calculations against some data for $CH_3D$ and $CHD_3$, he does not treat the other isotopic species. The potential function found by Gray and Robiette was written in terms of symmetry coordinates as

$$V=\frac{1}{2}\sum_{i,j}F_{ij}S_iS_j+\frac{1}{6}\sum_{i,j,k}F_{ik}S_iS_jS_k+\cdots. \tag{2}$$

For our purposes we can not make use of the force field in symmetry coordinates directly, because of the different symmetry point groups of all $CH_nD_{4-n}$ species. As one or more of its isotopes are substituted for hydrogen in $CH_4$, the point group of the molecule changes from $T_d$ to $C_{3v}$ for $CH_3D$ ( or $CHD_3$), $C_{2v}$ for $CH_2D_2$, and $C_s$ for $CH_2DT$ so that the nine possible normal modes are classified into different irreducible representations, with different degeneracies. Jones and McDowell[13] give the correlation table for all isotopic methanes including tritium-containing species. In order to discuss the additivity of isotope shifts we need to be able to calculate the mean bond displacements for all the isotopomers in the same general way. Therefore we chose to carry out the calculations entirely in internal coordinates.

We first have to transform Gray and Robiette's force field into internal coordinates using his $U$ matrix:

$$R=U^TS. \tag{3}$$

For the quadratic force constants we obtain

$$f_{ij}=\sum_m\sum_n U_{mi}U_{nj}F_{mn}. \tag{4}$$

In an analogous manner, the cubic force constants in the symmetry coordinates can be transformed into cubic force constants in the internal coordinates:

$$f_{ijk}=\sum_m\sum_n\sum_p U_{mi}U_{nj}U_{pk}F_{mnp}. \tag{5}$$

These transformations can only be carried out if we take into consideration also a redundance condition:

$$S_R=(1/\sqrt{6})(\Delta\alpha_{12}+\Delta\alpha_{13}+\Delta\alpha_{14}+\Delta\alpha_{23}+\Delta\alpha_{24}+\Delta\alpha_{34}). \tag{6}$$

This provides additional zero force constants for the $S_R$ coordinate. Now we are able to express the anharmonic force field in terms of the internal coordinates:

$$V=(1/2)\sum_i\sum_j f_{ij}R_iR_j+(1/6)\sum_i\sum_j\sum_k f_{ijk}R_iR_jR_k+\cdots. \tag{7}$$

In the calculation of mean bond displacements we use the basic idea first introduced by Bartell.[14] In a previous paper we used Bartell's idea to develop a general model for calculations of different $\langle\Delta r\rangle$ for molecular types with a central atom, based on a modified Urey–Bradley treatment of the potential energy. We applied this to the $YAZ_2$ molecular type ($OCF_2$ in particular).[15] We used the general anharmonic force field in curvilinear coordinates for $CO_2$ and NNO to calculate the mean bond displacements in linear triatomic molecules.[16] In this paper we apply Bartell's basic idea to the general case of a molecule with a central atom, with the assumption that the cubic internal force constants are known. As in Ref. 15 this model assumes that the mean bond angle changes can be neglected. This is valid when all the bonds are equivalent and all equilibrium bond angles are determined by the molecular symmetry. It is also approximately valid when the bond angle displacements sum to zero and the mean bond angle displacements nearly sum to zero, as in the substituted methanes, and even better for the isotopic homologous series that we consider here.

From the molecular quantum mechanical analog to the Ehrenfest theorem[17] it follows that the space average force is zero, or

$$\left\langle\frac{\partial V}{\partial\xi}\right\rangle=0, \tag{8}$$

where $\xi$ is an arbitrary Cartesian displacement coordinate. We adopt the usual internal Cartesian frame where the $z_i$ axes are taken in the directions of the A–$X_i$ bonds at their equilibrium position. (A denotes the central atom.) For methane we have four different bond displacement coordinates $\Delta r_i(R_1$–$R_4)$ and six different bond angle displacement coordinates $\Delta\alpha_{ij}(R_5$–$R_{10})$. We can express the quadratic term in $V$ also in the following form:

$$V_2=\frac{1}{2}\sum_{i,j=1}^{4}\sum^{4}f_{ij}R_iR_j+\sum_{i=1}^{4}\sum_{j=5}^{10}f_{ij}R_iR_j+\frac{1}{2}\sum_{i,j=5}^{10}\sum^{10}f_{ij}R_iR_j, \tag{9}$$

where the first term includes only bond–bond interaction, the second term bond–bond angle interaction, and the third term describes bond angle–bond angle interactions. The derivatives of $V_2$ with regard to $\Delta z_k$ ($k=1$ to 4) are conveniently expressed in Kronecker deltas, if we take only the linear terms:

(a) For the bond displacement coordinates

$$\frac{\partial R_i}{\partial\Delta z_k}=\delta_{ik}. \tag{10a}$$

(b) For the bond angle displacement coordinates

$$\frac{\partial R_i}{\partial\Delta z_k}=-\frac{R_i}{2r_i}\epsilon_{ki}. \tag{10b}$$

$r_i$ denotes the equilibrium bond length, and $\epsilon_{ki}=1$ if the bond angle coordinate $i$ includes bond $k$, zero otherwise:

$$\left\langle\frac{\partial V_2}{\partial\Delta z_k}\right\rangle=\sum_{j=1}^{4}f_{kj}\langle R_j\rangle+2\sum_{j=5}^{10}f_{kj}\langle R_j\rangle-\frac{1}{2r}\sum_{i=1}^{4}\sum_{j=5}^{10}f_{ij}\langle R_iR_j\rangle\epsilon_{kj}-\frac{1}{4r}\sum_{i=5}^{10}\sum_{j=5}^{10}f_{ij}\langle R_iR_j\rangle(\epsilon_{ki}+\epsilon_{kj}). \tag{11a}$$

As previously stated, we neglect the second term, which involves $\langle \Delta\alpha_{ij} \rangle$. In an analogous way we obtain the derivatives for the cubic part of $V$ as

$$\left\langle \frac{\partial V_3}{\partial \Delta z_k} \right\rangle = \frac{1}{2} \sum_{i=1}^{4} \sum_{j=1}^{4} f_{kij} \langle R_i R_j \rangle + \frac{1}{2} \sum_{i=5}^{10} \sum_{j=5}^{10} f_{kij} \langle R_i R_j \rangle + \sum_{i=1}^{4} \sum_{j=5}^{10} f_{kij} \langle R_i R_j \rangle. \tag{11b}$$

Here we neglected all terms higher than quadratic in the mean product amplitudes, i.e., all terms of the form $\langle R_i R_j R_k \rangle$. From Eq. (11) we get a set of four linear coupled equations, which connect the mean bond displacements $\langle \Delta r_k \rangle$ with the mean square amplitudes (MSA) $\langle R_i R_j \rangle$:

$$\sum_{i=1}^{4} f_{ki} \langle \Delta r_i \rangle = -\frac{1}{2} \sum_{i=1}^{4} \sum_{j=1}^{4} f_{kij} \langle \Delta r_i \Delta r_j \rangle - \frac{1}{2} \sum_{i=5}^{10} \sum_{j=5}^{10} \left[ f_{kij} - \frac{1}{2r} f_{ij} (\epsilon_{ki} + \epsilon_{kj}) \right] \langle \Delta\alpha_i \Delta\alpha_j \rangle - \sum_{i=1}^{4} \sum_{j=5}^{10} \left( f_{kij} - \frac{1}{2r} f_{ij} \epsilon_{kj} \right) \langle \Delta r_i \Delta\alpha_j \rangle. \tag{12}$$

The MSA's (which include nonvanishing cross products) are related to the mean square normal coordinates $\langle Q^2 \rangle$ in the usual way[18]:

$$\langle R_i R_j \rangle = \mathbf{L} \langle Q^2 \rangle \mathbf{L}^T, \tag{13}$$

where $\langle Q^2 \rangle$ is a quadratic matrix with the diagonal elements

$$\langle Q^2 \rangle_{ii} = (h / 4\pi^2 c \omega_i)(v_i + \tfrac{1}{2}). \tag{14a}$$

The thermal average of $(v_i + \frac{1}{2})$ taken with the harmonic oscillator partition function, is $\frac{1}{2} \coth(hc\omega_i / 2kT)$, giving

$$\langle Q^2 \rangle_{ii} = (h / 4\pi^2 c \omega_i) \tfrac{1}{2} \coth(hc\omega_i / 2kT). \tag{14b}$$

The nondiagonal elements are zero. The transformation matrix $\mathbf{L}$ from normal coordinates to internal coordinates can be obtained directly by the usual $GF$-matrix method[19]; again including a redundant normal mode $\omega_r = 0$, to get a quadratic $\mathbf{L}$ matrix. The mean bond displacements are obtained by solving the four coupled equations (12) in terms of the quantities in Eqs. (13) and (14).

TABLE I. Vibrational contributions to mean bond displacements (in $10^{-2}$ Å) in the methanes, $^{12}CX_{4-n}Y_n$ (X, Y = H, D, T) at 300 K, calculated using the anharmonic force field of Gray and Robiette (Ref. 10).

| | $\langle \Delta r_{CH} \rangle_{vib}$ | $\langle \Delta r_{CD} \rangle_{vib}$ | $\langle \Delta r_{CT} \rangle_{vib}$ |
|---|---|---|---|
| $CH_4$ | 2.0881 | | |
| $CH_3D$ | 2.0727 | 1.5873 | |
| $CH_2D_2$ | 2.0572 | 1.5699 | |
| $CHD_3$ | 2.0416 | 1.5522 | |
| $CD_4$ | | 1.5348 | |
| $CH_4$ | 2.0881 | | |
| $CH_3T$ | 2.0671 | | 1.3757 |
| $CH_2T_2$ | 2.0458 | | 1.3502 |
| $CHT_3$ | 2.0243 | | 1.3246 |
| $CT_4$ | | | 1.2988 |
| $CD_4$ | | 1.5348 | |
| $CD_3T$ | | 1.5281 | 1.3202 |
| $CD_2T_2$ | | 1.5213 | 1.3131 |
| $CDT_3$ | | 1.5147 | 1.3059 |
| $CT_4$ | | | 1.2988 |

TABLE II. Vibrational contributions to mean bond displacements.[a,b]

| | $\langle \Delta r_{CH} \rangle_{vib}$ | $\langle \Delta r_{CD} \rangle_{vib}$ |
|---|---|---|
| $^{12}CH_4$ | $d$ | |
| $^{13}CH_4$ | $d - \Delta_C$ | |
| $^{12}CD_4$ | | $d - \Delta_D$ |
| $^{13}CD_4$ | | $d - \Delta_C - \Delta'_D$ |
| $^{12}CH_{4-n}D_n$ | $d - n\delta_H$ | $d - \Delta_D + (4-n)\delta_D$ |
| $^{13}CH_{4-n}D_n$ | $d - \Delta_C - n\delta_H$ | $d - \Delta_C - \Delta'_D + (4-n)\delta_D$ |

[a] To each must be added the rotational contribution given in Table III.

[b] Values calculated with Gray and Robiette's force field: $d = 2.0881 \times 10^{-2}$ Å, $\Delta_D = 5.5345 \times 10^{-3}$ Å, $\Delta'_D = 5.553 \times 10^{-3}$ Å, $\Delta_C = 6.2 \times 10^{-5}$ Å, $\delta_H = 1.55 \times 10^{-4}$ Å, and $\delta_D = 1.75 \times 10^{-4}$ Å for T substitution, in $^{12}CH_{4-n}T_n$, $\Delta_T = 7.893 \times 10^{-3}$ Å, $\delta'_H = 2.13 \times 10^{-4}$ Å, $\delta'_T = 2.56 \times 10^{-3}$ Å.

We also should include the change in bond lengths due to rotation. We calculated the centrifugal distortion by assuming that the rotational level spacings are small compared to $kT$ so that the equipartition law can be used in the form of the Toyama, Oka, and Morino formulas[20]

$$\langle \Delta r \rangle_{rot} = kT \mathbf{U}^T \mathbf{F}_s^{-1} \mathbf{G}_s^{-1} \mathbf{U} \mathbf{\Omega} \mathbf{X}. \tag{15}$$

We found that the centrifugal distortion is nearly two magnitudes smaller than the effect due to anharmonic vibrations for methane.

Since we have set up our calculations entirely in terms of the internal coordinates, the only mass-dependent input are the elements of the $\mathbf{G}$ matrix. Our typical results are shown in Tables I–V. Here we indicate our findings which show the strict additivity of the effects of isotopic substitution on the mean bond displacements. We discuss the implications of these with respect to isotope shifts in general, in the accompanying paper.[9]

The calculated mean bond displacements due to vibration are given in Table I. By inspection of these results it is shown that they are strictly additive, and the numerical values of the constitutive parts are given in Table II. $\langle \Delta r_{CH} \rangle_{vib}$ and $\langle \Delta r_{CD} \rangle_{vib}$ are linearly related to $n$ and $4-n$, respectively. On the other hand, the mean bond displacement due to

TABLE III. Centrifugal distortion contribution to mean bond displacements in $^{12}CH_{4-n}D_n$.[a]

| | $\langle \Delta r_{CH} \rangle_{rot} / 10^{-4}$ Å | $\langle \Delta r_{CD} \rangle_{rot} / 10^{-4}$ Å |
|---|---|---|
| $CH_4$ | $5.2413 = d_{rot}$ | |
| $CH_3D$ | 4.3384 | 7.9498 |
| $CH_2D_2$ | 3.7148 | 6.7677 |
| $CHD_3$ | 3.2649 | 5.9009 |
| $CD_4$ | | $5.2413 = d_{rot}$ |

[a] These values can be reproduced by the following equations: $\langle \Delta r_{CH} \rangle_{rot} = d_{rot} / (1 + nc_H)$; $\langle \Delta r_{CD} \rangle_{rot} = d_{rot} / [1 - (4-n)c_D]$ where $c_H = 0.205$, $c_D = 0.113$.

TABLE IV. Mean bond displacements in selected isotopomers of methane, in $10^{-2}$ Å.

| | $\langle \Delta r_{\mathrm{CH}} \rangle$ | | | $\langle \Delta r_{\mathrm{CD}} \rangle$ | | |
|---|---|---|---|---|---|---|
| | vib | rot | tot | vib | rot | tot |
| $^{12}$CH$_4$ | 2.0881 | 0.0524 | 2.1405 | | | |
| $^{13}$CH$_4$ | 2.0819 | 0.0524 | 2.1343 | | | |
| $^{12}$CH$_3$D | 2.0727 | 0.0434 | 2.1161 | 1.5873 | 0.0795 | 1.6668 |
| $^{13}$CH$_3$D | 2.0664 | 0.0433 | 2.1097 | 1.5793 | 0.0798 | 1.6591 |

centrifugal distortion depends on $n$ as shown in Table III. This contribution is two orders of magnitude smaller than the vibrational terms, however. It has previously been noted that the centrifugal stretching contribution to the mean bond displacement is independent of mass for a highly symmetric molecule, $T_d$ for example, if substitution is done so as to preserve the symmetry.[1] We see this in Table III, the $\langle \Delta r_{\mathrm{CH}} \rangle_{\mathrm{rot}}$ in CH$_4$ and $\langle \Delta r_{\mathrm{CD}} \rangle_{\mathrm{rot}}$ in CD$_4$ are equal.

Our values for the mean bond displacements in Table IV can be compared with values calculated previously. Kuchitsu and Bartell's $\langle \Delta r_{\mathrm{CH}} \rangle$ and $\langle \Delta r_{\mathrm{CD}} \rangle$ at 300 K are 0.0221 and 0.0164 Å, respectively.[21] They later estimated corrections to these by about 10% with improved nonbonded parametrization in the model.[22] The agreement with our results using Gray and Robiette's force field is quite good, indicating that the model of Kuchitsu and Bartell gives a good account of the anharmonic force field. We also calculated the temperature dependence of $\langle \Delta r_{\mathrm{CH}} \rangle$ in $^{13}$CH$_4$, shown in Table V.

Although the secondary effects of isotopic substitution $\delta$ and the centrifugal distortion contributions to the mean bond displacement are small (both are of the order of $10^{-4}$ Å), we report them here to illustrate the additivity of the effects of isotopic substitution. The use of another anharmonic force field will undoubtedly yield mean bond displacements which differ from ours by the same order of magnitude as these small terms, but the systematic changes upon successive substitution of H with D will be the same as we have found here. The additivity must be due to the symmetry and the Born–Oppenheimer approximation. The relative magnitudes $\delta_{\mathrm{D}}$ and $\delta_{\mathrm{H}}$ are not invariant to the force field, however, we have found by choosing an arbitrary force field (unrelated to CH$_4$) and *maintaining only the symmetry of the problem*, that it is possible to get $\delta_{\mathrm{D}} > \delta_{\mathrm{H}}$ or $\delta_{\mathrm{D}} < \delta_{\mathrm{H}}$.

## CORRELATION TO NMR MEASUREMENTS

The theoretical basis for the rovibrational effects on nuclear shielding have been discussed in previous papers.[1] Our interpretation of the shielding in CH$_4$ in the zero-pressure limit can be summarized as follows:

$$\sigma_0^{\mathrm{C}}(\mathrm{T}) = \sigma_e^{\mathrm{C}} + (\partial \sigma^{\mathrm{C}} / \partial \Delta r_{\mathrm{CH}})_e \sum_i^4 \langle \Delta r_{\mathrm{CH}_i} \rangle^{\mathrm{T}} + \cdots . \tag{16}$$

$$\sigma_0^{\mathrm{H}}(\mathrm{T}) = \sigma_e^{\mathrm{H}} + (\partial \sigma^{\mathrm{H}_i} / \partial \Delta r_{\mathrm{CH}_i})_e \langle \Delta r_{\mathrm{CH}_i} \rangle^{T} + (\partial \sigma^{\mathrm{H}_i} / \partial \Delta r_{\mathrm{CH}_j})_e \sum_{j \neq i} \langle \Delta r_{\mathrm{CH}_j} \rangle^{\mathrm{T}} + \cdots . \tag{17}$$

TABLE V. Temperature dependence of $\langle \Delta r_{\mathrm{CH}} \rangle$ in $^{13}$CH$_4$ (in $10^{-2}$ Å).

| $T$ | Vib | Rot | Total |
|---|---|---|---|
| 250 | 2.0812 | 0.0437 | 2.1249 |
| 275 | 2.0815 | 0.0480 | 2.1295 |
| 300 | 2.0819 | 0.0524 | 2.1343 |
| 325 | 2.0825 | 0.0568 | 2.1393 |
| 350 | 2.0833 | 0.0611 | 2.1444 |

If we neglect all but the linear terms, the $^{2/1}$H-induced isotope shift in the $^{13}$C spectrum of CH$_4$ will be given by

$$\begin{aligned} &\sigma_0^{\mathrm{C}}(^{13}\mathrm{CH}_4) - \sigma_0^{\mathrm{C}}(^{13}\mathrm{CH}_3\mathrm{D}) \\ &\quad = (\partial \sigma^{\mathrm{C}} / \partial \Delta r_{\mathrm{CH}})_e \sum_i^4 [\langle \Delta r_{\mathrm{CH}_i} \rangle_{\mathrm{CH}_4} - \langle \Delta r_{\mathrm{CH}_i} \rangle_{\mathrm{CH}_3\mathrm{D}}] \\ &\quad = (\partial \sigma^{\mathrm{C}} / \partial \Delta r_{\mathrm{CH}})_e \{4 \langle \Delta r_{\mathrm{CH}} \rangle_{^{13}\mathrm{CH}_4} - \langle \Delta r_{\mathrm{CD}} \rangle_{^{13}\mathrm{CH}_3\mathrm{D}} \\ &\qquad - 3 \langle \Delta r_{\mathrm{CH}} \rangle_{^{13}\mathrm{CH}_3\mathrm{D}} \}. \end{aligned} \tag{18}$$

This isotope shift has been measured and the reported value is $-0.192 \pm 0.003$ ppm.[8] Using the values in Table IV for the mean bond displacements, we obtain

$$(\partial \sigma^{\mathrm{C}} / \partial \Delta r_{\mathrm{CH}})_e = -35 \pm 3 \text{ ppm/Å}.$$

From Eq. (17) we can express the one-bond $^1$H isotope shift as well as the two-bond isotope shift. Let us consider the one-bond isotope shift first because its magnitude will be dominated by only one term. There is of course the primary isotope shift, the difference between the shielding of the $^1$H and the $^2$H in the same position, but this is impossible to measure in the absolute sense. Therefore, even though the calculation is simple, we have no experiments with which we can compare. On the other hand, there is the $^{13/12}$C-induced shift in the $^1$H spectrum of CH$_4$. Using Eq. (17) we can express this as follows:

$$\begin{aligned} &\sigma_0^{\mathrm{H}}(^{12}\mathrm{CH}_4) - \sigma_0^{\mathrm{H}}(^{13}\mathrm{CH}_4) \\ &\quad = (\partial \sigma^{\mathrm{H}} / \partial \Delta r_{\mathrm{CH}})_e [\langle \Delta r_{\mathrm{CH}} \rangle_{^{13}\mathrm{CH}_4} \langle \Delta r_{\mathrm{CH}} \rangle_{^{13}\mathrm{CH}_4}]. \end{aligned} \tag{19}$$

We measured this isotope shift in CH$_4$ and obtained $-0.0024 \pm 0.0002$ ppm. Using Eq. (19) and the mean bond displacements from Table IV we obtain

$$(\partial \sigma^{\mathrm{H}_i} / \partial \Delta r_{\mathrm{CH}_i})_e = -38 \pm 3 \text{ ppm/Å}.$$

The two-bond isotope shift for $^1$H in CH$_4$ involves at least two important contributions. From Eq. (17), the $^{2/1}$H-induced isotope shift in CH$_4$ can be expressed as follows:

$$\begin{aligned} &\sigma_0^{\mathrm{H}}(\mathrm{CH}_4) - \sigma_0^{\mathrm{H}}(\mathrm{CH}_3\mathrm{D}) \\ &\quad = (\partial \sigma^{\mathrm{H}_i} / \partial \Delta r_{\mathrm{CH}_i})_e [\langle \Delta r_{\mathrm{CH}} \rangle_{\mathrm{CH}_4} - \langle \Delta r_{\mathrm{CH}} \rangle_{\mathrm{CH}_3\mathrm{D}}] \\ &\qquad + (\partial \sigma^{\mathrm{H}_i} / \partial \Delta r_{\mathrm{CH}_j})_e [3 \langle \Delta r_{\mathrm{CH}} \rangle_{\mathrm{CH}_4} \\ &\qquad - 2 \langle \Delta r_{\mathrm{CH}} \rangle_{\mathrm{CH}_3\mathrm{D}} - \langle \Delta r_{\mathrm{CD}} \rangle_{\mathrm{CH}_3\mathrm{D}}]. \end{aligned} \tag{20}$$

This isotope shift has also been reported: $-0.016$ ppm.[23] Using the value of $(\partial \sigma^{\mathrm{H}_i} / \partial \Delta r_{\mathrm{CH}_i})_e$ which we obtained from the $^{13/12}$C-induced $^1$H isotope shift, and the values of the mean bond displacements in Table IV, we obtain from the $^{2/1}$H-induced $^1$H isotope shift of $-0.016$ ppm the value of $(\partial \sigma^{\mathrm{H}_i} / \partial \Delta r_{\mathrm{CH}_j})_e = -1.3 \pm 0.2$ ppm/Å. The contributing terms to the $^{2/1}$H-induced $^1$H isotope shift are $-9.3 \times 10^{-3}$

TABLE VI. Some derivatives of $^1H$ shielding, $(\partial\sigma^H/\partial\Delta r)_e$, ppm/Å.

| Molecule | Source | $(\partial\sigma^H/\partial\Delta r)_e$ | Ref. |
|---|---|---|---|
| $H_2$ | theor | $-21.8$ | a |
| | theor | $-20.7$ | b |
| | isotope sh. | $-12.1\pm0.06$ | c |
| LiH | theor | $-2.69$ | d |
| | theor | $-4.14$ | b |
| HF | theor | $-40.7$ | e |
| | theor | $-41.7$ | b |
| $H_2O$ | theor | $-35.3$ | f |
| $CH_4$ | isotope sh. | $-38\pm3$ | this work |

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TABLE VII. Some derivatives of $^{13}C$ shielding, $(\partial\sigma^C/\partial\Delta r)_e$, ppm/Å.

| Molecule | Source | $(\partial\sigma^C/\partial\Delta r)_e$ | Ref. |
|---|---|---|---|
| CO | $T$ dep. $\sigma_0(T)$ | $-226\pm40$ | a |
| | theor | $-413.7$ | b |
| $CN^-$ | isotope sh. | $-473\pm90$ | c |
| $CO_2$ | T dep. $\sigma_0(T)$ | $-220\pm50$ | d |
| $CH_4$ | isotope sh. | $-35\pm3$ | this work |

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and $-6.7\times10^{-3}$ ppm, respectively in Eq. (20). The first term involves the (small) secondary effect on the bond length due to isotopic substitution elsewhere, detected by the change in $^1H$ shielding with the bond extension. The second term involves the large primary effect on a neighbor bond length, detected by the change in $^1H$ shielding with a neighboring bond extension. In this example, the two terms are comparable. The same was true of the $^{13/12}C$-induced isotope shift of $^{19}F$ in $O{=}CF_2$, in which the isotope effects on both the C=O and the C–F bond length had to be included.[15]

With the derivative $(\partial\sigma^C/\partial\Delta r_{CH})_e$ from the $^{2/1}H$-induced $^{13}C$ isotope shift we can now calculate the expected temperature dependence of the $^{13}C$ shielding in $CH_4$ gas in the zero-pressure limit, using the temperature dependent mean bond displacements in Table III. Over the 100 ° temperature change we calculate a shielding change of $2.7\times10^{-2}$ ppm. This corresponds to a 0.6 Hz change between 250 and 350 K with a 21.1 kG spectrometer. This explains why we were unable to observe a temperature dependence for $\sigma_0$ of $^{13}C$ in $CH_4$ gas.[7] There is a useful practical consequence of this. Since the density dependence of $^{13}C$ shielding in $CH_4$ is likewise known to be small and nearly temperature independent, (the $^{13}C$ shielding change with density is $-0.01+1.3\times10^{-5}(T-300)-9.8\times10^{-8}(T-300)^2$ ppm/amagat)[7] then the $^{13}C$ signal in a sample of $CH_4$ gas serves as a good temperature-independent reference, and a more convenient one than $^{129}Xe$ in xenon gas at the zero-pressure limit.

If our assumption that the expansion of nuclear shielding in terms of internal coordinates can be truncated after the linear terms is valid even for calculations of isotope shifts, then we have a convenient way of obtaining empirical derivatives of nuclear shielding with respect to bond extension in those systems where the temperature dependence of nuclear shielding in the zero-pressure limit is too small to measure.

In Table VI and VII we compare the empirical derivatives that we have obtained for $CH_4$ with other theoretical and empirical values for C and H in other molecules. For $^1H$ our value of $-38$ ppm/Å is consistent with the other values. For $^{13}C$ in $CH_4$ the derivative is about an order of magnitude smaller than the others. This is not unexpected, the highly symmetric nuclear site in $CH_4$ leads to a small paramagnetic contribution to the shielding. Calculations show that this is of the order of $-100$ ppm for $^{13}C$ in $CH_4$,[24] compared to $-315$ ppm in CO, for example.[25] It is our contention that the change in the paramagnetic contribution upon bond extension dominates the change in shielding. The small empirical value for $(\partial\sigma^C/\partial\Delta r)_e$ in $CH_4$ supports this. The smaller isotope shifts of nuclei in symmetric sites, as P in $PO_4^{3-}$, are undoubtedly due to the generally smaller derivatives associated with bond extension around a symmetric electronic environment.

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