# The Zero Point Vibrational Contribution to the $^{13}C$–H Spin–Spin Coupling Constant in Methane. An *ab initio* Result

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A large basis set *ab initio* quantum mechanical calculation reveals that the experimental value of 125.4 Hz for the $^{13}C$–H coupling constant in methane contains a zero point vibrational contribution of about 7 Hz.

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The measured value of a nuclear spin–spin coupling constant is not equal to the value it would have if the molecule were held fixed at its equilibrium geometry. The most important contribution to the difference comes from the zero point vibrational motion of the nuclei. As the molecule vibrates about its equilibrium geometry the spin–spin coupling covers a range of values which form a spin–spin coupling surface.[1] For small displacements about equilibrium this surface can be written as a power series in internal displacement co-ordinates with respect to equilibrium. Thus for coupling $J$ of the $^{13}C$ nucleus to H-1 in methane we write equation (1). The $r_i$ ($i$ = 1—4) represent increases in the lengths of the four C–H bonds with respect to the equilibrium bond length $r_e$: the $\alpha_{ij}$ represent increases in the six interbond angles with respect to their equilibrium value of 109° 28.3′. Unlike the $r_i$, the $\alpha_{ij}$ are not independent and for small displacements sum approximately (but not exactly[2]) to zero. $J_e$ is the coupling constant at equilibrium geometry and $J_r$, $J_s$, $J_\alpha$, and $J_\beta$ describe the sensitivity of the coupling to the various kinds of displacement. Using symmetry arguments it is possible to show that $J_\beta = -J_\alpha$. For substantial displacements from equilibrium equation (1) needs to be supplemented by terms quadratic in the co-ordinates. However, we have not considered such terms in this work.

$$J = J_e + J_r r_1 + J_s(r_2 + r_3 + r_4) + J_\alpha(\alpha_{12} + \alpha_{13} + \alpha_{14}) + J_\beta(\alpha_{23} + \alpha_{24} + \alpha_{34}) \quad (1)$$

A coupling constant averaged over the zero point motion $<J>$ can be obtained once the averages of the $r_i$ and the $\alpha_{ij}$ are known. (The $\alpha_{ij}$ do not average to zero, *i.e.* the mean angle between two CH bonds in the zero point level of methane is not the tetrahedral angle but slightly less than this.[3,4]) To obtain these averages we identify the ten internal co-ordinates with the internal curvilinear co-ordinates $\mathcal{R}_i$($i$ = 1—10) of Hoy *et al.*[5] which are related to the reduced normal co-ordinates $q_m$ by equation (2), where the elements $\bar{L}_i^m$, $\bar{L}_i^{mn}$ *etc.* of the '$\bar{L}$ tensor' can be determined from the harmonic force field, the atomic masses, and the equilibrium bond length.[5] The expectation values of the $q_m$ in methane are all zero except for the totally symmetric stretching mode $q_1$ for which[6] equation (3) applies. $\phi_{1mm}$ is a cubic anharmonic force constant in the expansion of the force field in terms of $q_1$ and $q_m$, $\omega_1$ is the (harmonic) frequency of $q_1$, $v_m$ is the vibrational quantum number of the $m$th mode, and $d_m$ is the degeneracy of that mode. For the zero point level of methane all $v_m$ are zero. The expectation value of $q_mq_n$ is[6,7] given by equation (4).

$$\mathcal{R}_i = \sum_m \bar{L}_i^m q_m + 1/2 \sum_{m,n} \bar{L}_i^{mn} q_m q_n + \ldots \quad (2)$$

$$<q_1> = -\sum_m \frac{\phi_{1mm}}{2\omega_1}(v_m + d_m/2), \ q_1 \text{ totally symmetric} \quad (3)$$

$$<q_m q_n> = (1/d_m)(v_m + d_m/2)\delta_{mn} \quad (4)$$

We have calculated the $^{13}C$–$^{1}H$ spin–spin coupling surface of methane using a large basis set at the RPA (random phase approximation) level. The bond lengths and bond angles were systematically varied about equilibrium to produce some seventy distinct geometries at each of which the coupling constant was calculated. As well as the dominant Fermi contact term[8] the spin dipolar and orbital diamagnetic and paramagnetic contributions were obtained. Upon fitting to equation (1) we find the following values for the coefficients: $J_r$ = 124.4 Hz Å$^{-1}$, $J_s$ = 81.0 Hz Å$^{-1}$, and $J_\alpha = -J_\beta$ = 44.0 Hz rad$^{-1}$. The coupling of the $CH^1$ bond increases very rapidly with increasing length of the bond; our value of 124.4 Hz Å$^{-1}$ compares with a value of 101 Hz Å$^{-1}$ for the corresponding coefficient of the $H_2$ molecule.[9] The former is larger by a factor of 5 after allowing for the difference in the magnetogyric ratios of $^1H$ and $^{13}C$. The $CH^1$ coupling is also quite sensitive to stretching of the other CH bonds; indeed increasing the $CH^2$ and $CH^3$ bonds by a given amount each increases $J(CH^1)$ by more than increasing $CH^1$ itself by the same amount. Depending upon the circumstances the coupling constant can vary considerably with angle change. For example if the $CH^2$, $CH^3$, and $CH^4$ bonds are held fixed with respect to each other then, to first order, no change in $J(CH^1)$ occurs for small displacements of H-1 at constant $r$ since $\alpha_{12} + \alpha_{13} + \alpha_{14} = 0$; on the other hand if the angle changes $\alpha_{12}$, $\alpha_{13}$, and $\alpha_{14}$ are each +0.1 radian (5.7°) then $J(CH^1)$ increased by 26.4 Hz since $\alpha_{12} + \alpha_{13} + \alpha_{14} = -(\alpha_{23} + \alpha_{24} + \alpha_{34}) = 0.3$.

The $\bar{L}$ tensor elements and the $\phi_{1mn}$ were calculated by the methods described by Hoy *et al.*[5] using the quadratic and cubic force fields and the equilibrium bond length of 1.0858 Å given by Gray and Robiette.[10] Upon evaluation we obtain equation (5) for $^{13}CH_4$ (in Hz). The experimental value of $J(CH)$ in methane is usually given as 125.0 Hz[11] although the best value

$$\langle J\rangle = J_e + 7.2 \tag{5}$$

would appear to be the 125.36(±0.01) Hz found after extrapolation to zero density of gas.[12] Although only about 6% of the total value, the zero point vibrational contribution is still large at 7.2 Hz and is many times the experimental error. We predict that zero point vibrational contributions to $^1J(CH)$ values in general will be large. Furthermore, the spin–spin coupling surfaces will differ sufficiently enough from CH bond to CH bond that, together with differing force fields for nuclear motion, zero point vibrational contributions to $^1J(CH)$ values will differ significantly between themselves. This must place an upper limit on attempts to correlate experimental $J(CH)$ values with parameters such as electronegativity, s-character, bond length *etc.*

The present result is not definitive. The most important error comes from the neglect of electron correlation. This contributes substantially to $J_e$; our calculated value is 153.84 Hz which is similar to the values found by Guest *et al.*[13] who used the SCF method with a range of large basis sets at the fixed equilibrium geometry and similar to a result of 149.9 Hz obtained by us.[14] However, our interest here is in the way in which $J(CH)$ varies with geometry in the vicinity of equilibrium rather than with $J_e$ itself. Secondly, some additional contributions will be made by terms quadratic in the displacement co-ordinates. Small contributions are also expected from the dependence of the coupling on rotational excitation which is always present in a gaseous sample under experimental conditions.

In a later paper we shall report the results of a more complete calculation to second order in reduced normal co-ordinates and incorporating statistical averaging over the rotational–vibrational levels, for all one-bond coupling constants in the $^{13}C$ isotopomers of methane. This will account for the primary isotope effect on the coupling constant *i.e.* the value of $(\gamma_H/\gamma_D)^1J(CD) - {}^1J(CH)$ which we predict to be negative. This is in line with the negative primary isotope effects observed for $CDCl_3$–$CHCl_3$ and other systems by Everett.[15] Sergeyev and Solkan[16] earlier studied the primary isotope effect for methane using the semi-empirical INDO method.

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