The Proton Spin–Spin Coupling Surface in Methane. A Test of the J(H,H) = $(\gamma_H/\gamma_D)J$(H,D) Rule for Geminal Protons

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Calculation shows that the proton–proton spin–spin coupling in methane is very sensitive to the interbond angle involving the coupled protons, a result which leads to the prediction of primary isotope effects on ^2J(H,H) in agreement with experimental results for geminal deuterium isotope effects in related compounds.

The proton resonance spectrum of the compound $^{12}CH_4$ displays only one signal and so the spin–spin coupling constant ^2J(H,H) in the $^{12}CH_4$ molecule cannot be measured directly. However, estimates of this constant can be obtained indirectly by measuring the spacing between multiplet components in the proton resonance spectra of deuteriated methanes and multiplying by the factor γ_D/γ_H. In this way Bernheim and Lavery[1] obtained for $|^2J(H,H)|$ in the $^{12}CH_4$ molecule, 12.4 (±1.4) Hz from $^{12}CH_3D$, 12.3 (±0.9) Hz from $^{12}CH_2D_2$, and 12.4 (±0.8) Hz from $^{12}CHD_3$. Combining these results and taking into account the negative sign of this coupling constant[2] we obtain an experimental value of −12.4 (±1.3) Hz for ^2J(H,H) in $^{12}CH_4$.

The procedure described above overlooks the unique 'dynamic state' of each molecule in the series from $^{12}CH_4$ to $^{12}CHD_3$. For example, in $^{12}CH_3D$ the C–D bond is on average shorter than the C–H bond in methane and the HCD angle is on average different from the HCH angle in $^{12}CH_4$. It is therefore of some importance to estimate the magnitudes of these vibrationally induced effects to test the validity of the relation $|^2J(H,H)| = (\gamma_H/\gamma_D)|^2J(H,D)|$ frequently used for geminal coupling constants.

In fact the spin–spin coupling constant between two protons in the $^{12}CH_4$ molecule is sensitive to the molecular geometry and, within the Born–Oppenheimer approximation, the variation forms a 'proton–proton spin–spin coupling surface.' This surface can conveniently be described by expanding the coupling constant as a Taylor series about equilibrium in terms of internal displacement co-ordinates. Thus for the spin–spin coupling constant J^{12} between two protons, labelled 1 and 2, we write equation (1), where we are neglecting quadratic and

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

higher terms in displacements. J_e is the coupling constant at equilibrium; the $r_i (i = 1—4)$ represent increases in the individual bond lengths with respect to equilibrium (r_e = 1.0858 Å);[3] the α's give increases in the interbond angles with respect to the equilibrium tetrahedral angle of 109°28.3′. Unlike the four r_i, the six α_{ij} are not independent but sum to zero for small displacements.[4] The coefficients $J_r{}^{12}$, $J_s{}^{12}$, $J_\alpha{}^{12}$, $J_\beta{}^{12}$, and $J_\omega{}^{12}$ describe the sensitivity of the coupling to the various types of co-ordinate. It can be shown that the last three of these are not independent but are related by equation (2). If

$$J_\alpha{}^{12} + 4J_\beta{}^{12} + J_\omega{}^{12} = 0 \qquad (2)$$

the term 'reduced spin–spin coupling constant' is defined in the usual way[2] then it is clear that the reduced ^2J spin–spin coupling surfaces are identical for all isotopomers of methane.

To proceed towards a vibrational average we now identify the ten internal co-ordinates with the internal curvilinear co-ordinates of Hoy, Mills, and Strey[5] *viz.* $\mathcal{R}_i (i = 1—10)$ and write equation (3). The q_m are the reduced normal co-

$$\mathfrak{R}_i = \sum_m \bar{L}_i^m q_m + \tfrac{1}{2}\sum_{m,n} \bar{L}_i^{mn} q_m q_n + \ldots \qquad (3)$$

ordinates and the coefficients $\bar{L}_i$, $\bar{L}_i^{mn}$ *etc.* are the components of the L tensor which, as shown in equation (3), relates the reduced normal co-ordinates to the internal co-ordinates. The second and higher order terms on the right hand side of equation (3) allow for the nonlinearity of the transformation between the q_m and the $\mathfrak{R}_i$ for finite displacements from equilibrium. Specific formula for these L tensor elements have been given by Hoy, Mills, and Strey.[5] In the present work we do not use components of the $\bar{L}$ tensor beyond those quadratic in the q's.

Upon averaging over the nuclear motion, q_m is zero for all but totally symmetric vibrations for which equation (4)

$$\langle q_m \rangle = -\sum_n \frac{\phi_{mnn}}{2\omega_m}(v_n + d_n/2),\ q_m \text{ totally symmetric} \qquad (4)$$

applies. The ϕ_{mnn} are cubic coefficients in the expression for the potential energy in terms of reduced normal co-ordinates and can be determined from the force field and the $\bar{L}$ tensor components.[5] ω_m is the harmonic frequency of the mth normal mode, v_n is the vibrational quantum number, and d_n is the degeneracy of that mode. We also need[6,7] equation (5). By

$$\langle q_m q_n \rangle = (1/d_m)\,(v_m + d_m/2)\,\delta_{mn} \qquad (5)$$

combining equation (1) with equations (3)—(5) we can evaluate the coupling constant in any vibrational state.

We have calculated surfaces for a number of properties of the methane molecule[8] using a large basis set (*viz.* IV of Lazzeretti and Zanasi[9]) and varying the bond lengths and bond angles about equilibrium to produce some seventy distinct geometries. All second-order properties were evaluated using the RPA method.[10] For the proton spin–spin coupling constant we calculated not only the dominant Fermi contact contribution but also the spin–dipolar and orbital diamagnetic and paramagnetic terms.[2] Upon fitting the results to equation (1) we find $J_r^{12} = -18.01$ Hz Å^{-1}, $J_s^{12} = +3.04$ Hz Å^{-1}, $J_\alpha^{12} = 45.57$ Hz rad^{-1}, $J_\beta^{12} = -8.43$ Hz rad^{-1}, and $J_\omega^{12} = -11.96$ Hz rad^{-1}.

Stretching either of the bonds involving the coupled protons is seen to reduce the coupling constant whilst stretching either of the other two bonds leads to a small increase in this constant. These results seem reasonable on physical grounds. The coupling is very sensitive to the interbond angle between the coupled nuclei. Our result of 45.57 Hz rad^{-1} for J_α^{12} is considerably larger than that calculated by Maciel *et al.*[11] some years ago using the INDO method. They do not give numerical results for J^{12} but show a plot of $^2J^{12}(\mathrm{H,H})$ in methane against the $\mathrm{H^1CH^2}$ angle. From Kowalewski's reproduction of this plot[2] with its more legible scales, we calculate that Maciel *et al.* obtained $J_\alpha^{12} = 11.5$ Hz rad^{-1}: approximately one quarter of the present result. Our value for J_ω^{12} appears surprising at first as one would not expect alteration of the $\mathrm{H^3CH^4}$ angle to affect $|J^{12}|$ by more than 25% of the value produced by the same alteration in the angle $\mathrm{H^1CH^2}$. However, the sensitivity is less than implied because of the interdependence of the angles. For example, if α_{12} is increased from zero to 0.1 radian (5.7°) with $\alpha_{34} = 0$, then $\Delta J^{12} = 0.1J_\alpha^{12} - 0.1J_\beta^{12} = +5.40$ Hz; whereas if α_{34} is increased to 0.1 radian with $\alpha_{12} = 0$ then $\Delta J^{12} = 0.1J_\omega^{12} - 0.1J_\beta^{12} = -0.35$ Hz. Thus changing the angle $\mathrm{H^1CH^2}$ has an even larger effect than at first sight whilst changing the angle $\mathrm{H^3CH^4}$ has a very small effect indeed.

The $\bar{L}$ tensor elements and the ϕ_{lmn} were calculated using the quadratic and cubic force field of Gray and Robiette.[3] This force field is not entirely experimental in origin as it incorporates some of the smaller cubic anharmonic constants calculated by Pulay, Meyer, and Boggs.[12] Nevertheless, despite a very recent determination of some of these cubic constants[13] we have used the Gray and Robiette force field as both quadratic and cubic coefficients were systematically varied in their work to fit a wide variety of experimental data.

Upon evaluation for the zero point level of $^{12}\mathrm{CH_4}$ we obtain equation (6) (in Hz). This result includes the contributions of

$$^2J(\mathrm{H,H}) = J_e - 0.625 \qquad (6)$$

all terms first order in internal co-ordinates; see equation (1). Similarly, for $^{12}\mathrm{CH_3D}$ we obtain equation (7) (in Hz). There

$$(\gamma_\mathrm{H}/\gamma_\mathrm{D})^2J(\mathrm{H,D}) = J_e - 0.490 \qquad (7)$$

is, therefore, a difference of 0.135 Hz in the vibrational corrections with that for $^{12}\mathrm{CH_4}$ being, as expected, the greater. For $^{12}\mathrm{CH_3T}$ we obtain a correction of -0.428 Hz. J_e is known[2] to be a negative quantity in methane and in the $>\mathrm{C(sp^3)H_2}$ group. Consequently, we predict for this group that use of the relation $(\gamma_\mathrm{H}/\gamma_\mathrm{D})|^2J(\mathrm{H,D})|$ underestimates the value of $|^2J(\mathrm{H,H})|$, or more generally that equation (8) applies.

$$|^2J(\mathrm{H,H})| > (\gamma_\mathrm{H}/\gamma_\mathrm{D})|^2J(\mathrm{H,D})| > (\gamma_\mathrm{H}/\gamma_\mathrm{T})|^2J(\mathrm{H,T})| \qquad (8)$$

The numerical results given here are not definitive since, in particular, electron correlation has not been taken into account. Our RPA result for J_e is -25.3 Hz which is about 12 Hz more negative than the experimental value and close to the coupled Hartree–Fock value of -22.3 Hz obtained by Guest *et al.*[14] who also used a large basis set SCF wavefunction. However we are mainly interested here in the variation of coupling with geometry. Kowalewski *et al.*[15] have shown that the correlation contributions to $^2J(\mathrm{H,H})$ in $\mathrm{H_2O}$, $\mathrm{NH_3}$, and $\mathrm{CH_4}$ are almost the same despite differences not only in the central atom but also in bond lengths and bond angles. It seems reasonable therefore *a priori* to take the view that correlation contributions to the bond length and bond angle dependences of the coupling are small.

Secondly, it is possible that second-order terms in equation (1) may make important contributions to the vibrational average. In particular the coefficients of equation (1) have been calculated at the theoretical equilibrium geometry (r = 1.082 58 Å). When we have calculated the second-order part of the property surface these coefficients will be improved by adjusting them to the experimental equilibrium geometry given above. Finally, the present results apply only to the zero-point level and further small corrections will be necessary to take account of the rotational–vibrational excitation present in any gaseous sample at room temperature.

At a later date we intend to publish 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 pairs of magnetic nuclei in the ^{12}C-methane isotopomers. This latter calculation is straightforward as both primary and secondary isotope effects can be calculated from the same property surface.

In the light of the above we offer comment on some earlier work. Fraser *et al.*[16] and Bloxsidge *et al.*[17] measured geminal proton–deuteron and proton–triton coupling constants respectively in several compounds in solution at 25 °C; see Table 1. Benzyl methyl sulphoxide [compound (**1**)] has a prochiral carbon atom and so the geminal proton–proton coupling constant can be directly observed. Although the observed results of 12.75 and 12.97 Hz are not in particularly good agreement with each other they are both larger than the values calculated from the observed $|^2J(\mathrm{H,D})|$ and $|^2J(\mathrm{H,T})|$

Table 1. Calculated and observed values of $|^2J(H,H)|$ in Hz at 25 °C.

		Calculated $|^2J(H,H)|$	
		From (γ_H/γ_T) $|^2J(H,T)|$[17]	From (γ_H/γ_D) $|^2J(H,D)|$[16]
PhCH(H,D,T)SOMe	(**1**)[a]	12.64(4)	12.51
PhCH(D,T)CN	(**2**)[b]	18.41(5)	18.50
PhCOCH(D,T)Br	(**3**)[c]	11.54(5)	11.28(13)
PhCOCH(D,T)Cl	(**4**)[c]	14.28(5)	13.98(39)

[a] 10% in acetone; observed $|^2J(H,H)|$ 12.75,[17] 12.97.[16] [b] Neat. [c] 10% in PhPr.

results. Assuming a negative absolute sign, this agrees with the prediction of equation (8) above and enables us to state that the larger value for the directly observed $|^2J(H,H)|$ is due to the larger vibrational correction in the isotopomer with two coupled protons. Equation (8) also suggests that the calculated values of $|^2J(H,H)|$ from the proton–deuteron coupling should be larger than those from the proton–triton coupling. This is true for compound (**2**) but not for compounds (**1**) and (**3**). For compound (**4**) the experimental uncertainty prevents any such distinction. Of course, in compounds (**1**)—(**4**) the geminal spin–spin coupling surfaces will be somewhat different from each other and from that of methane on account of the adjacent polar groups and of intermolecular interaction. Furthermore, the potential surfaces over which the coupled nuclei execute their vibrations will also be different. Nevertheless, one would expect, on general grounds, that the results for a deuterium isotopomer should lie between those for the corresponding proton and triton isotopomer.

Finally we note that vibrational corrections are estimated to be 9% of the total value of $^2J(H,H)$ in NH_3[18] and 'as much as 1/3 of the total H–H coupling constant' in H_2O[19] and remark that in SiH_4, where the value of $^2J(H,H)$ is +2.75 Hz[20,21] the vibrational correction may well be a substantial fraction of the total coupling constant.

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