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The Anomalous Deuterium Isotope Effect in the NMR Spectrum of Methane: An Analysis in Localized Molecular Orbitals

Stephan P. A. Sauer^{*[a]} and Patricio F. Provasi^[b]

Isotope effects^[1] on NMR indirect nuclear spin–spin coupling constants (SSCC) are less frequently studied than the corresponding effects on chemical shifts. Nevertheless, unusual effects have been observed for them and still lack a satisfying explanation. Raynes and co-workers^[2] measured the temperature dependence of the SSCC of the isotopomers of methane and found it puzzling that the reduced one-bond carbon–deuterium SSCC is larger than the carbon–proton coupling constant for all mixed isotopomers. This implies that the secondary isotope effect [Eq. (1)] on the carbon–hydrogen SSCC

$$\Delta_s^1 J(^{13}\text{CH})[^{2/1}\text{H}] \equiv |^1 J(^{13}\text{CH})_{\text{D}}| - |^1 J(^{13}\text{CH})_{\text{H}}| \quad (1)$$

is larger than the primary isotope effect shown in Equation (2)

$$\Delta_p^1 J(^{13}\text{C}^{2/1}\text{H}) \equiv |^1 J(^{13}\text{CD})|_{\text{yD}}^{\text{yH}} - |^1 J(^{13}\text{CH})| \quad (2)$$

Fitting the measured SSCCs of all isotopomers to a coupling constant surface^[3] they furthermore found that the derivative of this coupling with respect to the length of the bond to one of the other hydrogen atoms, $\partial^1 J(\text{CH})/\partial R_{\text{other}}$, should be approximately 4 times as large as the derivative with respect to the length of the bond between the coupled atoms, $\partial^1 J(\text{CH})/\partial R_{\text{own}}$. However, they rejected this fit as unacceptable on physical grounds. Later on, however, Raynes and co-workers^[4,5] calculated the SSCC surfaces and isotope effects of methane using various high level ab initio methods. They found a) that the calculated deuterium isotope and temperature effects are in perfect agreement with the measured data and b) that the ratio between $\partial^1 J(\text{CH})/\partial R_{\text{other}}$ and $\partial^1 J(\text{CH})/\partial R_{\text{own}}$ is indeed 4.5. This means that the carbon–hydrogen coupling constant in methane is more dependent on the length of the bond of carbon to one of the other hydrogen atoms than on the hydrogen atom involved in the coupling. Raynes et al.^[4] called this phenomena the unexpected differential sensitivity (UDS) and stated that it is not easy to explain in physical terms why this happens. Furthermore they noted that ab initio calculations at the Hartree–Fock level were not able to reproduce this phenomenon or the correct isotope shifts. It was necessary to include some treatment of electron

correlation as for example, in the second-order polarization propagator approximation with coupled-cluster singles and doubles amplitudes—SOPPA(CCSD).^[6,7]

Although this isotope effect is anomalous, it is apparently not uncommon. Similar isotope effects^[8] could also be deduced from the NMR spectra of phenylsilanes, acetylene, nitromethane, toluene and halomethanes. Furthermore an UDS was also found^[9,10] for the one-bond coupling constants in acetylene, in BH_4^- , NH_4^+ and SiH_4 as well as the carbon shielding in acetylene but not for water, or the oxonium ion.^[11] Sauer and Raynes^[10] concluded that a necessary condition for the UDS to arise is that the central atom has no lone pairs, but no deeper explanation was given.

In order to explain this phenomenon we present herein an analysis of the geometry dependence of the C–H spin–spin coupling constant in methane in terms of localized B3LYP Kohn–Sham orbitals. We discuss only the Fermi contact (FC) term, because only this term contributes significantly to the carbon–hydrogen coupling in methane or its geometry dependence.^[5] However, this should not be generalized because the number of examples where the non-contact terms are important or even dominating^[12] is increasing.

We have calculated the FC term as a sum over all exited states expressed in terms of Kohn–Sham molecular orbitals. This allows us to restrict the summation to the virtual orbitals only and thereby to obtain contributions to the FC term from pairs of occupied orbitals. The transition moments over the FC operators are prior to the summation transformed to localized occupied orbitals by the Foster–Boys procedure.^[13] We can thus analyze the Fermi contact term in terms of contributions from core and bond orbitals. This approach is a generalization of the CLOPPA method by Contreras and co-workers which, so far, was only used in combination with semiempirical wavefunctions.^[14] Two other schemes for the analysis of SSCCs in terms of localized Kohn–Sham orbitals have been presented recently,^[15,16] which, however, are not based on a sum-over-states expression for the coupling constant but on the coupled Kohn–Sham procedure.

In the present calculation we have employed a completely uncontracted version of the aug-cc-pVTZ-J basis sets.^[6,17] Although this basis set was originally optimized for high-level correlated wavefunction methods such as SOPPA(CCSD), it was recently also shown^[18] to accurately reproduce the results of density functional theory calculations with much larger basis sets. The FC term and the total SSCC were calculated at the equilibrium geometry and at geometries where one of the carbon–hydrogen bonds was changed by ± 0.05 and ± 0.1 Å. We have employed the B3LYP^[19] functional as implemented in the Dalton program.^[20] In Table 1 and 2 it is shown that the

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earlier SOPPA(CCSD) results^[5] for the UDS are satisfactorily reproduced with this functional. We have also investigated other functionals, as shown in Table 1, but B3LYP gave the best agreement.

Table 1. One-bond indirect spin–spin coupling constant $J(^{13}\text{C}^1\text{H})$ of methane, in Hz, calculated with different methods.

LDA	BLYP	B3LYP	SOPPA(CCSD)	Exp. ^[4]
100.56	133.60	132.49	122.32	120.87 (± 0.05)

In Table 2 the most important orbital contributions to the FC term are listed. One can see that the largest contribution to it comes from the 'bond-bond' term in agreement with earlier findings by Wu et al.,^[16] followed by the 'bond-core' and 'bond-other bond' contributions. The latter as well as the

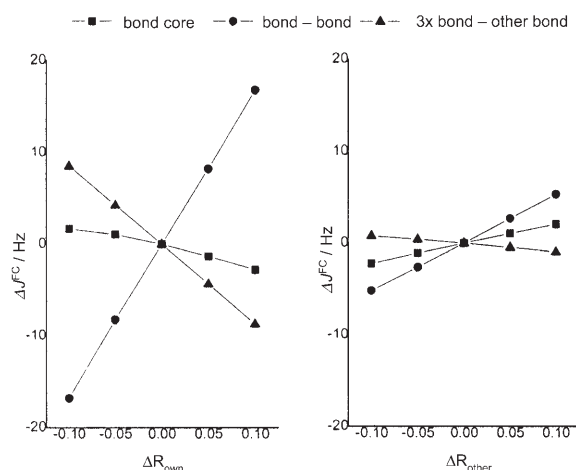


Figure 1. Variation of the dominant orbital contributions to the Fermi contact term of $J(^{13}\text{C}^1\text{H})$ of methane, in Hz, with the bond length of the coupled (R_{own}) or other bond (R_{other}).

Table 2. Localized B3LYP orbital contributions to the Fermi contact term of $J(^{13}\text{C}^1\text{H})$ of methane, in Hz, as well as total Fermi contact term and total coupling constant calculated at the B3LYP and SOPPA(CCSD) levels and their changes due to a change in the bond lengths by ± 0.1 Å.

	Contribution	R_e	Shortening		Elongation	
			R_{own}	R_{other}	R_{own}	R_{other}
B3LYP	Core–core	2.77	1.20	−0.07	−0.83	0.07
	Bond–core	35.98	1.66	−2.23	−2.77	2.05
	Bond–bond	120.69	−16.83	−5.15	16.74	5.33
	Bond–other bond	−17.91	8.49	0.78	−8.71	−0.97
	Other bond–other bond	−9.81	2.98	0.58	−3.07	−0.65
	Σ	131.72	−2.50	−6.10	1.37	5.82
	Σ without bond–core		−4.16	−3.87	4.14	3.77
	Total FC	130.40	−2.61	−6.19	1.87	5.90
SOPPA(CCSD)	Total $J(^{13}\text{C}^1\text{H})$	132.49	−2.35	−6.06	1.53	5.77
SOPPA(CCSD)	Total FC	120.53	−2.40	−5.98	1.24	5.71
	Total $J(^{13}\text{C}^1\text{H})$	122.32	−2.15	−5.86	0.93	5.59

'other bond–other bond' contribution have the opposite sign than the two dominant contributions, again in agreement with the findings of Wu et al.^[16]

The changes in these contributions due to an extension or contraction of either the bond between the coupled atoms (R_{own}) or the bond to one of the other hydrogen atoms (R_{other}) are also given in Table 2 and shown graphically in Figure 1. The most important observation is that the changes in the orbital contributions are much larger if the bond to the coupled hydrogen atom is extended or shortened than if the bond to one of the other hydrogen atoms is changed. This means that at the level of individual orbital contributions nothing unusual or unexpected happens with the one-bond SSCC in methane. However the sum of these changes is smaller for variations of the coupled bond than of the other bonds because some of the orbital contributions increase while others decrease on extending or shortening the bonds. The 'bond-bond' contribution increases on extending the bond length whereas the 'bond-other bond' contribution decreases. In addition and more important is that the 'bond-core' contribution shows the

opposite dependence for changes in the coupled bond than in the other bonds. It decreases when the bond between the coupled atoms is extended, whereas it increases when the bond to the other hydrogen atoms is extended. If one excludes the changes in this single contribution, the dependence of the one-bond SSCC on its own bond length becomes slightly larger than the dependence on the other bond length, that is, the UDS disappears.

Physically this means that the coupling pathway through the carbon 1s orbital and the bond orbital is weakened when the corresponding bond is extended, whereas it is strengthened when one of the other bonds is extended. This must mean that extending a bond in methane transfers spin-density to the other bonds and thus leads to a larger coupling there.

Acknowledgements

This research was supported financially by grants from SNF, FNU and from the Carlsberg Foundation and by computer time grants from DCSC. P.F.P. acknowledges financial support from CONICET (PIP 5119), FONCYT (PICT 21604/2004), UNNE and the CU-DNRC.

Keywords: chemical shifts • deuterium isotope effect • localized molecular orbitals • NMR spectroscopy • spin–spin coupling

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Received: March 2, 2008

Revised: April 10, 2008

Published online on May 6, 2008