Molecular Orbital Theory of Carbon-Fluorine Nuclear Spin Coupling Constants: Application to Fluorinated Methanes

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Summary Calculations show that it is necessary to include orbital and spin dipolar terms in addition to the usual Fermi contact term in order to reproduce the observed trend of J_{CF} in the fluorinated methanes.

NUCLEAR spin coupling constants between carbon and directly bonded atoms in a wide range of molecules have recently been investigated[1] by Maciel, McIver, Ostlund, and Pople using the INDO[2] molecular orbital approximation. Using only the Fermi contact interaction, they obtained qualitatively good agreement with experiment for calculated J_{CC} values but not for J_{CN} or J_{CF}.

A self-consistent-field perturbation theory has recently been developed by Blizzard and Santry which permits ready calculation of the orbital[3] and spin dipolar[4] interactions as well as the contact term. We report here the results of applying this method in the INDO approximation to the calculation of carbon–fluorine coupling constants. We confirm that the Fermi contact term is incapable by itself of reproducing the experimental trends of J_{CF} values in a wide range of molecules. It is only when the other two usually neglected terms are included that the experimental trends are obtained.

The results for the fluorinated methanes, using standard geometries,[5] are shown in the Figure. The contact term (Figure, c) predicts that J_{CF} will increase with increasing n in the series $CH_{4-n}F_n$ whereas experimentally (Figure, f) J_{CF} is found to decrease up to CHF_3 then increase to CF_4. However, if the dipolar and orbital terms (Figure, a and b) are added to the contact term, the resulting theoretical values (Figure, d) follow the same trend as experiment.

At the level of approximation of the molecular orbital

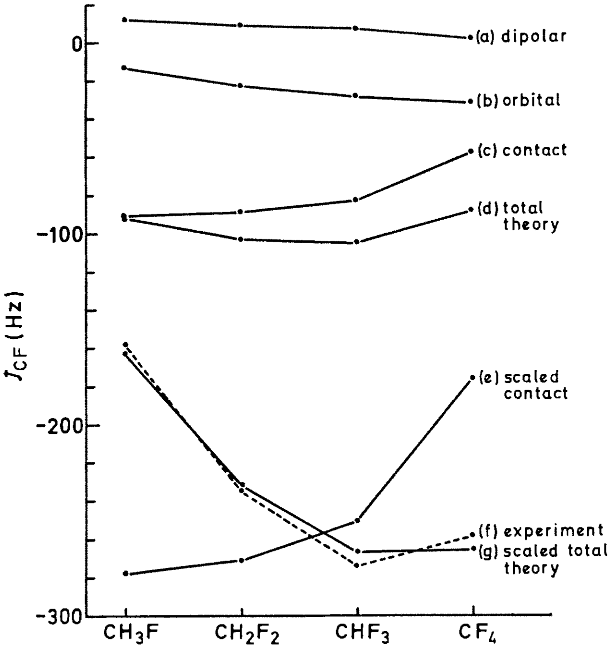

FIGURE. *Trends in the theoretical contributions to* J_{CF} *in the fluoromethanes, compared with experiment*:

(a)—(d) *Dipolar, orbital, and contact terms and their sum, with* $S_C^2(o)S_F^2(o) = 33{\cdot}1099$ *a.u.* *and* $\langle r^{-3}\rangle_C\langle r^{-3}\rangle_F = 12{\cdot}768$ *a.u.*

(e) *Contact term with* $S_C^2(o)S_F^2(o) = 100{\cdot}833$ *a.u.*

(f) *Experimental values.*[8]

(g) *Sum of all three terms, with* $S_C^2(o)S_F^2(o) = 58{\cdot}0417$ *a.u. and* $\langle r^{-3}\rangle_C\langle r^{-3}\rangle_F = 68{\cdot}721$ *a.u.*

theory used here, there are two types of integrals appearing in the theoretical expressions for J_{AB} which, as suggested by Pople, McIver, and Ostlund[6] for the contact term, may be treated as parameters. These are $S_A^2(o)$, the s-electron density at the nucleus of atom A, and $\langle r^{-3}\rangle_A$, the average value of r^{-3} for an electron in a p-orbital centred on atom A, where r is the position vector of the electron. The contact term is proportional to the product $S_A^2(o)S_B^2(o)$ and both the orbital and dipolar terms are proportional to $\langle r^{-3}\rangle_A$-$\langle r^{-3}\rangle_B$.

In the Figures a—d, the values $S_C^2(o)S_F^2(o) = 33{\cdot}1099$ a.u. and $\langle r^{-3}\rangle_C\langle r^{-3}\rangle_F = 12{\cdot}768$ a.u. were used. These values come from the atomic calculations of Morton, Rowlands, and Whiffen.[7] Considerably better quantitative agreement with experiment is obtained if different values are chosen. For the contact term alone, the best least-squares agreement is obtained when $S_C^2(o)S_F^2(o) = 100{\cdot}833$ a.u. (Figure, e). When all three terms are included, the best values are $S_C^2(o)S_F^2(o) = 58{\cdot}0417$ a.u. and $\langle r^{-3}\rangle_C\langle r^{-3}\rangle_F = 68{\cdot}721$ a.u. (Figure, g).

The Figure, e, shows that even when optimally scaled for these four molecules, the contact term alone incorrectly predicts the experimental trend. On the other hand, scaling of all three contributions (Figure, g) permits both the trend and the numerical values of J_{CF} in the fluoromethanes to be well reproduced.

In conclusion, we report that all three interactions must also be included for the series $CH_{3-n}F_nCN$, $CH_{3-n}F_nCH_2OH$, and $CH_{3-n}F_nCO_2H$ if the experimental trends are to be correctly predicted. A detailed report of these results and the theory employed is in preparation.

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