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# Substituent Effects on Scalar ${}^2J({}^{19}F,{}^{19}F)$ and ${}^3J({}^{19}F,{}^{19}F)$ NMR Couplings: A Comparison of SOPPA and DFT Methods

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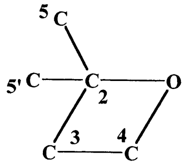
Substituent effects for ${}^2J(F,F)$ couplings in aliphatic and olefinic $CF_2$ moieties and ${}^3J(F,F)$ couplings in fluorinated derivatives of ethylene were studied using both high level ab initio and DFT/B3LYP calculations. Where possible, J variations have been compared with experimental values. In general, the SOPPA (second-order polarization propagator approximation) methodology matches absolute experimental values reasonably well, whereas the DFT/B3LYP approach performs poorly in describing ${}^2J(F,F)$ couplings. Fortunately, substituent effects for DFT J couplings are notably better reproduced. For a vinyl $CF_2$ moiety, the accurate prediction of ${}^2J(F,F)$ couplings is a challenging task even for high level ab initio methods such as SOPPA and SOPPA(CCSD) (second-order polarization propagator approximation with coupled cluster singles and doubles amplitudes). Aliphatic ${}^2J(F,F)$ couplings are very sensitive to the electronegativity of substituents placed α to the $CF_2$ group. The latter J perturbations are dominated largely by the noncontact PSO and SD Ramsey contributions, whereas the influence of the FC term is rather small. Substituent effects on ${}^2J(F,F)$ and ${}^3J(F,F)$ couplings in fluorinated derivatives of ethylene are also dominated by non-Fermi contributions. Because DFT/B3LYP strongly underestimates the FC contribution, but generally assesses the non-Fermi terms similar to SOPPA, the latter accounts for DFT's ability to predict substituent effects reasonably well.

## Introduction

Observation of structurally informative trans-hydrogen bond couplings between pairs of nucleic acids,[1] in proteins[2] and in protein−nucleotide complexes,[3] during the past few years has dramatically increased interest in NMR spectroscopy. Two concomitant factors have contributed to the situation: new experimental techniques appearing at an unexpected pace and a surprising increase in computational resources affecting both hardware and software. In this environment, a strong renewed interest in theoretical aspects of both magnetic shielding constants and spin−spin coupling constants[4] has surfaced. With respect to the latter, this interest includes studies which offer insight into the underlying interaction and transmission mechanisms. Scalar couplings are a composite of four Ramsey terms: Fermi contact (FC), spin dipolar (SD), paramagnetic spin−orbit (PSO), and diamagnetic spin−orbit (DSO). Experimentally, only total scalar couplings are amenable to measurement. The importance of each contribution can only be assessed by either high level calculations or indirect criteria. In many cases it is assumed that the couplings are strongly dominated by the Fermi contact term. However, recent calculations show that for both saturated and unsaturated compounds scalar couplings involving fluorine nuclei are dominated by noncontact contributions.[5−7] It should also be noted that in recent years fluorine has been incorporated into alpha-helices,[8] proteins,[9] and bioactive small molecules[10] as NMR probes for aggregation, microenvironmental structure, and binding site interactions.

**SCHEME 1: 1a: 2-$(CF_3)_2$;3-$F_2$;4-F,H; 1b: 2-$(CF_3)_2$;3-$F_2$;4-F,Cl; 1c: 2-$(CF_3)_2$;3-$F_2$;4-Cl,H; 1d: 2-$(CF_3)_2$;3-F,H;4-$F_2$; 1e: 2-$(CF_3)_2$;3-Cl,F;4-$F_2$; 1f: 2-$(CF_3)_2$;3-Cl,H;4-$F_2$.**



${}^{19}$F,${}^{19}$F) spin−spin coupling constants (hereafter J(F,F)) present some peculiarities which make them more difficult to rationalize than other types of couplings. For instance, it has not been possible to establish an empirical correlation between *vicinal* couplings and the corresponding dihedral angle, a trend that was thought to be due to dominant substituent effects.[11] Similarly, substituent effects on *geminal* couplings are known to be large and unpredictable. In general, two-bond couplings (${}^2J(F,F)$) in aliphatic $CF_2$ groups range from 200 to 350 Hz, whereas the olefinic values ($C(sp^2)F_2$) run from 10 to 100 Hz. Some conspicuous outliers are also known. For example, the $CF_2$ at C-4 in oxetane **1** is reported to show ${}^2J(F,F)$ as low as 83 Hz, whereas the corresponding couplings at C-3 are found to be larger than 200 Hz.[12] This suggests that an oxygen atom placed α to the carbon of the $CF_2$ moiety results in a very large and negative substituent effect. An outlier in the $C(sp^2)F_2$ class is tetrafluoroethylene with ${}^2J(F,F) = 121.8$ Hz (Scheme 1).[13]

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Based on DFT calculations, it has recently been shown that the dihedral angle dependence for $^3J(F,F)$ couplings is unusual, since noncontact contributions follow separate torsion angle dependences.[14] For F−CH$_2$−CH$_2$−F, it appears that the fluorine lone electron pairs contribute a very important negative contribution to the Fermi contact (FC) term for the trans conformation. As a result, the graphed dihedral angle dependence of the total $^3J(F,F)$ coupling appears quite different from that of standard Karplus curves[15] representing, for example, $^3J(H,H)$, $^3J(C,H)$, $^3J(N,H)$, $^3J(F,H)$, and $^3J(C,C)$ couplings.[16] In fluorinated pyridines, DFT/B3LYP calculated $^nJ(F,F)$ ($n = 3-7$) couplings in very good agreement with experimental values were found to comprise strong contributions from non−contact terms.[7] Another unusual feature of J(F,F) couplings is that in many cases such interactions have been reported to be dominated by a through-space mechanism.[17] According to recent studies,[6,18] substantial paramagnetic spin−orbital (PSO) terms may well contribute to such through-space couplings in certain instances.

These considerations suggest that the behavior of $^2J(F,F)$ and $^3J(F,F)$ couplings, both in saturated and unsaturated compounds, may be governed by substituent effects acting selectively on the four different Ramsey terms (FC, SD, PSO, and DSO).[19] To test this hypothesis, we have applied the second-order polarization propagator approximation (SOPPA)[20−22] and DFT/B3LYP[7,23] theory to calculation of the four terms of scalar $^2J(F,F)$ coupling in a set of model compounds incorporating FC(sp$^2$)F and FC(sp$^3$)F moieties. Total coupling trends are compared with experimental values for 1,1-vinyl-difluorides and derivatives of oxetane **1.** Similar calculations have been carried out for the $^3J(F,F)$ coupling components in a few di-, tri-, and tetra-fluorinated ethylenes.

It is known that DFT-based approaches to calculating coupling constants fail for some couplings involving at least one F atom.[24] Thus, results obtained at both the SOPPA and DFT/B3LYP levels should provide an idea of how the latter protocol performs for short range J(F,F) couplings by contrast with an inherently superior method. Such comparisons are important because high level ab initio J-calculations are prohibitively expensive for polyatomic compounds. Therefore, if DFT-calculated $^2J(F,F)$ and $^3J(F,F)$ couplings can be shown to describe the important trends semiquantitatively, then such an approach would be an adequate alternative for studying medium to large molecular weight polyatomic structures.

**Methods of Calculation.** *Geometry Optimizations.* All geometry optimizations were performed with the Gaussian 98 package of programs[25] at the MP2/cc-pVTZ level using very tight optimization.

*SOPPA Calculations.* The SOPPA method[20,21,22] is based on second-order Møller−Plesset perturbation (MP2) theory,[26] accounting for electron correlation effects through second order in the fluctuation potential. Replacement of the MP2 correlation coefficient in the SOPPA equations with the coupled cluster single and double (CCSD) amplitudes yields the SOPPA(CCSD) scheme.[22,27] In the present work, SOPPA and SOPPA(CCSD) calculations were performed with a local version of the Dalton 1.2 program package.[28] Locally dense basis sets (LDBS)[29,30] were employed in order to keep the basis set size within the current limitations of the SOPPA implementation in the program. The aug-cc-pVTZ-J [31,32] basis sets, which ensure the cusp behavior of the wave function and consequently a very good description of the FC term [ref 31 and references cited therein] were used for atoms considered important for defining the coupling pathway for nuclei involved in the calculated couplings (For each particular case see Table footnotes). For all other atoms, the cc-pVTZ and/or cc-pVDZ[33] basis sets were employed.

**TABLE 1: Comparison of SOPPA and DFT/B3LYP calculated $^2J(F,F)$ Couplings for Fluorinated Derivatives of Methane; MCSCF Values for $CF_2H_2$ and $CF_3H$ from ref 38 in Hz**

| | method | DSO | PSO | SD | FC | total |
|---|---|---|---|---|---|---|
| $CF_2\ H_2$$^a$ | SOPPA | −1.1 | 134.4 | 73.7 | 111.4 | 318.4 |
| | DFT | −1.1 | 152.6 | 89.2 | 51.8 | 292.5 |
| | MCSCF$^b$ | −1.1 | 132.8 | 74.5 | 140.0 | 346.2 |
| $CF_2HOH$$^a$ | SOPPA | −0.8 | −16.6 | 45.5 | 113.4 | 141.6 |
| | DFT | −0.7 | −23.7 | 52.6 | 53.6 | 81.8 |
| $CF_3H$$^a$ | SOPPA | −0.9 | −13.1 | 41.6 | 96.6 | 124.2 |
| | DFT | −0.9 | −22.4 | 47.6 | 33.9 | 58.2 |
| | MCSCF$^c$ | −0.8 | −13.4 | 40.7 | 125.9 | 152.4 |
| $CF_2HLi$$^d$ | SOPPA | −0.4 | 168.9 | 104.2 | 124.0 | 396.6 |
| | DFT | −0.4 | 194.1 | 127.8 | 49.8 | 371.3 |

[a] Basis set: aug-cc-pVTZ-J[31,32] for all atoms: F and C (15s6p3d1f/9s5p3d1f), H (10s3p1d/6s3p1d). [b] Values taken from ref 38. HIII[51, 52] basis set (11s7p2d/7s6p1d) for C and F and (6s2p/4s2p) for H. Active space: $^{2100}RAS^{4321}_{11;864}$ with single and doubles excitation from RAS 2 to RAS 3. [c] Values taken from ref 38. HIII[51,52] basis set (11s7p2d/7s6p1d) for C and F and (6s2p/4s2p) for H. Active space: $^{31}RAS^{85}_{16;16}$ with single and doubles excitation from RAS 2 to RAS 3. [d] Basis set: aug-cc-pVTZ-J[31,32] (15s6p3d1f/9s5p3d1f) for F and C and cc-pVTZ[33] for H (5s2p1d/3s2p1d) and Li (11s5p2d1f/4s3p2d1f).

*DFT/B3LYP Calculations.* DFT/B3LYP coupling constant calculations were carried out with a modified version of the Gaussian 98 program[25] following the theoretical scheme described previously.[7] It has since been observed that the aug-cc-pVTZ-J basis performs remarkably well in conjunction with DFT calculations, in the sense that it yields spin−spin couplings values close to the converged limit of the basis set.[34] The FC and PSO terms were obtained within the coupled perturbed framework, whereas the SD term was evaluated by means of finite perturbation theory.[35] PSO and the DSO integrals were obtained from the Dalton program.[28] For an even-handed comparison, in all cases, DFT and SOPPA J coupling calculations were carried out with the same basis sets.

Following ideas developed previously for the dissection of the FC term into natural localized molecular orbitals (NLMO),[36] we make use of the related decomposition of the PSO term into LMO contributions by transforming the first-order density matrix and the matrix elements of the PSO Hamiltonian from atomic orbitals to localized molecular orbitals. As in the previous work,[36] the NLMO were obtained from natural bond orbital (NBO) analysis[37] as implemented in the Gaussian 98 suite of programs.

## Results and Discussion

**$CF_2XH$ Model Compounds.** To obtain insight into the large differences observed for $^2J(F,F)$ couplings at different ring positions in oxetanes **1**,[12] difluoromethane and difluoromethanol were taken as model compounds to evaluate the effect on $^2J(F,F)$ of an oxygen atom placed α to the C atom of the FCF moiety. These acyclic and unstrained structures are small enough to allow a comparison between the DFT calculated values and those obtained with the high level ab initio SOPPA approach. The corresponding SOPPA and DFT/B3LYP values for all four scalar coupling terms are compiled in Table 1, together with those for $CF_3H$ and $CF_2LiH$. The latter structures add an additional electronegative fluorine and the electropositive lithium cation, respectively. When comparing SOPPA and DFT/B3LYP $^2J(F,F)$ couplings for $CF_2H_2$ and $CF_2HOH$, it is observed that

**TABLE 2: Comparison of Calculated Substituent Effects, Δ(X), on $^2$J(F,F) Couplings in Monosubstituted Derivatives of Difluoromethane, $CF_2XH$,[a] in Hz**

| subs. | method | DSO | PSO | SD | FC | total |
|---|---|---|---|---|---|---|
| Δ(F) | SOPPA | 0.2 | −147.5 | −32.1 | −14.8 | −194.2 |
| | DFT | 0.2 | −175.0 | −41.6 | −17.9 | −234.3 |
| | MCSCF[b] | 0.3 | −146.2 | −33.8 | −14.1 | −193.8 |
| Δ(OH) | SOPPA | 0.3 | −151.0 | −28.2 | 2.0 | −176.9 |
| | DFT | 0.4 | −176.3 | −36.6 | 1.8 | −210.7 |
| Δ(Li) | SOPPA | 0.7 | 34.5 | 30.5 | 12.6 | 78.2 |
| | DFT | 0.7 | 41.5 | 38.6 | −2.0 | 80.8 |

[a] Derived from Table 1. [b] Values taken from ref 38.

**TABLE 3: DFT/B3LYP[a] Values Predicted for J($F_{3'}$,$F_{3''}$) and J($F_{4'}$,$F_{4''}$) in 2,2,3,3-Tetrafluorooxetane (2) in Hz**

| | DSO | PSO | SD | FC | total | exp.[b] | | |
|---|---|---|---|---|---|---|---|---|
| J($F_{3'}$,$F_{3''}$) | −0.3 | 54.9 | 63.3 | 25.5 | 143.3 | 221[c] | 203[d] | 206[e] |
| J($F_{4'}$,$F_{4''}$) | −0.3 | −61.5 | 44.3 | 45.4 | 28.0 | 96[f] | 83[g] | 87[h] |
| Δ | 0.0 | −116.4 | −19.0 | 19.9 | −115.3 | −125 | −120 | −119 |

[a] The aug-cc-pVTZ-J basis set was used on all atoms. [b] Taken from ref 2. [c] In **1a**. [d] In **1b**. [e] In **1c**. [f] In **1d**. [g] In **1e**. [h] In **1f**.

both methods yield similar overall total coupling trends. Agreement with respect to Ramsey term partitioning, however, is not satisfying. Of particular note, the large differences between the FC term from the two approaches account for most of the discrepancy in the total *J* values. In all three cases, substituent effects on $^2$J(F,F) (Table 2) are dominated strongly by the sum of the noncontact PSO and SD contributions, the former being much more important than the latter. A substituent effect so decisively dominated by the PSO term is a rather unexpected result, one worth examining in detail. Two compound classes are evaluated below.

In Tables 1 and 2, MCSCF $^2$J(F,F) coupling calculations for $CF_2H_2$ and $CF_3H$ taken from the current literature[38] are also included. When they are compared with the SOPPA values obtained in the present work, very good agreement for the PSO and SD terms is noted, whereas a rather important difference for the FC term is evident. It may well be that the FC MCSCF calculation is not optimal with respect to the basis set for the chosen active space. However, if such a discrepancy operates, it is the same for both $CF_2H_2$ and $CF_3H$ leading to excellent agreement between the MCSCF and SOPPA fluorine substituent effect on the $^2$J(F,F) coupling in difluoromethane (cf. Table 2).

**Fluorinated Oxetanes.** We have obtained DFT−$^2$J(F,F) couplings and the four Ramsey terms for the analogue of compound **1** in which two fluorine atoms reside at C-3 ($^2$J($F_{3'}$,$F_{3''}$)), another two fluorines reside at C-4 ($^2$J($F_{4'}$,$F_{4''}$)), and the C-5 and C-5′ carbons are replaced by H atoms, i.e., 2,2,3,3-tetrafluorooxetane (**2**) (Table 3). Total couplings are compared with experimental values taken from Brey and Brey[12] for oxetanes **1a**−**f**. Calculated couplings follow the same trend as observed in the oxetane couplings, although the computed values are considerably underestimated. Reference to the SOPPA and DFT results depicted in Table 1 suggests that this shortcoming originates in the very small value calculated for the FC term, although in this case the PSO term is also somewhat smaller than predicted for $CF_2H_2$ (Table 1) and may be underestimated as well. Nonetheless, the regiospecific substituent effects displayed in Table 3 show very good agreement with experimental values taken from oxetane derivatives **1a**−**f**. It is important to note that these calculated substituent effects originate in the PSO term, whereas the SD and FC contributions nearly cancel each other. The result suggests this to be a good candidate for dissecting the PSO terms of $^2$J($F_{3'}$,$F_{3''}$) and $^2$J($F_{4'}$,$F_{4''}$) into localized molecular orbitals (LMOs) to probe the underlying cause of the sign differences in Table 3.

**TABLE 4: DFT/B3LYP−NJC[a] Dissection of the PSO Term into NLMO Contributions for J($F_{3'}$,$F_{3''}$) and J($F_{4'}$,$F_{4''}$) Couplings in 2,2,3,3-Tetrafluorooxetane (2) in Hz**

| contribution | J($F_{3'}$,$F_{3''}$) | J($F_{4'}$,$F_{4''}$) |
|---|---|---|
| Σ(C−C) | 10.8 | 4.2 |
| Σ (C−O) | 0.59 | 2.6 |
| Σ (C−H) | −2.1 | 0.06 |
| Σ (C−$F_j$)[b] | −13.4 | −30.4 |
| Σ (C−$F_k$)[c] | −0.16 | −0.19 |
| Σ (Core) | 0.72 | 0.84 |
| Σ (LP(O)) | −0.01 | −7.4 |
| Σ (LP($F_j$))[b] | 59.4 | −30.8 |
| Σ (LP($F_k$))[c] | −0.89 | −0.47 |
| total | 54.89 | −61.49 |

[a] The aug-cc-pVTZ-J basis set was used on all atoms. [b] $F_j$: coupled nuclei. [c] $F_k$: not coupled nuclei.

To obtain a qualitative description of factors affecting the PSO term, it should be recalled that the perturbative Hamiltonian corresponding to the PSO interaction can be written as

$$H_{\mathrm{PSO}} = \frac{\mu_o \hbar \mu_B}{2\pi i} \sum_A \gamma A \mathbf{I}_A \sum_k \frac{(\mathbf{r}_{kA} \times \nabla_k)}{{r_{kA}}^3} \qquad (1)$$

and the PSO term is obtained through second-order perturbation theory. Without committing oneself to any particular approximation, a qualitative description of certain factors affecting the PSO term can be obtained by referring to the coupled Hartree−Fock perturbative approach. Within this methodology, the PSO term can be split into a sum of terms, each depending on two occupied and two vacant LMOs. Because the Hamiltonian of eq 1 involves the rotation operator, ($r_{kA} \times \nabla_k$), such contributions will be significant when there is substantial overlap between an occupied LMO rotated by 90° and a vacant LMO localized at the site of a chemical bond. The energy gap between these two orbitals is also important for defining the magnitude of such contributions. However, we note that the present NJC dissection analysis explicitly considers only the occupied LMOs, whereas vacant MO are implicitly taken into account only through the coupled-perturbed procedure. The bond-localized contributions of the PSO term to $^2$J($F_{3'}$,$F_{3''}$) and $^2$J($F_{4'}$,$F_{4''}$) in **2** (59.4 and −30.8 Hz, respectively) are given in Table 4, where it is observed that the main difference comes from the sum of the lone electron pairs on the coupled fluorine atoms. The difference, −90.7 Hz, amounts to the majority of the substituent effect displayed in Table 3. From the qualitative description of LMO properties affecting the PSO term outlined above, it is possible to rationalize the −90.7 Hz difference. The substantial difference in fluorine lone pair contributions from $^2$J($F_{3'}$,$F_{3''}$) and $^2$J($F_{4'}$,$F_{4''}$) seems to originate in the interaction between an F lone pair and the vacant LMOs placed at the C−F bond involving the same fluorine atom. Qualitatively, this vacant LMO possesses features similar to the corresponding σ(C−F)* antibond as obtained by NBO analysis. The electronegative O atom is bonded α to the $F_{4'}C_4F_{4''}$ moiety. This widens the energy gap between the $F_{4'}$ and $F_{4''}$ lone pairs and the vacant $C_4$−$F_{4',4''}$ LMOs (or, approximately, the σ($C_4$−$F_{4',4''}$)* antibonds of the NBO analysis). Therefore, the PSO term of $^2$J(F,F) couplings should decrease when an electronegative group is bonded α to the FCF moiety. To test this rationalization, the calculated $^2$J(F,F) couplings in $CF_3H$ and $CF_2HLi$ are also included in Table 1, and the respective effects on the Ramsey terms of

**TABLE 5: Comparison of SOPPA, SOPPA (CCSD), DFT/B3LYP, and Experimental[a] $^2J$(F,F) and $^3J$(F,F) Couplings in 1,1-Difluoroethylene (3) and 1,2-Difluoroethylene (4 and 5) in Hz**

| comp | subs. | coupling | method [b] | DSO | PSO | SD | FC | total |
|---|---|---|---|---|---|---|---|---|
| 3 | 1,1-di | $^2J$(F,F) | SOPPA | −1.2 | −74.6 | 22.3 | 67.4 | 13.9 |
| | | | SOPPA(CCSD) | −1.1 | −67.4 | 22.6 | 64.0 | 18.1 |
| | | | DFT | −1.1 | −104.5 | 20.3 | 6.0 | −79.3 |
| | | | exp.[a] | | | | | 36.4 |
| 4 | (*Z*)-1,2-di | *cis*-J(F,F) | SOPPA | −0.4 | −38.3 | 24.3 | 0.7 | −13.7 |
| | | | SOPPA(CCSD) | −0.4 | −35.9 | 22.2 | 0.5 | −13.6 |
| | | | DFT | −0.4 | −47.6 | 30.2 | 1.8 | −16.0 |
| | | | exp.[a] | | | | | −18.7 |
| 5 | (*E*)-1,2-di | *trans*-J(F,F) | SOPPA | −1.8 | −143.1 | 22.8 | −11.5 | −133.6 |
| | | | SOPPA(CCSD) | −1.8 | −136.5 | 20.6 | −11.5 | −129.2 |
| | | | DFT | −1.8 | −162.7 | 27.9 | −26.7 | −163.3 |
| | | | exp.[a] | | | | | −132.7 |

[a] Experimental values were taken from ref 53. [b] Basis set: aug-cc-pVTZ-J (ref 31, 32) for all atoms: F and C (15s6p3d1f/9s5p3d1f), H (10s3p1d/6s3p1d).

**TABLE 6: Comparison of SOPPA, SOPPA (CCSD), DFT/B3LYP, and Experimental[a] $^2J$(F,F) and $^3J$(F,F) Couplings in Trifluoroethylene (6) in Hz**

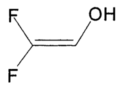
| coupling | method[b] | DSO | PSO | SD | FC | total |
|---|---|---|---|---|---|---|
| $^2J$(F,F) | SOPPA | −1.1 | −16.5 | 27.0 | 51.7 | 61.1 |
| | SOPPA(CCSD) | −1.1 | −12.1 | 27.2 | 48.4 | 62.3 |
| | DFT | −1.1 | −39.5 | 27.5 | −6.8 | −19.0 |
| | exp.[a] | | | | | 82 |
| *cis*-$^3J$(F,F) | SOPPA | −0.3 | 5.3 | 30.9 | 2.2 | 38.1 |
| | SOPPA(CCSD) | −0.3 | 5.0 | 28.7 | 2.2 | 35.7 |
| | DFT | −0.3 | 6.4 | 39.1 | 2.1 | 47.3 |
| | exp.[a] | | | | | 33 |
| *trans*-$^3J$(F,F) | SOPPA | −1.8 | −128.9 | 18.7 | −8.4 | −120.4 |
| | SOPPA(CCSD) | −1.8 | −122.8 | 17.2 | −8.5 | −116.0 |
| | DFT | −1.8 | −145.6 | 22.7 | −21.3 | −146.1 |
| | exp.[a] | | | | | 118 |

[a] Experimental values were taken from ref 54. [b] Basis set: aug-cc-pVTZ-J (ref 31, 32) on F and C2 (15s6p3d1f/9s5p3d1f), cc-pVTZ (ref 33) on C1 (10s5p2d1f/4s3p2d1f), cc-pVDZ (ref 33) on H (4s1p/2s1p).

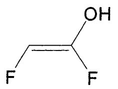
$^2J$(F,F) are displayed in Table 2. Somewhat surprisingly, the potent electronegative OH and F substitutents both elicit a similar decrease in PSO. Nonetheless, such results strongly support the above rationalization concerning the effect of an α group on the PSO term of $^2J$(F,F) couplings. Although no rationalization of the substituent effect on the SD term of $^2J$(F,F) couplings is attempted, it appears that it is also strongly influenced by the electronegativity of an α substituent.

**Flourinated Ethylenes.** The interesting influence of substituents on two bond couplings for the FC(sp$^3$)F functionality discussed above prompted us to extend the work to the FC(sp$^2$)F moiety in the context of several vinyl fluorides. The poor performance of the DFT/B3LYP approach for describing such coupling underscores the importance of studying how DFT/B3LYP calculated $^2J$(F,F) and $^3J$(F,F) couplings compare with high level ab initio values. For the olefinic structures, such comparisons are made against both SOPPA and SOPPA(CCSD) J(F,F) couplings. The corresponding Ramsey terms are summarized in Tables 5−8. In Table 5, it is observed that all three computational approaches agree poorly with the experimental $^2J$(F,F) coupling in 1,1-difluoroethylene (**3**). It seems that the accurate calculation of this coupling is challenging not only for the DFT approach but also for the high level ab initio schemes. On the other hand, for the $^3J$(F,F) coupling in (*Z*)1,2-difluoroethylene (**4**), the three predictive approaches perform reasonably well. Note that in all cases the FC term is found to be much smaller, in absolute value, than the SD and PSO terms. The agreement between SOPPA and SOPPA(CCSD) values is excellent, although this agreement results from a small compensation between PSO and SD terms. The total DFT value is also in notably better agreement with the corresponding ab initio quantities than are the different Ramsey terms.

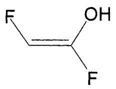
For *trans*-$^3J$(F,F) coupling in (*E*)-1,2-difluoroethylene (**5**), all three approaches yield negative values for the PSO and FC terms, although the absolute value from the DFT result is somewhat overestimated by comparison with those obtained with the SOPPA approaches. It is noteworthy that the trans configuration of the fluorine atoms in 1,2-difluoroethane (i.e., $F-CH_2-CH_2-F$) delivers negative values for the PSO and FC terms by DFT.[14] NJC analysis of the latter term showed that the negative value originates in the F lone pairs in the F−C−C−F plane of the trans conformer.



**7**



**8**



**9**

In Table 6, calculated J(F,F) couplings in trifluoroethylene (**6**) are compared with experimental values taken from Koroniak et al.,[54] whereas in Tables 7 and 8, the values for the three isomers of difluoroethenol, **7**, **8**, and **9**,[39−42] and tetrafluoroethylene (**10**), respectively, are provided. Comments similar to those made above for values reported in Table 5 hold for those shown in Table 6. From results displayed in Tables 6 and 7, fluorine and OH substituent effects on $^2J$(F,F), *cis*-$^3J$(F,F), and *trans*-$^3J$(F,F) couplings are obtained by subtracting the couplings shown in Table 5 from the corresponding values given in Tables 6 and 7. The calculated substituent effects obtained with SOPPA and DFT approaches are compared among themselves and, in the fluorine case, with experimental values. Results thus obtained are given in Table 9. The following features, corresponding to *β*-substituent effects, are worth comment. The PSO and SD terms of $^2J$(F,F) are of opposite signs to those displayed in Table 2 for α-substituent effects. The substituent effect for the FC term is of the same sign and of similar absolute value for both α- and *β*-substituent effects. It is also noteworthy that the PSO terms for the fluorinated analogue are smaller than those for the hydroxyl analogue in accord with the qualitative rationalization given above for the $CF_2$ moiety. For $^3J$(F,F) couplings, the FC substituent effect is smaller in absolute value than the PSO and SD substituent effects. For *trans*-$^3J$(F,F), the total substituent effects are notably smaller than for *cis*-$^3J$(F,F) couplings.

Interestingly, the total DFT fluorine substituent effects are markedly better reproduced than total coupling constants. If values of J(F,F) couplings for trifluoroethylene are subtracted

**TABLE 7: Comparison of SOPPA, SOPPA (CCSD), and DFT/B3LYP $^{2}$J(F,F) and $^{3}$J(F,F) Couplings in Difluoroethenol Isomers 7−9 in Hz**

| compd | subs. | coupling | method | DSO | PSO | SD | FC | total |
|---|---|---|---|---|---|---|---|---|
| 7 | 2,2-di[a] | $^{2}$J(F,F) | SOPPA | −1.1 | 7.0 | 31.8 | 56.5 | 94.3 |
| | | | SOPPA(CCSD) | −1.0 | 10.5 | 31.6 | 52.8 | 93.9 |
| | | | DFT | −1.1 | −27.9 | 29.1 | −6.9 | −6.7 |
| 8 | (*Z*)-1,2-di[b] | *cis*-$^{3}$J(F,F) | SOPPA | −0.2 | −7.5 | 24.5 | 1.8 | 18.7 |
| | | | SOPPA(CCSD) | −0.2 | −7.3 | 22.9 | 1.8 | 17.3 |
| | | | DFT | −0.2 | −8.4 | 30.1 | 2.5 | 24.0 |
| 9 | (*E*)-1,2-di[b] | *trans*-$^{3}$J(F,F) | SOPPA | −1.8 | −123.6 | 13.7 | −10.6 | −122.3 |
| | | | SOPPA(CCSD) | −1.8 | −117.9 | 12.7 | −10.7 | −117.7 |
| | | | DFT | −1.7 | −145.2 | 17.7 | −22.5 | −151.7 |

[a] Basis sets: aug-cc-pVTZ-J (ref 31, 32) on F and C2 (15s6p3d1f/9s5p3d1f), cc-pVTZ (ref 33) on C1 and O (10s5p2d1f/4s3p2d1f), cc-pVDZ (ref 33) on H (4s1p/2s1p). [b] Basis set: aug-cc-pVTZ-J (ref 31, 32) on F (15s6p3d1f/9s5p3d1f), cc-pVTZ (ref 33) on C and O (10s5p2d1f/4s3p2d1f), cc-pVDZ (ref 33) on H (4s1p/2s1p).

**TABLE 8: Comparison of SOPPA, SOPPA (CCSD), DFT/B3LYP, and Experimental[a] $^{2}$J(F,F) and $^{3}$J(F,F) Couplings in Tetrafluoroethylene (10) in Hz**

| coupling | method [b] | DSO | PSO | SD | FC | total |
|---|---|---|---|---|---|---|
| $^{2}$J(F,F) | SOPPA(CCSD) | −1.0 | 31.4 | 33.4 | 40.1 | 103.9 |
| | DFT | −1.0 | 9.6 | 35.0 | −11.4 | 32.3 |
| | exp.[a] | | | | | 121.756 |
| *cis*-$^{3}$J(F,F) | SOPPA(CCSD) | −0.2 | 35.8 | 32.8 | 2.3 | 70.7 |
| | DFT | −0.1 | 45.4 | 44.4 | 1.8 | 91.5 |
| | exp.[a] | | | | | 74.567 |
| *trans*-$^{3}$J(F,F) | SOPPA(CCSD) | −1.8 | −119.6 | 15.8 | −2.1 | −107.7 |
| | DFT | −1.8 | −143.3 | 20.1 | −11.6 | −136.9 |
| | exp.[a] | | | | | −111.877 |

[a] Experimental values were taken from ref 13. [b] Basis sets: aug-cc-pVTZ-J[31,32] on three F atoms ($F_1$, $F_2$ and $F_{2'}$) and $C_2$; on $C_1$: cc-pVTZ and on $F_{1'}$: cc-pVDZ[33].

**TABLE 9: Comparison of Calculated Substituent Effects on $^{2}$J(F,F) and $^{3}$J(F,F) Couplings in Fluoroethylenes and Difluoroethenol Isomers 7−9, i.e. J(F,F)(Trifluoro)−J(F,F)(Difluoro),[a] in Hz**

| subs. | | | DSO | PSO | SD | FC | total |
|---|---|---|---|---|---|---|---|
| Δ(F) | $^{2}$J(F,F) | SOPPA | 0.1 | 58.1 | 4.7 | −15.7 | 47.2 |
| | | SOPPA(CCSD) | 0 | 55.3 | 4.6 | −15.6 | 44.2 |
| | | DFT | 0 | 65.0 | 7.1 | −12.8 | 59.3 |
| | | exp.[a] | | | | | 50 |
| | *cis*-$^{3}$J(F,F) | SOPPA | 0.1 | 43.6 | 6.6 | 1.5 | 51.8 |
| | | SOPPA(CCSD) | 0.1 | 40.9 | 6.5 | 1.7 | 49.3 |
| | | DFT | 0.1 | 54.0 | 8.9 | 0.3 | 63.3 |
| | | exp.[a] | | | | | 42 |
| | *trans*-$^{3}$J(F,F) | SOPPA | 0 | 14.2 | −4.1 | 3.1 | 13.2 |
| | | SOPPA(CCSD) | 0 | 13.7 | −3.4 | 3.0 | 13.2 |
| | | DFT | 0 | 17.1 | −5.2 | 5.4 | 17.2 |
| | | exp.[a] | | | | | 15 |
| Δ(OH) | $^{2}$J(F,F) | SOPPA | 0.1 | 81.6 | 9.5 | −10.9 | 80.4 |
| | | SOPPA(CCSD) | 0.1 | 77.9 | 9.0 | −11.2 | 75.8 |
| | | DFT | 0.1 | 76.6 | 8.8 | −12.9 | 72.6 |
| | *cis*-$^{3}$J(F,F) | SOPPA | 0.2 | 30.8 | 0.2 | 1.1 | 32.4 |
| | | SOPPA(CCSD) | 0.2 | 28.6 | 0.7 | 1.3 | 30.9 |
| | | DFT | 0.2 | 39.2 | −0.1 | 0.7 | 40.0 |
| | *trans*-$^{3}$J(F,F) | SOPPA | 0 | 19.5 | −9.1 | 0.9 | 11.3 |
| | | SOPPA(CCSD) | 0 | 18.6 | −7.9 | 0.8 | 11.5 |
| | | DFT | 0.1 | 17.5 | −10.2 | 4.2 | 11.6 |

[a] Differences taken from data in Tables 5−7.

from the respective couplings in tetrafluoroethylene, then the substituent effect for a second fluorine atom can be estimated. It is noteworthy that such a difference is very close to the Δ(F) value shown in Table 9 only for the *cis*-$^{3}$J(F,F) coupling. This means that for this coupling a substituent additivity rule holds, whereas for $^{2}$J(F,F) and *trans*-$^{3}$J(F,F), additivity is not operating. It is worth noting that in tetrafluoroethylene the worst agreement between SOPPA (CCSD) and experimental values is found again for the $^{2}$J(F,F) coupling, confirming the trend shown above for 1,1-difluoroethylene and trifluoroethylene.

## Concluding Remarks

High level ab initio SOPPA calculations of α-substituent effects on $^{2}$J(F,F) couplings for the $CF_2$ aliphatic moiety are found to be dominated by the PSO term. The SD contribution is second in importance followed by the FC term which governs most other coupling relationships involving non-F/F pairs of magnetically active nuclei. Substituent effects on PSO and SD are negative for an electronegative group and positive for an electropositive one. Comparing SOPPA couplings with those obtained by the DFT/B3LYP level of theory, the latter turns in a poor performance for $^{2}$J(F,F). However, substituent effects on such couplings are reasonably well reproduced. This fact was used to perform an NJC dissection analysis of the PSO term in a model compound mimicking an oxetane derivative (**2**) in order to obtain insight into the origin of the large PSO α-substituent effect. Such analysis highlights the role played by the lone-pairs on J-coupled fluorine with respect to both the very large contribution to $^{2}$J(F,F) and the α-substituent effect. Comparing SOPPA calculations with data taken from the literature, it can be concluded that substituent effects are easier to reproduce than coupling constants. A similar observation has been made for fluorine substituent chemical shifts, which are notably better reproduced than fluorine chemical shifts for F atoms bonded to different structures.[43] It is also interesting to note that SOPPA and SOPPA(CCSD) total couplings are in better agreement than the individual Ramsey contributions, because differences in the latter tend to compensate by cancellation.

Prediction of $^{2}$J(F,F) couplings for fluorine bonded to a vinyl moiety were found to be a challenging task even for the SOPPA and SOPPA(CCSD) approaches. Even so, both *cis*- and *trans*-$^{3}$J(F,F) calculated couplings agree more closely with experimental values than do the $^{2}$J(F,F) couplings. Calculations within the DFT/B3LYP framework for *cis*-$^{3}$J(F,F) couplings seem to perform better than for other couplings considered in this work. It is interesting to note that in previous investigations[7,18b] it was found that the DFT approach yields promising results for J(F,F) couplings in aromatic compounds. Recently, several studies have appeared in which the performance of the DFT approach for calculating NMR spin−spin couplings is discussed.[44] It seems that concordance with experiment depends more on the particular coupling pathway than on the nature of the coupled nuclei.

Shtarev and co-workers recently reported $^{2}$J(F,F) couplings for a series of bridge-fluorinated dimethyl bicyclo[1.1.1]pentane-1,3-dicarboxylates.[5] They obtained values ranging from 141.5 to 162.0 Hz which fall outside the normal 200 Hz to 350 Hz range for a $CF_2$ aliphatic moiety.[11] Similarly, Battiste and Posey[45] reported $^{2}$J(F,F) couplings which range from 145.5 and

163.3 Hz for a series of exo-3,3−difluorotricyclo[3.2.1.0$^{2,4}$] octane derivatives. Such values suggest that the PSO (and to a lesser extent, the SD) term of $^2$J(F,F) for aliphatic $CF_2$ moieties are very sensitive to bond angle strain at the fluorinated carbon atom. Such an effect can be viewed as a surrogate for an electronegative substituent placed $\alpha$ to the C atom, which increases the energy gap between the fluorine nonbonding electron pairs and the vacant C−F LMOs, thereby decreasing the magnitudes of the PSO and SD terms (in an algebraic sense). This widening of the lone pair-virtual orbital energy gap, $\Delta\epsilon$, increases in strained small-ring structures, thereby increasing this center's effective electronegativity. The generality of this viewpoint is reinforced by the $^2$J(F,F) values found for a wide range of fluorinated and strained cyclopropanes (150−185 Hz).[46] Similarly, the majority of fluorinated cyclobutanes follows suit with $^2$J(F,F) = 180−215.[46] Optimization of 2,2-difluoropropane, 1,1-difluorocyclobutane, and 1,1-difluorocyclopropane (B3LYP/6-311G**) followed by NBO analysis,[37,47] is supportive by reporting that the $CF_2$ $\Delta\epsilon$ gap increases along the series. Accordingly, some fraction of the lowering of J(F,F) for analogues of oxetane **2** to 83−96 Hz arises from the ring strain effect. However, it should be noted that these values are almost 100 Hz lower than those found for fluorinated cyclobutanes. The overwhelming influence of the electronegative $\alpha$-oxygen on J(F,F) in **2** is accompanied by an increase in $\Delta\epsilon$ for the (O)$CF_2$ moiety as measured by NBO analysis, identical to that for 1,1-difluoro-cyclopropane. It should be noted further that such trends for the PSO and SD terms of $^2$J(F,F) hold when passing from a C(sp3)$F_2$ moiety to a more electronegative C(sp$^2$) one. In fact, from difluoromethane (Table 1) to 1,2-difluoroethylene (Table 5), the PSO, SD, and FC terms (SOPPA values) change from +134.4, +73.7, and +111.4 Hz to −74.6, +22.3, and +67.4 Hz, respectively.

The NJC−PSO-DFT analysis employed in this work has provided unique insights into substituent effects on J(F,F) couplings. Despite the poor agreement between total DFT couplings and those provided by high level ab initio calculations, the general trends are followed closely by the PSO contributions. The NJC−PSO dissection extends our previous development[36] and application[14,18b,48] of the NJC-FC methodology and complements the related NJC−NBO formulation by the Wisconsin group.[49] Details concerning the formulation of the method and its implementation will be provided shortly.[50]

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