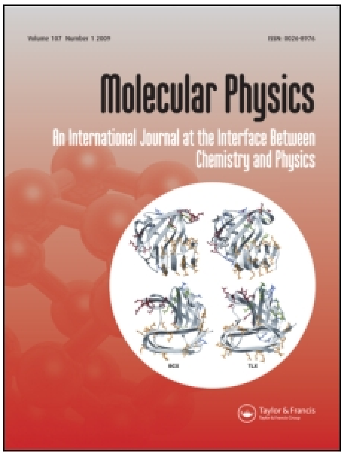

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# $^1$H and $^{19}$F dynamic nuclear polarization studies at X-band: $^{19}$F differential enhancements

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# $^1$H and $^{19}$F dynamic nuclear polarization studies at X-band : $^{19}$F differential enhancements†

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X-band dynamic nuclear polarization (DNP) measurements on $^1$H and $^{19}$F nuclei in 1,4-bis(trifluoromethyl)benzene, 1,2,4-trifluorobenzene and $^{19}$F nuclei in octafluorotoluene are reported. The free radical used in all these cases is tri-t-butylphenoxyl. Chemically shifted fluorines have been resolved and clear differential $^{19}$F DNP trends have been established in these systems. *Q*-enhancement corrections to ultimate–ultimate enhancement values are discussed. Three theoretical models of the radical–solvent interaction involving, respectively, transfer of an electron spin, M.O. treatment of solvent–radical interaction at separations around the van der Waals distance, and exchange polarization of the solvent molecule are reported. The latter, treated as a closed-shell perturbation in the molecular orbital framework, leads to an $sp_\sigma$ polarizability parameter which reflects the present experimentally observed $^{19}$F DNP trends reasonably well. Apart from the present work, the only other experimental results on $^{19}$F differential DNP are those of Dwek *et al.* at *Q*-band and their results have also been satisfactorily interpreted in terms of our $sp_\sigma$ polarizability approach.

## 1. INTRODUCTION

Differential dynamic nuclear polarization (DNP) of chemically shifted nuclei in a given molecule have attracted attention as a potential source of valuable information on molecular structure as well as molecular interactions [1]. Nuclei lying in the interior of molecules have more often been the subject of such investigations. Thus, correlations of differential DNP effects with structure have been possible for carbon-13 [2]. However, differential effects exhibited by nuclei lying at the molecular periphery have been rarely studied. To our knowledge, only one group of workers have reported studies [3] on differential $^{19}$F DNP. Their results pertain to *Q*-band studies and no satisfactory theoretical interpretation of these results is available. It has been our aim to study differential $^{19}$F DNP at X-band, where the requirements of resolution and Overhauser enhancement are generally in less serious conflict than at *Q*-band and to seek a theoretical framework in terms of which differential $^{19}$F DNP effects can be generally understood. Here we present our $^1$H and $^{19}$F DNP results on 1,2,4-trifluorobenzene and $^{19}$F DNP results on octafluorotoluene. We

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have been able to demonstrate clearly differential enhancements of the chemically shifted fluorines in these two systems. We also report $^{19}F$ and $^{1}H$ DNP studies at X-band on 1,4-bis(trifluoromethyl)benzene. The free radical employed in the present studies is tri-t-butylphenoxyl (TTBP).

## 2. Experimental

All the DNP measurements were carried out at room temperature (25° ± 2°C) on a spectrometer built in our laboratory and described in detail elsewhere [4]. The fluorine compounds were laboratory preparations and were used without further purification. The radical was prepared in the N.M.R. sample tube itself by adding excess, freshly-prepared nickel peroxide to the radical precursor, tri-t-butylphenol. The precursor was obtained from K. & K. Laboratories, U.S.A., and was freshly recrystallized from methanol before use. Dissolved oxygen in the DNP sample was removed by bubbling oxygen-free nitrogen gas through it. The radical concentration was estimated in all cases to be $\sim 5 \times 10^{-2}$ M on the basis of complete conversion of the precursor. Nuclear relaxation times in the DNP samples were obtained by rapid repetitive scan of the N.M.R. spectrum following sudden switch-off of the microwave power subsequent to establishing Overhauser polarization. In all cases relaxation times amounted to a fraction of a second, so that the leakage factor could be safely approximated to unity. At the maximum microwave power available to us (less than 300 mW), observed fluorine enhancements in the systems 1,2,4-trifluorobenzene and octafluorotoluene were small and hence extrapolation to obtain ultimate–ultimate enhancements ($U_\infty$ values) has not been attempted. Instead, relative enhancements were measured for the various resonances of a molecule. However, it proved possible to obtain $U_\infty$ values for both $^{1}H$ and $^{19}F$ in 1,4-bis-(trifluoromethyl)benzene.

## 3. Results and discussion

DNP results on the systems that we have studied are summarized in table 1. The values in parentheses correspond to those obtained after $Q$-enhancement correction (*vide infra*).

### 3.1. *Q-enhancement corrections*

It has been pointed out [1, 5] that the effect of precessing nuclear magnetism at resonance is to change the amplitude of the r.f. field $H_1$ exciting the N.M.R. Corrections to the observed enhancements should be applied in order to take this effect into account and arrive at the real enhancements. The equation we have employed for this purpose is

$$\delta\left(\frac{1}{A}\right) = A_a^{-1} - A_r^{-1} = \frac{\phi N \gamma_I^2 \hbar^2 \omega_0 Q_0}{2kT\Delta\nu}. \tag{1}$$

Here, $A_a$ is the apparent enhancement while $A_r$ is the real enhancement ; $\phi$ is the filling factor, $Q_0$ the quality factor, $\Delta\nu$ the linewidth and the other symbols have their usual significance. Equation (1) is identical to that given in [5] except that a ± sign was erroneously introduced and applied in [5].

Table 1. Summary of X-band DNP results on some fluorocarbon/TTBP systems (25° ± 2°C).

| Fluorocarbon | Nucleus | Relative enhancements (A) | $U_\infty$† |
|---|---|---|---|
| 1,4-Bis(trifluoromethyl)benzene | H | — | $-98 \pm 10$<br>$(-87)$ |
|  | F | — | $-71 \pm 9$<br>$(-64)$ |
| 1,2,4-Trifluorobenzene | H | — | $-153 \pm 27$<br>$(-126)$ |
|  | $F_1$ | 0·0 |  |
|  | $F_2$ | +0·4 | — |
|  | $F_4$ | −0·5 |  |
| Octafluorotoluene | $F_{al}$ | −2·0 |  |
|  | $F_o$ | −0·3 |  |
|  | $F_m$ | +3·6 |  |
|  | $F_p$ | +5·4 |  |

† Values in parentheses correspond to $U_\infty$ values after $Q$-enhancement correction (see equation (1) of text).

## 3.2. *Results*

### 3.2.1. *DNP in* 1,4-*bis(trifluoromethyl)benzene*

Proton DNP measurements carried out on the sample 1,4-bis(trifluoromethyl)benzene/TTBP yield a $U_\infty$ value of $-98 \pm 10(-87)$. Here the $Q$-enhancement correction has been obtained with $Q_0 = 27$, $\Delta\nu = 10$ Hz and $\phi = 0{\cdot}7$. The error in $U_\infty$ is the standard deviation estimated from the scatter observed in $U_\infty$ values upon repeating the experiments five to ten times. Assuming the generally valid model of pure dipolar interaction modulated by translational diffusion for the proton case [6], this $U_\infty$ value leads to a correlation time $\tau_t = (13{\cdot}5 \pm 2) \times 10^{-11}$ s. Upon further assuming that the fluorines in this molecule have the same dipolar correlation time as the protons, an assumption often used and rationalized [7], we should expect for the fluorines $U_{\infty,{}^{19}\mathrm{F}} = U_{\infty,{}^{1}\mathrm{H}} \times \gamma_\mathrm{H}/\gamma_\mathrm{F} = -104(-92)$, for pure dipolar interaction modulated by translational diffusion. The observed value of $U_{\infty,{}^{19}\mathrm{F}}$ is $-71 \pm 9(-64)$ in this molecule, which clearly indicates the presence of a scalar component of relaxation. This result is in agreement with the general observation [8] that aliphatic fluorines, especially those bonded to aromatic rings, show scalar interaction, though the dipolar component of relaxation usually dominates.

### 3.2.2. *DNP in* 1,2,4-*trifluorobenzene*

Proton DNP measurements carried out on the sample 1,2,4-trifluorobenzene/TTBP yield a $U_\infty$ value of $-153 \pm 27(-126)$. Assuming the model of pure dipolar interaction modulated by translational diffusion, this $U_\infty$ value

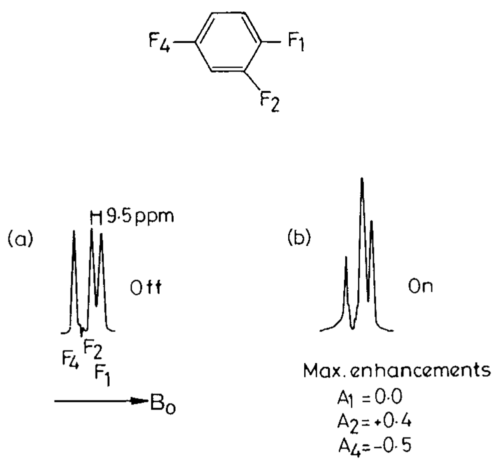

Figure 1. ${}^{19}F$ N.M.R. spectrum of 1,2,4-trifluorobenzene/TTBP with (*a*) microwave power off and (*b*) microwave power on (arbitrary level).

leads to a correlation time $\tau_t = (7{\cdot}1 \pm 2) \times 10^{-11}$ s. The ${}^{19}F$ spectrum of this sample is shown in figure 1 both under unenhanced and enhanced conditions. The differential enhancements of the three chemically-shifted fluorines are unmistakable, with the ordering $A_4 < A_1 < A_2$, $A$ being the maximum observed enhancement ($A = v/v_0 - 1$, $v_0$ being the unenhanced N.M.R. signal intensity and $v$, the enhanced intensity).

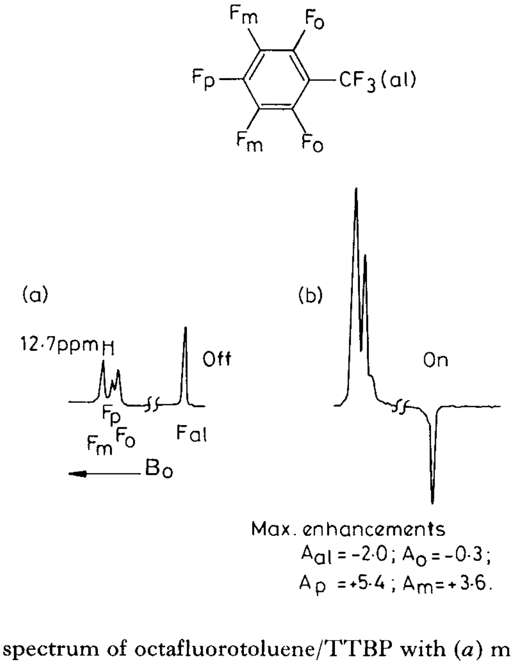

Figure 2. ${}^{19}F$ N.M.R. spectrum of octafluorotoluene/TTBP with (*a*) microwave power off and (*b*) microwave power on (arbitrary level).

### 3.2.3. *DNP in octafluorotoluene*

Figure 2 shows a recording of the $^{19}$F N.M.R. spectrum of the system octafluorotoluene/TTBP, both under unenhanced and enhanced conditions. Clear differential enhancements are exhibited in this case also, with the ordering $A_{\text{aliphatic}} < A_{\text{ortho}} < A_{\text{meta}} < A_{\text{para}}$. These results reflect the same trends as reported earlier [3] in *Q*-band studies.

## 3.3. *Scalar interaction and differential effects in $^{19}$F DNP*

It is reasonable [7] to assume that all the inequivalent fluorines in a molecule have equal dipolar correlation times, equal, in the case of 1,2,4-trifluorobenzene, to the value obtained from the proton DNP measurements. The differential effects are therefore to be ascribed to differences in scalar interactions at the three fluorines. These, in turn, could in general arise from differences in the hyperfine coupling constant, or in the scalar correlation time, or both. In the present study, the radical we used was the sterically well-shielded TTBP species which is well known to interact with solvent molecules by exchange polarization rather than by specific chemical interaction [9]. We may, therefore, ascribe the observed DNP trends to differences in hyperfine couplings i.e., spin densities at the fluorines, assuming equal scalar correlation times.

## 3.4. *Theoretical models for $^{19}$F differential DNP enhancements*

### 3.4.1. *Complete spin transfer*

If an odd electron is transferred from the radical to the solvent it would occupy the lowest unoccupied molecular orbital of the solvent. On the other hand if an electron is transferred from the solvent to the radical the highest occupied molecular orbital of the solvent is to be considered. The spin densities at the various fluorine sites of the solvent can then be calculated by an open-shell treatment of the corresponding ion. We were interested in finding out whether such calculated spin densities would correlate with the observed trends in $^{19}$F differential DNP. Open-shell calculations in the INDO framework [10] were carried out on 1,2,4-trifluorobenzene (TFB) and octafluorotoluene radical ions and the square of the coefficient of the *s*-orbital of fluorines in the appropriate M.O. was employed to calculate the spin density. The calculations based on the models discussed in this section were all carried out using an appropriately modified version of the program ' CNINDO ' [11]. Input atom coordinates were generated from standard bond lengths and bond angles [10]. Molecular structure parameters from microwave data [12] were used for 1,2,4-trifluorobenzene. Some representative results are given in table 2. It is clear that spin transfer as measured by *s*-orbital coefficients squared in radical ions is not an appropriate model to describe the fluorocarbon/TTBP differential DNP results.

### 3.4.2. *Solvent–radical complex*

Supermolecule calculations for radical–solvent separations around the appropriate van der Waals distance were carried out on the system TFB/phenoxyl. (Spin density distribution in the phenoxyl radical in the INDO scheme is not very different from that in TTBP and was employed in the calculations to

Table 2. $s$-Orbital spin densities in some radical ions.

| System | Position | Spin density × $10^4$ |
|---|---|---|
| 1,2,4-Trifluorobenzene | $F_1$ | −1·57 |
| (radical anion) | $F_2$ | 1·89 |
| | $F_4$ | −1·47 |
| Octafluorotoluene | $F_{al}$ | 12·40 |
| (radical anion) | $F_o$ | 1·18 |
| | $F_m$ | −1·06 |
| | $F_p$ | 4·07 |

save computer time.) Radical–solvent interactions have been classified [8] as occurring in the $\sigma$-, $\pi$- and plane–plane modes. For the sterically inaccessible TTBP radical, the $\pi$-mode has been shown [8] to be most effective in inducing spin density at the solvent nuclei. Our $\pi$-mode calculations, however, displayed convergence problems which could not be overcome satisfactorily even with the level-shift [13] and damping [14] procedures.

### 3.4.3. *$sp_\sigma$-polarizability*

Considering that the DNP situation corresponds to transfer of $10^{-2}$–$10^{-3}$ electron spin only [8], and since chemical interactions are unimportant with the TTBP radical, we have employed a modified version of the closed-shell pertubation treatment given by Dwek *et al.* [15], in order to account for the experimental ordering of enhancements in terms of spin density ordering. To this end, we start with the equation for spin density induced at nucleus $M$ on the solvent molecule :

$$\delta_M = -2 \sum_i^{\text{occ}} \sum_j^{\text{unocc}} \sum_{\substack{b', b'' \\ M', M''}} C_{is,M} C_{js,M} C_{ib',M'} C_{jb'',M''} (\epsilon_i - \epsilon_j)^{-1} \times (\phi_{s,M} | \delta_M(r) | \phi_{s,M}) \left( \phi_{b',M'} \psi_R{}^0 \left| \frac{e^2}{r} \right| \psi_R{}^0 \phi_{b'',M''} \right). \quad (2)$$

This equation treats the exchange interaction between the radical unpaired electron and electrons of the solvent molecule as the perturbation and is similar to that given by Dwek *et al.* [15] except that we have used the difference in M.O. energies, $\epsilon$s, as a measure of the triplet excitation energy, whereas Dwek *et al.* have used the average energy approximation, $C_{is,M}$ and $C_{jb'',M''}$ are, respectively, the coefficient of the valence $s$-orbital $\phi_{s,M}$ centred on nucleus $M$ in the occupied M.O. $i$, and that of a valence-shell a.o. $\phi_{b'',M''}$ centred on nucleus $M''$ in the unoccupied M.O. $j$. $\psi_R{}^0$ is the radical oxygen a.o. $\delta_M(r)$ is the Dirac delta function operator centred on nucleus $M$. Here we have retained only one-centre integrals of this operator. Equation (2) is further simplified by retaining only terms with $M' = M'' = M$ in the summation over $M'$, $M''$, since the fluorine atoms lie at the periphery of the molecule. Further, the electrostatic perturbation is likely to be large for the valence-shell fluorine $p$-orbitals only, since the valence-shell fluorine $s$-orbital is deeply buried both energetically and spatially, in comparison with the *p*-orbitals. Consequently, we retain only the terms involving *p*-orbitals in the summation over $b'$, $b''$ in (2). Finally, we classify the *p*-orbitals as $p_\sigma$, $p_l$ and $p_z$, where $p_\sigma$ is the *p*-orbital in the bond direction, $p_l$ is the lone-pair orbital in the molecular plane (well defined for the aromatic fluorines) and $p_z$ is the lone-pair orbital perpendicular to the molecular plane. In this representation, the contribution to $\delta_M$ from the terms $b'$, $b''=p_l$, $p_z$ is necessarily very small due to symmetry. Equation (2) thus reduces to

$$\delta_M = -2 \sum_i^{\text{occ}} \sum_j^{\text{unocc}} C_{is,M} C_{js,M} C_{ip_\sigma,M} C_{jp_\sigma,M} (\epsilon_i - \epsilon_j)^{-1} \times (\phi_{s,M} | \delta_M(r) | \phi_{s,M}) \left( \phi_{p_\sigma,M} \psi_R{}^0 \left| \frac{e^2}{r} \right| \psi_R{}^0 \phi_{p_\sigma,M} \right). \quad (3)$$

We have therefore used the quantity

$$(sp_\sigma)_{M,M} = 4 \sum_i^{\text{occ}} \sum_j^{\text{unocc}} (\epsilon_i - \epsilon_j)^{-1} C_{is,M} C_{js,M} C_{ip_\sigma,M} C_{jp_\sigma,M}. \quad (4)$$

Table 3. Calculated $(sp_\sigma)$ parameter for some fluorine compounds.

| Compound | EHT |  |  | SCF(INDO) |  |  |
|---|---|---|---|---|---|---|
|  | o | m | p | o | m | p |
| Pentafluorobenzene | 0·1643 | 0·1695 | 0·1708 | 0·1002 | 0·1046 | 0·1045 |
| Pentafluorochlorobenzene† | 0·1681 | 0·1716 | 0·1710 | 0·0944 | 0·0971 | 0·0968 |
| Pentafluorovinylbenzene | 0·1610 | 0·1679 | 0·1708 | 0·0980 | 0·1038 | 0·1045 |
| Octafluorotoluene‡ | 0·1629 | 0·1688 | 0·1708 | 0·1017 | 0·1060 | 0·1054 |
|  | α | β |  | α | β |  |
| Octafluoronaphthalene | 0·1629 | 0·1681 |  | 0·1015 | 0·1042 |  |
|  | (1) | (2) | (4) | (1) | (2) | (4) |
| 1,2,4-Trifluorobenzene | 0·1634 | 0·1633 | 0·1588 | 0·0987 | 0·0982 | 0·0945 |

† SCF calculations in the CNDO framework.

‡ $(sp_\sigma)$ parameter for the aliphatic fluorines : EHT ~0·13 ; SCF(INDO) : ~0·08.

Table 4. Comparison between spin densities based on $sp_\sigma$ polarizability and experimental DNP trends.

| System | Experimental ordering | EHT ordering | SCF(INDO) ordering |
|---|---|---|---|
| Pentafluorobenzene‡ | $F_o < F_m < F_p$ | $F_o < F_m < F_p$ | $F_o < F_m \sim F_p$ |
| Pentafluorochlorobenzene†‡ | $F_o < F_m < F_p$ | $F_o < F_p < F_m$ | $F_o < F_m \sim F_p$ |
| Pentafluorovinylbenzene‡ | $F_o < F_m < F_p$ | $F_o < F_m < F_p$ | $F_o < F_m < F_p$ |
| Octafluoronaphthalene‡ | $F_\alpha < F_\beta$ | $F_\alpha < F_\beta$ | $F_\alpha < F_\beta$ |
| Octafluorotoluene‡ § | $F_{al} < F_o < F_m < F_p$ | $F_{al} < F_o < F_m < F_p$ | $F_{al} < F_o < F_p < F_m$ |
| 1,2,4-Trifluorobenzene § | $F_4 < F_1 < F_2$ | $F_4 < F_1 \sim F_2$ | $F_4 < F_2 < F_1$ |

† SCF calculations in the CNDO framework.

‡ Experimental ordering from [3].

§ Present work.

to compare spin densities at different nuclei $M$ in the same molecule. By analogy with Coulson and Longuet-Higgins' mutual $\pi$-polarizabilities [16], we may term this the $(sp_\sigma)$-polarizability parameter. We have carried out calculations of this parameter in both the extended Hückel theory (EHT) and SCF INDO/CNDO framework [10]. The molecules that we have treated include 1,2,4-trifluorobenzene, octafluorotoluene, pentafluorobenzene, pentafluorochlorobenzene, pentafluorovinylbenzene and octafluoronaphthalene. Experimental differential $^{19}F$ enhancements in the last five molecules have been reported [3] at $Q$-band.

Table 3 summarizes the results of our calculations, while table 4 compares the theoretical results with experiment. The overall agreement in ordering between the experimental and calculated results is gratifying. However, the meta- and para-fluorines, which normally exhibit rather close relative enhancements, are not always correctly ordered by the theoretical calculations. In particular, the meta- and para-ordering is often seen to switch the EHT and SCF–INDO/CNDO results. This could be related to problems associated with the virtual orbitals in finite basis set calculations of this nature. The reliability of the theoretical results probably does not warrant such close comparisons as frequently have to be made between the meta- and para-fluorines.

Table 5. Valence-shell diagonal density matrix elements (SCF INDO)

| Compound | | $s$-orbital | $p_\sigma$ | $p_l$ | $p_z$ | Total |
|---|---|---|---|---|---|---|
| Pentafluorobenzene | o | 1·8447 | 1·4372 | 1·9821 | 1·9452 | 7·2092 |
| | m | 1·8437 | 1·4208 | 1·9819 | 1·9509 | 7·1973 |
| | p | 1·8437 | 1·4215 | 1·9820 | 1·9464 | 7·1935 |
| Pentafluorochlorobenzene† | o | 1·8224 | 1·4056 | 1·9844 | 1·9474 | 7·1598 |
| | m | 1·8212 | 1·3955 | 1·9840 | 1·9550 | 7·1557 |
| | p | 1·8212 | 1·3975 | 1·9847 | 1·9491 | 7·1525 |
| Pentafluorovinylbenzene | o | 1·8447 | 1·4391 | 1·9785 | 1·9447 | 7·2070 |
| | m | 1·8438 | 1·4238 | 1·9821 | 1·9496 | 7·1993 |
| | p | 1·8436 | 1·4215 | 1·9819 | 1·9474 | 7·1944 |
| Octafluoronaphthalene | $\alpha$ | 1·8445 | 1·4318 | 1·9815 | 1·9443 | 7·2021 |
| | $\beta$ | 1·8437 | 1·4223 | 1·9821 | 1·9471 | 7·1952 |
| Octafluorotoluene‡ | o | 1·8445 | 1·4304 | 1·9813 | 1·9412 | 7·1974 |
| | m | 1·8436 | 1·4144 | 1·9815 | 1·9502 | 7·1897 |
| | p | 1·8435 | 1·4175 | 1·9819 | 1·9425 | 7·1854 |
| 1,2,4-Trifluorobenzene | $F_1$ | 1·8448 | 1·4438 | 1·9827 | 1·9501 | 7·2214 |
| | $F_2$ | 1·8449 | 1·4458 | 1·9828 | 1·9455 | 7·2190 |
| | $F_4$ | 1·8458 | 1·4596 | 1·9828 | 1·9449 | 7·2331 |

† SCF CNDO density matrix elements are reported.

‡ The aliphatic fluorines have : $s$ density $\sim 1{\cdot}87$ ; $p_\sigma$ density $\sim 1{\cdot}5$ ; total valence-shell electron density : 7·2535.

In table 5, electron densities and valence-shell orbital occupation numbers at the different fluorines have been presented for all the molecules studied. Lower electron densities clearly correlate with higher scalar rates. The orbital analysis indicates that the differences arise mainly from the $p_\sigma$ density values.

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