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## Theoretical calculations of the magnetizability of some small fluorine-containing molecules using London atomic orbitals

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### Abstract

We report a systematic investigation of the magnetizability of a series of small molecules. The use of London atomic orbitals ensures gauge invariance and a fast basis set convergence. Good agreement is obtained with experimental magnetizabilities, both isotropic and anisotropic. The calculations suggest a reinvestigation of some of the semi-experimental isotropic magnetizabilities. We have verified experimentally observed changes in the out-of-plane minus the average in-plane magnetizability anisotropy upon fluorine substitution in some planar molecules. Our results do not support the experimental changes observed for similar fluorine substitutions in linear molecules.

### 1. Introduction

In recent years there has been renewed interest in the *ab initio* calculation of molecular magnetizabilities. One reason for this is the advent of more powerful computers, which has made it possible to use large basis sets to reduce the gauge origin dependence that hampers the conventional finite basis set calculations. However, although the use of large basis sets may give near gauge-invariant results for small systems, this approach is not suitable for large molecules since the basis set becomes prohibitively large [1–3].

One way to overcome the arbitrariness in the choice of gauge origin is to use some predefined origin. This may be accomplished in two ways – either by using a common gauge origin for the entire molecule or by using local origins for the individual atomic or molecular orbitals.

In the common gauge origin approach – which is often used – it is difficult to select a single origin that

is equally well suited for the entire molecule. Several schemes have been proposed [4–8]. Often the gauge origin is chosen to be the center of mass or the center of electronic charge. Since there is no arbitrariness in these choices, such calculations may be regarded as gauge-origin independent. Unfortunately, they are not size extensive.

Size-extensive and gauge-origin independent calculations require the use of local origins. Kutzelnigg and Schindler have proposed using local gauge origins for the individual molecular orbitals in the IGLO method (individual gauges for localized orbitals) [9,10]. In the London orbital approach [11], pioneered by Hameka [12–14] and used by Ditchfield [15], each atomic orbital is equipped with its own gauge origin. We recently presented a modern formalism for the calculation of molecular magnetizabilities based on London atomic orbitals (also known as gauge-invariant atomic orbitals (GIAOs)) and demonstrated that this method converges consider-

ably faster than IGLO [16]. The faster convergence of the London method has also been observed for other properties such as nuclear magnetic shieldings [17,18] and vibrational circular dichroism [19,20], both at the correlated and uncorrelated levels.

Dahle et al. [21] have shown that Hartree–Fock limit magnetizabilities can be obtained with relatively small basis sets provided London orbitals are used. Unfortunately, it is harder to judge the agreement between the Hartree–Fock limit and the true magnetizabilities since the isotropic magnetizability for gases is difficult to measure owing to the small effects associated with diamagnetism [22]. However, in high-field molecular Zeeman studies using microwave spectroscopy – first described by Flygare and co-workers [23,24] – the two anisotropic components of the magnetizability are measured directly and with greater reliability. Comparisons with such experiments should provide a critical test of the applicability of the London method, especially since the calculated anisotropic components are harder to converge than the isotropic magnetizability [16].

Flygare [25] pointed out that the successive replacements of hydrogens by fluorines in CH bonds give positive contributions of decreasing magnitude to the out-of-plane minus the average in-plane magnetizability anisotropy,  $\zeta_{11} - \frac{1}{2}(\zeta_{22} + \zeta_{33})$ . Several molecules were investigated, for instance ethane, ethylene, methane and hydrogen cyanide [26–29], and changes in the magnetizability anisotropy were observed for  $sp^2$ - and  $sp^3$ -hybridized atoms only, not for  $sp$ -hybridized carbon atoms.

We have undertaken a systematic study of the change in the out-of-plane minus the average in-plane magnetizability anisotropy of methane, ethane, ethylene, acetylene, propyne, formaldehyde, and hydrogen cyanide. This provides us with an estimate of the reliability of the calculated magnetizability anisotropies. Since microwave spectroscopy is restricted to molecules with permanent dipole moments, this study also provides information not obtainable from such experiments. Calculated values for the isotropic magnetizability of the molecules studied are also presented.

## 2. Basis set and geometries

In a study of basis set requirements for the calculation of magnetic properties using London atomic orbitals, Dahle et al. [21] describe a medium size basis set which they recommend for routine calculations of molecular magnetizabilities. The basis set gives isotropic magnetizabilities within 1.5% of the Hartree–Fock limit, and anisotropic magnetizabilities that are generally within 2% of the Hartree–Fock limit, although a deviation as large as 10% was reported for the anisotropic component for one of the molecules.

The proposed basis set is based on Dunning's correlation consistent set cc-pVDZ [30–32]. For hydrogen we use Dunning's augmented cc-pVDZ set, and for the second row atoms we use the standard cc-pVDZ set to which a single set of diffuse p orbitals has been added. The exponent of these orbitals is the same as for the additional p orbitals in Dunning's augmented cc-pVDZ set.

For a consistent theoretical treatment of all molecules, we have optimized their geometries using the same basis set as for the magnetizabilities. In this way we can check the predictability of the method from a purely theoretical point of view. The geometry optimization and the calculation of the magnetizability anisotropy were carried out using the HERMIT-SIRIUS-ABACUS program package [33–35]. The optimized geometries and electronic energies are given in Table 1.

## 3. Results and discussion

In Table 2 we summarize the calculated isotropic magnetizabilities and compare with experimental and semi-experimental values. One of the problems faced in studies of magnetizabilities, is the lack of a single experimental technique capable of extracting all the pertinent information. The experimentally determined isotropic magnetizabilities are therefore taken from different sources, and are often obtained by combining experimental results with calculated quantities.

In the study of basis sets requirements for magnetizabilities, Dahle et al. found that the experimental values were  $-6.8 \pm 0.7\%$  off the estimated Hartree–

Table 1  
Optimized molecular geometries and electronic energies

Molecule	Energy (au)	Geometry
CH <sub>2</sub> O	-113.883694	$r_{\text{CO}}=118.36$ pm, $r_{\text{CH}}=110.05$ pm, $\angle \text{HCH}=116.24^\circ$
CHFO	-212.772880	$r_{\text{CO}}=116.16$ pm, $r_{\text{CF}}=121.69$ pm, $r_{\text{CH}}=108.99$ pm, $\angle \text{FCO}=122.73^\circ$ , $\angle \text{HCO}=127.28^\circ$
CF <sub>2</sub> O	-311.643927	$r_{\text{CO}}=115.40$ pm, $r_{\text{FC}}=128.94$ pm, $\angle \text{FCF}=108.27^\circ$
C <sub>2</sub> H <sub>4</sub>	-78.042318	$r_{\text{CC}}=132.36$ pm, $r_{\text{CH}}=108.30$ pm, $\angle \text{HCH}=116.76^\circ$
C <sub>2</sub> H <sub>3</sub> F <sup>a</sup>	-176.903155	$r_{\text{CC}}=131.33$ pm, $r_{\text{CF}}=133.01$ pm, $r_{\text{CH}^1}=107.96$ pm, $r_{\text{CH}^2}=108.09$ pm, $r_{\text{CH}^3}=107.96$ pm, $\angle \text{FCH}=112.00^\circ$ , $\angle \text{FCC}=122.31^\circ$ , $\angle \text{HCH}=119.22^\circ$ , $\angle \text{H}^2\text{CC}=121.65^\circ$
CF <sub>2</sub> CH <sub>2</sub>	-275.767574	$r_{\text{CC}}=130.76$ pm, $r_{\text{CF}}=130.26$ pm, $r_{\text{CH}}=107.73$ pm, $\angle \text{FCF}=109.28^\circ$ , $\angle \text{HCH}=120.70^\circ$
cis-CHFCHF	-275.753655	$r_{\text{CC}}=131.17$ pm, $r_{\text{CF}}=132.16$ pm, $r_{\text{CH}}=107.73$ pm, $\angle \text{FCC}=123.05^\circ$ , $\angle \text{FCH}=114.61^\circ$
trans-CHFCHF	-275.752539	$r_{\text{CC}}=131.05$ pm, $r_{\text{CF}}=132.80$ pm, $r_{\text{CH}}=107.83$ pm, $\angle \text{FCC}=120.29^\circ$ , $\angle \text{FCH}=114.46^\circ$
C <sub>2</sub> HF <sub>3</sub> <sup>b</sup>	-374.610229	$r_{\text{CC}}=130.75$ pm, $r_{\text{CH}}=107.54$ pm, $r_{\text{CF}^1}=132.39$ pm, $r_{\text{CF}^2}=130.15$ pm, $r_{\text{CF}^3}=129.57$ pm, $\angle \text{FCH}=116.20^\circ$ , $\angle \text{HCC}=122.86^\circ$ , $\angle \text{FCF}=111.34^\circ$ , $\angle \text{F}^2\text{CC}=123.01^\circ$
C <sub>2</sub> F <sub>4</sub>	-473.460026	$r_{\text{CC}}=130.33$ pm, $r_{\text{CF}}=129.80$ pm, $\angle \text{FCF}=112.61^\circ$
CH <sub>4</sub>	-40.199331	$r_{\text{CH}}=109.01$ pm
CH <sub>3</sub> F	-139.053400	$r_{\text{CF}}=137.01$ pm, $r_{\text{CH}}=108.81$ pm, $\angle \text{FCH}=108.68^\circ$ , $\angle \text{HCH}=110.25^\circ$
CH <sub>2</sub> F <sub>2</sub>	-237.656926	$r_{\text{CF}}=147.12$ pm, $r_{\text{CH}}=113.04$ pm, $\angle \text{FCF}=86.95^\circ$ , $\angle \text{HCH}=101.06^\circ$ , $\angle \text{FCH}=86.00^\circ$
C <sub>2</sub> H <sub>6</sub>	-79.236399	$r_{\text{CC}}=152.63$ pm, $r_{\text{CH}}=109.22$ pm, $\angle \text{HCH}=107.56^\circ$ , $\angle \text{HCC}=111.32^\circ$
CH <sub>3</sub> CH <sub>2</sub> F <sup>c</sup>	-178.098669	$r_{\text{CC}}=151.00$ pm, $r_{\text{CF}}=137.91$ pm, $r_{\text{C(F)H}}=108.96$ pm, $r_{\text{C(H)H}}=109.05$ pm, $r_{\text{C(H)H}'}=109.19$ pm, $\angle \text{FCH}=107.03^\circ$ , $\angle \text{FCC}=109.85^\circ$ , $\angle \text{HC(F)H}=108.89^\circ$ , $\angle \text{HC(F)C}=111.90^\circ$ , $\angle \text{H}'\text{CH}=108.49^\circ$ , $\angle \text{H}'\text{CC}=109.76^\circ$ , $\angle \text{HC(H)H}=108.53^\circ$ , $\angle \text{HC(H)C}=110.76^\circ$
CH <sub>3</sub> CHF <sub>2</sub> <sup>d</sup>	-276.973712	$r_{\text{CC}}=150.12$ pm, $r_{\text{CF}}=134.86$ pm, $r_{\text{C(F)H}}=108.71$ pm, $r_{\text{C(H)H}}=108.93$ pm, $r_{\text{C(H)H}'}=108.94$ pm, $\angle \text{FCF}=106.62^\circ$ , $\angle \text{FCC}=110.39^\circ$ , $\angle \text{FCH}=107.49^\circ$ , $\angle \text{HC(F)C}=114.14^\circ$ , $\angle \text{H}'\text{CH}=109.29^\circ$ , $\angle \text{H}'\text{CC}=109.61^\circ$ , $\angle \text{HCH}=109.20^\circ$ , $\angle \text{HC(H)C}=109.72^\circ$
CH <sub>2</sub> FCH <sub>2</sub> F <sup>e</sup>	-276.955293	$r_{\text{CC}}=151.22$ pm, $r_{\text{CF}}=137.20$ pm, $r_{\text{CH}}=108.83$ pm, $\angle \text{FCH}=108.40^\circ$ , $\angle \text{FCC}=108.02^\circ$ , $\angle \text{HCH}=109.50^\circ$ , $\angle \text{HCC}=111.21^\circ$
C <sub>2</sub> H <sub>2</sub>	-76.828287	$r_{\text{CC}}=119.31$ pm, $r_{\text{CH}}=106.33$ pm,
C <sub>2</sub> HF	-175.661499	$r_{\text{CC}}=118.38$ pm, $r_{\text{CF}}=126.62$ pm, $r_{\text{CH}}=106.14$ pm
C <sub>2</sub> F <sub>2</sub>	-274.486197	$r_{\text{CC}}=117.14$ pm, $r_{\text{CF}}=127.16$ pm
HCN	-92.886977	$r_{\text{CH}}=106.67$ pm, $r_{\text{CN}}=113.48$ pm
FCN	-191.716216	$r_{\text{CF}}=124.88$ pm, $r_{\text{CN}}=113.34$ pm
CH <sub>3</sub> CCH	-115.877137	$r_{\text{C-C}}=146.88$ pm, $r_{\text{C=C}}=119.45$ pm, $r_{\text{CH}_3}=108.97$ pm, $r_{\text{CH}}=106.29$ pm, $\angle \text{HCH}=108.47^\circ$ , $\angle \text{HCC}=110.45^\circ$
CH <sub>3</sub> CCF	-214.708863	$r_{\text{C-C}}=147.13$ pm, $r_{\text{C=C}}=118.42$ pm, $r_{\text{CH}}=108.93$ pm, $r_{\text{CF}}=127.30$ pm, $\angle \text{HCH}=108.45^\circ$ , $\angle \text{HCC}=110.73^\circ$

<sup>a</sup> The hydrogens are numbered such that number 1 is on the same carbon atom as the fluorine atom, number 2 is cis to, and number 3 trans to the fluorine atom.

<sup>b</sup> The labeling is as in footnote a, but it is now the fluorine's position with respect to the hydrogen atom.

<sup>c</sup> The primed hydrogen indicates the hydrogen in anti-position to the fluorine atom.

<sup>d</sup> The primed hydrogen indicates the hydrogen in anti-position to the sole hydrogen atom.

<sup>e</sup> The fluorine atoms are in anti-position.

Fock limit for the eight molecules studied. In addition the basis was found to give results between 0 and +1.5% off the Hartree-Fock limit, and they proposed to scale the theoretical results by  $-7.5 \pm 1.5\%$ . We use this scaling factor to arrive at the scaled GIAO results in Table 2.

The scaled values for the isotropic magnetizability

are in excellent agreement with the purely experimental isotropic gas phase magnetizabilities of Barter et al. [22]. This suggests that the lack of agreement between our scaled isotropic magnetizabilities and the semi-empirical/quasi-experimental numbers may be due to errors in the determination of the latter quan-

Table 2

Isotropic magnetizability of the different molecules investigated, this work, IGLO calculations and experimentally determined values (aggregation state used in the experimental determination indicated in parentheses)

Molecule	GIAO	GIAO scaled	IGLO <sup>a</sup>	Exp.
CH <sub>2</sub> O	-142.8	-132 ± 2	-160 (H II)	-114 ± 5 <sup>b</sup> (ℓ)
CHFO	-317.2	-293 ± 4	-	-227 ± 66 <sup>c</sup>
CF <sub>2</sub> O	-428.7	-397 ± 5	-475 (H I)	-438 <sup>d</sup>
C <sub>2</sub> H <sub>4</sub>	-356.3	-330 ± 4	-375 (H II)	-312 ± 13 <sup>e</sup> (g)
C <sub>2</sub> H <sub>3</sub> F	-432.1	-400 ± 5	-	-360 ± 66 <sup>c</sup>
CH <sub>2</sub> CF <sub>2</sub>	-525.3	-486 ± 7	-570 (H I)	-475 <sup>d</sup>
cis-CHFCHF	-487.1	-451 ± 6	-530 (H I)	-452 <sup>d</sup>
trans-CHFCHF	-472.6	-437 ± 6	-520 (H I)	-
C <sub>2</sub> HF <sub>3</sub>	-567.2	-525 ± 7	-	-535 ± 33 <sup>f</sup> (ℓ)
C <sub>4</sub> F <sub>4</sub>	-635.9	-588 ± 8	-	-
CH <sub>4</sub>	-315.3	-292 ± 4	-322 (H II)	-289 ± 13 <sup>c</sup> (g)
CH <sub>3</sub> F	-317.4	-294 ± 4	-337 (H I)	-295 ± 13 <sup>c</sup> (g)
CH <sub>2</sub> F <sub>2</sub>	-379.2	-351 ± 5	-403 (H I)	-398 <sup>d</sup>
C <sub>2</sub> H <sub>6</sub>	-493.2	-456 ± 6	-513 (H II)	-445 ± 13 <sup>c</sup> (g)
C <sub>2</sub> H <sub>5</sub> F	-528.4	-489 ± 7	-557 (H I)	-548 ± 66 <sup>d</sup>
CH <sub>3</sub> CHF <sub>2</sub>	-602.4	-557 ± 8	-	-606 ± 66 <sup>d</sup>
CH <sub>2</sub> FCH <sub>2</sub> F	-561.8	-520 ± 7	-	-
C <sub>2</sub> H <sub>2</sub>	-386.5	-358 ± 5	-	-346 ± 13 <sup>c</sup> (g)
C <sub>2</sub> HF	-454.2	-420 ± 6	-	-432 <sup>g</sup>
C <sub>2</sub> F <sub>2</sub>	-505.7	-468 ± 6	-	-
HCN	-284.6	-263 ± 4	-	-279 <sup>f</sup>
FCN	-380.7	-352 ± 5	-	-385 <sup>f</sup>
CH <sub>3</sub> CCH	-574.6	-532 ± 7	-	-
CH <sub>3</sub> CCF	-641.3	-593 ± 8	-	-

<sup>a</sup> All results taken from the work of Schindler and Kutzelnigg [36].

<sup>b</sup> Cited by Hüttner et al. [37].

<sup>c</sup> Estimated from Pascals constants by Rock et al. [27].

<sup>d</sup> Obtained from experimental determination of  $\zeta^{\text{para}}$  and estimated values for  $\zeta^{\text{dia}}$  by Blickensderfer et al. [26].

<sup>e</sup> Barter et al. [22].

<sup>f</sup> Determined by Park et al. [38].

<sup>g</sup> Obtained from experimental determination of  $\zeta^{\text{para}}$  and theoretical estimation of  $\zeta^{\text{dia}}$ , cited by Appleman and Dailey [39].

tities. We therefore propose that these values for the magnetizability tensor be reexamined.

In Table 2 we have listed IGLO results where these are available. As in previous studies [16,40], the IGLO results are more diamagnetic than those obtained using the London method. It should be noted that the basis sets are different, although the H II basis used in the IGLO calculations is of comparable size with our basis set.

The calculated and experimentally determined magnetizability anisotropies are in Table 3. We denote the principal axis perpendicular to the heavy atom plane by  $\xi_{11}$ , the axis parallel to the molecular

axis by  $\xi_{22}$ , and the in-plane axis perpendicular to the principal axis by  $\xi_{33}$ . Using these definitions we have tabulated  $\Delta\xi_1 = \xi_{11} - \frac{1}{2}(\xi_{22} + \xi_{33})$  and  $\Delta\xi_2 = \xi_{22} - g_{x_{11}} + \xi_{33}$ . For symmetric top molecules there is only one distinct anisotropy, usually given as  $\Delta\xi = \xi_{\parallel} - \xi_{\perp}$ . For consistency with the asymmetric tops, we tabulate their anisotropies as  $\Delta\xi_1 = \frac{1}{2}(\xi_{\perp} - \xi_{\parallel})$ .

The agreement between our calculated anisotropies and the experimentally determined values for  $\Delta\xi_1$  is good, especially taking into account the sensitivity of the anisotropy to the quality of the wavefunction. The theoretical values are usually within or slightly outside the experimental error bars.

Table 3  
Anisotropic magnetizability of the different molecules studied

Molecule	$\Delta\zeta_1$		$\Delta\zeta_2$	
	theoret.	exp.	theoret.	exp.
CH <sub>2</sub> O	-176.3	-179 ± 7	194.4	212 ± 8
CHFO	-97.5	-100 ± 5	58.0	50.6 ± 5
CF <sub>2</sub> O	-41.5	-56 ± 13	2.1	-13 ± 15
C <sub>2</sub> H <sub>4</sub>	-130.3	-	26.0	-
C <sub>2</sub> H <sub>3</sub> F	-77.7	-73 ± 3	-8.8	-13 ± 3
CH <sub>2</sub> CF <sub>2</sub>	-55.6	-45 ± 10	-14.4	-19 ± 10
cis-CHFCHF	-25.6	-33 ± 7	28.0	47 ± 7
trans-CHFCHF	-36.8	-	131.3	-
C <sub>2</sub> HF <sub>3</sub>	-34.7	-30 ± 5	-53.2	-70 ± 3
C <sub>2</sub> F <sub>4</sub>	-6.9	-	30.5	-
C <sub>2</sub> H <sub>6</sub>	37.2	-	-	-
C <sub>2</sub> H <sub>5</sub> F	59.5	60 ± 8	-36.5	-55 ± 7
anti-CH <sub>2</sub> FCH <sub>2</sub> F	76.2	-	-164.7	-
CH <sub>3</sub> CHF <sub>2</sub>	42.2	42 ± 13	-21.1	-28 ± 12
CH <sub>4</sub>	0	0	-	-
CH <sub>3</sub> F	64.5	71 ± 10	-	-
CH <sub>2</sub> F <sub>2</sub>	28.4	26 ± 8	11.0	7 ± 7
C <sub>2</sub> H <sub>2</sub>	18.3	37 ± 5	-	-
C <sub>2</sub> HF	38.0	43 ± 2	-	-
C <sub>2</sub> F <sub>2</sub>	68.5	-	-	-
HCN	48.5	60 ± 7	-	-
FCN	48.1	60 ± 13	-	-
C <sub>3</sub> H <sub>4</sub>	59.2	63.9 ± 2	-	-
C <sub>3</sub> H <sub>3</sub> F	78.2	-	-	-

The good agreement between theory and experiment is also evident from Table 4, where the changes in  $\Delta\zeta_1$  upon fluorine substitution are given. Except for the sp-hybridized molecules, we reproduce the experimental findings of Flygare [25]. Substitution of fluorine makes a positive contribution to the anisotropy, largest for the first fluorine, smaller for the second and so on. Some of the gaps due to lack of experimental observations are filled by our calculations, and these results follow the same pattern. For example, the substitution of a single fluorine atom in ethylene produces a change in the anisotropy of the same magnitude as the effect observed when a second fluorine atom is substituted on the opposite carbon atom. In contrast, the change in the anisotropy observed upon further substitution on the *same* carbon atom is smaller by a factor of two. Similarly, the change in the anisotropy in going from cis/trans-1,2-

difluoroethylene to trifluoroethylene is smaller than the change observed when going from 1,1-difluoroethylene to trifluoroethylene. The change in the anisotropy when going to tetrafluoroethylene does not fit this pattern.

Some remarks should be made concerning the non-planar molecules methane and ethane. In methane the anisotropy increases upon substitution of a single fluorine atom, but decreases upon the further substitution of a second fluorine atom, in agreement with experiment. Since this second substitution is most properly regarded as an in-plane substitution, this behaviour does not fit the pattern observed in the planar molecules. Exactly the same behaviour is observed in ethane upon substitution of two fluorine atoms on the same carbon atom – the anisotropy first increases and then decreases. However, if the second fluorine atom is substituted on the opposite carbon

Table 4  
Change in the magnetizability anisotropy upon fluorine substitution

Molecule 1	Molecule 2	$\Delta (\Delta\xi_1(2-1))$	
		theoret.	exp.
CH <sub>2</sub> O	CHFO	78.8	79 ± 7
CHFO	CF <sub>2</sub> O	56	44 ± 13
C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>3</sub> F	52.6	–
C <sub>2</sub> H <sub>3</sub> F	cis-CHFCHF	52.1	40 ± 7
C <sub>2</sub> H <sub>3</sub> F	trans-CHFCHF	40.9	–
C <sub>2</sub> H <sub>3</sub> F	CH <sub>2</sub> CF <sub>2</sub>	22.1	28 ± 10
cis-CHFCHF	C <sub>2</sub> HF <sub>3</sub>	–9.1	3 ± 7
trans-CHFCHF	C <sub>2</sub> HF <sub>3</sub>	2.1	–
CH <sub>2</sub> CF <sub>2</sub>	C <sub>2</sub> HF <sub>3</sub>	22.1	28 ± 10
C <sub>2</sub> HF <sub>3</sub>	C <sub>2</sub> F <sub>4</sub>	27.8	–
C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> HF	19.7	6 ± 5
C <sub>2</sub> HF	C <sub>2</sub> F <sub>2</sub>	30.5	–
CH <sub>4</sub>	CH <sub>3</sub> F	64.5	71 ± 10
CH <sub>3</sub> F	CH <sub>2</sub> F <sub>2</sub>	–36.1	–45 ± 11
C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub> CH <sub>2</sub> F	22.3	–
CH <sub>3</sub> CH <sub>2</sub> F	anti-CH <sub>2</sub> FCH <sub>2</sub> F	16.7	–
HCN	FCN	–0.4	0.0
C <sub>3</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>3</sub> F	19.0	–

atom in anti-position, so that the carbon and fluorine atoms are all in the same plane, then the anisotropy increases upon both substitutions in accordance with our experience from ethylene.

Finally, we comment on the linear molecules hydrogen cyanide and acetylene. The agreement with experiment is here less satisfactory. As in experiment, the anisotropy of HCN does not change appreciably upon substitution of fluorine, but the calculated anisotropy is significantly lower than experiment. In acetylene, the calculated anisotropy is only half of the observed value and there is a strong increase upon the substitution of fluorine, in contrast to the small increase found by experiment. Substitution of a second atom further increases the anisotropy as in all planar molecules. There is no experimental value for difluoroacetylene.

We have obtained good agreement between the theoretical and experimental values for  $\Delta\xi_1$ . Unlike the isotropic magnetizability, it has not been necessary to scale the results. This indicates that the correlation energy is unevenly distributed among the

principal directions of the molecules. We may therefore expect worse agreement between theory and experiment for other anisotropies. From Table 3 we see that this is indeed the case. The agreement between theory and experiment for  $\Delta\xi_2$  is less satisfactory than  $\Delta\xi_1$ . However, no clear trends as to which component is most in error can be seen from the results. As there is no way to determine both the isotropic and anisotropic magnetizabilities in the same experiment for molecules in the gas phase, such an analysis is hard to perform. We finally note that a similar uneven distribution of correlation effects among the different components has been observed for molecular quadrupole moments by Woliński, Sadlej and Karlström [41].

#### 4. Concluding remarks

We have shown that the use of London atomic orbitals for the calculation of magnetizabilities gives accurate results, both for the isotropic and the anisotropic parts. Although the correlation corrections are unevenly distributed in the different directions of the molecules, the isotropic magnetizabilities are within experimental error bars for most molecules if a previously proposed scaling scheme is used.

The out-of-plane minus the average in-plane magnetizability anisotropy can be accurately determined by the London atomic orbital approach, and experimentally observed trends for the change in this quantity upon fluorine substitution have been reproduced for planar molecules. For non-planar molecules, our results are in agreement with experiment and do not support the proposed positive increase of the magnetizability anisotropy upon fluorine substitution [25]. For linear molecules it is not clear from our results what effect fluorine substitution has on the magnetizability anisotropy.

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