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Molecular Magnetizabilities: Zero-Point Vibrational Effects and the Breakdown of Pascal's Rule

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We demonstrate, by ab initio calculations on more than 60 molecules, that zero-point vibrational corrections to isotropic magnetizabilities in general are negligible, being less than 0.5% for almost all molecules studied. The exceptions to this rule are aromatic and anti-aromatic ring systems where the effect may be as large as 1% due to a sizable vibrational contribution to the component of the magnetizability perpendicular to the molecular plane. For the magnetizability anisotropy, zero-point vibrational corrections are much more important, often contributing 5−10% of the total vibrationally averaged magnetizability anisotropy. We also demonstrate that the additivity of magnetizabilities (known as Pascal's rule) breaks down in the case of fluorine-containing molecules.

I. Introduction

The calculation of molecular magnetizabilities and molecular polarizabilities offers some interesting contrasts. An electric field perturbation causes a linear distortion of the electron distribution, which can be rather readily described by augmenting the basis set with diffuse higher angular momentum functions.[1,2] Electron correlation effects are very important for the polarizability, however, which substantially increases the difficulty of calculating reliable polarizabilities.[3] There is of course a major basis set problem associated with describing electron correlation in general,[4−6] but once this has been tackled, the *extension* of the basis set to obtain reliable polarizabilities is modest.[1,7]

Experience with calculated magnetizabilities suggest the exact opposite. Correlation effects appear to be negligible,[8−12] other than situations of serious near-degeneracy that require multireference wave functions.[8,10,13] The effect of an external magnetic field is to induce a circulation of the electrons, an effect that is very difficult to describe with conventional basis sets. For example, the isotropic magnetizability of PF_3 is not converged to within 10% of the basis set limit even in a basis of more than 500 functions.[14] Fortunately, these basis set convergence difficulties can be circumvented by introducing basis functions that depend on local gauge origins. Such basis sets not only yield enormously improved convergence of the results with basis set size but also, when chosen appropriately, yield results that are independent of the global gauge origin.[15−17] This approach was pioneered by Kutzelnigg and Schindler some twenty years ago, using localized molecular orbitals with a local gauge origin for each orbital.[18−20] To avoid calculating difficult two-electron integrals, they introduced a resolution of the identity: as with many such approaches this IGLO method (individual gauges for localized orbitals) shows a strong basis-set dependence, at least when small basis sets are used.[20,21] Even better results can be obtained using London atomic orbitals, introduced into the calculation of magnetizabilities about 10 years ago.[22,23] These London orbital calculations involve no approximations or resolution of the identity, and very impressive basis set convergence is then observed.[14,24] For example, basis sets as small as aug-cc-pVDZ yield magnetizabilities within a few percent of the basis set limit in Hartree−Fock calculations.[23]

With the basis set convergence issue solved, and the empirical observation that correlation effects on magnetizabilities are small (in well-behaved single-reference cases), the stage would appear to be set for calculations of magnetizabilities that agree well with (gas-phase) experimental measurements. The one remaining issue that still needs consideration is the effect of nuclear motion: the molecular rotation and vibration. A few studies have been presented,[25−28] but detailed investigations on a range of polyatomic molecules are nonexistent. In general, the conclusion is that rovibrational effects are small, but a definitive answer is lacking. It is the purpose of this paper to try to rectify this situation.

II. Computational Details

In this paper we use London orbital Hartree−Fock calculations to investigate zero-point vibrational effects on the isotropic magnetizability for a comprehensive set of molecules, ranging in size from methane to benzoic acid. We use an approach recently introduced for the calculation of zero-point vibrational corrections to molecular properties.[28−30] In this approach, the vibrational wave function is expanded around an *effective geometry* defined such that it minimizes the sum of the potential

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TABLE 1: Electronic and Vibrational Contributions to the Molecular Magnetizabilities Reported in Units of 10^{-30} J T^{-2} [a]

molecule	ξ_e	ξ_{eff}	$\xi_{eff} - \xi_e$	$\langle \xi_2^{(0)} \rangle$	$\langle \xi \rangle_{ZPV}$	$\langle \xi \rangle$	percentage
methane	−314.6	−316.4	−1.8	−2.0	−3.8	−318.4	1.2
ethane	−493.5	−496.1	−2.6	2.3	−0.3	−493.2	0.1
propane	−693.1	−695.5	−2.4	2.9	0.5	−692.6	0.1
cyclopropane	−703.5	−705.8	−2.3	5.5	3.2	−700.3	0.5
butane	−890.8	−893.8	−3.0	3.9	0.9	−889.9	0.1
2-methylpropane	−905.9	−908.3	−2.4	1.7	−0.7	−906.6	0.1
ethene	−354.1	−355.3	−1.2	3.5	2.3	−351.8	0.7
propene	−548.9	−550.4	−1.5	2.5	1.0	−547.9	0.2
cyclopropene	−480.3	−481.6	−1.3	6.1	4.8	−475.5	1.0
propadiene	−480.3	−481.0	−0.7	0.1	−0.6	−480.9	0.1
1-butene	−750.9	−752.9	−2.0	3.8	1.8	−749.1	0.2
trans-2-butene	−739.3	−741.3	−2.0	1.8	−0.2	−739.5	0.0
cis-2-butene	−744.2	−745.9	−1.7	3.2	1.5	−742.7	0.2
cyclobutane	−754.6	−754.5	0.1	9.1	9.2	−745.4	1.2
cyclobutene	−612.4	−613.9	−1.5	5.2	3.7	−608.7	0.6
butadiene	−610.4	−611.9	−1.5	4.0	2.5	−607.9	0.4
cyclobutadiene	−281.2	−282.9	−1.7	11.0	9.3	−271.9	3.4
ethyne	−381.5	−381.9	−0.4	1.0	0.6	−380.9	0.2
propyne	−571.7	−572.3	−0.6	0.8	0.2	−571.5	0.0
methanol	−367.2	−369.5	−2.3	−1.5	−3.8	−371.0	1.0
ethanol	−580.1	−582.3	−2.2	2.7	0.5	−579.6	0.1
1-propanol	−779.1	−781.9	−2.8	4.2	1.4	−777.7	0.2
2-propanol	−798.6	−800.3	−1.7	1.6	−0.1	−798.7	0.0
3-hydroxipropene	−639.3	−640.5	−1.2	4.3	3.1	−636.2	0.5
formaldehyde	−139.9	−140.4	−0.5	3.8	3.3	−136.6	2.4
ethanal	−375.1	−374.8	0.3	−0.1	0.2	−374.9	0.1
propanal	−582.2	−583.4	−1.2	3.1	1.9	−580.3	0.3
cyclopropanone	−551.0	−553.0	−2.0	3.4	1.4	−549.6	0.3
dimethyl ether	−541.4	−543.0	−1.6	0.2	−1.4	−542.8	0.3
oxirane	−538.7	−540.4	−1.7	2.8	1.1	−537.6	0.2
formic acid	−355.3	−355.3	0.0	1.3	1.3	−354.0	0.4
ethanoic acid	−566.0	−564.6	1.4	0.4	1.8	−564.2	0.3
propanoic acid	−773.5	−774.1	−0.6	0.7	0.1	−773.4	0.0
ethaneamine	−641.4	−643.7	−2.3	3.4	1.1	−640.3	0.2
1-propaneamine	−839.5	−842.3	−2.8	4.6	1.8	−837.7	0.2
2-propaneamine	−857.2	−858.9	−1.7	2.2	0.5	−856.7	0.1
benzene	−1001.9	−1004.8	−2.9	16.5	13.6	−988.3	1.4
phenol	−1095.9	−1099.2	−3.3	11.9	8.6	−1087.3	0.8
aniline	−1127.5	−1130.5	−3.0	12.6	9.6	−1117.9	0.9
toluene	1183.3	−1186.9	−3.6	15.0	11.4	−1171.9	1.0
benzoic acid	−1277.4	−1280.0	−2.6	16.0	13.4	−1264.0	1.1
fluoromethane	−315.0	−316.3	−1.3	0.4	−0.9	−315.9	0.3
difluoromethane	−374.9	−375.8	−0.9	1.6	0.7	−374.2	0.2
trifluoromethane	−470.1	−470.7	−0.6	1.5	0.9	−469.2	0.2
tetrafluoromethane	−563.0	−563.8	−0.8	1.5	0.7	−562.3	0.1
fluoroethane	−526.5	−527.9	−1.4	1.3	−0.1	−526.6	0.0
1,1-difluoroethane	−599.5	−600.2	−0.7	0.1	0.6	−600.1	0.1
1,2-difluoroethane	−561.0	−562.2	−1.2	1.6	0.4	−560.6	0.1
1,1,1-trifluoroethane	−686.1	−686.9	−0.8	0.0	−0.8	−686.9	0.1
hexafluoroethane	−896.7	−897.3	−0.6	2.6	2.0	−894.7	0.2
fluoroethene	−428.6	−429.4	−0.8	0.8	0.0	−428.6	0.0
1,1-difluoroethene	−519.5	−520.2	−0.7	−0.1	−0.8	−520.3	0.2
cis-1,2-fluoroethene	−483.3	−484.3	−1.0	1.5	0.5	−482.8	0.1
trans-1,2-fluoroethene	−470.7	−471.5	−0.8	1.1	0.3	−470.4	0.1
trifluoroethene	−561.1	−561.9	−0.8	1.4	0.6	−560.5	0.1
1-fluoropropane	−729.1	−731.1	−2.0	2.7	0.7	−728.6	0.1
2-fluoropropane	−743.5	−744.6	−1.1	0.0	−1.1	−744.6	0.1
2,2-difluoropropane	−814.1	−815.0	−0.9	−1.0	−1.9	−816.0	0.2
1-fluorobutane	−924.9	−927.4	−2.5	4.5	2.0	−922.9	0.
2-fluorobutane	−944.2	−946.0	−1.8	1.4	−0.4	−944.6	0.0
fluorobenzene	−1063.2	−1066.0	−2.8	13.3	10.5	−1052.7	1.0
o-difluorobenzene	−1124.6	−1127.3	−2.7	9.7	7.0	−1117.6	0.6
m-difluorobenzene	−1120.5	−1123.2	−2.7	9.7	7.0	−1113.5	0.6
p-difluorobenzene	−1121.0	−1123.6	−2.6	9.6	7.0	−1114.0	0.6

[a] In addition, the percentage contribution of the zero-point vibrational correction to the total magnetizability is given.

and zero-point vibrational energies.[31] At this effective geometry, the leading anharmonic corrections vanish,[29,30] being implicitly accounted for through the change in the molecular property as we shift the expansion point from the equilibrium to the effective geometry. The contribution to the vibrationally averaged molecular property arising from averaging it over the harmonic oscillator vibrational wave function is given as

$$\langle \xi_2^{(0)} \rangle_{\mathrm{eff}} = \frac{1}{4} \sum_{i=1}^{N} \frac{\langle \xi_{\mathrm{eff},ii}^{(2)} \rangle}{\omega_{\mathrm{eff},i}} \qquad (1)$$

where the summation runs over all normal coordinates in the

TABLE 2: Electronic and Zero-Point Vibrational Corrections to the Magnetizability Anisotropies in Planar Organic Ring Systems (Magnetizability Anisotropies Reported in Units of 10^{-30} J T^{-2})[a]

molecule	$\Delta\xi_e$	$\Delta\xi_{eff}$	$\Delta\xi_{eff} - \Delta\xi_e$	$\langle\Delta\xi_2^{(0)}\rangle$	$\langle\Delta\xi\rangle_{ZPV}$	$\langle\Delta\xi\rangle$	percentage
formaldehyde[b]	−179.0	−178.8	−0.2	−1.3	−1.5	−177.5	0.8
cyclopropane	−182.4	−182.7	−0.3	−3.6	−3.9	−186.3	2.1
cyclopropene	−298.4	−300.0	−1.6	1.4	−0.2	−298.6	0.1
cyclobutane	231.8	238.0	6.2	−0.4	5.8	237.6	2.4
cyclobutene	−47.3	−45.7	1.6	1.8	3.4	−43.9	7.7
cyclobutadiene	337.5	335.3	−2.2	25.5	23.3	360.8	6.5
benzene	−1130.5	−1134.8	−4.3	45.7	41.4	−1089.1	3.8
phenol	−1010.2	−1016.1	−5.9	33.1	27.2	−983.0	3.6
aniline	−960.1	−962.1	−2.0	38.4	36.4	−923.7	3.9
toluene	−1080.3	−1084.4	−4.1	43.2	39.1	−1041.2	3.8
benzoic acid	−1260.9	−1264.0	−3.1	44.6	41.5	−1219.4	3.4

[a] For the cylindrical molecules, the anisotropies are defined as $\Delta\xi = \xi_{\parallel} - \xi_{\perp}$; otherwise they are defined as $\Delta\xi = \xi_{aa} - {}^1/_2(\xi_{bb} + \xi_{cc})$, where ξ_{bb} and ξ_{cc} are the two principal components of the magnetizability most similar in value. The percentage denotes the contribution of the zero-point vibrational corrections to the total vibrationally averaged magnetizability anisotropy. [b] $\Delta\xi = \xi_{cc} - {}^1/_2(\xi_{aa} + \xi_{bb})$, where ξ_{cc} and is the component with the largest absolute value of the magnetizability.

molecule, $\omega_{eff,i}$ is the harmonic frequency at the effective geometry for normal mode i, and $\xi^{(2)}_{eff,ii}$ is the second derivative of the magnetizability with respect to normal coordinate i.

The work presented here is to a large extent based on two recent studies presented for zero-point vibrational correction to nuclear shieldings,[32,33] and more details about our approach and the computational procedure can be found in these papers. In particular, if we use the same basis set and wave function as refs 32 and 33, we can reuse the effective geometries when calculating the zero-point vibrational corrections to the magnetizabilities.[30] We will still need, however, to determine second derivatives of the magnetizability with respect to the normal modes at the effective geometry. Following our previous studies, we will use a Hartree−Fock wave function and the polarized valence triple-ζ basis set of Ahlrichs and co-workers.[34] Although not the basis set we normally use in calculations of magnetizabilities, we expect it to be large and flexible enough to provide accurate magnetizabilities. We note, for instance, that the magnetizability calculated with this basis set for ethene -354.1×10^{-30} J T^{-2} is in excellent agreement with that obtained using the aug-cc-pVTZ basis set at the same geometry, -353.8×10^{-30} J T^{-2}. All calculations have been done with the Dalton quantum chemistry program.[35]

III. Zero-Point Vibrational Corrections to Magnetizabilities

Our magnetizabilities calculated at the equilibrium and effective geometries, as well as the harmonic contributions to the zero-point vibrational corrections and the total magnetizability, are collected in Table 1. We note that the effects of zero-point vibrational corrections are small, the average percentage contribution of the vibrational corrections to the total magnetizability being a negligible 0.4%, which, combined with the known insensitivity to electron correlation effects, gives further support to the notion that Hartree−Fock isotropic magnetizabilities calculated at the equilibrium geometry give very accurate and realistic estimates of the magnetizability of an isolated molecule in the gas phase. A direct comparison with experiment is, however, difficult due to the large experimental error bars and the potential systematic errors in the experimental results.[23]

For methane, we can compare our results with large-scale MCSCF calculations.[28] Our zero-point vibrational correction of -3.8×10^{-30} J T^{-2} is in excellent agreement with the Hartree−Fock result of ref 28, and in that paper the electron correlation effects were found to reduce the magnitude of the zero-point vibrational correction by about 10%. The effect of electron correlation on the zero-point vibrational correction itself is thus quite large in the case of methane. However, the zero-point vibrational correction is a modest 1.2% of the total electron correlated magnetizability—and this is one of the largest vibrational contributions to the magnetizability of any of the molecules studied here—and the effect of electron correlation on the total vibrationally averaged magnetizability is thus negligible. It is important to note that electron correlation effects may affect both the harmonic force field and the magnetizability derivatives. However, large electron correlation effects cannot be expected, as the reason for the minor vibrational corrections are the small magnetizability derivatives. This can be realized by noting the small change in the magnetizability that results when we change the expansion point. This lack of sensitivity of the magnetizability to the molecular geometry also provides a partial explanation for the remarkable additivity of the molecular magnetizability, normally referred to as Pascal's rule.[36−38] We will return to this point later.

If we focus on the molecules in Table 1 for which the zero-point vibrational corrections to the magnetizability is the largest, we note one striking feature. With the exception of methane and methanol, all these molecules are planar systems. More interestingly, investigating the vibrational contribution to the different components of the magnetizability shows that almost all the effect comes from vibrational corrections to one component only, the component perpendicular to the molecular plane. This would indicate that zero-point vibrational effects may be substantial on the magnetizability anisotropies, and these are collected in Table 2.

Table 2 reveals another interesting observation, namely that with the exception of cyclobutene, for which the magnetizability anisotropy is rather small, all molecules for which there are significant zero-point vibrational corrections to the magnetizability are what is traditionally classified as aromatic or anti-aromatic molecules. The concept of electronic ring currents has been extensively discussed in the literature with respect to isotropic and anisotropic magnetizabilities.[39,40] Our results for the zero-point vibrational corrections to the magnetizabilities give some indication that these effects may play an important role also for the *vibrational* corrections to the magnetizability, although the mechanism behind this is unclear.

Let us briefly discuss the zero-point vibrational corrections to the magnetizability anisotropies. The calculated anisotropies and their zero-point vibrational corrections are presented in Table 3. As evident from Tables 2 and 3, zero-point vibrational

TABLE 3: Electronic and Vibrational Contributions to the Magnetizability Anisotropies Reported in Units of 10^{-30} J T^{-2} [a]

molecule	$\Delta\xi_{1,e}$	$\langle\Delta\xi_1\rangle$	$\langle\Delta\xi_1\rangle_{ZPV}$	$\langle\Delta\xi_1\rangle_{ZPV}/\langle\Delta\xi_1\rangle \times 100\%$	$\Delta\xi_{2,e}$	$\langle\Delta\xi_2\rangle$	$\langle\Delta\xi_1\rangle_{ZPV}$	$\langle\Delta\xi_2\rangle_{ZPV}/\langle\Delta\xi_2\rangle \times 100\%$
ethane	−75.5	−82.6	−7.1	8.5				
propane	−47.1	−49.9	−2.8	5.7	37.7	40.0	2.3	5.7
cyclopropane	−182.4	−186.4	−4.0	2.1				
butane	−83.6	−88.3	−4.7	5.4				
2-methylpropane	37.6	51.0	13.4	26.3				
ethene	−131.4	−127.0	4.4	3.4	104.1	101.1	−3.0	3.0
propene	−118.9	−112.8	6.1	5.4	133.1	132.5	−0.6	0.5
cyclopropene	−298.4	−298.6	−0.2	0.1	222.6	223.1	0.5	0.2
propadiene	2.4	−0.3	−2.7	907.7				
1-butene	−152.8	−149.9	2.9	2.0	140.2	136.5	−3.7	−2.7
trans-2-butene	−104.1	−97.6	6.5	6.7	191.8	191.7	−0.1	0.0
cis-2-butene	−113.6	−107.4	6.3	5.9	80.1	74.5	−5.6	7.6
cyclobutane	231.8	237.6	5.8	2.4				
cyclobutene	−47.3	−43.9	3.4	7.8	46.0	42.6	−3.4	7.9
butadiene	−270.8	−261.2	9.6	3.7	235.3	227.4	−7.9	3.5
cyclobutadiene	−203.2	−223.1	−19.8	8.9	337.5	360.8	23.3	6.5
ethyne	−35.6	−41.6	−6.0	14.4				
propyne	−116.0	−122.7	−6.7	5.4				
methanol	−131.4	−128.4	3.0	2.4	71.0	67.0	−4.0	6.0
ethanol	−71.1	−67.1	4.0	5.9	48.5	47.8	−0.7	1.4
1-propanol	−67.2	−64.8	2.4	3.8	67.0	69.0	2.0	3.0
2-propanol	−47.1	−44.0	3.1	7.0	53.7	54.4	0.7	1.3
3-hydroxypropene	−182.8	−175.8	7.0	4.0	153.4	147.1	−6.3	4.3
formaldehyde	−179.0	−180.1	−1.1	0.1	196.4	199.7	3.3	1.6
ethanal	−162.7	−159.1	3.6	2.2	198.1	194.9	−3.2	1.7
propanal	−179.3	−172.9	6.4	3.7	213.4	212.3	−1.1	0.5
cyclopropanone	−241.8	−239.6	2.2	0.9	279.6	277.9	−1.7	0.6
dimethyl ether	−90.6	−97.6	−7.0	7.2	73.8	77.8	4.0	5.2
oxirane	−141.5	−146.0	−4.5	3.1	144.6	145.6	1.0	0.7
formic acid	−106.7	−105.7	1.0	1.0	70.9	69.6	−1.3	1.9
ethanoic acid	−77.9	−75.7	2.2	2.9	77.6	73.4	−4.2	5.7
propanoic acid	−99.5	−98.8	0.7	0.7	106.6	104.7	−1.9	1.9
ethaneamine	−69.3	−68.0	1.3	1.9	47.5	48.2	0.7	1.5
1-propaneamine	−119.1	−120.2	−1.1	0.9	69.7	70.7	1.0	1.4
2-propaneamine	−51.4	−50.4	1.0	1.0	56.7	58.8	2.1	3.7
benzene	−1130.5	−1089.1	41.4	3.8				
phenol	−1010.2	−983.0	27.2	2.8	566.2	551.5	−14.7	2.7
aniline	−960.1	−923.7	36.4	3.9	565.7	544.7	−21.0	3.9
toluene	−1080.3	−1041.2	39.1	3.8	610.8	592.8	−18.0	3.0
benzoic acid	−1260.9	−1219.4	41.5	3.4	645.5	627.9	−17.6	2.8
fluoromethane	−128.1	−130.1	−2.0	1.5				
difluoromethane	−34.5	−34.4	0.1	0.3	27.8	26.9	−0.9	3.2
trifluoromethane	23.8	23.0	−0.8	3.4				
fluoroethane	−74.7	−72.6	2.1	2.9	61.1	60.4	−0.7	1.1
1,1-difluoroethane	−21.2	−22.4	−1.2	5.4	41.4	40.9	−0.5	1.2
1,2-difluoroethane	−65.7	−65.0	0.7	1.1	90.8	90.7	−0.1	0.1
1,1,1-trifluoroethane	−21.1	−24.2	−3.1	12.8				
hexafluoroethane	49.5	48.7	−0.8	1.6				
fluoroethene	−76.2	−74.2	2.0	2.7	85.9	83.8	−2.1	2.5
1,1-difluoroethene	−54.3	−52.6	1.7	3.2	71.6	70.8	−0.8	1.1
cis-1,2-fluoroethene	−26.1	−24.5	1.6	6.7	24.7	24.4	−0.3	1.2
trans-1,2-fluoroethene	−90.1	−88.9	1.2	1.3	130.4	128.7	−1.7	1.3
trifluoroethene	−51.0	−51.5	−0.5	1.0	86.1	85.2	−0.9	1.1
1-fluoropropane	−120.1	−121.1	−1.0	0.8	62.0	64.7	2.7	4.2
2-fluoropropane	−50.0	−46.3	3.7	8.0	61.1	60.6	−0.5	0.8
2,2-difluoropropane	−14.8	−18.2	−3.4	18.5	19.1	19.0	−0.1	0.5
1-fluorobutane	−85.4	−82.6	2.8	3.3	64.7	62.7	−2.0	3.2
2-fluorobutane	−64.1	−70.1	−6.0	8.5	75.7	80.1	4.4	5.5
fluorobenzene	−1044.0	−1008.6	35.4	3.5	558.4	540.0	−18.4	3.4
o-difluorobenzene	−981.2	−948.4	32.8	3.5	545.9	528.9	−17.0	3.2
m-difluorobenzene	−941.5	−910.1	31.4	3.5	504.3	487.3	−17.0	3.5
p-difluorobenzene	−948.3	−917.6	30.7	3.4	547.7	530.0	−17.7	3.3

[a] In addition, the percentage contribution of the zero-point vibrational correction to the total magnetizability is given. The anisotropies are defined as $\Delta\xi_1 = \xi_{aa} - {}^1/_2(\xi_{bb} + \xi_{cc})$ and $\Delta\xi_2 = \xi_{cc} - {}^1/_2(\xi_{aa} + \xi_{bb})$, where $|\xi_{aa}| \geq |\xi_{bb}| \geq |\xi_{cc}|$. For cylindrical molecules, we report $\Delta\xi = \xi_{\parallel} - \xi_{\perp}$.

corrections to the magnetizability anisotropies are much larger than for the isotropic part, often being about 5−10% of the total magnetizability anisotropies. Thus, for an accurate determination of the magnetizability anisotropy, zero-point vibrational corrections appear to be necessary. However, for this property, electron correlation effects are also important,[11,41] and because of this we do not consider our results to be of predictive quality.

IV. The Breakdown of Pascal's Rule

Let us finally focus on the fluorine-containing molecules included in Table 1. It was established early that molecular magnetizabilities could be accurately determined by adding up "atomic" magnetizability contributions,[36] and this is known as Pascal's rule.[37,38] Recent theoretical investigations have verified this almost perfect additivity.[23,42,43] If we consider methane and fluoromethane, we note that they have an almost identical isotropic magnetizability, which would indicate that the atomic "Pascal"-type magnetizability of fluorine is identical to that of hydrogen, and thus that $\xi(CF_4) \approx \xi(CH_4)$. However, Table 1 shows that the magnetizability of CF_4 is very different from that of CH_4, being instead almost twice as large. Interestingly, in going from CH_4 to CF_4 the increase in the absolute value of the isotropic magnetizability as we substitute a hydrogen atom with a fluorine atom is 0, 60, 96, and 93 $\times 10^{-30}$ J T^{-2}, respectively.

The same trend can be observed for the series ethane, fluoroethane, 1,1-difluoroethane, and 1,1,1-trifluoroethane, although the effect is somewhat more damped. Interestingly, going from fluoroethane to 1,2-difluoroethane, the absolute value of the isotropic magnetizability increases by 34 $\times 10^{-30}$ J T^{-2}, which is almost identical to the increase observed between ethane and fluoroethane, 32 $\times 10^{-30}$ J T^{-2}. In contrast, the change in the isotropic magnetizability is almost twice as large if we attach the second fluorine to the same carbon as the first—that is, going from fluoroethane to 1,1-difluoroethane—the change then being 72 $\times 10^{-30}$ J T^{-2}. The same observation can be made for the ethene and propane derivatives. In other words, the presence of fluorines on a carbon atom causes such large perturbations to the local electronic structure that the additivity scheme for the magnetizability breaks down. However, the effect is local, and the substitution of fluorines on other carbon atoms in the molecule shows the expected additivity of the magnetizability. For this reason, the substitution of fluorines to benzene shows a perfect additivity, which explains how atomic fluorine magnetizabilities could be derived using fluorobenzenes as model systems.[42] We note, however, that the increase in the isotropic magnetizability when we substitute a hydrogen with a fluorine is almost twice as large in benzene as it is in the alkanes, with the other extreme being methane where the fluorine has the same atomic magnetizability as hydrogen going from methane to fluoromethane. It therefore appears difficult to extract a Pascal-like atomic magnetizability for fluorine which does not depend on the rest of the molecular framework.

V. Summary

We have demonstrated—by calculations on 64 organic molecules—that zero-point vibrational corrections to isotropic magnetizabilities are negligible. Combining this result with the excellent basis set convergence observed when London orbitals are used and the small electron correlation effects,[11,22,23] we have shown that Hartree–Fock isotropic magnetizabilities calculated at an equilibrium geometry provide results that are accurate enough to allow for a direct comparison with gas-phase experiments. For aromatic and anti-aromatic ring systems there appears to be a sizable vibrational contribution to the out-of-plane component of the magnetizability, and for these systems the inclusion of zero-point vibrational corrections is recommended if highly accurate results for the isotropic magnetizability are required. We have also shown that the well-known additivity of the isotropic magnetizability breaks down in the case of multiple substitutions of fluorine atoms to a single carbon center.

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