On the Magnetic Susceptibility of Fluorine

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The isotropic magnetic susceptibility, χ_{iso}, for F_2 has been measured experimentally for the first time and found to be $(-9.627 \pm 0.062) \times 10^{-6}$ (cgs). The value was measured on a paramagnetic gas analyzer (PGA) configured to be compatible with the aggressive F_2. The PGA was shown to respond linearly with χ_{iso} and was calibrated using the response from several pure gases and their literature χ_{iso} values. The major source of error in the analysis is the inaccuracy of the literature χ_{iso} values. The experimental result for F_2 was compared to ab initio calculations using both Hartree−Fock (HF) theory and gradient-corrected density functional theory (DFT) theory with a variety of basis sets. DFT calculations were found to converge to a value much closer to the experimental value compared to HF calculations, underlining the importance of the many-electron correlation effect in F_2.

Introduction

Although F_2 was first isolated by Moissan over 100 years ago,[1] it is the only nonradioactive element that lacks an experimentally determined value for its magnetic susceptibility[2] χ_{iso}. An occasionally cited[3] "experimental" value is actually a derived quantity from the sum of the diamagnetic susceptibility χ_d, calculated from a perturbed Hartree−Fock (HF) approach,[4] and the paramagnetic magnetic susceptibility χ_p, obtained from the experimental determination of the molecular *g*-value by a molecular beam experiment.[5]

The reason that no experimental determination of χ_{iso} for F_2 has been reported is undoubtedly because of the experimental difficulties arising from its reactivity. The highly aggressive F_2 is incompatible with instruments used in literature methods for the determination of the magnetic susceptibility of gases.[6] Another experimental problem arises from the contamination of commercial F_2 with varying levels of O_2, which are difficult to measure precisely. Concentrations of the paramagnetic O_2 as low as 10 ppm can noticeably change χ_{iso}; thus, O_2 contamination level must be known precisely or preferably eliminated in order to measure the magnetic susceptibility of F_2. Moreover, F_2 can generate O_2 by reaction with metal oxides typically found on the surfaces of materials used in the construction of F_2 gas-handling systems. This generated O_2 would lead to additional bias in the magnetic susceptibility determination, especially in methods where the measurement is taken under static conditions.

In the absence of an experimental value, the calculation of χ_{iso} for F_2 has received considerable attention. Estimations have ranged[7] from -13.10×10^{-6} (cgs) to -11.6×10^{-6} for group additivity methods developed by Pascal and -9.48×10^{-6} to -18.65×10^{-6} for ab initio calculations.[4,8] Early ab initio calculations utilized small basis sets with a perturbed HF approach. They have had reasonable success[9] in predicting other molecular properties of F_2 that have been experimentally measured.[5,10] Recent advances in density functional theory (DFT) have prompted a number of theoretical studies to calculate molecular magnetic properties chiefly driven by the demand to develop first-principles methods to simulate NMR spectra. By comparison, little attention has been paid to the calculations of molecular magnetic susceptibilities and shielding tensors. In particular, there has been a lack of systematic studies on the calculations of the magnetic susceptibility as a function of basis sets, which is an important issue to establish confidence on the calculated values.

In this paper we present the first true experimental determination of the magnetic susceptibility of fluorine[11] and systematic theoretical studies on its magnetic properties. The experiment was carried out by using a commercial paramagnetic gas analyzer (PGA), the Siemens Oxymat 6E paramagnetic oxygen analyzer, configured to be compatible with undiluted fluorine. Ab initio quantum mechanical calculations were performed systematically to evaluate the magnetic susceptibility and chemical shielding tensor of F_2 with a variety of basis sets using both the Hartree−Fock method and the gradient-corrected density functional theory. A comparison was then made between the experimental values with the ab initio results.

Experimental Section

Safety Note: Molecular fluorine is a highly reactive, strongly oxidizing, toxic gas with an OSHA permissible exposure limit, time-weighted average (PEL-TWA) of 0.1 ppm. Extreme caution must be exercised when handling F_2, especially at the elevated temperatures and pressures described for the procedure for the removal of O_2. The PGA and the stainless steel/Monel metal gas handling system were progressively passivated with F_2 to eliminate surface oxides and form a stable fluoride surface layer.

Gas Purity. With the exception of F_2, all of the single-component cylinder gases (Air Products and Chemicals) were certified to contain not more than 1 ppm of O_2 and used as received. The oxygen content was verified using either a Delta F Platinum series or Illinois Instruments model 3000 oxygen analyzer. The N_2 was sourced from a 120 psig house line supplied from a bulk liquid N_2 tank certified to contain less than 5 ppm O_2 and less than 25 ppm total impurities. The O_2 in the house N_2 was found to be typically in the range 0.06−0.2

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ppm. Neon was certified to contain not more than 10 ppm He. Undiluted F_2 was received with a batch certificate of analysis stating that the CO_2 concentration was less than 30 ppm and that the CF_4 and SF_6 concentrations were less than 5 ppm. The HF concentration was less than 1000 ppm. The unknown quantity of O_2 in the F_2 was removed by the purification method described below.

Gas Analysis Procedure. The PGA, a Siemens Oxymat 6E paramagnetic oxygen analyzer, was configured with titanium tubing, a stainless steel cell, and a high-pressure reference input. The reference line was supplied with pure nitrogen at 60 psig unless noted otherwise. The PGA response at a detector temperature between 41 and 43 °C was read as an equivalent O_2 concentration in ppm and calibrated with a primary cylinder gas mixture of 5020 ppm O_2 in N_2. The results for a sample gas analysis on the PGA were measured relative to the response from pure N_2. The gas of interest was flowed through the analyzer at 400 sccm, while the output from the PGA was recorded electronically at 20 samples/s. The average of all individual readings from the PGA over 1 minute was taken as one independent reading. In a typical analysis, five independent readings would be recorded for N_2 followed by five independent readings from the gas to be analyzed. The average response from N_2 was subtracted from the average response of the test gas to yield an estimate of the response of the test gas relative to N_2. Unless noted otherwise, three runs were made for each gas.

Linearity with Respect to Varying O_2 Concentrations. A primary cylinder gas mixture of 5020 ppm O_2 in N_2 was blended with N_2 to make various test mixtures containing different levels of O_2. Blending was accomplished dynamically using mass flow controllers. The output of the mass flow controllers was verified using a BIOS International Dry-Cal DC-2M primary air flow meter. Oxygen concentrations of 5020, 3500, 2420, 1000, 485, and 275 ppm were measured. Two additional points were acquired using primary cylinder gas mixtures containing 97 and 10.7 ppm O_2 in N_2. A plot of the PGA response versus the known O_2 concentration gives a line with a slope of 0.999 34, an intercept of 0.105 ppm O_2, a coefficient of determination (r^2) of 0.999 993, and a standard error for the PGA response estimate of 4.70 ppm.

Linearity with Respect to Varying Ar Concentrations. A cylinder of Ar was blended with N_2 to make various test mixtures containing different levels of Ar in the same manner described in the preceding experiment using dilute O_2. Nitrogen concentrations of 100%, 78.8%, 57.3%, 39.3%, 20.8%, 18.5%, and 0% in Ar were measured. A plot of the PGA response versus % N_2 gives a line with a slope of 26.082, an intercept of −2607.8 ppm, a coefficient of determination (r^2) of 0.999 982, and a standard error for the PGA response estimate of 3.84 ppm.

PGA Response vs χ_{iso} Calibration. The PGA response relative to N_2 was recorded for pure He, H_2, Ne, CO, CH_4, Ar, and CO_2. The H_2 and He were run with a reference pressure of 112 psig to reduce the back diffusion of the sample gas through the reference line, which affects the reading of the PGA. The span of the PGA was recalibrated with the 5020 ppm O_2 in N_2 standard prior to running the H_2 and He at the higher reference pressure.

Removal of O_2 from F_2. A modified method of Jacob and Christe[12] was followed to remove the O_2 as nonvolatile $O_2^+SbF_6^-$. A thoroughly dried, fluorine-passivated 500 cm^3 Monel cylinder was filled with 1 atm of dry N_2. In a drybox, 5 g of SbF_5 (Aldrich) was transferred into the cylinder. The cylinder was reconnected to the F_2 gas delivery system and the bottom of the flask cooled with dry ice to freeze the SbF_5. The N_2 was removed from the flask by evacuation and the flask thoroughly purged with 1 atm of undiluted F_2. The cylinder was cooled to liquid N_2 temperatures to condense the F_2, and an additional 5.9 sL (10 g) of F_2 was condensed into the flask. The flask was isolated and allowed to warm to room temperature (final pressure ≈ 200 psia) and then heated to 200 °C for 1.5−3.5 h. After allowing the gas to cool to room temperature, the flask was cooled to 0 °C to lower the volatility of the SbF_5 to a partial pressure of less than 1 mmHg.[13] The average PGA response from the purified F_2 over seven measurements was 715.4 ± 3.57 ppm.

TABLE 1: Literature[a] χ_{iso} and Average PGA Responses vs N_2 for Several Specialty Gases

gas	$\chi_{iso} \times 10^6$ cgs	PGA response (O_2 ppm equivalent)	$\chi_{iso} \times 10^6$ cgs estimated from calibration[e]
He	−1.88	3274.5 ± 4.8	−1.95
H_2	−4.01	2626.2 ± 1.3	−3.90
Ne	−7.65[b]	1414.8 ± 2.3	−7.53
CO	−11.8[c]	−83.1 ± 2.8	−12.0
CH_4	−17.4[d]	−2198.6 ± 0.6	−18.4
Ar	−19.6	−2590.5 ± 2.7	−19.5
CO_2	−21.0	−3032.3 ± 3.0	−20.9

[a] Values taken from Foëx[17] unless otherwise indicated. [b] Havens.[18] [c] Jaanus and Shur.[19] [d] Barter, Meinsenheimer, and Stevenson.[20] [e] Calculated from the linear regression of the results of all the gases except CH_4.

Computational Methods

Several ab intio methods[14] have been developed to deal with the gauge problem in the calculation of the second-order magnetic response properties of a molecule. In this article, we utilized the continuous set of gauge transformation (CSGT) method[14a−c] to achieve the gauge-invariant. It has been shown by Keith and Bader[14b] that, in general, for moderately sized or large basis sets, the CSGT method, employing the coupled perturbed HF wave functions, calculates χ_{iso} in reasonably good agreement with experimental results. However, that approach failed to produce an accurate χ_{iso} for F_2.

The present approach utilizes wave functions obtained from both HF theory and the gradient-corrected DFT to calculate the magnetic susceptibility as well as the magnetic shielding tensor for F_2 with a range of basis sets. The gradient-corrected DFT calculations employed BLYP and B3LYP functionals.[15] Full geometry optimization was performed followed by calculations of magnetic response properties. The CSGT method was implemented in the Gaussian 94 program suite,[16] and the calculations were performed on a SGI/Power Challenge workstation.

Results

Experimental Determination of χ_{iso} for F_2. The specialty gases selected to calibrate the PGA response to χ_{iso} were those that have literature χ_{iso} values close to the expected value for F_2 and could be obtained free from O_2 contamination. Table 1 shows the literature χ_{iso} and PGA responses vs N_2 for several pure specialty gases as well as the estimated χ_{iso} values based on the calibration line with a slope of 333.45, an intercept of 3925.67 ppm, a coefficient of determination (r^2) of 0.999 73, and a standard error for the PGA response estimate of 41.7 ppm. The calibration line used to estimate χ_{iso} of F_2 included data points from all the gases except CH_4, which had a PGA response that fell off the calibration line, casting doubt on the accuracy of the literature χ_{iso} value for CH_4.

TABLE 2: PGA Response of F_2 after Reaction with SbF_5 at 200 °C

run	reaction time (h)	PGA response (O_2 ppm equivalent)
1	2.5	718.8 ± 3.6
2	3.5	715.8 ± 2.3
3	2.7	711.9 ± 3.0
4	2.4	720.7 ± 4.9
5	1.5	715.2 ± 4.1
6	1.8	715.0 ± 2.7
7	2.0	710.5 ± 5.7
average		715.4 ± 3.6

The removal of O_2 from F_2 was accomplished by the method of Jacob and Christe.[12] At elevated temperatures, SbF_5 reacts with O_2 and F_2 to form the nonvolatile $O_2{}^+SbF_6{}^-$ salt. After the reaction the purified F_2 was analyzed on the PGA. The reaction flask containing the purified F_2 was cooled to 0 °C to ensure that no significant amount of SbF_5 would contaminate the analyzed F_2.[13] Table 2 shows the results of reacting the O_2 contaminant in the F_2 with SbF_5 at 200 °C. Over the course of the seven runs the O_2-containing F_2 was heated between 1.5 and 3.5 h at 200 °C. The PGA response of the purified F_2 did not vary with the heating time, showing that the O_2 was reacted away to levels below the detection limit of the PGA. By use of the calibration line, the χ_{iso} for F_2 is estimated to be $(-9.627 \pm 0.062) \times 10^{-6}$.

Ab Initio Calculations. The optimized bond distance of F_2 calculated using a variety of basis sets and methods is shown in Table 3.

The calculated magnetic susceptibility is shown in Table 4, where $\chi_{\|}$ represents the component parallel to the molecular axis and $\chi_{\perp}$ the component perpendicular to the molecule. The isotropic and anisotropic magnetic susceptibilities are defined as

$$\chi_{iso} = \frac{1}{3}(\chi_{\|} + 2\chi_{\perp}) \quad (1)$$

and

$$\chi_{ani} = \chi_{\|} - \chi_{\perp} \quad (2)$$

respectively.

The calculated magnetic shielding tensor and anisotropy are shown in Table 5. Similarly, the isotropic and anisotropic shielding tensors are defined as

$$\sigma_{iso} = \frac{1}{3}(\sigma_{\|} + 2\sigma_{\perp}) \quad (3)$$

and

$$\sigma_{ani} = \sigma_{\|} - \sigma_{\perp} \quad (4)$$

respectively, where $\sigma_{\|}$ and $\sigma_{\perp}$ are the components parallel and perpendicular to the symmetry axis. For convenience of comparison, we list the values of the experimental bond length of F_2 and its reported magnetic susceptibility and shielding tensor in Table 6.

Discussion

The suitability of the Siemens Oxymat 6E as the PGA for this work depended on two factors: compatibility with F_2 and precision of determining χ_{iso} of any gas. The Oxymat 6E operates by detecting flow variations induced in a reference gas stream by an oscillating magnetic field operating on the sample gas stream.[22] Several features make this PGA compatible with F_2. The sample-gas-wetted portions of this instrument are fabricated of metals that form stable metal fluorides upon exposure to F_2. Both the sample gas and the N_2 reference gas flow continuously during an analysis, thereby mitigating dead-leg and oxygen generation effects. Also, the detection element, which resides in reference gas stream, is not directly contacted by the F_2.

TABLE 3: Optimized F−F Bond Distance (Å)

basis set	HF	BLYP	B3LYP
3-21+G(d)	1.4113	1.4723	1.4723
6-31G(d)	1.3446	1.4340	1.4029
6-31+G(d)	1.3466	1.4449	1.4108
6-311+G(2d,p)	1.3304	1.4000	1.4000
D95(d,p)	1.3368	1.4002	1.4002
D95++(d,p)	1.3353	1.4355	1.4008
cc-pVDZ	1.3476	1.4100	1.4100
Aug- cc-pVDZ	1.3382	1.4379	1.4031
cc-pVTZ	1.3295	1.4325	1.3975
Aug- cc-pVTZ	1.3282	1.4326	1.3970
cc-pVQZ	1.3276	1.4323	1.3967
Aug- cc-pVQZ	1.3267	1.4323	1.3967

The potential precision in measuring χ_{iso} was estimated by determining the linearity of the PGA response with χ_{iso} using both paramagnetic (O_2) and diamagnetic (Ar) gases. The PGA responses relative to nitrogen for several O_2 in N_2 mixtures ranging from 9.8 to 5020 ppm were measured. A least-squares solution of the PGA response vs the known O_2 concentration gives a correlation factor of 0.999 993 and a standard error for the PGA response estimate of 4.70 ppm. Taking χ_{iso} of O_2 to be 3449.0×10^{-6}, the maximum resolution of the PGA is $(4.7 \times 10^{-6})(3449 \times 10^{-6}) = 0.016 \times 10^{-6}$. The PGA response relative to N_2 of several N_2−Ar blends from 0 to 100% was measured. A plot of these responses versus % N_2 yielded a linear fit with a correlation factor of 0.999 982 and a standard error for the PGA response estimate of 3.84 ppm. These studies show that the response of the PGA varies linearly with χ_{iso} and that the χ_{iso} of F_2 can be measured without damaging the instrument to a potential precision of $\pm 0.016 \times 10^{-6}$.

Previous reports on the experimental determination of χ_{iso} for gases generally rely on a single-point calibration using literature values for H_2,[23] Ar,[20] O_2,[18,24] air,[25] water,[26] or an aqueous solution of a paramagnetic salt.[27] The risk in this approach is that any bias in the standard measurement or in the literature value applied to that measurement will be carried through the entire study. To mitigate this potential bias, we constructed a calibration curve for the PGA response vs χ_{iso} for several different gases using published χ_{iso} values from different studies. While constructing the calibration curve, it became apparent that the largest source of error would be the unknown precision and accuracy of the reported χ_{iso} for the calibration gases. Reviews of published experimental χ_{iso} values for gases by Foëx[17] and Joussot-Dubien[6] show that there is severe disagreement among authors for the measured χ_{iso} for several gases, even when similar methods and reference fluids are used. Many of these studies certainly suffered from sample contamination, and there are other less obvious sources of errors in the techniques employed.[28] The Foëx review, which covers the literature up to 1956, attempted to identify the most reliable value based on author consensus and reliability of the measurement method.

Figure 1 is a plot of the data in Table 1. Also included are the χ_{iso} values from Foëx[17] for Ne, CO, and CH_4. The graph shows that the χ_{iso} values accepted by Foëx for Ne, CO, and CH_4 are in considerable error.

TABLE 4: Calculated Isotropic Magnetic Susceptibility (cgs ppm)[a]

	HF				BLYP				B3LYP			
basis set	$\chi_\perp$	$\chi_\parallel$	χ_{iso}	χ_{ani}	$\chi_\perp$	$\chi_\parallel$	χ_{iso}	χ_{ani}	$\chi_\perp$	$\chi_\parallel$	χ_{iso}	χ_{ani}
3-21+G(d)	−6.16	−17.07	−9.80	−10.91	−1.05	−17.92	−6.67	−16.87	−1.63	−17.68	−6.98	−16.05
6-31G(d)	−10.51	−16.31	−12.44	−5.80	−5.32	−16.35	−8.99	−11.03	−7.15	−16.31	−10.21	−9.16
6-31+G(d)	−10.24	−16.77	−12.42	−6.53	−4.93	−17.55	−9.14	−12.62	−6.85	−17.29	−10.33	−10.44
6-311+G(2d,p)	−10.66	−16.71	−12.67	−6.05	−6.95	−17.45	−10.45	−10.50	−7.40	−17.25	−10.68	−9.85
D95(d,p)	−10.70	−16.56	−12.66	−5.86	−10.09	−16.71	−10.09	−6.62	−7.28	−16.68	−10.41	−9.40
D95++(d,p)	−10.35	−16.68	−12.46	−6.33	−5.18	−17.44	−9.27	−12.26	−7.06	−17.18	−10.44	−10.12
cc-pVDZ	−9.56	−16.46	−11.86	−6.90	−5.46	−16.46	−9.12	−11.00	−5.91	−16.46	−9.43	−10.55
Aug- cc-pVDZ	−10.40	−16.85	−12.55	−6.45	−5.37	−17.61	−9.45	−12.24	−7.21	−17.34	−10.58	−10.13
cc-pVTZ	−11.18	−16.51	−12.96	−5.33	−6.17	−17.02	−9.79	−10.85	−8.02	−16.87	−10.97	−8.85
Aug- cc-pVTZ	−10.57	−16.65	−12.60	−6.08	−5.68	−17.50	−9.62	−11.82	−7.47	−17.23	−10.72	−9.76
cc-pVQZ	−11.12	−16.54	−12.92	−5.42	−6.24	−17.19	−9.89	−10.95	−8.05	−17.00	−11.03	−8.95
Aug- cc-pVQZ	−10.52	−16.60	−12.55	−6.08	−5.60	−17.46	−9.56	−11.86	−7.39	−17.19	−10.66	−9.8

[a] The experimental value is $(-9.627 \pm 0.062) \times 10^{-6}$ cgs ppm.

TABLE 5: Calculated Magnetic Shielding Tensors and Anisotropies (ppm)

	HF				BLYP				B3LYP			
basis set	$\sigma_\perp$	$\sigma_\parallel$	σ_{iso}	σ_{ani}	$\sigma_\perp$	$\sigma_\parallel$	σ_{iso}	σ_{ani}	$\sigma_\perp$	$\sigma_\parallel$	σ_{iso}	σ_{ani}
3-21+G(d)	−527.86	484.92	−190.27	1012.78	−869.61	483.62	−418.54	1353.23	−856.38	483.73	−409.67	1340.11
6-31G(d)	−236.32	489.29	5.55	725.62	−684.04	487.52	−293.52	1171.56	−525.70	488.09	−187.77	1013.80
6-31+G(d)	−255.48	488.93	−7.34	744.41	−747.12	486.68	−335.85	1233.80	−572.04	487.39	−218.89	1059.43
6-311+G(2d,p)	−230.07	489.96	9.94	720.03	−596.08	488.95	−234.40	1085.03	−575.30	488.87	−220.58	1064.18
D95(d,p)	−244.85	489.85	0.05	734.70	−571.01	488.29	−217.91	1059.31	−553.67	488.32	−206.34	1041.99
D95++(d,p)	−249.50	489.82	−3.06	739.32	−750.44	487.50	−337.79	1237.94	−571.56	488.16	−218.32	1059.72
cc-pVDZ	−306.12	489.78	−40.82	795.90	−609.36	488.35	−243.45	1097.91	−599.92	488.45	−237.13	1088.37
Aug- cc-pVDZ	−218.22	489.72	17.76	707.94	−703.83	487.24	−306.81	1191.08	−529.04	488.04	−190.01	1017.08
cc-pVTZ	−208.34	489.66	24.33	698.00	−712.84	487.71	−318.65	1209.54	−539.95	488.29	−197.20	1028.24
Aug- cc-pVTZ	−195.56	489.57	32.81	685.13	−716.07	487.42	−314.91	1203.49	−531.87	488.06	−191.89	1019.93
cc-pVQZ	−196.54	489.71	32.21	686.25	−731.78	488.02	−325.18	1219.83	−543.23	488.54	−199.30	1031.77
Aug- cc-pVQZ	−198.17	489.71	31.12	687.87	−739.03	487.93	−330.05	1226.96	−549.61	488.46	−203.59	1038.07

TABLE 6: Literature Data on F_2 Bond Length, Magnetic Susceptibility, Magnetic Shielding Tensor, and Anisotropies (ppm)[a]

R (Å)[21]	$\chi_\perp$	$\chi_\parallel$	χ_{iso}[b]	χ_{ani}	$\sigma_\perp$	$\sigma_\parallel$	σ_{iso}	σ_{ani}
1.4119	−6.0	−17.0	−9.627	−11.0	−560	490	−210	1050 ± 50
			±0.062	−233	1055			

[a] Values taken from ref 3 except as noted. [b] This work.

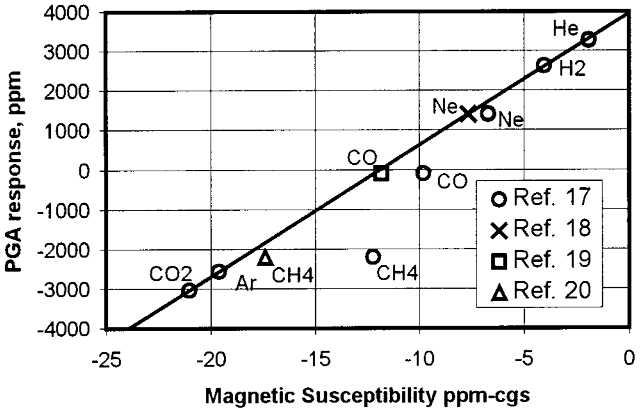

Figure 1. Literature χ_{iso} vs PGA response and calibration line used to estimate χ_{iso} for F_2.

Foëx accepted the -6.7×10^{-6} for Ne, citing Mann[24] and Sugden,[29] and rejected the Havens[18] value of -7.6×10^{-6} as well as other different values from earlier investigations using inferior methods.[30] The Mann and Sugden studies for Ne most likely were biased by He contamination. In the early part of this century when all of these studies were conducted, Ne free of He contamination was not readily available. Ne obtained from air distillation lights typically contains 25% He.[31] Of all the investigators, only Havens notes that his source Ne was certified to have little He contamination (<1000 ppm). The addition of 17% He to Ne would raise the χ_{iso} from -7.6×10^{-6} to -6.7×10^{-6}. The -7.6×10^{-6} value for Ne is in better agreement with theoretical calculations.[32]

Foëx's value for CO appears to be a misprint that has been carried through to all secondary references.[2] The Jaanus and Shur reference[19] cited by Foëx reports the χ_{iso} for CO to be -11.8×10^{-6} and not -9.8×10^{-6}.

The -12.2×10^{-6} value for CH_4 from the report by Bitter[33] was the only published value available at the time of the Foëx review. Although the more recent value of -17.4×10^{-6} reported by Barter[20] is much improved over that of Bitter, CH_4 still falls substantially away from the line in Figure 1. Barter offers no explanation why their value differs so greatly from that reported by Bitter.

Including data for CH_4 in the calibration leads to a poor linear model with a correlation factor of 0.997 78 and a standard error for the PGA response estimate of 118.7 ppm. This calibration predicts the χ_{iso} for F_2 to be $(-9.525 \pm 0.170) \times 10^{-6}$. Rejecting the CH_4 point improves the correlation factor for the regression to 0.999 73 and reduces the standard error for the PGA response estimate to 41.7 ppm. It is in using this calibration line that the χ_{iso} for F_2 is estimated to be $(-9.627 \pm 0.062) \times 10^{-6}$. The calibration line may also be used to estimate the χ_{iso} for N_2, on the basis of a zero response of the PGA for pure N_2 as both the sample and reference gas. The χ_{iso} for N_2 is estimated to be $(-11.77 \pm 0.03) \times 10^{-6}$, which agrees well with the -12×10^{-6} value accepted by Foëx.

This standard error of 41.7 ppm for the PGA is an order of magnitude higher than that observed from the Ar/N_2 results (3.84 ppm), which showed the true linear response of the PGA with χ_{iso}. The imprecision in the linear calibration model is caused by inaccuracies in the literature χ_{iso} used for the calibration gases. Although these inaccuracies are small, on the order of $\pm 0.1 \times 10^{-6}$, they are large enough so that the potential precision of this method for measuring χ_{iso} is not realized.

In light of the fact that almost all the previous calculations of magnetic susceptibility and shielding tensor on F_2 were done with the HF methods with small basis sets and that DFT has become an increasingly important alternative to the HF theory in providing accurate structure and energetics information for a molecule, there is strong motivation to recalculate the magnetic response properties of F_2 with both HF and DFT methods using increasingly larger basis sets.

Table 3 shows that for the optimized bond distance of F_2 as the size of the basis sets increases, the HF calculation converges to a value significantly smaller than the experimental value. The DFT calculations yield bond distances in better agreement with experimental results. In general, we found inclusion of diffuse functions in the basis sets helps to improve the quality of the optimized bond distance. Our calculation with the CISD(T)/6-31+G(d) method gave a F_2 bond length of 1.4109 Å, in much better agreement with the experimental value of 1.4119 Å. It is worth noting that the bond length calculated at the HF/3-21+G(d) level is also in good agreement with experiment.

It is seen from Table 4 that the HF calculations essentially failed to accurately reproduce the experimental magnetic susceptibility, even when large basis sets are used. It is, however, surprising that the magnetic susceptibility calculated at the HF/3-21+G(d) level is in excellent agreement with the experimental value, although the calculated quantities are clearly not converging as the basis set increases. It is likely that the good agreement is coincidental. In general, we found that the BLYP calculations with large basis sets gave converged magnetic susceptibilities in good agreement with experimental results. B3LYP calculations also significantly improved the results, although the convergence with the basis sets seems slower. This suggests that the electron correlation effect is important for the magnetic susceptibility to converge to the correct value. This is consistent with the fact that the electron correlation effect in F_2 is strong owing to the strong many-electron interaction in the low-lying states.

The magnetic shielding tensor cannot be directly measured with our current experimental system. Therefore, we compare the calculated magnetic shielding tensors with the available "experimental data" reported in the literature, bearing in mind that these data were not measured directly from experiments as explained at the beginning of this article. As demonstrated in Table 5, for the magnetic shielding tensor and anisotropy for F_2, the HF calculations in general severely underestimated even with a large basis set. The calculated magnetic shielding tensors are significantly improved in the DFT calculations, indicating the sensitivity to the electron correlation effect. In particular, the calculated shielding tensors obtained with the B3LYP method converge accurately to the literature values. We note that the HF/3-21+G(d) calculation is also in good agreement with the literature results. However, this is again likely to be a coincidence, since the calculated values are obviously not converging with the size of basis sets.

Conclusions

By use of an F_2-compatible paramagnetic gas analyzer, the first true experimental measurement of the magnetic susceptibility of F_2 yielded a result of $(-9.627 \pm 0.062) \times 10^{-6}$ (cgs). A multipoint calibration of the PGA response to varying χ_{iso} was employed to avoid the potential bias errors from a single-point calibration. The major source of error in the measurement is due to the inaccuracies of literature χ_{iso} values for the gases used to calibrate the apparatus. Ab initio calculations using HF methods do not converge on this result with increasing size of basis sets. We show that the good agreement between the relatively low-level HF/3-21+G(d) calculations and experiment is most likely a coincidence, since both the calculated magnetic susceptibility and shielding tensor do not converge as the basis set increases. In fact, HF/3-21+G(d) calculations were also performed for other molecules and found to differ considerably from the experimental values. The gradient-corrected DFT calculations give much improved results. In particular, the magnetic susceptibility of F_2 calculated with the BLYP method converges rapidly as the size of the basis set increases, yielding a value in good agreement with the experimental value. The magnetic shielding tensor calculated with the hybrid method also converges to the reported literature data. The theoretical calculations underline the importance of the many-electron correlation effect in F_2.

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References and Notes

(1) Flahaut, J.; Viel, C. In *Fluorine: The First Hundred Years (1886−1986)*; Banks, R. E., Sharp, D. W. A., Tatlow, J. C., Eds.; Elsevier Sequioia: Luasanne, 1986; pp 27−43 and references therein.

(2) (a) Lide, D. R. *CRC Handbook of Chemistry and Physics*; CRC Press: Boston, 1990; pp 9-14−9-18. (b) Grigoriev, I. S.; Meilikhov, E. Z.; Radzig, A. A. *Handbook of Physical Quantities*; CRC Press: New York, 1997; pp 26-1−26-2.

(3) Applemen, B. R.; Dailey, B. P. *Adv. Magn. Resonance* **1974**, *7*, 231−320.

(4) Stevens, R. M.; Lipscomb, W. N. *J. Chem. Phys.* **1964**, *41*, 3710−3716.

(5) Ozier, I.; Crapo, L. M.; Cederberg, J. W.; Ramsey, N. F. *Phys. Rev. Lett.* **1964**, *13*, 482−484.

(6) Joussot-Dubien, J. *J. Chim. Phys.* **1960**, *57*, 734−744.

(7) (a) Perceau, R. *Compt. Rend.* **1954**, *239*, 170−171. (b) Pascal, P. *Compt. Rend.* **1911**, *152*, 1010−1012. (c) Pascal, P. *Rev. Gen. Sci.* **1923**, *34*, 388−399.

(8) (a) Zaucer, M.; Pumpernik, D.; Hladnik, M.; Azman, A. *Z. Naturforsch.* **1977**, *32a*, 411−414. (b) Karplus, M.; Kolker, H. J. *J. Chem. Phys.* **1963**, *38*, 1263−1275. (c) de la Vega, J. R.; Hameka, H. F. *J. Chem. Phys.* **1967**, *47*, 1834−1836. (d) Lyon, W. D.; Hirschfelder, J. O. *J. Chem. Phys.* **1967**, *46*, 1788−1796 (only calculates χ^{d}).

(9) (a) Kern, C. W.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *37*, 260−266. (b) Kolker, H. J.; Karplus, M *J. Chem. Phys.* **1964**, *41*, 1259−1266. (c) Hindermann, D. K.; Cornwall, C. D. *J. Chem. Phys.* **1968**, *48*, 4148−4154. (d) Geirke, T. D.; Flygare, W. H. *J. Am. Chem. Soc.* **1972**, *94*, 7277−7283. (e) Flygare, W. H. *Chem. Rev.* **1973**, *74*, 653−687.

(10) Gutowsky, H. S.; Hoffman, C. J. *J. Chem. Phys.* **1951**, *19*, 1259−1267.

(11) Preliminary results were presented orally by the authors at the 15th International Symposium on Fluorine Chemistry, August 5, 1997, Vancouver. A value of $(-9.65 \pm 0.14) \times 10^{-6}$ was reported.

(12) Jacob, E.; Christe, K. O. *J. Fluorine Chem.* **1977**, *10*, 169−172.

(13) Hoffman, C. J.; Jolly, W. L. *J. Phys. Chem.* **1957**, *61*, 1574−1575.

(14) (a) Keith, T. A.; Bader, R. F. W. *Chem. Phys. Lett.* **1992**, *194*, 1−8. (b) Keith, T. A.; Bader, R. F. W. *Chem. Phys. Lett.* **1993**, *210*, 223−231. (c) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497−5509. (d) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251−8260.

(15) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski,

V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision B.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(17) Foëx, G.; Gorter, C. J.; Smits, L. J. *Constantes Sélectionnées Diamagnétisme et Paramagnétisme Relaxation Paramagnétique*; Masson & Cie: Paris, 1957; Vol. 7.

(18) Havens, G. G. *Phys. Rev.* **1933**, *43*, 992−1000.

(19) Jaanus, R. J.; Shur, J. S. *Phys. Z. Sowjetunion* **1935**, *7*, 19−25.

(20) Barter, C.; Meisenheimer, R. G.; Stevenson, D. P. *J. Phys. Chem.* **1960**, *64*, 1312−1316.

(21) Lide, D. R.; Frederikse, H. P. R. *CRC Handbook of Chemistry and Physics*; CRC Press: New York, 1997; p 9-18.

(22) Refer to Siemens Oxymat 6E product literature and operations manual for a detailed description.

(23) Abonnenc, L. *Compt. Rend.* **1939**, *208*, 986−988.

(24) Mann, K. E. *Z. Physik* **1936**, *98*, 548−558.

(25) Vaidyanathan, V. I. *Philos. Mag.* **1928**, *5*, 380−386.

(26) Sone; T. *Proc. Phys. Math. Soc. Jpn.* **1919**, *1*, 136−137.

(27) Wills, A. P.; Hector, L. G. *Phys. Rev.* **1924**, *23*, 209−220.

(28) Mulay, L. N.; Mulay, I. L. *Anal. Chem.* **1970**, *42*, 325R−333R.

(29) Sugden, S. *J. Chem. Soc. (London)* **1943**, 328−333.

(30) (a) Glaser, A. *Ann. Phys.* **1924**, *75*, 459−488. (b) Hector, L. G. *Phys. Rev.* **1924**, *24*, 418−425.

(31) Schrobilgen, G. J.; Whalen, J. M. In *Kirk−Othmer Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz, J. I., Howe-Grant, M., Eds.; John Wiley and Sons: New York, 1996; Volume 13, pp 18−19.

(32) (a) Sidwell, T. W.; Hurst, R. P. *J. Chem. Phys.* **1962**, *37*, 203−204. (b) Gold, A.; Knox, R. S. *Phys. Rev. Ser. 2* **1959**, *113*, 843−838.

(33) Bitter, F. *Phys. Rev.* **1929**, *33*, 389.