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# Comment on "On the Magnetic Susceptibility of Fluorine"

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In a recent paper, Cheng et al.[1] presented an experimental determination of the isotropic magnetizability of the fluorine molecule. In contrast to many earlier experimental determinations of isotropic magnetizabilities,[2−5] care was exercised in order to reduce the errors arising from the use of potentially inaccurate magnetizabilities when calibrating the experimental apparatus. This was achieved by fitting the observed paramagnetic gas analyzer (PGA) responses against the magnetizability of six gases, for which there exists critically examined experimental data. These experimental results were taken from a comprehensive review that attempted to identify the most reliable experimental determinations.[6] However, these experimental observations inevitably depend on potentially inaccurate single- or few-point calibrations of the experimental apparatus.

Indeed, Cheng et al. started out with a set of seven molecules to be used in the calibration, but were forced to reject the data recorded by Barter, Meisenheimer, and Stevenson[2] for methane because it fell too far off the calibration line. It has been pointed out, on the basis of *ab initio* calculations,[7] that there is a calibration error in the data of Barter et al., and that the results of ref 2 should be scaled by a factor 1.07 to correct for the incorrect magnetizability of argon used to calibrate the experimental setup. Rescaling the results of Barter et al. would lead to a magnetizability for methane of −18.6 ppm cgs, which is in much better agreement with the value obtained by Cheng et al., − 18.4 ppm cgs,[1] on the basis of their own calibration measurements.

It is our opinion that the accuracy of modern ab initio calculations of magnetizabilities of small molecules has now reached a stage at which accurately calculated magnetizabilities may be a better source of calibration data than magnetizabilities derived from a repeated recalibration against one or more ill-determined experimental results. We will here reinvestigate the PGA responses of Cheng et al. using accurately determined ab initio isotropic magnetizabilities as reference for the calibration.

We will only consider the atoms and molecules that Cheng et al. used for calibration. In each case we will briefly describe the ab initio techniques that have been used to determine the magnetizability and argue why we have included or excluded that value in our fit of the experimental PGA response. We will only consider atoms and molecules for which there exist calculations with an accurate treatment of electron correlation effects and in the case of molecules rovibrational effects have been accounted for. In Table 1 we have collected the magnetizabilities estimated by Cheng et al. from their experimental calibration, together with the experimental reference data they used for the calibration curve. We also report in Table 1 the theoretical reference data available for these molecules, which we have correlated the PGA responses in ref 1 against.

**TABLE 1. Magnetizabilities**[a]

| atom or molecule | ref 1 expt reference data | ref 1 estimated from fit | ab initio data | this work estimated from fit |
|---|---|---|---|---|
| He | −1.88 | −1.95 | −1.8915[b] | −1.84 |
| $H_2$ | −4.01 | −3.90 | −4.043[b] | −3.92 |
| Ne | −7.65 | −7.53 | −7.565[b] | −7.79 |
| $F_2$ |  | −9.627 | −10.48[c]/−10.57[c] | −10.03 |
| CO | −11.8 | −12.0 | −12.79[d]/−13.11[d] | −12.58 |
| $CH_4$ | −17.4 | −18.4 | −19.16[e] | −19.35 |
| Ar | −19.6 | −19.5 | −20.66[b] | −20.61 |
| $CO_2$ | −21.0 | −20.9 | −22.44 | −22.02 |

[a] In ppm cgs units. [b] Included as a reference in the fit (see text). [c] The MP2 estimate for the rovibrational correction (0.24 ppm cgs) not included in these numbers. [d] The MP2 estimate for the rovibrational correction (0.06 ppm cgs) not included in these numbers. [e] The MCSCF estimate for the rovibrational correction (−0.20 ppm cgs) not included in this number, but has been accounted for in the fit.

For helium and hydrogen, the ab initio data have been obtained using full CI (FCI) wave functions with a large basis set[7,8] (as we said, the rovibrational corrections to the hydrogen magnetizability have also been accounted for). Since the FCI wave function is an exact solution to the electron correlation problem for a given choice of basis set, these results can be considered to be more accurate than any available experimental data.

For the other two noble gases, neon and argon, the results derive from Complete Active Space Self-Consistent Field (CASSCF) calculations[9] in which the eight valence electrons have been correlated in a space of 13 orbitals.[7,10] Although only the valence electrons are correlated, this level of the treatment of electron correlation can be expected to be reasonably good since the sum-over-states contribution to the magnetizability vanishes for a noble gas, leaving only an expectation-value contribution (the diamagnetic contribution). Furthermore, we would not expect core correlation[11] to be important for a property such as the magnetizability, as it is mainly dominated by the valence electronic structure. The calculated magnetizability of neon is also in very good agreement with the most recent experimental value determined using electron diffraction (where no calibration is necessary) of 7.613 ± 0.114 ppm cgs.[12] For argon, we have also done a CCSD calculation using the aug-cc-pVQZ basis set, obtaining a magnetizability of −20.62 ppm cgs, thus supporting the active space used in the MCSCF calculations on the noble gases.

For CO, the theoretical data, calculated using second-order Møller−Plesset (MP2) theory,[13] linearized coupled-cluster doubles theory (L-CCD),[14] and CASSCF wave functions,[15] scatter from −12.79 ppm cgs to −13.11 ppm cgs, with an MP2 estimate for the rovibrational correction of 0.06 ppm cgs.[13] Although the MP2 and CASSCF results are in good agreement, we find the disagreement with L-CCD disturbing and the spread to be too wide, and have for this reason chosen not to use the magnetizability of CO in the fit. We will instead use our new fit to reevaluate the magnetizability of CO in order to compare the performance of the different methods used for calculating the magnetizability of CO.

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For $CH_4$, we have obtained a CASSCF magnetizability of −19.16 ppm cgs, obtained with a wave function similar to that used for neon (the two systems are isoelectronic).[16] The correction due to zero-point vibrational motion calculated with the same MCSCF wave function is −0.20 ppm cgs,[16] and we thus estimate the magnetizability of $CH_4$ to be −19.36 ppm cgs.

For $CO_2$, we are only aware of an MCSCF investigation using London atomic orbitals and a modest-sized active space.[17] Although electron correlation is considered (the correlation effect being a modest 0.15 ppm cgs), we cannot consider this wave function to be accurate enough for our purposes. Furthermore, we are not aware of any estimates of the rovibrational corrections to the magnetizability of this molecule.

The two fits we have used (with and without the inclusion of the datum for $CH_4$) include the data for He, $H_2$, Ne, and Ar. The two fits are almost identical, indicating the good quality of our $CH_4$ calculation. With $CH_4$ included in the fit (the fit without $CH_4$ included is given in parentheses), we get an intercept of 3850.57 ppm (3849.60 ppm) and a slope of 312.53 ppm (312.26 ppm), and in both cases with a correlation of better than 0.99988. The difference between these two fits is only apparent for He and $H_2$. These results may be compared with the fit of Cheng et al., which has an intercept at 3925.67 ppm, a slope of 333.45, and a correlation of 0.99973. We have listed the new experimental data obtained from our fit (without the inclusion of $CH_4$) in Table 1.

On the basis of our new fits, we recommend that the experimental value for the magnetizability of fluorine be adjusted to −10.03 ± 0.06 ppm cgs, which can be seen to be significantly larger than the experimental estimate of −9.627 ± 0.062 ppm cgs. It is also worth noticing that our fit clearly favors the L-CCD result for CO over the MP2 and CASSCF estimates. However, there is still a discrepancy of 0.17 ppm cgs, which is likely due to higher-order correlation effects. It would clearly be of interest to verify this by more elaborate coupled-cluster calculations. We also note that the correlated result for $CO_2$[17] clearly favors our fit over that based on experimental data.

It is also instructive to compare our new experimental estimate for the magnetizability of fluorine with available ab initio data. The most accurate result published so far is the L-CCD study of Cybulski and Bishop,[14] where a value of −10.48 ppm cgs was obtained. Adding to this value their MP2 zero-point vibrational correction of 0.24 ppm cgs[13] yields a total magnetizability of −10.24 ppm cgs. Considering the approximations in the L-CCD approach, this result must be considered in good agreement with our new experimental estimate. To corroborate the L-CCD results of Cybulski and Bishop, we have performed some restricted active space SCF calculations using the Dalton quantum chemistry program,[18] and our best result (without zero-point vibrational corrections) was − 10.57 ppm cgs, in close agreement with the L-CCD result.

In summary, we believe that modern ab initio data for small molecules today are of an accuracy higher than that of the older magnetizability measurements still often used to calibrate modern experimental determinations of magnetizabilities. On this basis we have recalibrated the recent magnetizability of fluorine determined by Cheng et al.,[1] and we propose that a more accurate value based on their experimental data would be −10.03 ± 0.06 ppm cgs. We have also proposed new experimental estimates for the isotropic magnetizability of CO and $CO_2$, and it would clearly be of interest to verify our proposed recalibration through high-level ab initio calculations of the magnetizability of CO, $F_2$, and $CO_2$.

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## References and Notes

(1) Cheng, H.; Fowler, D. E.; Henderson, P. B.; Hobbs, J. P.; Pascolini, M. R. *J. Phys. Chem. A* **1999**, *103*, 2861.

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

(3) Abonnenc, L. *Compt. Rend.* **1939**, *208*, 986.

(4) Mann, K. E. *Z. Phys.* **1935**, *98*, 548.

(5) Havens, G. G. *Phys. Rev.* **1933**, *43*, 992.

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

(7) Ruud, K.; Skaane, H.; Helgaker, T.; Bak, K. L.; Jørgensen, P. *J. Am. Chem. Soc.* **1994**, *116*, 10135.

(8) Ruud, K.; Åstrand, P.-O.; Helgaker, T.; Mikkelsen, K. V. J. Mol. Struct. (*THEOCHEM*) **1996**, *388*, 231.

(9) Roos, B. O. Adv. Chem. Phys. **1987**, *69*, 399.

(10) Jaszunski, M.; Jørgensen, P.; Rizzo, A. *Theor. Chim. Acta* **1995**, *90*, 291.

(11) Helgaker, T.; Taylor, P. R.. In *Modern Electronic Structure Theory. Part II.*; Yarkony, D. R., Ed.; World Scientific: New York, 1995.

(12) Zhang, Y.; Fink, M. Phys. Rev. **A 1987**, *35*, 1943.

(13) Cybulski, S. M.; Bishop, D. M. *J. Chem. Phys.* **1994**, *100*, 2019.

(14) Cybulski, S. M.; Bishop, D. M. *J. Chem. Phys.* **1997**, *106*, 4082.

(15) Ruud, K.; Helgaker, T.; Jørgensen, P. *J. Chem. Phys.* **1997**, *107*, 10599.

(16) Ruud, K.; Åstrand, P.-O.; Taylor, P. R. *J. Chem. Phys.* **2000**, *112*. In press.

(17) Jonsson, D.; Norman, P.; Ågren, H.; Rizzo, A.; Coriani, S. Personal communication.

(18) Helgaker, T.; Jensen, H. J. A.; Jørgensen, P.; Olsen, J.; Ruud, K.; Ågren, H.; Andersen, T.; Bak, K. L.; Bakken, V.; Christiansen, O.; Dahle, P.; Dalskov, E. K.; Enevoldsen, T.; Fernandez, B.; Heiberg, H.; Hettema, H.; Jonsson, D.; Kirpekar, S.; Kobayashi, R.; Koch, H.; Mikkelsen, K. V.; Norman, P.; Packer, M. J.; Saue, T.; Taylor, P. R.; Vahtras, O. Dalton, an ab initio electronic structure program, Release 1.0; 1997. See http://www.kjemi.uio.no/software/dalton/dalton.html.