Reply to Comment on "On the Magnetic Susceptibility of Fluorine[1]"

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An examination of the calibration lines derived by us using literature experimental results for the isotropic magnetic susceptibility χ_{iso} and by the commentors using ab initio calculations shows that the only meaningful difference is in the χ_{iso} value used for Ar. With Ar at one end of the calibration line, scaling its calibration value up by 5% would change the slope and raise the predicted χ_{iso} for F_2 by +4.2%. The small changes from the literature χ_{iso} values to ab initio χ_{iso} values for the other three gases (He, H_2, and Ne) do not modify the linear calibration significantly. Thus, the issue of whether the χ_{iso} for F_2 is closer to −9.627 or −10.03 ppm hinges on whether the χ_{iso} for Ar is closer to −19.6 or −20.66 ppm.

The literature experimental values for the χ_{iso} for Ar range from −18 to −21.5 ppm,[2] with −19.6 ppm proposed as the best value in the Foëx review,[3] apparently after averaging values obtained by both the manometric balance[4] and Faraday test-body[5] methods. Having in hand an experimental value for Ar measured by a less disputable method, for example electron diffraction or high-resolution nuclear magnetic resonance (HRNMR), would allow the estimation of the χ_{iso} for F_2 to remain purely experimentally derived. Unfortunately, no such study has been published; however, as pointed out by the commentors in one of their references[6] there are experimental HRNMR χ_{iso} values[7] for both CH_4 and C_2H_4 of -18.7 ± 0.4 and -19.7 ± 0.4 ppm, respectively. The predicted χ_{iso} for CH_4 of −18.4 ppm from the experimental calibration agrees better with the HRNMR result than the −19.39 ppm prediction from the ab initio calibration.

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Furthermore, we now have measured the paramagnetic gas analyzer (PGA) response[8] of C_2H_4 (CP grade, Air Products and Chemicals, $O_2 + Ar < 50$ ppm) and obtained an offset from N_2 of -2631.7 ± 2.53 O_2 ppm equivalent. From this offset, the experimental linear model predicts an χ_{iso} of −19.67 ppm whereas the ab initio linear model predicts −20.78 ppm.

From these data we must conclude that either the ab initio calculations provide better χ_{iso} values and three different experimental methods (manometric balance, Faraday test-body, and HRNMR) have a similar systematic bias for atoms and molecules larger than Ne, which in our opinion is unlikely, or that ab initio calculations tend to systematically overestimate χ_{iso} slightly for these same molecules. Indeed, we note that the ab initio data calculated by the commentors are consistently larger than the reported experimental values. As long as the data from the ab initio calculations are self-consistent, one would expect the ab initio linear model would predict accurately the calculated χ_{iso} of an atom or molecule from its experimental PGA offset.

There has been remarkable development in improving the accuracy of ab initio quantum mechanical calculations in recent years. However, while the calculations by the commentors were performed at considerably high level, it is still debatable whether the values of χ_{iso} predicted from the theoretical calculations are more reliable than the experimental data, particularly in view of the various approximations used in the theoretical models and the fact that the experimental data set is also self-consistent.

References and Notes

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(8) See ref 1 for experimental method.

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