JOURNAL OF CHEMICAL PHYSICS VOLUME 118, NUMBER 22 8 JUNE 2003

Calculation of the ^{129}Xe chemical shift in Xe@C_{60}

Devin N. Sears and Cynthia J. Jameson[a)]
Department of Chemistry, M/C-111, University of Illinois at Chicago, Chicago, Illinois 60607-7061

(Received 11 February 2003; accepted 18 March 2003)

We report, for the first time, a reasonably good calculation of Xe shielding in a fullerene. We find the ^{129}Xe intermolecular shielding value $[\sigma(^{129}\mathrm{Xe@C_{60}})-\sigma(\mathrm{Xe\ atom})]=-181.58\ \mathrm{ppm\ (B3LYP)}$, in very good agreement with the value observed for ^{129}Xe@C_{60} dissolved in liquid benzene. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1573190]

INTRODUCTION

^{3}He nuclear magnetic resonance (NMR) spectroscopy has proven to be a powerful application of rare gas NMR spectroscopy when used to identify isomers of the fullerene cages and to follow the events of chemical reactions such cages undergo.[1–8] The fraction of starting material that has been consumed in a reaction can be determined, and the number of peaks and their intensities indicate how many products have been formed and their relative amounts. Furthermore, after separation methods are used and individual products are isolated, individual He shifts can be assigned to specific structures. Incorporation into fullerenes of larger rare gas atoms required more extreme conditions.[9] The size of the Xe atom is approaching the size of the cavity in C_{60}. Nevertheless, with an improved method of incorporation, Saunders and co-workers have recently demonstrated ^{129}Xe NMR spectroscopy of endohedral xenon in C_{60}.[10] The expectation of the authors was that the chemical shifts of Xe will be very different from the helium chemical shifts, and that they might change differently as a result of chemical reactions or reduction. In this paper we report theoretical calculations of the ^{129}Xe shielding for Xe@C_{60} for comparison with experiment. We also report the ^{3}He shielding in ^{3}He@C_{60}, and the neutron shielding at the center of C_{60} in order to provide a theoretical assessment of the accuracy of the description of the molecular shielding of C_{60} itself at the level of the theory used here.

METHOD

The Xe basis set is the same one we have used for previous calculations,[11,12] consisting of a $(21s16p10d)$ core taken from Ref. 13, expanded according to the recipe of Bishop and Cybulski.[14] The core was increased with three *s* orbitals, three *p* orbitals, five *d* orbitals, and nine *f* orbitals to give $(24s19p15d9f)$, a total of 240 basis functions. The basis set used for C is 6-311G**. For He shielding calculations we used 50 basis functions consisting of $(11s13p)$. The C_{60} geometry was taken from the minimum energy geometry at the second-order Møller–Plesset (MP2) level using a triple zeta plus polarization (TZP) basis by Häser *et al.*,[15] i.e., equilibrium bond lengths 1.406 and 1.446 Å. Shielding calculations were carried out using gauge-including atomic orbitals (GIAO) in GAUSSIAN 98,[16] at the Hartree–Fock level and also in density functional theory using the B3LYP hybrid functional, employing 240 and 1080 basis functions on Xe and C_{60}, respectively. In previous work we have found that the ^{129}Xe shielding calculated using the three-parameter hybrid functional of Becke which combines the Lee–Yang–Parr functional with exact Hartree–Fock exchange (B3LYP) overestimates the electron correlation contribution to the Xe response. Where it is possible to have a clear comparison with gas phase density coefficients in the linear density regime, Xe shielding surfaces calculated at the Hartree–Fock level and B3LYP level lead to density coefficients that are on each side of the experimental data, with the B3LYP overestimating the (deshielding) electron correlation contributions that are not included in the Hartree–Fock results for Xe.[12,17] In those cases, such as rare gas pairs, the Hartree–Fock shift relative to the free Xe atom was about 15% too low in magnitude and the B3LYP result was about 15% too high. For the particular case of C_{60}, however, electron correlation is clearly very important in describing the electronic structure of C_{60} itself. Furthermore, we have found that Hartree–Fock calculations of Xe shielding response to aromatic systems can lead to clearly incorrect positive shielding relative to the free Xe atom when Xe is placed at the face of the pi system at van der Waals distances.[17] Thus, the preferred method for Xe@C_{60} is clearly not Hartree–Fock.

RESULTS

Unlike our other work, we do not carry out a calculation of a shielding surface generated by placing the Xe at various positions within the cage. Because of the relative sizes of Xe atom and the interior of the cavity, the Xe has very little probability of being found off-center. ^{3}He may have room to move around inside the cage, but it has so few electrons that it cannot create a deep potential energy trough along the walls of a confining cavity like Xe can. Our single point calculation of the ^{129}Xe shielding at the center of the C_{60} gives $[\sigma(^{129}\mathrm{Xe@C_{60}})-\sigma(\mathrm{free\ Xe\ atom})]=-181.58\ \mathrm{ppm\ (B3LYP)}$, with counterpoise corrections. The counterpoise-corrected intermolecular shielding takes the difference between the $\sigma(^{129}\mathrm{Xe@C_{60}})$ and the σ(Xe atom) calculated with 1080 ghost orbitals centered on the carbons. The difference between Xe atom shielding calculation with and without the ghost orbitals on the carbons

---

[a)] Electronic mail: cjj@sigma.chem.uic.edu

amounts to 0.0775 ppm, only 0.04% of the intermolecular shielding, attesting to the high quality of the basis set we use for Xe.

Our single point calculation of the ^{3}He shielding at the center of the C_{60} gives $[\sigma(^3\mathrm{He@C_{60}})-\sigma(\text{free He atom})] = +0.7195\ \mathrm{ppm}\ (\mathrm{B3LYP})$ with counterpoise corrections. Here, the difference between the He atom calculation with and without the ghost orbitals on the carbons amounts to 0.0009 ppm, only 0.12% of the intermolecular shielding. Finally, we also calculate the shielding of a neutron at the center of the C_{60}; this is +1.0829 ppm (B3LYP). Both the ^{3}He nucleus in He and the neutron experience a positive shielding at the center of the C_{60}, which may be attributed to "ring currents" of the C_{60}.[18,19] However, the two electrons of He provide an intermolecular deshielding response due to overlap and exchange and some electron correlation contributions amounting to −0.36 ppm. The sign of the latter (deshielding) is that expected from the known intermolecular shielding of rare gas atoms, and the magnitude is also as expected. For example, the observed range of intermolecular shieldings relative to the free atom, in ppm measured in exactly the same set of solvents, is 200:102.5:12.5:0.552 for Xe:Kr:Ne:He.[20,21] In a medium, He atom behaves almost like a naked spin, but not quite.

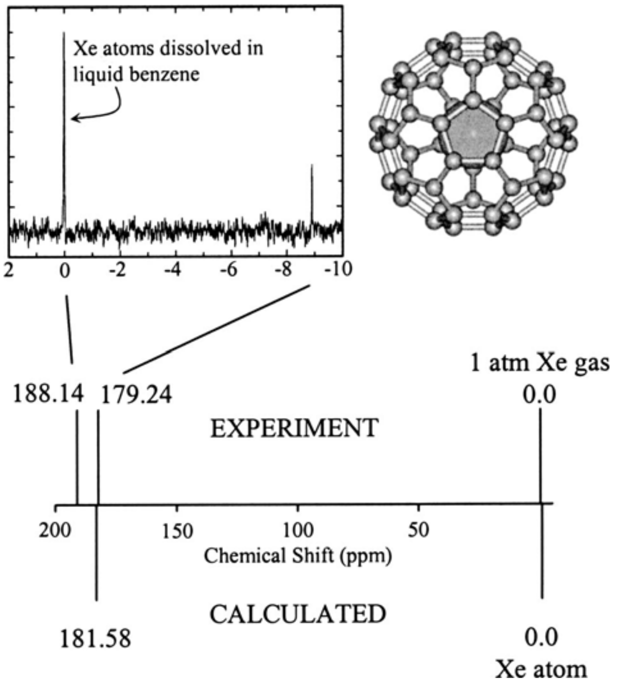

FIG. 1. Comparison of theoretical ^{129}Xe NMR spectrum with experiment. The theoretical values are in vacuum, whereas the experimental values were obtained in liquid benzene. The experimental spectrum is reprinted with permission from Ref. 10. © 2002 American Chemical Society.

COMPARISONS WITH EXPERIMENT

The chemical shift δ is related to the shielding as follows: $[\sigma(\text{reference state})-\sigma(\text{sample})]/[1-\sigma(\text{reference state})]$. Since σ(reference state) is in ppm, the denominator is usually close enough to 1 that chemical shift differences can be considered approximately as shielding differences, but with opposite sign. The experimental chemical shift for Xe in $\mathrm{Xe@C_{60}}$, relative to Xe gas at 1 atm is reported to be +179.24 ppm by Syamala *et al.*[10] That is, $\sigma(^{129}\mathrm{Xe@C_{60}},\text{liq.bz},\text{cyl}\|B_0)-\sigma(^{129}\mathrm{Xe},\text{gas},1\ \text{atm}) \approx -179.24$ ppm. The chemical shift of Xe gas at 1 atm, 300 K, is +0.536 ppm from the value at the zero-density limit.[22] The experimental chemical shift relative to Xe gas at zero density is therefore +179.78 ppm for $\mathrm{Xe@C_{60}}$ dissolved in liquid benzene in a cylindrical sample oriented parallel to the magnetic field. This still needs to be corrected for bulk susceptibility. If we do this correction, we find a Xe chemical shift of 182.35 ppm for $\mathrm{Xe@C_{60}}$ dissolved in liquid benzene that would have been observed in a spherical sample. We compare this ^{129}Xe chemical shift of 182.35 ppm with our calculated value of 181.58 ppm for $\mathrm{Xe@C_{60}}$ in vacuum:

$$[\sigma(^{129}\mathrm{Xe@C_{60}},\text{liq. bz, sph.})-\sigma(^{129}\mathrm{Xe},\text{ free Xe atom})]/$$

$$[1-\sigma(^{129}\mathrm{Xe},\text{ free Xe atom})]$$

$$=-182.35\ \text{ppm (experimental)},$$

$$[\sigma(^{129}\mathrm{Xe@C_{60}},\text{isolated})-\sigma(^{129}\mathrm{Xe},\text{ free Xe atom})]$$

$$=-181.58\ \text{ppm (B3LYP, theoretical)}.$$

In Fig. 1 we show the comparison of our calculations with the observed ^{129}Xe NMR spectrum of $\mathrm{Xe@C_{60}}$. The experimental value includes solvent effects on C_{60}, in the nature of an electric polarization or cage geometry alteration. Although the agreement with experiment is excellent, B3LYP may not provide a sufficiently accurate electron-correlated electronic structure of C_{60} to elicit the accurate shielding response in the Xe atom. Our calculated intermolecular shielding of −181.58 ppm for $\mathrm{Xe@C_{60}}$ in vacuum may be somewhat too deshielded, as B3LYP calculations of Xe intermolecular shielding response sometimes tend to be. On the other hand, the Hartree–Fock (HF) results for $\mathrm{Xe@C_{60}}$ using the same basis sets and geometry is −135.419 ppm. With smaller basis sets, especially for Xe, the only other previous theoretical result for $\mathrm{Xe@C_{60}}$ is −71.7 ppm at the HF level by Bühl *et al.*[23] The quality of the basis set used for Xe is a major determinant of good estimates of Xe intermolecular shielding.

To compare the ^{3}He calculations with experiment, we use the free He atom as the reference system to define the chemical shift. We find the ^{3}He nucleus in $\mathrm{He@C_{60}}$ to be more shielded than the ^{3}He nucleus in a free He atom. Our B3LYP chemical shift for $^3\mathrm{He@C_{60}}$ in vacuum relative to free He atom, −0.7195 ppm can be compared with the observed ^{3}He NMR spectrum of Saunders *et al.*,[1] which gives −6.3 ppm for $^3\mathrm{He@C_{60}}$ in solution relative to ^{3}He dissolved in liquid methylnaphthalene. The comparison is not strictly valid since the reference states used in defining the chemical shifts are different from each other. How large can the difference between the reference states He in liquid methylnaphthalene and free He atom be? The chemical shift range of the ^{3}He gas-to-solution shifts is known to be rather small: The ^{3}He chemical shifts relative to free He atom range from −0.224 ppm in benzene to +0.800 in $\mathrm{CH_2I_2}$, bulk-susceptibility-corrected to spherical sample geometry.[24] Thus, the difference between our calculated result, −0.7195 ppm, and the experimental −6.3 ppm value should not be attributed to the differences between the reference states (the He in-solution versus the free He atom), which are rather small for ^{3}He. Instead, the two calculations, the neutron and He atom shieldings at the center of C_{60} are indicators of the inaccuracy of the theoretical description used here for C_{60} itself, using B3LYP/6-311G** at the MP2/TZP-optimized geometry. Bühl *et al.* calculated a chemical shift of −8.4 ppm at the HF level,[25] using the same C_{60} geometry as we have used and a smaller (dz) basis set for shielding calculations. More recently Chen and Thiel reported −8.0 for the shielding of a neutron at the center, using B3LYP/6-31G* level of geometry optimization and self-consistent field calculation of shielding using 3-21G basis for C.[26] (Their unexpectedly good agreement with the experimental −6.3 ppm appears to be coming from a combination of neglect of electron correlation and use of too small a basis set for the carbons in C_{60}.)

In addition to B3LYP giving ∼−5.6 ppm error for the molecular shielding of C_{60} itself, Xe shielding responses calculated using B3LYP have been shown to be usually somewhat too deshielded, when comparison with gas phase experiments can be made.[12] We also note that the experimental value we are comparing with has not been corrected for solvent effects. Since the C_{60} is a fairly rigid cage, we do not expect the solvent outside the C_{60} to affect the Xe shielding through cage distortion. A measure of the solvent effects on the molecular shielding of C_{60} is given by the ^{3}He@C$_{60}$ shielding changes in various solvents, and these are known to be small.[1] Finally, we address the inaccuracies that come from having carried out all our calculations with nonrelativistic wave functions. The absolute shielding of the free Xe atom has been calculated by Vaara and Pyykko with relativistic four-component wave functions using a very large one-particle basis set.[27] The results are an improvement over the earlier calculations by Kolb, Johnson, and Shorer[28] and the magnitude of the relativistic correction is indeed important in defining the absolute shielding of the free Xe atom itself. While there are as yet no calculations of the relativistic correction to the intermolecular *change* in shielding of Xe atom, such corrections are not expected to be large since the largest relativistic corrections arise from the tightly bound inner core while intermolecular interactions arise primarily from changes in the outer reaches of the wave function.

CONCLUSIONS

We report, for the first time, a reasonably good calculation of Xe shielding in a fullerene. We find the ^{129}Xe intermolecular shielding value $[\sigma(^{129}\mathrm{Xe@C_{60}})-\sigma(\mathrm{Xe\,atom})] = -181.58\,\mathrm{ppm}\,(\mathrm{B3LYP})$. Agreement with the value obtained in solution is very good. The reported experimental chemical shift, +179.78 ppm, can be corrected for bulk susceptibility of the solvent and the Xe gas at 1 atm can be corrected to the zero pressure limit, leading to $[\sigma(^{129}\mathrm{Xe@C_{60}})$ in liquid benzene, spherical sample $-\sigma(\mathrm{Xe\,atom})]\approx -182.35\,\mathrm{ppm}$. The high quality of the basis set used for Xe is attested to by the negligible counterpoise correction. If the ^{3}He chemical shift dispersion observed in various derivatives of fullerenes arises entirely from ''ring current'' molecular shielding of C_{60} changing with derivatization, then there would be no advantage in using endohedral ^{129}Xe rather than ^{3}He. The ''ring current'' molecular shielding at a location is independent of the identity of the probe atom located there. However, if the dispersion of ^{3}He chemical shifts arises in part from changes in cage electronic structure that can induce significant changes in the shielding response in the electrons of the rare gas atom, then the chemical shift dispersion will be greatly amplified in endohedral Xe compared to He, and the ordering of the peak positions will be quite different from that found in ^{3}He NMR spectra. Experiments on Xe@[C$_{60}$]$^{-6}$ may provide a definitive answer.

ACKNOWLEDGMENT

This research was supported by the National Science Foundation (Grant CHE99-79259).

[1] M. Saunders, H. A. Jimenez-Vazquez, R. J. Cross, S. Mroczkowski, D. I. Freedberg, and F. A. L. Anet, Nature (London) **367**, 256 (1994).
[2] M. Saunders, H. A. Jimenez-Vazquez, R. J. Cross, W. E. Billups, C. Gesenberg, A. Gonzalez, W. Luo, R. C. Haddon, F. Diederich, and A. Herrmann, J. Am. Chem. Soc. **117**, 9305 (1995).
[3] M. Saunders, R. J. Cross, H. A. Jimenez-Vazquez, R. Shimshi, and A. Khong, Science (Washington, DC, U.S.) **271**, 1693 (1996).
[4] E. Shabtai, A. Weitz, R. C. Haddon, R. E. Hoffman, M. Rabinovitz, A. Khong, R. J. Cross, M. Saunders, P.-C. Cheng, and L. T. Scott, J. Am. Chem. Soc. **120**, 6389 (1998).
[5] M. Saunders, H. A. Jimenez-Vazquez, B. Bangerter, R. J. Cross, S. Mroczkowski, D. I. Freedberg, and F. A. L. Anet, J. Am. Chem. Soc. **116**, 3621 (1994).
[6] M. Rüttimann, R. F. Haldimann, L. Isaacs, F. Diederich, A. Khong, H. A. Jimenez-Vazquez, R. J. Cross, and M. Saunders, Chem. Eur. J. **3**, 1071 (1997).
[7] G.-W. Wang, B. R. Weedon, M. S. Meier, M. Saunders, and R. J. Cross, Org. Lett. **2**, 2241 (2000).
[8] G.-W. Wang, M. Saunders, and R. J. Cross, J. Am. Chem. Soc. **123**, 256 (2001).
[9] M. Saunders, H. A. Jimenez-Vazquez, and R. J. Cross, J. Am. Chem. Soc. **116**, 2193 (1994).
[10] M. S. Syamala, R. J. Cross, and M. Saunders, J. Am. Chem. Soc. **124**, 6216 (2002).
[11] A. C. de Dios and C. J. Jameson, J. Chem. Phys. **107**, 4253 (1997).
[12] C. J. Jameson, D. N. Sears, and A. C. de Dios, J. Chem. Phys. **118**, 2575 (2003).
[13] H. Partridge and K. Faegri, Jr., NASA Tech. Memo. **103918** (1992).
[14] D. M. Bishop and S. M. Cybulski, Chem. Phys. Lett. **211**, 255 (1993).
[15] M. Häser, J. Almlöf, and G. E. Scuseria, Chem. Phys. Lett. **181**, 497 (1991).
[16] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A.9, Gaussian, Inc., Pittsburgh, PA, 1998.
[17] C. J. Jameson and D. N. Sears (unpublished).
[18] R. Zanasi and P. W. Fowler, Chem. Phys. Lett. **238**, 270 (1995).
[19] P. Lazzeretti, Prog. Nucl. Magn. Reson. Spectrosc. **36**, 1 (2000).
[20] P. Diehl, O. Muenster, and J. Jokisaari, Chem. Phys. Lett. **178**, 147 (1991).
[21] J. Jokisaari, Prog. Nucl. Magn. Reson. Spectrosc. **26**, 1 (1994).
[22] C. J. Jameson, A. K. Jameson, and S. M. Cohen, J. Chem. Phys. **59**, 4540 (1973).
[23] M. Bühl, S. Patchkovskii, and W. Thiel, Chem. Phys. Lett. **275**, 14 (1997).
[24] R. Seydoux, P. Diehl, R. K. Mazitov, and J. Jokisaari, J. Magn. Reson. A **101**, 78 (1993).
[25] M. Bühl, W. Thiel, H. Jiao, P. v. R. Schleyer, M. Saunders, and F. A. L. Anet, J. Am. Chem. Soc. **116**, 6005 (1994).
[26] Z. Chen and W. Thiel, Chem. Phys. Lett. **367**, 15 (2003).
[27] J. Vaara and P. Pyykkö, J. Chem. Phys. **118**, 2973 (2003).
[28] D. Kolb, W. R. Johnson, and P. Shorer, Phys. Rev. A **26**, 19 (1982).