Endohedral Magnetic Shielding in the C_{60} Cluster

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Among the many unique properties of polyhedral carbon clusters (fullerenes), their ability to form endohedral complexes[1,2] is particularly interesting. Endohedral complexes with atoms of noble gases trapped inside the C_{60} cage have been produced only very recently by inserting the guests with the help of high-energy collisions[3,4] or high temperature and pressure[5,6]. Although many properties of endohedral complexes are well understood,[2,7,8] theoretical predictions for the endohedral magnetic shielding have been mired in controversy.[9–12] The very recent synthesis of the $^3He@C_{60}$ species[6] has created the exciting opportunity for measuring shielding in the interior of the C_{60} cluster.[13] Here we report on the first rigorous electronic structure calculations on the NMR chemical shift of the endohedral ^3He atom. Good agreement with the experimental data[13] is obtained, and the differences among the previous theoretical results are resolved. The present calculations open the avenue for accurate predictions of NMR spectra of endohedral complexes that will aid in isolation and characterization of these truly unusual chemical systems.

In order to assess the influence of the cage geometry on the computed shifts, two calculations were performed. The first calculation used the previously published[8] HF/DZP optimized geometry of $He@C_{60}$ (with C–C bond lengths of 1.374 and 1.449 Å virtually identical to those of pristine C_{60}). The MNDO optimized geometry of C_{60}, with bond lengths of 1.400 and 1.474 Å that are much closer to the experimental values of 1.401 and 1.458 Å[14] than their HF/DZP counterparts, was employed in the second calculation. In both cases, the helium atom was placed at the cage center. According to electronic structure calculations,[8] such a location of the guest corresponds to the energy minimum. All calculations were carried out at the Hartree–Fock (HF) level of theory with the gauge-invariant atomic orbitals (GIAO), coupled-perturbed HF (CPHF) formalism.[15,16] The GIAO-CPHF approach yields values of magnetic properties that are invariant to the choice of gauge origin. The molecular orbitals were expanded within the split-valence 6-31G basis sets for carbon atoms and the double-ζ plus polarization (DZP) basis set for the helium atom. Such a choice of approximation is expected[16] to afford quite accurate values of the NMR chemical shifts while keeping the computational cost within reasonable limits.

The calculations yielded the value of 59.8 ppm for the diagonal components of the shielding tensor of an isolated ^3He atom. For the endohedral helium atom located at the center of the C_{60} cage, shieldings of 68.5 and 66.5 ppm were found at the HF/DZP and MNDO geometries, respectively, corresponding to the predicted upfield shifts of 8.7 and 6.7 ppm. The agreement between the experimental shift of 6.3 ± 0.2 ppm[13] and our theoretical predictions is very good, especially if one takes into account that electron correlation effects and librational motion of the guest were completely neglected in the calculations. However, the substantial sensitivity of the computed shifts to the bond lengths demonstrates that the use of accurate geometries is important in this type of calculation.

It is instructive to relate the above data to various estimates based upon semiquantitative arguments. With the gauge origin coinciding with the center of the C_{60} cage, the isotropically averaged shielding tensor of a centrally located guest atom is given by (in atomic units)[15]

$$\sigma = (\alpha^2/2)\langle\Psi_0^{HG}|\hat{r}^{-1}|\Psi_0^{HG}\rangle - \alpha^2\sum_j(E_j^{HG} - E_0^{HG})^{-1}|\langle\Psi_0^{HG}|\hat{L}|\Psi_j^{HG}\rangle\cdot\langle\Psi_j^{HG}|\hat{L}r^{-3}|\Psi_0^{HG}\rangle| \quad (1)$$

where α is the fine structure constant and $\hat{L}$ is the angular momentum operator. Ψ_0^{HG} and Ψ_j^{HG} are the wave functions of the ground and the j-th excited states of the endohedral complex, whereas E_0^{HG} and E_j^{HG} are the corresponding energies. If one neglects the orbital mixing between the guest and the host cage of C_{60} (an approximation that is well justified for $He@C_{60}$[7,8]), the change in the chemical shift of the guest atom upon encapsulation is given by

$$\Delta\sigma = -(\alpha^2/2)\langle\Psi_0^{H}|\hat{r}^{-1}|\Psi_0^{H}\rangle + \alpha^2\sum_j(E_j^{H} - E_0^{H})^{-1}|\langle\Psi_0^{H}|\hat{L}|\Psi_j^{H}\rangle\cdot\langle\Psi_j^{H}|\hat{L}\hat{r}^{-3}|\Psi_0^{H}\rangle| \quad (2)$$

where the superscripts H refer to the host cage itself. The above expression is somewhat similar to that for the isotropically averaged magnetic susceptibility of the host, which reads

$$\chi = -(\alpha^2/4)\langle\Psi_0^{H}|\hat{r}^{2}|\Psi_0^{H}\rangle + (\alpha^2/2)\sum_j(E_j^{H} - E_0^{H})^{-1}|\langle\Psi_0^{H}|\hat{L}|\Psi_j^{H}\rangle\cdot\langle\Psi_j^{H}|\hat{L}|\Psi_0^{H}\rangle| \quad (3)$$

Therefore, one may be tempted to assume that the electrons of C_{60} are largely confined to the vicinity of the cage surface and write

$$\Delta\sigma \approx 2\chi R^{-3} \quad (4)$$

where R is the cage radius. Equation 4 is the same as that obtained with arguments of classical electrodynamics.

Using eq 4 in conjunction with the London theory, Elser and Haddon[9] predicted the endohedral chemical shift in C_{60} to be less than 1 ppm, i.e., 1 order of magnitude smaller than the experimental value. The question of whether this large discrepancy results from the qualitative character of the London theory or the approximation 4 can be easily resolved by using the recently measured[10,11] magnetic susceptibility of C_{60}. Noting that the experimental molar χ of −260 ppm cgs/mol is equivalent to −2.9

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$\times 10^{-3}$ au and that the cage radius of C_{60} is ca. 3.52 Å or 6.66 au,[28] one obtains $\Delta\sigma = -19.6$ ppm from eq 4. The theoretical χ of -4.0×10^{-3} au,[12] extrapolated from calculations that are not gauge invariant, yields an even worse estimate of -27.8 ppm.

The reasons for the failure of the previous calculations to provide reasonable estimates of the endohedral shielding in C_{60} are clear. While the predictions[9] based on the London theory badly underestimate χ, eq 4 overestimates the shielding by at least a factor of 3. A simple explanation of this overestimation is provided by the fact that the diamagnetic component of shielding (the first term in eq 2) amounts to about -1440 ppm and is almost exactly canceled by the paramagnetic component (the second term) to yield the final diamagnetic shift of ca. -7 ppm. Therefore, even a relatively small percentage error introduced in each of these components by the approximations used in deriving eq 4 from eq 2 is bound to result in large deviation of the estimated shift from its exact value.

The calculations reported here demonstrate that it is now feasible to accurately predict the NMR spectra of host molecules in endohedral complexes and other large supramolecular systems. Such theoretical predictions are bound to guide the experimentalists in their quest for isolation and characterization of endohedral complexes. The magnitude of the computed endohedral magnetic shielding confirms the previously postulated,[9-11] almost exact cancellation of the diamagnetic and paramagnetic contributions to magnetic properties of the C_{60} cluster, but the inability of simple approaches to yield useful estimates for the endohedral chemical shift is apparent. Thus, to paraphrase the original remark,[17] the chemical shift in the NMR spectrum of a central atom *is* remarkable, *but not just* because of ring currents.

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