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ATOMIC CLOCK BASED ON ENDOHEDRAL FULLERENE NO@C_{60}: DETERMINATION OF ELECTRON PARAMAGNETIC RESONANCE (EPR) PARAMETERS

Michael E. Miller

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The goal of this study was to apply density functional theory (DFT) to determine if a nitric oxide (NO) radical encapsulated in a 60-carbon (C_{60}) fullerene, endohedral fullerene NO@C_{60}, is a suitable candidate for the development of portable condensed-matter, molecular atomic clocks. In order to assess the potential of NO@C_{60} to function as an accurate and reliable frequency standard, electron paramagnetic resonance (EPR) parameters (hyperfine coupling constant and electronic g-factor) were calculated using the DFT method.

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Michael E. Miller	(973) 724-9525

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INTRODUCTION

An atomic clock makes use of an atomic resonance to control a periodic phenomenon. Similarly, a resonance in a molecule could be used to control the periodic phenomenon. The atomic or molecular clock is a very precise clock because the resonances are determined by the atom's properties, which are among the most stable and accurately measured phenomena known to man. Since all clocks are just devices that count and display the total of a series of periodic events, the accuracy of the clock depends directly on the stability and accuracy of the periodic phenomenon used to establish the rate of the clock (refs. 1 and 2).

Precise and portable frequency references underpin a range of military weaponry for synchronization of communication networks, for environmental sensing, and in positioning systems such as the global positioning system (GPS). The state-of-the-art miniature frequency standard is the chip-scale atomic clock, which uses optical interrogation of a vapor/gas of alkali metal atoms, such as Cesium (Cs) or Rubidium (Rb). However, a condensed matter (i.e., solid-state) could further improve size, weight, power, and cost by avoiding the need for optical and vacuum elements. The goal and approach here is to characterize and exploit a radio-frequency spin resonance transition of a nitric oxide (NO) radical encapsulated in a 60-carbon (C_{60}) fullerene (fig. 1). The fullerene is an ideal molecular substrate since it exhibits a Faraday cage effect, thus shielding the inside from external stray electric fields. This is a critically important feature for an atomic clock to possess, in particular for military applications and systems.

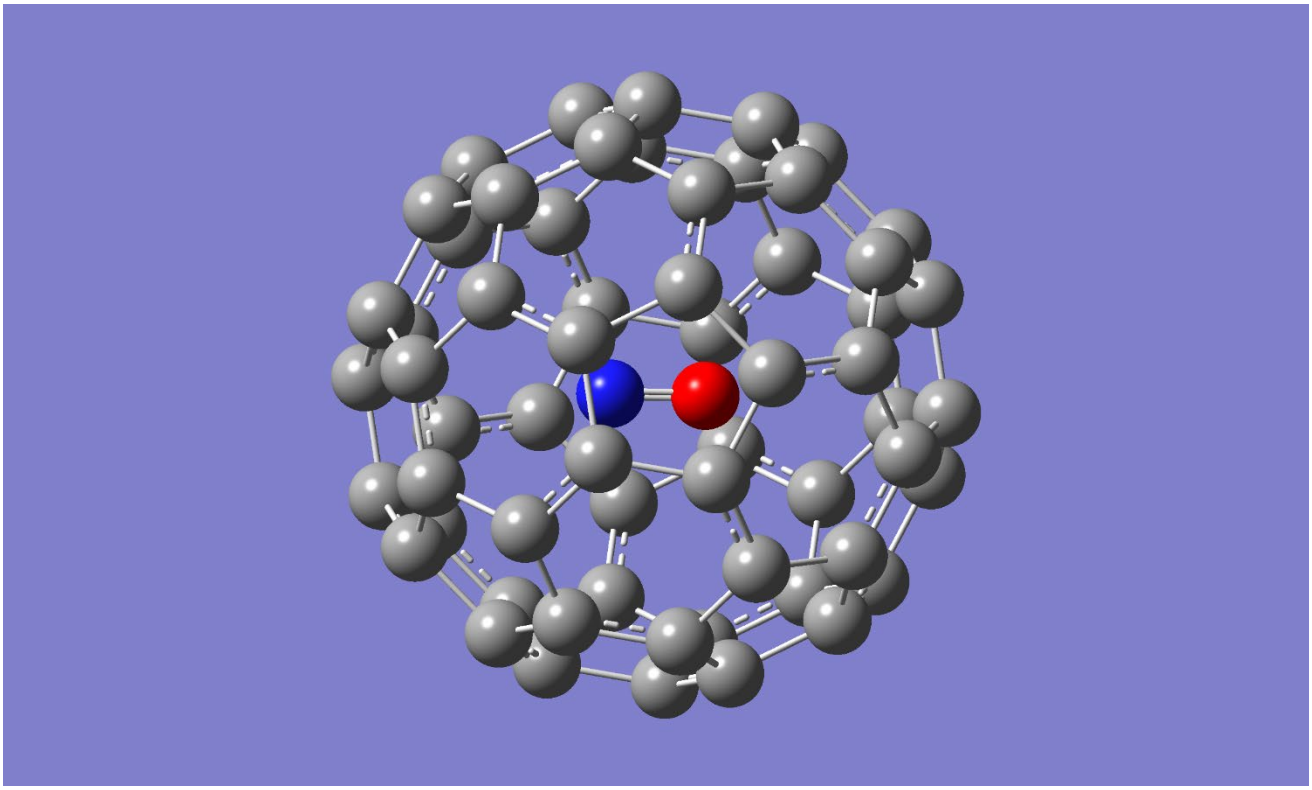

Figure 1
Optimized structure of NO radical encapsulated in a C_{60} fullerene (endohedral fullerene NO@C_{60})

The basic time-keeping element of atomic clocks is the hyperfine interaction between outer electron(s) and the nuclear spin. The hyperfine interaction is robust against perturbations from vibration or temperature since it exclusively involves the density and spin of the electron wave

function at the nucleus. High-quality atomic clocks have time precision of better than 1 part in 10^{15} (refs. 2 and 3).

There has been a great deal of interest by the U.S. Department of Defense (DoD) and the electronics industry in reducing the size, complexity, and power requirements of atomic clocks. A precise and stable time base that can fit within the packaging and power envelope of modern devices will greatly increase the efficiency and robustness of mobile computing and sensor elements. Spectral bandwidth allocation is fundamentally limited by the accuracy and stability of the reference frequency used to define the clock period. Interestingly, one of the fundamental limits to reducing the size of electronic wireless sensors is the fact that crystal oscillators cannot be shrunk beyond the current package size. A micro-electromechanical systems (MEMS) or nano-electromechanical systems (NEMS) chip-scale atomic or molecular clock could replace complex clock synchronization methods within computers and improve arbitration protocols between chips by supplying precise local clocks (refs. 2 and 4).

As mentioned previously, atomic clocks currently operate by using vapors of Cs or Rb coming off an oven. This results in approximately one atom per cubic micron. In some optical atomic clocks, buffer gas is used to slow the collision rate of the atoms with the walls where the spin flipping occurs, which results in broadening the hyperfine line width, an undesirable feature. Each atom produces a magnetic field due to the spin of the nucleus. When the atomic system has been excited, the magnetic field oscillates at the hyperfine transition frequency of 100 MHz to 20 GHz, depending on the atomic species being used. The best current systems use stabilized lasers to interact with the atomic system by means of optical transitions. This method is costly in size, weight, and power required (refs. 1 and 2).

Buckminsterfullerenes (buckyballs), such as C_{60}, which contain a single atomic or molecular passenger are referred to as endohedral fullerenes and offer an alternative approach. For most of these endohedral fullerenes, a charge transfer of the enclosed atom to the fullerene cage occurs, resulting in a chemical bond and distorted structure. In the case of the Group 5 atoms of the periodic table, the trapped atom is confined by a harmonic-like potential to the center of the cage. The atom is trapped within the covalent bonds of the buckyball, with its outer electrons symmetrically repelled away from the walls of the cage. In almost all respects, the atom behaves as a free, unbonded atomic species, though spatially restricted to be within the fullerene cage. The distributed pi bonding electrons also act as an almost perfect Faraday cage. The inner atom is fully capable of entering into magnetic interactions since the C_{60} cage is spin neutral. Because the endohedral species is shielded from the environment by the symmetrical all-carbon cage, this means that both the electron and nuclear spin lifetime and coherence time of the endohedral species can be very long, which is advantageous for stable frequency operation (refs. 5 and 6).

The NO molecule is a 15-electron diatomic molecule. Pauli pairing among the odd number of electrons leads to a single unpaired electronic spin in the neutral molecule associated with a single occupied pi-bonding valence molecular orbital, making NO a diatomic free radical. As a result, NO is a paramagnetic gas with a spin doublet (S = 1/2) ground state exhibiting an effective permanent magnetic dipole moment of 1.86 Bohr magnetons at room temperature (refs. 7 and 8). Electron paramagnetic resonance (EPR) spectroscopy, also referred to as electron spin resonance, is a technique that detects paramagnetic species. These include any atom, molecule, or compound with one or more unpaired electrons. A basic description of EPR will now be presented since it provides helpful background information for understanding the meaning of the results presented in this report.

Unpaired electrons are spinning charges, and a spinning charge generates a magnetic field. Consequently, each unpaired electron is a magnetic dipole (similar to a bar magnet with a north and south pole). Magnetic dipoles align themselves along magnetic fields (again, borrowing the analogy to bar magnets, this is what causes a compass needle to point to magnetic north). Stated another

way, the presence of an external magnetic field creates a situation in which it is energetically favorable for the dipole to point in a particular direction. In order to rotate the dipole (rotate the compass needle away from pointing north), energy has to be applied. While it is possible to force a compass needle to point at any angle away from north and generate a continuum of energetic states, the magnetic dipole of an electron can only take on two energy states, i.e., it is quantized. As a result, the amount of energy required to flip the electron from its favorable direction to its unfavorable direction is a discrete value. It follows that if this discrete amount of energy is supplied, the system will absorb the energy as the electron is flipped, and the detection of this absorbed energy is the basis of the EPR signal. For an electron in a magnetic field of approximately 0.35 tesla, the energy required is in the X-band microwave range (approximately 9.5 GHz), and most spectrometers operate in this range (refs. 7 and 9). The EPR spectrometer is essentially a machine that shines microwave radiation on a sample and measures how much of that radiation is absorbed by the sample as a function of an externally applied magnetic field. The fundamental equation of EPR spectroscopy is shown in equation 1:

$$h \nu = g \beta B \tag{1}$$

where ν is the frequency of the microwaves, h is Planck's constant, B is the external magnetic field, β is a constant known as the Bohr magneton, and g is a dimensionless quantity known as the electronic g-factor and is characteristic of the sample being studied. To take an EPR spectrum, the microwave frequency (ν) is held constant, and the magnetic field is swept across the desired range. When this equation is true (referred to as the resonance condition), energy will be absorbed.

The detection of absorbed microwave energy as a function of magnetic field is referred to as the EPR spectrum. As can be seen from equation 1, h and β are fundamental constants and ν is held constant for the experiment, so B is inversely proportional to g. As B increases, g decreases. For this reason, features at high magnetic field have low g-values and features at low magnetic field have high g-values. One g-factor value that is of particular interest is that of the free electron, which has a value of 2.0023. The difference in g-factor value between an unpaired electron in an atom/molecule and the free electron can provide important information about the magnetic properties of the microenvironment of the unpaired electron. More specifically, this free electron possesses an inherent spin angular momentum but no orbital angular momentum. For electrons in an atom, the g-factor can shift from the free electron value due to spin-orbit coupling. Spin-orbit coupling has the effect of broadening the EPR peaks, which is not desirable for the application of an atomic clock (ref. 6).

The EPR spectrum also reports the presence of paramagnetic nuclei in the vicinity of the unpaired electron. Such nuclei also possess an intrinsic spin and therefore can be understood as tiny quantum mechanical magnets that can only point in one of two directions. So, the presence of these nuclei can either add or subtract from the external magnetic field applied by the spectrometer. The result of this is that the actual magnetic field experienced by the unpaired electron may not be equal to the applied field but may be either more or less than this depending on the orientation of the local magnetic nuclei. For example, a proton nucleus in close association with the unpaired electron will have the effect of adding or subtracting from the magnetic field experienced by the electron. Due to the fact that approximately half of the magnetic dipoles generated by the protons will be aligned with the external field and half will be aligned against the field, the effect will be that about half of the unpaired electrons will experience a higher magnetic field and half will experience a lower magnetic field than expected. The result of this is that the resonance condition described by equation 1 will be true at different values of B for these two populations, so instead of a single EPR feature (peak), there will be two features (peaks) of roughly equal intensity. This effect is referred to as the hyperfine effect and is usually reported as the difference in magnetic field between the two EPR features. For example, for a proton, a difference of six Gauss means that the two EPR lines are six Gauss apart. This value is referred to as the hyperfine coupling constant. The nitrogen nucleus is a slightly

different case, as each nucleus can be thought of as containing two of these tiny quantum mechanical magnets. Consequently, there are three possible combinations of alignment, which are approximately equally populated: both aligned with the field, both aligned against the field, and one with and one against the field. In the last case, the contribution to the external field will be zero, so the effect will be to generate three EPR lines of equal intensity, with the middle line positioned at the g-factor value (ref. 10).

Both the g-factor and the hyperfine coupling constants are tensors in that they can attain a different value in every direction. If the molecule is freely diffusing, these values average out to a single directionless value (referred to as the isotropic value). However, in frozen solution, the molecule orientations will be random and fixed, such that all possible values will be present in the spectrum. In this case, the g-value and the hyperfine coupling constant are given as three orthogonal values in the x, y, and z directions. The quantum mechanical calculations performed in this study used the freely diffusing endohedral fullerene, so an isotropic value is expected.

It is important to note that atomic nitrogen (N) possesses an isotope with nuclear spin I = 1/2 (^{15}N). This nuclear spin value is preferred because it has only two possible values along any given axis, such as an axis imposed by an applied magnetic field, namely +1/2 and -1/2. This eliminates sources of decoherence such as nuclear quadrupole broadening and carbon hyperfine broadening and ultimately aids in atomic clock device design and fabrication. Therefore, in the preferred embodiment, the nitrogen atom of NO and the carbon atoms of the fullerene are to be isotopically purified. The preferred endohedral fullerene is therefore $^{15}N@^{12}C_{60}$ (refs. 6 and 10).

With this background in EPR spectra in mind, the intent of this study was to demonstrate that in lieu of experimentally collecting spectra, it is possible to apply theoretical quantum mechanical methods to obtain EPR parameters for the endohedral fullerene $^{15}N@^{12}C_{60}$. This is to be accomplished using an electron correlation method known as density-functional theory (DFT) as implemented in the Gaussian 16 code. Using a method that includes electron correlation is important because it includes the interactions of electrons with opposite spin (refs. 11 and 12).

METHODS, ASSUMPTIONS, AND PROCEDURES

Gas-phase, DFT spin-unrestricted calculations were applied to the endohedral configurations with the encapsulated free radical NO. Since the NO species possesses an unpaired electron, this requires the application of open-shell calculations, i.e., spin-unrestricted multiplicity (ref. 11). As part of the input to the Gaussian 16 code (ref. 12), approximate Cartesian coordinates must be specified as well as the DFT functional and the basis set. All the DFT calculations were performed using the gradient-corrected Becke, three parameter, Lee-Yang-Parr (B3LYP) hybrid functional in combination with a triple-zeta basis set, where the valence orbitals are split and polarization functions have okay included. The name for this basis set is triple-zeta valence with polarization (TZVP). The electronic g-factor was extracted from the data involving the Fermi contact terms and the electronic g-tensor. Isotropic hyperfine coupling constants were calculated for the encapsulated radical. These calculations also compute force constants for a geometry optimization and frequency calculation. Therefore, data output from the Gaussian 16 calculations also includes the optimized Cartesian coordinates with calculated infrared frequencies. This data is not shown in this report because it is not directly relevant to the calculation of the EPR parameters. What is important in this regard is to ensure that the $NO@C_{60}$ molecule has reached a stable minimum on the molecular potential energy surface (PES). A stable minimum is reflected in the frequency output by an absence of any negative frequencies. A stable minimum indicates that, in accordance with the laws of quantum mechanics and the approximations of quantum chemistry and DFT, this molecule will be stable and therefore can be synthesized in a laboratory under conditions of standard temperature and pressure.

The TZVP basis set utilized here includes polarization functions but is not specifically designed for EPR calculations. An assumption has been made that the coefficients of the polarization functions are weighted optimally, i.e., balanced, and are able to capture EPR properties accurately.

RESULTS

Overview of Data

The route section of the Gaussian input consists of the route card and the molecular specification. The route card begins with a pound sign (#) in the first column. This line details the theoretical procedure, the basis set, and the type of calculation. This is usually accomplished via two separate keywords within the route section of the input file, although a few method keywords imply a choice of basis set. Some procedures are Hartree-Fock (HF), restricted Hartree-Fock (RHF), unrestricted Hartree-Fock (UHF), and DFT. The most commonly used standard basis sets are Slater-type orbital (STO)-3G, 3-21G, 3-21G*, 4-31G, 6-31G, 6-31G*, 6-31G**, 6-311G*, 6-311G** and 6-31G(d). All Gaussian calculations reported here used the DFT procedure, and the basis set was TZVP. The route card also determines the way the output will be presented at the end of the run. The terse option (#T) outputs only essential information and results and was used in the reported calculations.

The molecular specification section contains specifics on the molecule, namely its charge, multiplicity, and initial geometry. The charge and multiplicity are on the same line and separated by a white space.

All molecular species studied in these calculations were neutral charge; therefore charge = 0 (zero).

Multiplicity = 2S + 1 where S is the total spin. Alpha and beta electrons have spins of +1/2 and -1/2, respectively. Equal numbers of each completely cancel and the total spin in that case is 0 and the multiplicity = 1 (singlet). An odd number of electrons gives at least spin = +1/2 and therefore multiplicity = 2 (doublet). Since the free nitrogen atom has three unpaired p-electrons, the spin S of 1/2 +1/2 +1/2 = 3/2 yields a multiplicity = 2S + 1 = 2(3/2) + 1 = 4 (a so-called quartet state). This was the multiplicity used for the $^{14}N@C_{60}$ and $^{15}N@C_{60}$ inputs. In the molecular configuration of NO, there is one unbonded p-electron (spin = +1/2) and is therefore a doublet.

In the Cartesian coordinate format, the atom is defined in the following way: element label, x, y, z.

As discussed previously, the absence of negative frequencies in the frequency output of the data is important since this indicates the presence of a stable minimum on the molecular PES. In particular, the lowest frequency must be positive valued. For all four molecular species, the Gaussian output reported positive harmonic frequencies, namely, $^{14}N@C_{60}$: 93.15 cm^{-1}, $^{15}N@C_{60}$: 90.02 cm^{-1}, $^{14}NO@C_{60}$: 24.33cm^{-1}, and $^{15}NO@C_{60}$: 24.11 cm^{-1}.

The Gaussian input and output data are listed in the appendix. Note that experimental values for the hyperfine coupling constants for the $NO@C_{60}$ molecules are not available since these molecules have not yet been synthesized.

Calculations

$$b_F = (16 \pi / 3) (g / 2) g_I * K * B_F$$

where b_F = isotropic hyperfine coupling constant in MHz, g = observed free-electron factor equal to 2.0023, K = composite conversion factor equal to 47.705336 MHz, B_F = isotropic hyperfine coupling constant in atomic units, and g_I = nuclear gyromagnetic ratio for the atom type in question. Note that g_I is computed from the magnetic moment of the atom divided by the spin.

The calculated and experimental isotropic hyperfine coupling constants (b_F) in MHz are listed in table 1. Note that at present experimental b_F values for the two NO@C_{60} molecules are unknown.

Table 1
Calculated and experimental isotropic hyperfine coupling constants (b_F) (refs. 6 and 7)

Molecule	Calculated (MHz)	Experimental (MHz)
^{14}N@C_{60}	11.0	15.7
^{15}N@C_{60}	15.0	22.2
^{14}NO@C_{60}	13.0	?
^{15}NO@C_{60}	18.1	?

Calculated electronic g-factors are extracted from table 1 as 1/3[Tr(g)], i.e., one-third the value of the trace of the g-matrix.

The calculated and experimental electronic g-factors (which are dimensionless quantities) are listed in table 2.

Table 2
Calculated and experimental electronic g-factors (refs. 6 and 7)

Molecule	Calculated	Experimental
^{14}N@C_{60}	2.00097	2.00204
^{15}N@C_{60}	2.00096	2.00043
^{14}NO@C_{60}	1.95333	?
^{15}NO@C_{60}	1.95333	?

Note that the experimental value for ^{15}N@C_{60} was determined by using the frequency peak ν = 56 x 10^9 Hz and magnetic field strength B = 2 tesla directly from the EPR spectrum at resonance for ^{15}N@C_{60} and inserting these values into equation 1 and solving for g, where h = Planck's constant = 6.626 x 10^{-34} joule-seconds and β = Bohr magneton = 9.274 x 10^{-24} joules per tesla. Also, note that experimental EPR spectra, and therefore the g-factors, have not been measured at present.

DISCUSSION AND PATH FORWARD

The relative errors for the hyperfine coupling constants for the $^{14}N@C_{60}$ and $^{15}N@C_{60}$ molecules are 30% and 32%, respectively. The DFT quantum chemical calculations performed underestimate the experimental values by those percentages. Based on these results, it can be concluded that the experimental values for the hyperfine coupling constants for the $^{14}NO@C_{60}$ and $^{15}NO@C_{60}$ molecules will be 31% higher on average than the values calculated here using the DFT as implemented in Gaussian 16.

The magnitude of the hyperfine coupling constant is a measure of the unpaired electron spin density and indicates the extent of delocalization of the unpaired electron over the molecule. The greater the value of this constant, the more stable is the molecule. According to the calculations, the hyperfine coupling constant is greatest for the $^{15}NO@C_{60}$ molecule. It is calculated to be 18.1 MHz. Adding 31% yields a probable experimental value of 23.7 Mhz.

The calculated electronic g-values for all molecules are very close to the free electron value of 2.0023, the maximum difference being approximately 5% for the $NO@C_{60}$ molecules. This indicates that the unpaired electron has very little orbital contribution to the magnetic moment, i.e., spin-orbit coupling is small. Small spin-orbit coupling is advantageous for development of a molecular atomic clock.

Based on these results, the $^{15}NO@C_{60}$ molecule has better potential to serve as the basis for an endohedral, molecular atomic clock than the $N@C_{60}$ endohedral fullerene.

A full-scale quantum-theoretical numerical simulation that includes more than only polarization functions is necessary to reproduce the EPR spectrum and to recover the underlying structural and dynamic parameters of radical-based molecules, such as the NO endohedral fullerenes. Spectral simulation is therefore an important ingredient of the successful application of EPR spectroscopy. EasySpin is a software package that is able to simulate EPR spectra of most paramagnetic systems under a wide range of dynamic conditions. EasySpin is a collection of functions and programs intended to run on MATLAB. This is the next step to take in continuing the work reported herein.

CONCLUSIONS

The availability of very high-stability frequency standards and the timekeeping that they provide are utilized extensively in military and commercial technologies, including the synchronization of communications networks, and in positioning systems such as the satellite-based global positioning system (GPS). Conventional atomic clocks are generally quite large and delicate and have significant operating-power requirements. Thus, there is a need for providing compact, reliable, portable, low-power atomic clocks. Endohedral fullerenes are attractive for use in an atomic clock because the endohedral species is shielded from the environment by the carbon cage. This means that both the electron and nuclear spin lifetimes and coherence time of the endohedral species, i.e., the nitric oxide (NO) radical, can be very long, which is advantageous for stable frequency operation.

The goal of this study was to determine if a NO radical encapsulated in an endohedral fullerene is a suitable candidate for the development of portable, condensed-matter, molecular atomic clocks. In order to assess the potential of $NO@C_{60}$ to function as an accurate and reliable frequency standard, electron paramagnetic resonance (EPR) parameters (hyperfine coupling constant and electronic g-factor) were calculated using the density functional theory (DFT) method.

At present, laboratory methods to produce a radical encapsulated in an endohedral fullerene, such as $NO@C_{60}$, are prohibitively expensive. However, this should not deter further experimental synthesis efforts since the calculated EPR parameters indicate that the endohedral fullerene has the potential to serve as the basis for a portable atomic clock.

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APPENDIX
GAUSSIAN 16 INPUT AND OUTPUT DATA

$^{14}N@C_{60}$ Input:

```
#T opt freq=noraman ub3lyp/TZVP guess=NoSymm int=(grid=superfinegrid)
 scf=xqc nmr prop=EPR density=current

 Symbolic Z-matrix:
 Charge = 0 Multiplicity = 4
 C                    -3.39476   0.92853  -0.36265
 C                    -3.38138  -0.38899  -0.96603
 C                    -2.75331   1.98785  -0.99283
 C                    -2.727    -0.59297  -2.17463
 C                    -1.92511  -1.78373  -2.37263
 C                    -3.26182  -1.36704   0.09665
 C                    -2.49298  -2.50878  -0.09313
 C                    -1.81056  -2.72148  -1.3537
 C                    -1.86648   2.77185   1.16195
 C                    -2.53551   1.66706   1.81923
 C                    -1.97312   2.92891  -0.21455
 C                    -3.28349   0.7647    1.0729
 C                    -3.20131  -0.65402   1.35679
 C                    -1.67306   1.18937   2.8814
 C                    -1.5942   -0.17091   3.15356
 C                    -2.3745   -1.11199   2.37525
 C                     0.41485   3.49439  -0.36511
 C                     0.52603   3.33058   1.07043
 C                    -0.80843   3.29776  -0.99411
 C                    -0.59064   2.97689   1.81789
 C                    -0.47112   1.99889   2.88058
```

C	1.81018	2.72157	1.35357
C	1.92475	1.78379	2.37246
C	0.76015	1.41492	3.15208
C	0.29647	2.0975	-2.83332
C	1.5723	2.30268	-2.17744
C	-0.86883	2.58456	-2.25415
C	1.63026	2.98646	-0.96924
C	2.49263	2.50885	0.09299
C	2.3742	1.112	-2.3754
C	3.20102	0.654	-1.35692
C	3.26151	1.3671	-0.0968
C	-2.05797	0.51178	-2.83184
C	-0.84267	0.00387	-3.436
C	-2.07081	1.77505	-2.2534
C	0.30982	0.78005	-3.4367
C	1.59395	0.17094	-3.15367
C	-0.76054	-1.41486	-3.15224
C	0.47073	-1.99883	-2.8807
C	1.67274	-1.18934	-2.88155
C	3.39437	-0.92851	0.36249
C	3.28317	-0.76473	-1.07309
C	2.53517	-1.66707	-1.81941
C	2.75292	-1.98781	0.99268
C	2.05763	-0.51175	2.83179
C	2.72659	0.593	2.17447
C	3.381	0.38903	0.96586
C	2.07049	-1.77508	2.25331
C	-0.29675	-2.09746	2.83322

```
 C                   -0.31018  -0.78001   3.43658
 C                    0.84237  -0.00376   3.4359
 C                    0.86852  -2.58461   2.25405
 C                   -0.4152   -3.49436   0.36495
 C                   -1.63058  -2.98638   0.96908
 C                   -1.57261  -2.30265   2.17731
 C                    0.80807  -3.29773   0.99395
 C                    1.86611  -2.77187  -1.16213
 C                    0.59025  -2.97686  -1.81804
 C                   -0.52642  -3.33052  -1.07057
 C                    1.97272  -2.92887   0.21436
 N                    0.00886  -0.00083   0.00363
```

$^{14}N@C_{60}$ Output:

```
g value of the free electron [g_e]: 0.20023193D+01
 relativistic mass correction [g_RMC]: -0.19030208D-02
 diamagnetic correction to g tensor [g_DC]:
   XX= 0.45098623D-03   YX=-0.56875299D-08   ZX= 0.96338789D-08
   XY=-0.20069108D-08   YY= 0.45100554D-03   ZY=-0.97918622D-08
   XZ= 0.66022538D-08   YZ=-0.77368220D-08   ZZ= 0.45099136D-03
 orbital Zeeman and spin-orbit coupling contribution to g tensor [g_OZ/SOC]:
   XX= 0.97096355D-04   YX= 0.37432326D-06   ZX=-0.23617293D-06
   XY= 0.35377596D-06   YY= 0.97586822D-04   ZY=-0.21880103D-06
   XZ=-0.15855503D-06   YZ=-0.25938539D-06   ZZ= 0.97802970D-04
 g tensor [g = g_e + g_RMC + g_DC + g_OZ/SOC]:
   XX= 0.20009644D+01   YX= 0.36863573D-06   ZX=-0.22653905D-06
   XY= 0.35176905D-06   YY= 0.20009649D+01   ZY=-0.22859289D-06
```

```
  XZ=-0.15195277D-06   YZ=-0.26712221D-06   ZZ= 0.20009651D+01


                      Isotropic Fermi Contact Couplings

       Atom                 a.u.       MegaHertz

       N(14)              0.03317       3.57269
```

$^{15}N@C_{60}$ Input:

```
#T opt freq=noraman ub3lyp/TZVP guess=NoSymm int=(grid=superfinegrid)
 CPHF(MaxInv=10000) scf=xqc nmr prop=EPR density=current


 Symbolic Z-matrix:

 Charge = 0 Multiplicity = 4
 C                    -3.39476   0.92853  -0.36265
 C                    -3.38138  -0.38899  -0.96603
 C                    -2.75331   1.98785  -0.99283
 C                    -2.727    -0.59297  -2.17463
 C                    -1.92511  -1.78373  -2.37263
 C                    -3.26182  -1.36704   0.09665
 C                    -2.49298  -2.50878  -0.09313
 C                    -1.81056  -2.72148  -1.3537
 C                    -1.86648   2.77185   1.16195
 C                    -2.53551   1.66706   1.81923
 C                    -1.97312   2.92891  -0.21455
 C                    -3.28349   0.7647    1.0729
 C                    -3.20131  -0.65402   1.35679
 C                    -1.67306   1.18937   2.8814
 C                    -1.5942   -0.17091   3.15356
 C                    -2.3745   -1.11199   2.37525
```

C	0.41485	3.49439	-0.36511
C	0.52603	3.33058	1.07043
C	-0.80843	3.29776	-0.99411
C	-0.59064	2.97689	1.81789
C	-0.47112	1.99889	2.88058
C	1.81018	2.72157	1.35357
C	1.92475	1.78379	2.37246
C	0.76015	1.41492	3.15208
C	0.29647	2.0975	-2.83332
C	1.5723	2.30268	-2.17744
C	-0.86883	2.58456	-2.25415
C	1.63026	2.98646	-0.96924
C	2.49263	2.50885	0.09299
C	2.3742	1.112	-2.3754
C	3.20102	0.654	-1.35692
C	3.26151	1.3671	-0.0968
C	-2.05797	0.51178	-2.83184
C	-0.84267	0.00387	-3.436
C	-2.07081	1.77505	-2.2534
C	0.30982	0.78005	-3.4367
C	1.59395	0.17094	-3.15367
C	-0.76054	-1.41486	-3.15224
C	0.47073	-1.99883	-2.8807
C	1.67274	-1.18934	-2.88155
C	3.39437	-0.92851	0.36249
C	3.28317	-0.76473	-1.07309
C	2.53517	-1.66707	-1.81941
C	2.75292	-1.98781	0.99268

C	2.05763	-0.51175	2.83179
C	2.72659	0.593	2.17447
C	3.381	0.38903	0.96586
C	2.07049	-1.77508	2.25331
C	-0.29675	-2.09746	2.83322
C	-0.31018	-0.78001	3.43658
C	0.84237	-0.00376	3.4359
C	0.86852	-2.58461	2.25405
C	-0.4152	-3.49436	0.36495
C	-1.63058	-2.98638	0.96908
C	-1.57261	-2.30265	2.17731
C	0.80807	-3.29773	0.99395
C	1.86611	-2.77187	-1.16213
C	0.59025	-2.97686	-1.81804
C	-0.52642	-3.33052	-1.07057
C	1.97272	-2.92887	0.21436
N(Iso=15)	0.00886	-0.00083	0.00363

$^{15}N@C_{60}$ Output:

```
g value of the free electron [g_e]: 0.20023193D+01
 relativistic mass correction [g_RMC]:-0.19030208D-02
 diamagnetic correction to g tensor [g_DC]:
   XX= 0.45098624D-03   YX=-0.56616104D-08   ZX= 0.96568402D-08
   XY=-0.20010088D-08   YY= 0.45100553D-03   ZY=-0.97717095D-08
   XZ= 0.66094223D-08   YZ=-0.77187395D-08   ZZ= 0.45099130D-03
 orbital Zeeman and spin-orbit coupling contribution to g tensor [g_OZ/SOC]:
   XX= 0.97067164D-04   YX= 0.40752156D-06   ZX=-0.19633693D-06
```

```
  XY= 0.41206808D-06   YY= 0.97506851D-04   ZY=-0.30087624D-06
  XZ=-0.19145882D-06   YZ=-0.21165523D-06   ZZ= 0.97843778D-04
 g tensor [g = g_e + g_RMC + g_DC + g_OZ/SOC]:
  XX= 0.20009643D+01   YX= 0.40185995D-06   ZX=-0.18668009D-06
  XY= 0.41006707D-06   YY= 0.20009648D+01   ZY=-0.31064795D-06
  XZ=-0.18484940D-06   YZ=-0.21937397D-06   ZZ= 0.20009651D+01

                        Isotropic Fermi Contact Couplings
       Atom                 a.u.       MegaHertz
       N(15)              0.03317      -5.01163
```

$^{14}NO@C_{60}$ Input:

```
#T opt freq=noraman ub3lyp/TZVP guess=NoSymm scf=(IntRep,NoVarAcc,Tigh
 t) int=(grid=superfinegrid) nmr prop=EPR density=current

 Symbolic Z-matrix:
 Charge = 0 Multiplicity = 2
 C                     2.1833    2.78617  -0.05378
 C                     3.04679   1.74701   0.47624
 C                     1.13057   3.27612   0.71146
 C                     2.81852   1.24009   1.75086
 C                     2.92203  -0.18692   1.99359
 C                     3.38876   0.84863  -0.61134
 C                     3.48857  -0.5196   -0.37872
 C                     3.25002  -1.04832   0.95192
 C                    -0.34269   3.28991  -1.25817
 C                     0.75465   2.77741  -2.0566
```

C	-0.15842	3.53373	0.09714
C	1.9906	2.53101	-1.46818
C	2.73447	1.33386	-1.81286
C	0.20738	1.83756	-3.01562
C	0.91895	0.68998	-3.34553
C	2.20854	0.43245	-2.73178
C	-2.36744	2.56934	0.6007
C	-2.56013	2.31495	-0.81408
C	-1.19207	3.16532	1.04583
C	-1.56815	2.66749	-1.72296
C	-1.22749	1.76938	-2.80948
C	-3.25593	1.04855	-0.95163
C	-2.92776	0.18695	-1.993
C	-1.89253	0.55562	-2.94119
C	-1.09207	1.61694	2.95341
C	-2.31774	0.99408	2.4888
C	-0.54095	2.6796	2.24724
C	-2.94363	1.46007	1.3376
C	-3.49428	0.51962	0.37869
C	-2.21407	-0.43246	2.73129
C	-2.74028	-1.33394	1.81249
C	-3.39461	-0.84864	0.61121
C	1.71948	1.75162	2.54899
C	1.14414	0.64218	3.28495
C	0.89379	2.748	2.04083
C	-0.23114	0.5765	3.48285
C	-0.92466	-0.68988	3.34561
C	1.88681	-0.55561	2.94172

C	1.22154	-1.76916	2.80964
C	-0.21329	-1.83757	3.01581
C	-2.18987	-2.78684	0.0538
C	-1.99685	-2.53146	1.4682
C	-0.76082	-2.77743	2.05672
C	-1.137	-3.27661	-0.71147
C	-1.7255	-1.75173	-2.54879
C	-2.8245	-1.24019	-1.75048
C	-3.05312	-1.74737	-0.47607
C	-0.89994	-2.74828	-2.0408
C	1.08633	-1.61683	-2.95329
C	0.22543	-0.57636	-3.4824
C	-1.14989	-0.6422	-3.28469
C	0.53487	-2.67932	-2.24708
C	2.36105	-2.56873	-0.60069
C	2.93776	-1.45993	-1.33786
C	2.31218	-0.99404	-2.48925
C	1.1857	-3.16482	-1.04565
C	0.3365	-3.28968	1.25822
C	1.56185	-2.66699	1.72295
C	2.55378	-2.31442	0.81412
C	0.15212	-3.53356	-0.09706
N	-0.53824	0.00206	0.00359
O	0.60623	-0.00272	-0.00492

$^{14}NO@C_{60}$ Output:

```
g value of the free electron [g_e]: 0.20023193D+01
```

```
 relativistic mass correction [g_RMC]:-0.29684919D-03
 diamagnetic correction to g tensor [g_DC]:
   XX= 0.12119068D-03   YX=-0.20228332D-06   ZX=-0.13339401D-05
   XY=-0.44055784D-06   YY= 0.11633745D-04   ZY= 0.57314194D-06
   XZ=-0.16690943D-05   YZ= 0.62188022D-06   ZZ= 0.21106805D-04
 orbital Zeeman and spin-orbit coupling contribution to g tensor [g_OZ/SOC]:
   XX=-0.13948584D+00   YX= 0.59225566D-03   ZX= 0.10684949D-02
   XY= 0.57406167D-03   YY=-0.13561639D-03   ZY= 0.28478396D-03
   XZ= 0.10623572D-02   YZ= 0.28477018D-03   ZZ= 0.36487944D-02
 g tensor [g = g_e + g_RMC + g_DC + g_OZ/SOC]:
   XX= 0.18626578D+01   YX= 0.59205337D-03   ZX= 0.10671610D-02
   XY= 0.57362111D-03   YY= 0.20018985D+01   ZY= 0.28535710D-03
   XZ= 0.10606881D-02   YZ= 0.28539206D-03   ZZ= 0.20056924D+01

                        Isotropic Fermi Contact Couplings
       Atom                  a.u.       MegaHertz
       N(14)               0.03982      12.86534
```

$^{15}NO@C_{60}$ Input:

```
#T opt freq=noraman ub3lyp/TZVP guess=NoSymm scf=(IntRep,NoVarAcc,Tigh
 t) int=(grid=superfinegrid) nmr prop=EPR density=current

 Symbolic Z-matrix:
 Charge = 0 Multiplicity = 2
 C                     2.18361  -2.7852    0.07803
 C                     3.0465   -1.75148  -0.46382
 C                     1.12968  -3.28276  -0.6804
```

C	2.81576	-1.25719	-1.74297
C	2.91861	0.16725	-2.00027
C	3.39029	-0.84232	0.61426
C	3.48927	0.52349	0.36759
C	3.24853	1.03879	-0.96793
C	-0.34028	-3.27652	1.29146
C	0.75834	-2.75604	2.08286
C	-0.15827	-3.5342	-0.06146
C	1.99335	-2.51561	1.48995
C	2.7378	-1.31535	1.82165
C	0.21234	-1.80675	3.03306
C	0.92461	-0.65614	3.351
C	2.21317	-0.40491	2.73235
C	-2.36795	-2.57538	-0.5712
C	-2.55875	-2.30697	0.84135
C	-1.19337	-3.1758	-1.0123
C	-1.56527	-2.65022	1.75209
C	-1.2228	-1.74091	2.82882
C	-3.25445	-1.03908	0.9673
C	-2.92434	-0.16717	1.99924
C	-1.88763	-0.5261	2.94976
C	-1.09676	-1.64667	-2.93566
C	-2.32164	-1.01905	-2.47511
C	-0.54435	-2.70225	-2.21988
C	-2.94521	-1.47347	-1.31813
C	-3.49462	-0.52347	-0.36789
C	-2.2182	0.40492	-2.732
C	-2.74337	1.31554	-1.8217

C	-3.3958	0.84242	-0.61444
C	1.7155	-1.77697	-2.53406
C	1.13892	-0.67523	-3.28053
C	0.89075	-2.76827	-2.01477
C	-0.23671	-0.6116	-3.47686
C	-0.93001	0.6561	-3.35147
C	1.88209	0.52619	-2.95093
C	1.21708	1.74092	-2.82986
C	-0.21805	1.80704	-3.0341
C	-2.1899	2.78599	-0.07854
C	-1.99937	2.5162	-1.49048
C	-0.76434	2.75625	-2.08366
C	-1.13589	3.28332	0.67995
C	-1.7213	1.77705	2.53336
C	-2.82173	1.25743	1.74222
C	-3.05267	1.75203	0.46323
C	-0.89672	2.76856	2.01429
C	1.09132	1.64657	2.93514
C	0.23128	0.61147	3.47585
C	-1.14442	0.67526	3.27968
C	0.53839	2.70179	2.2192
C	2.36135	2.57436	0.57075
C	2.93972	1.47331	1.3181
C	2.31659	1.01907	2.47538
C	1.18715	3.17536	1.01175
C	0.33428	3.27617	-1.29202
C	1.55915	2.64983	-1.75275
C	2.55214	2.30612	-0.84172

```
 C                     0.15218   3.53384   0.06088
 N(Iso=15)            -0.54054  -0.00237   0.00287
 O                     0.60379   0.00242   0.00977
```

$^{15}NO@C_{60}$ Output:

```
g value of the free electron [g_e]: 0.20023193D+01
 relativistic mass correction [g_RMC]:-0.29684923D-03
 diamagnetic correction to g tensor [g_DC]:
   XX= 0.12118145D-03   YX=-0.23871833D-06   ZX=-0.13246344D-05
   XY=-0.49752922D-06   YY= 0.11609695D-04   ZY= 0.32953009D-06
   XZ=-0.16625988D-05   YZ= 0.38868866D-06   ZZ= 0.21150616D-04
 orbital Zeeman and spin-orbit coupling contribution to g tensor [g_OZ/SOC]:
   XX=-0.13948808D+00   YX= 0.59100546D-03   ZX= 0.10681590D-02
   XY= 0.57282768D-03   YY=-0.14605911D-03   ZY= 0.20528931D-03
   XZ= 0.10620371D-02   YZ= 0.20523010D-03   ZZ= 0.36592180D-02
 g tensor [g = g_e + g_RMC + g_DC + g_OZ/SOC]:
   XX= 0.18626556D+01   YX= 0.59076675D-03   ZX= 0.10668344D-02
   XY= 0.57233016D-03   YY= 0.20018880D+01   ZY= 0.20561884D-03
   XZ= 0.10603745D-02   YZ= 0.20561879D-03   ZZ= 0.20057028D+01


                        Isotropic Fermi Contact Couplings
       Atom                  a.u.       MegaHertz
       N(15)                0.03982     -18.04711
```

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Title / Project

Michael E. Miller

Author/Project Engineer	Report number/Date received (to be completed by LCSD)
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