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FIRST PRINCIPLES THEORY OF HYPERFINE INTERACTIONS
IN GUANINE NUCLEOBASE

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Abstract

The electronic structure and the muonium hyperfine interactions in guanine nucleobase were investigated using the unrestricted Hartree-Fock cluster procedure in combination with the 6-311G(d,p) basis set. The effect of muonium on the planar shape of the guanine nucleobase varies depending on the trapping sites. Non-planar characteristic of guanine base was observed when muonium is trapped at C4, C5, or C6 atoms. The guanine base retains its planar geometry when muonium is present at C2, C8, N3, N7, or O6 atoms. The muonium hyperfine coupling constant at the different sites ranges from -31.3 MHz to 366.3 MHz. Based on the minimum total energy consideration, C8 is the most stable trapping site. The calculated value of the muonium Fermi contact coupling constant in the guanine nucleobase is in good agreement with the μ SR data. This study provides an excellent overall understanding of the effect of muonium addition to the various trapping sites in the guanine base and the associated hyperfine properties.

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1. Introduction

Muon Spin Rotation/ Relaxation/ Resonance (μ SR) experiment has been successfully developed in order to study microscopic structure, properties, and processes in wide range materials at electron level (Nagamine, 2003). Several μ SR experiments have been conducted using biological samples (Nagamine & Torikai, 2004). μ SR technique is a potential tool for obtaining microscopic information in biological systems such as protein (Nagamine & Torikai, 2004; Pant et al., 2015; Sugawara et al., 2014) and DNA (Hubbard, Oganessian, Sulaimanov, Butt, & Jayasooriya, 2004; Nagamine, Torikai, Shimomura, Ikedo, & Schultz, 2009) because μ SR technique is sensitive to dynamic and weak magnetism.

Torikai, Hori, Hirose, and Nagamine (2006), Nagamine and Torikai (2004) performed μ SR measurement to study electron transport in DNA at microscopic level. In this technique, 100% spin-polarized continuous positive muon (μ^+) beam is injected into samples such as DNA. During the slowing down process, the injected μ^+ picks up one electron to form a neutral atomic state called as muonium as shown in Figure 01. After its formation in the sample, muonium is then thermalized. At the end of the thermalization process, muoniums could be trapped at a number of sites in the DNA sample. The captured electron is then released and leaving behind μ^+ at the trapping sites. As the electron starts to move, it produces a fluctuating magnetic field at the μ^+ site which leads to spin-lattice relaxation of the μ^+ (Figure 01).

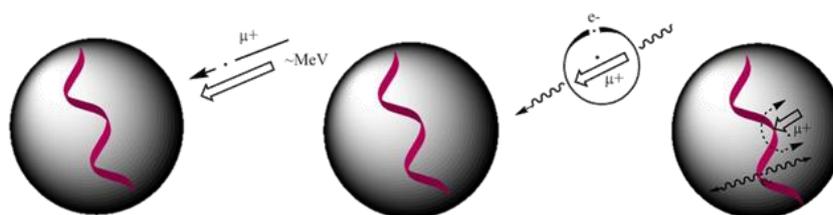


Figure 01. Schematic of μ SR experimental technique

The structural data for guanine nucleobase was obtained from PubChem database (Kim et al., 2015). Guanine base ring possesses planar characteristic in the starting geometry. Figure 02 shows the guanine nucleobase structure. The atoms numbering are implemented according to Sinden, Pearson, Potaman, and Ussery (1998) numbering scheme. Only the atoms that belong to the guanine base ring were included in the cluster. The link to the sugar phosphate group is terminated with a methyl (CH_3) group. The methyl group is attached at the nitrogen atom (N9) to simulate the electronic interaction effect of the sugar phosphate backbone with the nitrogenous base. The use of a methyl group to replace the sugar phosphate can be a justifiable approximation as it can imitate the effect of sugar phosphate group through hyperconjugation effects (Mahato et al., 2008).

Muonium-adduct free radical could be formed by the addition of muonium to the unsaturated molecule such as guanine nucleobase (Oganessian, Hubbard, Butt, & Jayasooriya, 2003). Muonium can add to a double bond and form free radicals in which muonium is chemically bound as a polarized spin state in the guanine nucleobase. The hyperfine interaction of muonium at all possible muonium trapping sites in

guanine nucleobase was investigated by using the first-principle computational studies. There are eight possible muonium trapping sites in guanine base located near to the atoms with an unsaturated bond (C2, C4, C5, C6, C8, N3, N7, and O6 in Figure 02).

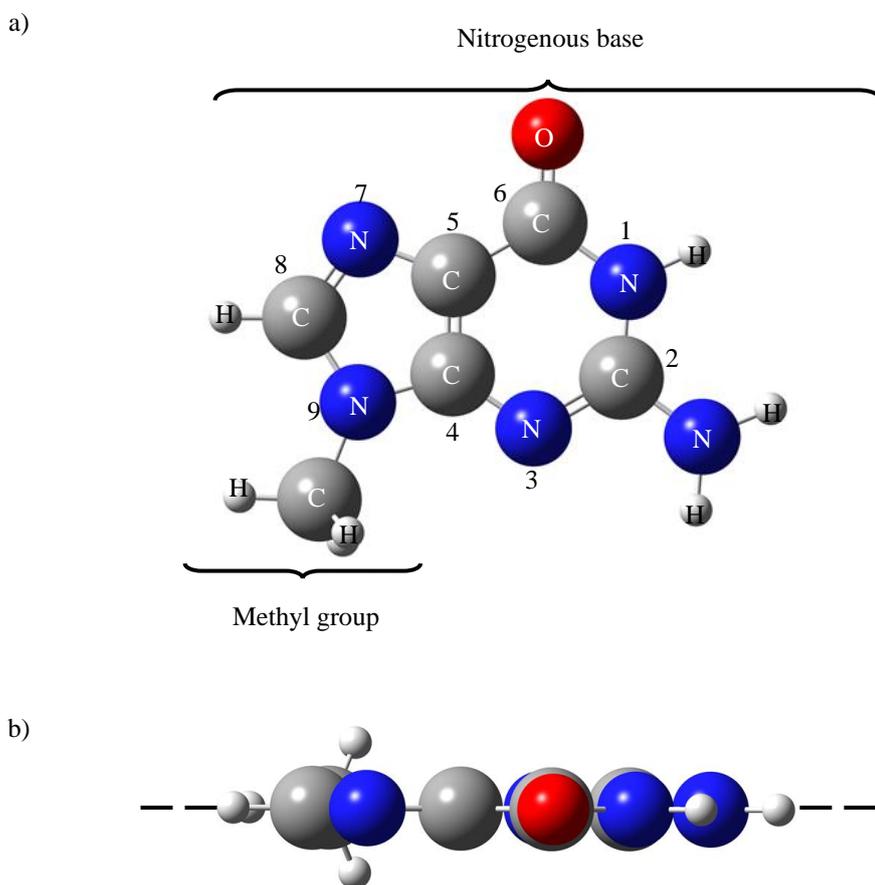


Figure 02. Guanine nucleobase structure. a) in the nucleobase conformation, a methyl group is attached to the N9 atom. b) guanine base ring has planar geometry. The red color represents oxygen; blue: nitrogen, gray: carbon, and white: hydrogen

2. Problem Statement

In this investigation, the eight muoniated systems were optimized such that the muonium and all atoms in the guanine nucleobase were allowed to relax. The Cluster Method was employed and the Hartree-Fock procedure (Sulaiman et al., 1994) at 6-311G(d,p) level (Zaharim et al., 2019) was applied to optimize the structure of the muoniated system. 6-311G(d,p) basis set describes the core atomic orbital by using one basis function (Zaharim et al., 2019). The representation of the valence electron is more flexible where three basis functions describe the valence atomic orbitals. The chosen basis set contains polarization function which is important to allow the distortion of the atomic orbitals in a molecular environment. The polarization function in 6-311G (d,p) basis set has p-type function added to the hydrogen atom and d-type function added to all other atoms. Spin unrestricted type of calculation was selected due to the existence of

an unpaired electron in the muoniated systems. The converged molecular orbitals were then used to examine the electronic structures of the systems and the muon HFCC at each possible Mu sites.

3. Research Questions

In this investigation, the eight muoniated systems were optimized such that the muonium and all atoms in the guanine nucleobase were allowed to relax. The Cluster Method was employed and the Hartree-Fock procedure (Sulaiman et al., 1994) at 6-311G(d,p) level (Zaharim et al., 2019) was applied to optimize the structure of the muoniated system. 6-311G(d,p) basis set describes the core atomic orbital by using one basis function (Zaharim et al., 2019).

4. Purpose of the Study

The electronic structure and the muonium hyperfine interactions in guanine nucleobase were investigated using the unrestricted Hartree-Fock cluster procedure in combination with the 6-311G(d,p) basis set.

5. Research Methods

The chosen basis set contains polarization function which is important to allow the distortion of the atomic orbitals in a molecular environment. The polarization function in 6-311G (d,p) basis set has *p*-type function added to the hydrogen atom and *d*-type function added to all other atoms. Spin unrestricted type of calculation was selected due to the existence of an unpaired electron in the muoniated systems.

6. Findings

The distortion test in the geometry of guanine nucleobase when muonium is added to the possible trapping sites was conducted. An analysis on the optimized muoniated systems structure was done to investigate whether the presence of muonium caused the guanine base ring to deviate from the planar shape. The results on the effect of muonium at the possible trapping sites have on the geometry of guanine nucleobase are summarized in Table 01.

Table 01. The geometrical effects of the muonium added to the guanine base ring of guanine nucleobase. 'Yes' means that muonium perturbs the planar geometry of guanine base ring, while 'no' means that muonium did not perturb the guanine base ring

Muonium trapping site	Distortion of the guanine base ring planar geometry (yes or no)
C2	No
C4	Yes
C5	Yes
C6	Yes
C8	No
N3	No
N7	No
O6	No

The NH₂ group forms a single bond with the C2 atom. The position of the NH₂ group in the initial guanine nucleobase structure is in-plane with the guanine base ring. When muonium is trapped and forms a bond with the C2 atom, the NH₂ group bends out of the plane to balance out the disturbing effect of muonium. However, the existence of muonium near the C2 atom causes no distortion to the planar geometry of the guanine base ring. A similar effect was observed when muonium is trapped and forms a bond with the C8 atom. The planar geometry of the guanine base ring is maintained when muonium is trapped near the C8 atom. The hydrogen atom at the C8 atom was observed to dislocate out of the plane to compensate with the existence of muonium. When muonium is trapped near the N3, N7 or O6 atoms, the guanine base ring maintains its planar geometry.

This kind of geometrical effect does not occur when muonium is trapped near the C4, C5, or C6 atoms. The two rings of guanine base appear tilted when muonium is trapped near the C4 or C5 atoms. For the C6 atom trapping site, the guanine base ring is severely altered from its planar geometry. The bond length between N1 and C6 atoms in the host system is 1.4 Å. From the calculated results, the bond length between these two atoms is increased to 3.4 Å when muonium is trapped and forms a bond with C6 atom.

The hyperfine parameter of all possible muoniated system was calculated. The stable trapping position of muonium was obtained by analyzing the possible sites that lead to the minimum total energy of the system (Cammarere, Scheicher, Sahoo, Das, & Nagamine, 2000; Sulaiman et al., 1994). Table 02 lists the possible muonium sites arranged in increasing order of the respective total energies. The relative energy is taken with respect to the possible muonium trapping site that has the lowest total energy. Muonium that is trapped and forms a bond with the C8 atom of guanine base has the lowest energy, followed by C2 where the energy increases by 0.3 eV.

Table 02. Calculated FCCC values for all possible muonium trapping sites in guanine nucleobase arranged in the ascending order of the relative energy. The relative energy is taken with respect to the possible muonium trapping site that has minimum total energy which is C8

Muonium trapping site	Relative energy, (eV)	FCCC, (MHz)
C8	0.0	336.2
C2	0.3	88.8
C4	0.5	321.7
N7	0.6	162.8
C5	0.8	366.3
O6	0.8	-37.3
C6	0.9	80.2
N3	2.7	-14.2

Our investigation on the hyperfine interaction shows that the muonium Fermi Contact Coupling Constant (FCCC) is positive for all possible muonium trapping sites, except for muonium trapped near the O6 and N3 atoms. The low Fermi contact interaction at the O6 atom is a consequence of a small overlap between the orbitals of the muonium and the O6 atom (Stride, Jayasooriya, & Reid, 2002). High muonium Fermi contact interaction (> 300 MHz) is observed for the muonium adducted to the C4, C5, and C8 atoms.

The present calculations result implies that the most possible muonium trapping sites based on the total energy consideration is when muonium is trapped at the C8 atom. The distance between muonium and C8 atom is 1.1 Å. The muonium FCCC value when muonium trapped near C8 atom is 336.2 MHz. The

calculated muonium FCCC of guanine nucleobase are in reasonable agreement with experimental value obtained in previous study (Hubbard et al., 2004).

The present investigation on muonium trapping sites in guanine nucleobase has demonstrated that muonium is likely to break the double bond between carbon-nitrogen (C8=N7) and attaches itself to the carbon atom (C8) by forming a single covalent bond. A muonium trapped near the C8 atom does not result in any significant changes to the planar geometry of guanine base rings.

7. Conclusion

This study has identified all radical species that could result from the addition of muonium at the trapping sites in the guanine nucleobase structure. This first principle investigation result has important implication in the interpretation of μ SR experiments. This study provides an excellent overall understanding of the effect of muonium addition to the various trapping sites in the guanine base and the associated hyperfine properties.

The addition of muonium at certain trapping sites provides a significant effect to the planar geometry of the guanine base ring. The results suggest that the most probable muon trapping sites are at the atoms with unsaturated bond. The variation in the FCCC values at different trapping sites made it possible to experimentally differentiate the trapping sites in the guanine base. It would be beneficial in the future to study the muonium addition to other three nitrogenous bases which are adenine, thymine, and cytosine.

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