Muonium behavior in N-acetylglycine-N-methylamide

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ABSTRACT

In muon spin rotation and relaxation (μSR) method, theoretical work using first-principles calculations helps to understand the stopping sites and charge states of muon in the sample materials. To support the μSR measurement on protein and DNA, a systematic first-principles study starting from the constituents of the protein has been performed. In this work, the behavior of muonium (Mu = μ^+e^-, bound state of a muon and an electron which is like a light isotope of H atom with similar chemical properties) in a N-acetylglycine-N-methylamide (AGMA), a part of peptide bond, is presented. It is found that the stopping site of Mu is around O of unsaturated bonds between C and O in the AGMA. Further calculations towards whole protein and DNA will be performed to support μSR studies.

1. Introduction

In order to apply the muon spin rotation and relaxation (μSR) method to study the life phenomena, K. Nagamine *et al* initiated the μSR measurements in cytochrome c protein [1, 2], DNA [3] to understand the electron transfer process and aqueous biological solutions [4] to detect the concentration of oxygen in the bio-solutions. But the stopping sites of muon and its charge states in the bio-samples have not understood yet. Theoretically, T. P. Das *et al* [5, 6] reported the unsaturated bond of carboxyl group in the amino acids passivated by H is possible stopping site of muon however in real bio-samples amino acids are connected/formed to peptide bonds rather than H passivation. In our systematic theoretical study, we found the termination of main chain of computational model plays the significant role for the variation of potential energy depth for muon and muonium (Mu = μ^+e^-, bound state of a muon and an electron which is like a light isotope of H atom with similar chemical properties) in the amino acids [7]. In glycine, the stopping site of Mu is estimated around O of unsaturated C=O bond [8]. In triglycine, the possible stopping site is calculated around O of the peptide bond [8] that is around the

O of central glycine moiety. In histidine and other aromatic amino acids, the stopping sites for Mu is estimated around aromatic side chain [7, 9, 10]. In this paper, the stopping site of Mu in N-acetylglycine-N-methylamide (hereafter AGMA), a part of peptide bond, is presented.

Positive muon (μ^+) is like a light proton (mass $m_\mu \approx 1/9\ m_p$; magnetic moment $\mu_\mu = 3.18\ \mu_p$) which acts as sensitive probe to study the local electronic and dynamic states of the materials. The muon can be produced by decay of pion. In accelerator facilities, muon can be generated by bombarding a muon production target (graphite etc.) by high energy proton beam. The muon decays (average life 2.2 μs) to positron along the direction of muon spin at the time of decay. By collecting the positrons using spectrometers around the sample, the information about the interested properties of materials can be extracted. The wide time window ($\sim$ ps to few μs), measurement without external perturbations (at any temperature, without external field) and characteristics of muon (100% spin polarized and asymmetric decay to positron in weak interaction) are advantages of this method over other spectroscopic/resonance methods. We can found the details of μSR technique elsewhere [11, 12].

2. Method

The theoretical calculations were performed using hybrid density function B3LYP with basis sets 6-31G(d) in Gaussian 09 set of programs [13]. In the B3LYP level of calculations, both gradient and exchange correlations are included. The basis set 6-31G(d) describes well the orbitals of first and second rows elements. The optimization of structures with different basis sets were confirmed as mentioned in previous works [7, 10]. The initial charge state of muon is taken as Mu as mentioned in the muon labelled electron method [11]. The stopping site is estimated based on the minimum potential energy (PE) for H or Mu (hereafter Mu) in the system. The PE in term of optimized energies for Mu was calculated as, PE = E(amino acid + H)

– [E(amino acid) + E(H)], where E(X) represents the minimum energy of system X. The PE for Mu around electronegative sites of N-acetylglycine-N-methylamide (Fig. 1) were calculated. The Bader charge analysis [14] to approximate the total charge with each atom is also calculated.
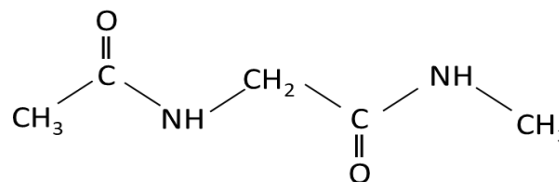
Fig. 1: Chemical formula (schematics) of N-acetylglycine-N-methylamide.

3. Results and Discussion

The potential energy for Mu at different sites of AGMA is calculated. The relatively more deeper values of PE are found around two sites - O1 and O2 (Fig. 2) with PE -0.41 eV and -0.45 eV, respectively. It indicates the stopping site of Mu is around O of unsaturated C=O of the AGMA.

The Bader charge analysis and highest occupied molecular orbitals (HOMO)-lowest unoccupied molecular orbitals (LUMO) gap for Mu stopping around those sites have been calculated as seen in table 1 and Fig. 3, respectively. The Bader charge analysis indicates that the nearby C of C=O bond acquired more negativity than other parts. It indicates the possibility of formation of radical at C after stopping of the Mu nearby the O.

From Fig. 3, the HOMO-LUMO gap of the system when Mu stopped around O2 is relatively smaller than that stopped around O1. The negative HOMO energy indicates the bonding state and positive LUMO energy indicates the antibonding state. A large gap (LUMO-HOMO) in the case of Mu stopping around O1 implies good thermodynamic stability of the compound, whereas a small gap suggests an easy electronic transition in the case of Mu stopping around O2.

Theoretically, even though two possible sites for Mu in AGMA are pointed out but the intensity of muon beam available in accelerator facilities in the worlds is not such a high to stop each Mu near each C=O bonds. So, in this small part of peptide bond, AGMA, the Mu stopping site would be around the O2.
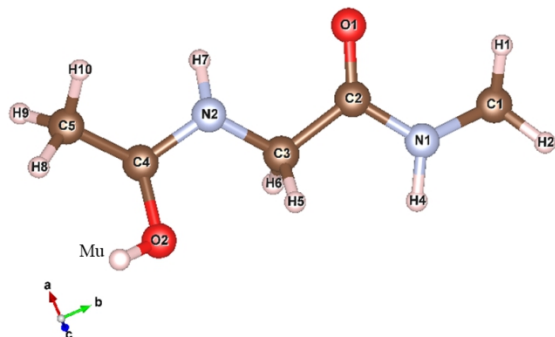
Fig. 2: Optimized structure of muonium in N-acetylglycine-N-methylamide.
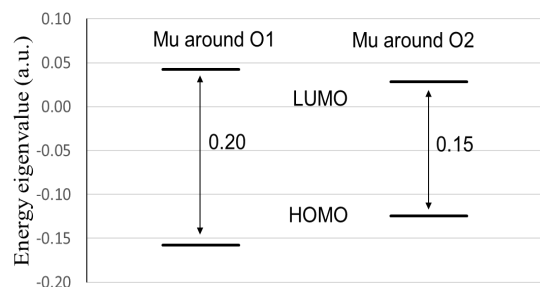
Fig. 3: HOMO-LUMO gap of two possible stopping sites of muonium in N-acetylglycine-N-methylamide. The gap is 0.20 a.u. and 0.15 a.u. for muon stopping around O1 and O2, respectively.

Table 1: Bader charge analysis for AGMA, and Mu stopping around O1 and O2.

Atom	Number of valance electrons with each atoms		
	AGMA	**AGMA + Mu around O1**	**AGMA + Mu around O2**
Mu	-	0	0
C1	3	3	3
C2	1	2	1
C3	3	3	3
C4	1	1	2
C5	4	4	4
H1	1	1	1
H2	1	1	1
H3	1	1	1
H4	0	0	0
H5	1	1	1
H6	1	1	1
H7	0	0	0
H8	1	1	1
H9	1	1	1
H10	1	1	1
N1	8	8	8
N2	8	8	8
O1	8	8	8
O2	8	8	8

4. Conclusions

The stopping site of muonium in N-acetylglycine-N-methylamide – a part of peptide bond is estimated around O of C=O bonds. The potential energy of muonium around both O (O1 and O2) indicates the possible stopping sites in the system. However, HOMO-LUMO gap indicates the easy electronic transition occurred when Mu stops around O2. The behavior of muonium will be studied via µSR studies and compared with current result using ultra slow muon microscopy under development in Japan Proton Accelerator Research Complex, Japan [15-18].

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