Theory of ^{14}N and ^{17}O Nuclear Quadrupole Interactions in Polyglycine and Glycine in the Protein Chain of Cytochrome c

R. H. Scheicher[a], D. Cammarere[a,b], N. Sahoo[a,c], K. Nagamine[d,e], and T. P. Das[a]

[a] Department of Physics, State University of New York at Albany, Albany, NY, 12222, USA
[b] Tamarac High School, Brittenkill, NY, USA
[c] Department of Radiation Oncology, Albany Medical College, Albany, NY, 12208, USA
[d] Muon Science Laboratory, RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama 351-0198, Japan
[e] Meson Science Laboratory, Institute of Materials Structure Science, KEK, Tsukuba, Ibaraki 305-0801, Japan

Reprint requests to Prof. T. P. Das; Fax: 1-518-442-5260, E-mail: tpd56@albany.edu

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As part of our ongoing investigations on hyperfine properties of nuclei and attached probes (like muon and muonium) in the protein chain of Cytochrome c (Cyt c), we have been studying the ^{14}N and ^{17}O nuclear quadrupole interactions in the amino acids in the protein chain at different sites where they occur. As a specific example of one of the amino acids in this context, we shall present our results on Glycine in the homo-molecular polymer Polyglycine and expectations for the hetero-molecular environment occurring at a particular region of the protein chain of Cyt c which is far enough away from the heme unit to make the results more characteristic of the chain.

In the Polyglycine polymer, our results for the ^{14}N and ^{17}O coupling constants e^2qQ and asymmetry parameters η for a central Glycine in a chain of odd numbered molecules are used to study how the e^2qQ and η vary with the chain length and to compare with the results for the isolated Glycine molecule. The aim is to study the convergence of the results with respect to chain length to find out the appropriate length at which the results become characteristic of the polymer chain. This conclusion is expected to provide insights into the chain length to be used in the protein to simulate the results for the protein chain in Cyt c. The Hartree-Fock Cluster procedure is being used for the investigations for all the results to be reported.

Key words: Hartree-Fock calculations; Polyglycine; Muon and Muonium Trapping; Nuclear Quadrupole Interactions.

1. Introduction

The microscopic details of the path that electrons take in the electron-transfer molecule Cyt c are being investigated [1] by the muon spin rotation (μSR) technique. In these experiments, a positive muon (μ^+) is injected into a crystalline Cyt c sample where it is expected to pick up an electron, thereby becoming muonium (Mu), and after slowing down, trap somewhere along the protein chain. The Mu would then release its electron, changing back to μ^+, and as such can probe the motion of the released electron through the muon spin-lattice relaxation it produces.

In our theoretical investigations of the trapping behavior of μ^+ and Mu in the protein chain of Cyt c [2], we have started by looking at individual amino acid molecules [3], which are the basic units of every protein chain. However, to see what effect the chain environment has on such quantities as the binding energy of μ^+ or Mu or the electric field gradient (EFG) tensors at various nuclei, our goal is to combine several amino acid molecules into finite chains and investigate the accompanying changes in these quantities as the chain length increases. For the sake of simplicity, as a first step in our investigations, we have worked with a homopolypeptide chain consisting of only one

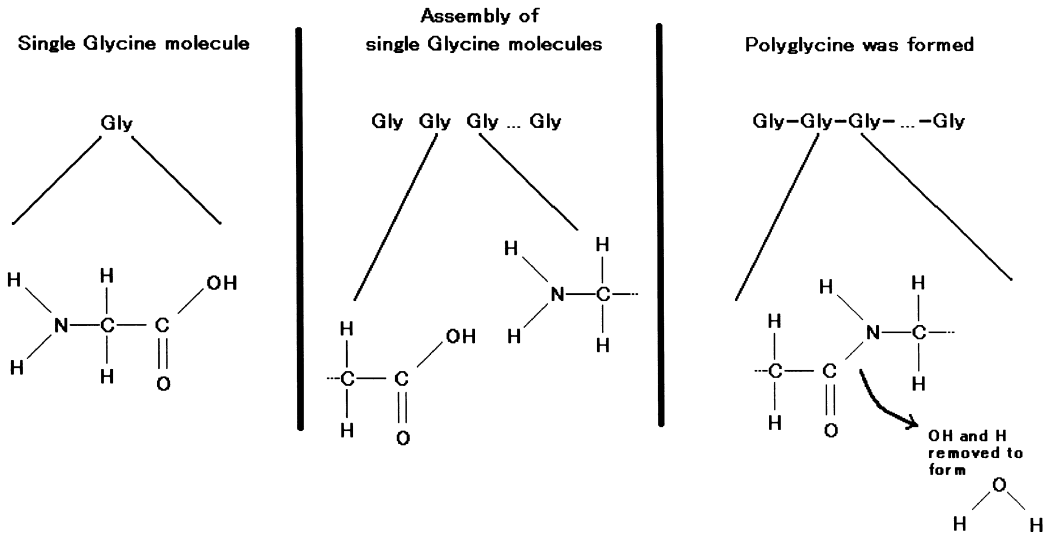

Fig. 1. When two Glycine molecules are combined in a polymer, one amino acid will lose the OH from its carboxyl group while the other amino acid loses an H from its amino group. A water molecule is formed and the bond between C and N from adjacent Glycine molecules is established.

type of amino acid, in particular Glycine, as it is the simplest amino acid, having only a single H atom for the residual part. Figure 1 shows the structure of an isolated Glycine molecule and that of a typical part of the chain with the focus on the connection of two adjacent amino acids. In the chain, the O atoms of the OH group in the isolated amino acid do not exist because of the bond formation between adjacent molecules, which leads to the creation of an H_2O molecule that leaves the system.

2. Procedure

In our Hartree-Fock Cluster investigations [4] of pure Polyglycine and Polyglycine with μ^+ or Mu attached, we stick to the following rule: only chains consisting of an odd number of Glycine molecules were taken into account, and in each of them it was always the amino acid in the center that was considered for the trapping site for μ^+ and Mu. This was done so that both ends of the chain would always be equally far away from the molecule under investigation. The trapping sites of interest for μSR study of electron transport in proteins in the amino acids are the ones that can trap both Mu and μ^+. These sites have been found [2, 3] to refer to the C=O group for all of the amino acids in recent investigations of individual amino acids of Cyt c. In our present investigation of Polyglycine we therefore concentrate on the trapping of Mu and μ^+ at the oxygen of the C=O part of the carboxyl group in the center Glycine molecule.

By comparing the energy for the case when μ^+ or Mu was attached, to that for a bare Polyglycine cluster of the same size, one is able to determine the binding energy of μ^+ or Mu. Furthermore, the EFG tensor, at the ^{14}N nucleus in the amino group and at the ^{17}O nucleus of the center Glycine were determined for the bare molecule and with attached μ^+ or Mu, from which the resulting quadrupole coupling constants e^2qQ and the asymmetry parameters η [5] were found.

3. Results and Discussion

It is found that the binding energy of μ^+ and Mu in Polyglycine decreases as more Glycine molecules are added to the chain. At a length of about five to seven combined amino acid molecules one observes that the results for the binding energy are converging since they do not change significantly when more molecules are added. Further details of our results on the binding energy of μ^+ and Mu, when trapped in Polyglycine, as a function of the size of the cluster will be reported elsewhere. In this paper we focus on the bare chain and the influence that the presence of μ^+ and Mu have on the EFG tensors at the ^{14}N and ^{17}O nuclei.

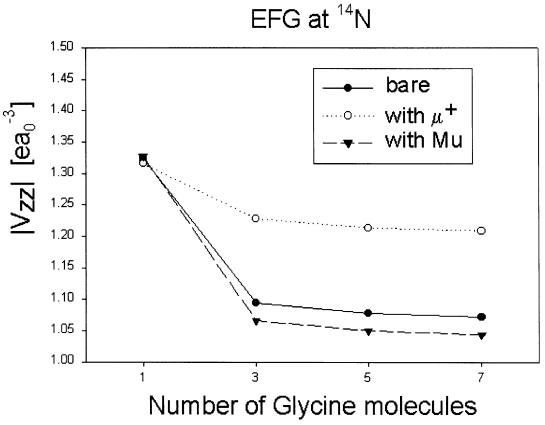

Fig. 2. The maximum principal component of the electric field gradient tensor at ^{14}N for a bare system, with μ^+ trapped and with Mu trapped, as a function of the chain length. The field gradient is expressed in atomic units (ea_0^{-3}), where e is the electronic charge and a_0 the Bohr radius.

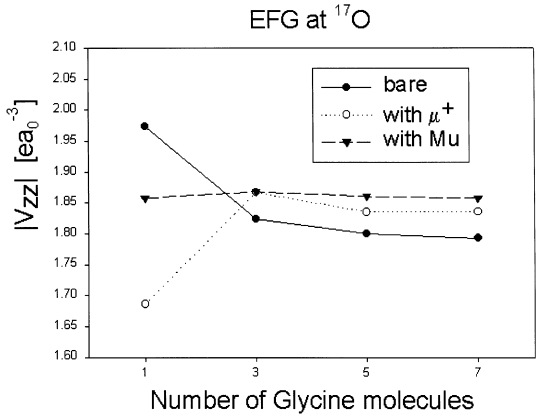

Fig. 3. The maximum principal component of the electric field gradient tensor at ^{17}O for a bare system, with μ^+ trapped and with Mu trapped, as a function of the chain length.

From Figs. 2 and 3 it is seen that the maximum principal component V_{zz} of the EFG tensor converges rather rapidly for both ^{14}N and ^{17}O as the number of combined amino acid molecules is increased. For ^{14}N the value of $|V_{zz}|$ in a single Glycine molecule starts out as almost identical for the bare system as well as when μ^+ or Mu is trapped, but then the results for the three different cases become different from each other, settling down to three different values representative of the infinite chain. For ^{17}O the behavior is opposite, with $|V_{zz}|$ for the three cases being quite

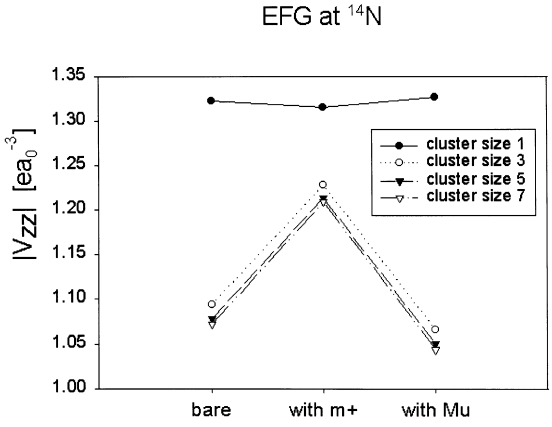

Fig. 4. The maximum principal component of the electric field gradient tensor at ^{14}N for the four different chain lengths used, in the case of a bare system, with μ^+ trapped and with Mu trapped.

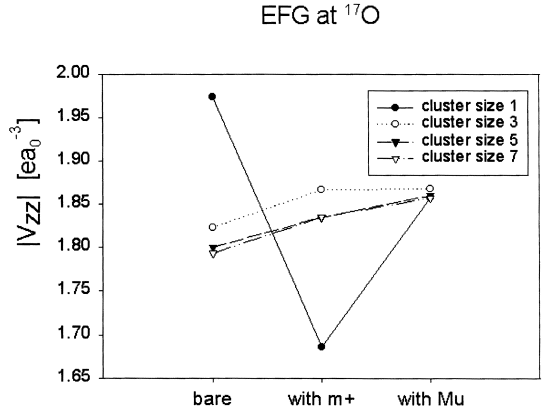

Fig. 5. The maximum principal component of the electric field gradient tensor at ^{17}O for the four different chain lengths used, in the case of a bare system, with μ^+ trapped and with Mu trapped.

different initially but becoming more similar as the length of the chain is increased, settling down to values that are very similar with much smaller difference as compared to ^{14}N for the infinite chain.

These features can be seen from a different perspective in Figs. 4 and 5, where the $|V_{zz}|$ curves are shown for the three cases of bare, μ^+ trapped and Mu trapped, for different chain lengths.

The corresponding results for the asymmetry parameters η for ^{14}N and ^{17}O are listed in Tables 1 and 2, for the cases of the bare chains and with μ^+ and Mu trapped, for different chain lengths. The results again show convergence with respect to chain length, with

Table 1. Asymmetry parameter η for ^{14}N in the center Glycine molecule of a Polyglycine chain consisting of N connected amino acids.

	N = 1	N = 3	N = 5	N = 7
bare	0.199	0.249	0.227	0.225
μ^+	0.361	0.334	0.292	0.286
Mu	0.165	0.222	0.180	0.182

Table 2. Asymmetry parameter η for ^{17}O in the center Glycine molecule of a Polyglycine chain consisting of N connected amino acids.

	N = 1	N = 3	N = 5	N = 7
bare	0.146	0.225	0.232	0.245
μ^+	0.096	0.275	0.227	0.237
Mu	0.841	0.989	0.967	0.967

the convergence being somewhat better for ^{14}N than for ^{17}O (about 1% as compared to about 5% in the worst case).

It is interesting to see that for ^{14}N, the values of η follow the same order as V_{zz} in Fig. 2, namely lowest for Mu trapped, highest for μ^+ trapped, with the result for the bare system in between these two values. For ^{17}O, on the other hand, it is found that for different chain lengths, the values of η for the bare system are quite close to the ones when μ^+ is trapped, but for trapped Mu, η is rather large and approaches unity. The latter feature is due to the fact that V_{yy} and V_{zz} have nearly equal magnitude but opposite signs.

4. Conclusions

It is clear from this investigations that for a chain length of about five to seven amino acids, one reaches converged values for bare as well as trapped muon and muonium cases. It would be interesting to see if similar convergence applies also to the hetero-chains characteristic of proteins, especially in Cyt c, which is the system we are investigating.

The situation with respect to the variations in the quadrupole coupling constants and asymmetry parameters is found to be rather interesting from theory. Experimental results would be very helpful to have, both to test the theoretical predictions and to be combined with theory to provide increased insight regarding the electron distributions in this interesting polymer system.

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[4] See for instance T. P. Das in "Electronic Properties of Solids Using Cluster Methods", T. A. Kaplan and S. D. Mahanti ed., Plenum Press, New York 1995, p. 1.

[5] T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy", Academic Press Inc., New York 1958.