

Change of ^7Be Decay Rate in Exohedral and Endohedral C_{60} Fullerene

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ABSTRACT

The half-life of exohedral $^7\text{Be}-\text{C}_{60}$ complex and that of ^7Be implanted in a gold foil have been found to be about the same within $\approx 0.2\%$. Using a radiochemical technique, we also measured that the probability of formation of endohedral $^7\text{Be}@C_{60}$ complex by nuclear implantation technique was $(5.6 \pm 0.45)\%$. We also find that the half-life of endohedral $^7\text{Be}@C_{60}$ complex is shorter than that of exohedral complex by more than 1%. An analysis of these results using linear muffin-tin orbital method calculations indicates that most of the implanted ^7Be ions in fullerene C_{60} stay at a distance of ≈ 5.3 Angstrom from the centers of nearest C_{60} molecules forming exohedral compounds and those who enter the fullerene cages go to the centers of the cages forming endohedral $^7\text{Be}@C_{60}$ compounds.

Keywords Half-life, ^7Be , endohedral $^7\text{Be}@C_{60}$

1 INTRODUCTION

It is known from earlier works[1-6] that the rate of orbital electron capture of ^7Be is susceptible to the surrounding environment and depends on both the lattice structure and electron affinity of the host atoms. Calculations [2,5,6] also showed that the decay rate of ^7Be should depend on its position in the host lattice. So the decay rate of ^7Be in an atomic cluster such as fullerene C_{60} or large biomolecule should also depend on its position with respect to the molecule and could be used as a tool to learn about the position of the implanted radioactive ion in the atomic cluster. In the future, this kind of study might also tell us about any abnormal change of DNA molecule in a living cell.

It is already well-known[7-9] that different types of metal atoms(Be, Kr, Xe etc.) can be inserted into C_{60} fullerene cage forming endohedral compound by nuclear implantation technique. Many theoretical studies [10-14] have been done regarding the charge and equilibrium positions of the implanted ion in both endohedral and exohedral fullerene complexes, but there is no corresponding experimental measurement. So it is important to address these questions experimentally. By comparing the measured half-lives of exohedral $^7\text{Be}-\text{C}_{60}$ and endohedral $^7\text{Be}@C_{60}$ with that of implanted ^7Be in another well understood material such as gold, we can learn

about the charge and equilibrium positions of ^7Be in endohedral and exohedral fullerene C_{60} complexes.

2 EXPERIMENT

In this work, we have measured the difference of half-lives of ^7Be implanted in a gold (Au) foil and fullerene C_{60} pellet. A $25\mu\text{m}$ thick gold(Au) foil and a $500\mu\text{m}$ thick fullerene C_{60} pellet were bombarded by a 18 MeV ^7Be beam from Nuclear Science Center, New Delhi, India. The ^7Be implanted samples were brought to Variable Energy Cyclotron Center, Kolkata, India for off-line counting. Following electron capture, a ^7Be nucleus has a 10.4% probability[17] of populating the first excited state of ^7Li which decays subsequently to its ground state emitting a 478-keV γ -ray photon. The half-life of ^7Be was determined by monitoring the intensity of this 478 keV γ -ray line with time. Two HPGe detectors (detector-1 and detector-2) having efficiency of 30% were used to count the samples— ^7Be implanted Au foil and ^7Be implanted fullerene pellet. In addition, a standard ^{133}Ba source was also placed in front of each HPGe detector. The detectors were well shielded by lead bricks to avoid any cross-talk between them and also to reduce the background level. The count rate of 478 keV γ -ray was about 1 count per sec at the beginning of the run. Both the HPGe detectors were started at the same time, data was accumulated for 24 hours, stored in a computer and the spectra were cleared and the counting restarted. After counting for 7 days, the positions of the samples were interchanged and counted again. This was done to take care of any systematic error. The counting was continued for about 6 months. From each day's spectra, we determined the counts under 478 keV ($N_{\gamma}(478)$) and 356 keV ($N_{\gamma}(356)$) photo-peaks coming from ^7Be and ^{133}Ba respectively. The ratio $N_{\gamma}(478)/N_{\gamma}(356)$ should be independent of computer dead time and systematic errors and decay exponentially with time. In the case of data sets for ^7Be in fullerene C_{60} and ^7Be in Au samples taken with detector-1, the reduced chisquare values of the exponential fits are 1.5 and 1.6 respectively. We also have similar data taken by detector-2 for ^7Be in fullerene C_{60} and Au and the reduced chisquare values of these exponential fits are 2.7 and 2.9 respectively. So we compared data sets taken by the same detector and analyzed the same way with similar quality of fits (reduced chisquare values) to cancel out the effect of any systematic

error. We obtain the percentage difference of the two decay rates i.e. $((\lambda_{Au}-\lambda_{C60})/\lambda_{C60})= (0.060\pm 0.405)\%$ and $(0.087\pm 0.264)\%$ for detector-1 and detector-2 respectively, where only statistical errors have been considered. Taking weighted average, we finally obtain the percentage difference in decay rates of ^7Be in gold and fullerene to be $((\lambda_{Au}-\lambda_{C60})/\lambda_{C60})=(0.079\pm 0.221)\%$. So we find that the half-life of ^7Be in gold and fullerene is about the same within $\approx 0.2\%$. In a subsequent experiment, we performed a radiochemical separation of endohedral $^7\text{Be}@C_{60}$ compound. ^7Be implanted fullerene C_{60} catcher was dissolved in 5 ml 1,2,4 trichlorobenzene. Equal volume of 6N hydrochloric acid containing carriers was added to the solution and the mixture was thoroughly shaken for 5 minutes in a separating funnel. The organic and the aqueous phases were separated and the activities of both the phases were determined accurately by γ -spectroscopy using a 20% HPGe detector. The aqueous fraction was again mixed with equal volume of organic solvent and a second extraction was carried out. The second organic fraction contained $<4\%$ of radioactivity compared to the first extraction. The organic fraction was also filtered through a millipore filter (pore size = 0.45 μm) to remove any insoluble material. No activity could be detected in the filter paper fraction. It is known [7] from Ohtsuki et al.'s high pressure liquid chromatography (HPLC) work that the ^7Be radioactivities observed in the organic phase come from molecules having similar mobility as C_{60} molecules implying ^7Be is somehow attached to fullerene C_{60} molecule. So the possibilities are ^7Be activities in organic phase are coming from either endohedral $^7\text{Be}@C_{60}$ complex or heterofullerene complex or exohedral $^7\text{Be}-C_{60}$ complex. Since only elements of group IVb and Vb of periodic table are known [9] to form heterofullerene compounds, so beryllium is not expected to form a heterofullerene compound with C_{60} . ^7Be ions stopped in the interstitial positions forming exohedral complex with C_{60} fullerene are not expected to form strong covalent bond with carbon atoms of C_{60} and should be readily dissolved in the hydrochloric acid and remain in the aqueous fraction. Therefore, as concluded earlier [7] also, the ^7Be activities observed in the organic phase should be associated only with the formation of endohedral $^7\text{Be}@C_{60}$ fullerene complex. So the yield of radioactive endofullerene can be accurately determined from the ratio of activities present in the organic and aqueous fractions. We found that the yield of endohedral $^7\text{Be}@C_{60}$ i.e. the probability of insertion of ^7Be in C_{60} by nuclear implantation technique is $(5.6\pm 0.45)\%$, where the estimated uncertainty includes both the statistical and systematic errors. ^7Be ions remain at interstitial space forming exohedral $^7\text{Be}-C_{60}$ complexes for the remaining 94.4% of the time. The radiochemically separated organic fraction containing endohedral $^7\text{Be}@C_{60}$ complex was dried in a plastic crucible. Two HPGe detectors having efficiency of 30% were used to count endohedral $^7\text{Be}@C_{60}$ and ^7Be in Au samples along with a ^{133}Ba source for 3 months following identical procedure as described earlier. However the amount of extracted

endohedral $^7\text{Be}@C_{60}$ complex was only 5.6% and so the statistical uncertainty on one day count of 478 keV γ -ray from endohedral complex was rather large (initially about 4.5% and 14% at the end of the run) for each detector. We finally obtained from our measurement that the half-life of endohedral $^7\text{Be}@C_{60}$ complex is shorter than that of ^7Be in Au by $(3.3\pm 2.3)\%$. Recently Ohtsuki et al. [19] measured half-life (52.68 ± 0.05) days of endohedral $^7\text{Be}@C_{60}$ complex with high accuracy. Comparing their number with our measured half-life (53.60 ± 0.19) days of ^7Be in Au, we find that the half-life of endohedral $^7\text{Be}@C_{60}$ complex is shorter than that of ^7Be in Au by $(1.71\pm 0.37)\%$. If we compare Ohtsuki et al.'s measured half-life [19] of endohedral $^7\text{Be}@C_{60}$ complex with that of ^7Be in Au as measured by Norman et al. [3], then the half-life of endohedral complex is shorter by $(1.20\pm 0.12)\%$. All these results agree with one another within about one standard deviation. The lower difference seen in the case of comparison with Norman et al.'s measured half-life of ^7Be in Au might be because of radiation damage of Au lattice in Norman et al.'s experiment [3]. We also conclude that the half-life of exohedral $^7\text{Be}-C_{60}$ complex and that of ^7Be implanted in Au foil are about the same within $\approx 0.2\%$. So the half-life of endohedral $^7\text{Be}@C_{60}$ complex is significantly (more than 1%) shorter than that of exohedral complex.

3 EXPLANATION

Let us first try to get a qualitative understanding of our results in terms of electron affinity. We have found experimentally that an implanted ^7Be ion has a very low probability $(5.6\pm 0.45)\%$ of entering the fullerene cage and they mostly stay in interstitial space forming exohedral $^7\text{Be}-C_{60}$ complex. The electron affinities of a fullerene molecule C_{60} and gold atom are 2.6 eV [20] and 2.3 eV [21] respectively. Both gold and fullerene have face-centered cubic (FCC) lattice structure, but the lattice parameter of fullerene C_{60} lattice is much larger (14.17 Angstrom) than that (4.08 Angstrom) of Au lattice. So if an implanted ^7Be ion occupies the same geometrical position in both C_{60} and Au lattices, then its distance from the center of the nearest Au atom and C_{60} molecule would be very different. When ^7Be would occupy the octahedral site of Au lattice, then its distance from the nearest Au atom would be ≈ 2 Angstrom, whereas in the case of C_{60} lattice, the corresponding distance would be ≈ 7 Angstrom and the distance from the nearest carbon atom of C_{60} molecule would be ≈ 3.7 Angstrom. Hence ^7Be should retain a significantly higher fraction of its 2s electrons in C_{60} lattice and so the decay rate of ^7Be should be significantly faster in C_{60} lattice than in Au lattice. So the observation of the same (within 0.2%) half-life of ^7Be in C_{60} and Au lattices should imply different geometrical positions for the implanted ^7Be ions in the two lattices. It should also imply that the bond lengths of $^7\text{Be}-C_{60}$ (i.e. the distance between ^7Be and the nearest carbon atom of C_{60}) and $^7\text{Be}-\text{Au}$ are about equal.

In order to understand the results quantitatively, we have done tight binding linear muffin-tin orbital (TB-LMTO) method calculations [2,5,6,22] to determine the average number of 2s electrons of ^7Be for both endohedral and exohedral fullerene complexes. A fullerene molecule consists of 60 carbon atoms placed on a sphere of radius 3.54 Angstrom. These fullerene C_{60} molecules are arranged in a face-centered cubic structure with 14.17 Angstrom lattice constant. For both endohedral and exohedral complex, ^7Be should go to equilibrium positions where the total energy of the system has local minima and the calculated decay rate of ^7Be at those positions should agree with the experimental results.

However we found that TB-LMTO code [22] was not very suitable for the determination of equilibrium positions in the fullerene C_{60} lattice, because its spheridization of potential requires filling up of the available empty space with close packed empty spheres and since such division is not unique, it introduces an uncertainty in the determination of the total energy of the system. In the case of fullerene C_{60} lattice, this uncertainty could be of the order of 0.4% in some cases and this is unacceptably large because the differences in binding energies of ^7Be at different sites are very small (of the order of 10 eV). The uncertainty in the determination of the charge density and number of 2s electrons of ^7Be could be up to twenty percent in some cases, but this is acceptable for the purpose of estimating the change in half-life of ^7Be and comparing with the experimental results. So the equilibrium position of ^7Be in endohedral $^7\text{Be}@\text{C}_{60}$ was taken from a previous density functional calculation [13] and TB-LMTO code was used to determine the average number of 2s electrons of ^7Be at that position.

Lu et al. [13] performed density functional calculations for endohedral $^7\text{Be}@\text{C}_{60}$ and found that the equilibrium position of beryllium ion should be exactly at the center of C_{60} cage. So we performed TB-LMTO calculation placing a ^7Be atom exactly at the center of fullerene C_{60} cage. The calculation was performed assuming such endofullerenes will form a face-centered cubic lattice with lattice parameter 14.17 Angstrom. Empty spheres were placed in the interstitial space and one inside the cage for close packing. TB-LMTO calculation shows that the radius of the muffin-tin sphere of the ^7Be atom at the center of C_{60} cage is ≈ 3 Angstrom and it almost fills up the entire space inside the C_{60} cage. Let Ψ_{total} be the complete electronic wave function and $\Psi_{\text{Be}2s}$ be beryllium 2s state wave function. Then the square of the overlap of Ψ_{total} with $\Psi_{\text{Be}2s}$ i.e. $|\langle \Psi_{\text{total}} | \Psi_{\text{Be}2s} \rangle|^2$ represents the average number of 2s electrons in beryllium ion. Our TB-LMTO calculation shows that the average number of 2s valence electrons of ^7Be atom placed at the center of a C_{60} cage is = 1.07. However, the convergence of the code for this calculation was not very good and the total energy was determined within 10 eV. The uncertainty on the average number of 2s valence electrons of ^7Be atom is not expected to be better than 20%.

We also calculated the average number of 2s electrons of ^7Be in Au. As shown earlier [6], in the case of implantation of ^7Be in Au lattice, ^7Be should go to octahedral and tetrahedral sites of Au lattice. TB-LMTO calculations were performed placing a ^7Be atom at octahedral and tetrahedral positions of a face-centered cubic Au lattice having lattice parameter 4.08 Angstrom. The average number of 2s electrons $|\langle \Psi_{\text{total}} | \Psi_{\text{Be}2s} \rangle|^2$ was found to be 0.54 and 0.36 for ^7Be occupying octahedral and tetrahedral positions of gold lattice respectively. The convergences of these calculations were excellent and the uncertainties in the number of 2s electrons should not be more than a few percent [6]. We expect that as a result of random implantations, the number of ^7Be atoms occupying tetrahedral sites would be twice that of occupying octahedral sites, because the number of tetrahedral sites are twice that of octahedral sites in a face-centered cubic lattice. Hence taking weighted average, we found ^7Be would have 0.42 electrons in its 2s orbital when implanted in Au. So the decay rate of ^7Be in endohedral $^7\text{Be}@\text{C}_{60}$ should be faster than that of ^7Be in Au. According to Hartree and Hartree's calculation [23], the overlap of valence 2s electrons to the total electronic overlap at beryllium nucleus is only 3.32% for a neutral beryllium atom. As shown in ref [6], there is a linear relationship between the decay rate of ^7Be and its number of valence 2s electrons. Using Hartree and Hartree's result [23] along with the linear relationship found earlier [6], we obtain that the decay rate of endohedral $^7\text{Be}@\text{C}_{60}$ should be faster by $\approx 1.1\%$ compared to that of ^7Be in Au lattice. The uncertainty on this calculated number is around 20% because of the poor convergence of TB-LMTO calculation for endohedral $^7\text{Be}@\text{C}_{60}$ complex as discussed earlier. This result is in reasonable agreement with the result that the decay rate of endohedral $^7\text{Be}@\text{C}_{60}$ complex is faster than that of ^7Be in Au by $(1.71 \pm 0.37)\%$. In order to calculate the decay rate of ^7Be when it goes to interstitial space of C_{60} lattice forming exohedral complex, we have to first determine its equilibrium positions in the fullerene C_{60} lattice. Although we have not come across any calculation for determining equilibrium positions of ^7Be in a fullerene C_{60} lattice, there are a large number of calculations [10-14] for equilibrium geometries of isolated exohedral fullerene C_{60} complex. From those calculations, it is known that the typical bond length between a carbon and the other ion forming exohedral fullerene complex is ≈ 2 Angstrom. The distance of the other ion from the center of the C_{60} cage is usually [10-12,14] around 5.5 Angstrom and the equilibrium position of the other ion is most likely to be along a line bisecting normally a C-C bond of C_{60} molecule. Using this information, we carried out TB-LMTO calculations for beryllium in C_{60} lattice and found that there were total energy minima positions when beryllium was on any face of the face-centered cubic C_{60} lattice between a corner C_{60} molecule and a face-centered C_{60} molecule along a line bisecting normally C-C bond of a C_{60} molecule. At equilibrium position, the distance of beryllium ion from the

center of C_{60} molecule is about 5.3 Angstrom and C-Be bond length comes out around 2 Angstrom. We find from TB-LMTO calculation that at this position, the average number of valence 2s electrons of beryllium ion is = 0.44. The uncertainty on this number is around 20% because of comparatively poor convergence of the code for these calculations. So using Hartree and Hartree's result [23], the decay rate of exohedral ${}^7\text{Be}-C_{60}$ complex should be faster by $\approx 0.03\%$ compared to that of ${}^7\text{Be}$ in Au. This result agrees with our experimental observation that the decay rate of exohedral ${}^7\text{Be}-C_{60}$ and that of ${}^7\text{Be}$ in Au are equal within 0.2%.

If we assume that ${}^7\text{Be}$ ions go to the octahedral or tetrahedral sites of face-centered cubic C_{60} lattice, then according to TB-LMTO calculations, the average number of 2s electrons of ${}^7\text{Be}$ should be 1.12 and 1.51 respectively. So using the method of ref[6], the decay rate of ${}^7\text{Be}$ should be faster than that of ${}^7\text{Be}$ in Au by 1.16% and 1.8% respectively, in complete disagreement with our experimental observation. Moreover if ${}^7\text{Be}$ is at octahedral site, then its distance from the center of the nearest C_{60} molecule would be about 7 Angstrom and so the length of shortest C-Be bond would be about 3.7 Angstrom. Similarly when ${}^7\text{Be}$ is at tetrahedral site of C_{60} lattice, then its distance from the center of the nearest C_{60} molecule is 6.1 Angstrom and the length of shortest C-Be bond is about 3 Angstrom. At this position, the line joining the center of the C_{60} molecule and ${}^7\text{Be}$ ion does not bisect C-C bond of C_{60} molecule, but passes through the center of the hexagonal opening of C_{60} molecule. It is also expected [14] that for most stable exohedral configuration, a beryllium atom should go to a site of high electron density. Our TB-LMTO calculations show that the electron density at tetrahedral site of C_{60} lattice should be about 50% more than that at octahedral site. However the electron density on a face of the lattice midway between two C_{60} molecules is about five times the electron density at the octahedral site. So from these qualitative arguments, we expect that the octahedral and tetrahedral sites should not be the equilibrium positions of ${}^7\text{Be}$ in fullerene C_{60} lattice. However our TB-LMTO calculations for the total energy of the system do not support this expectation, perhaps due to the model limitations mentioned above. In the case of endohedral ${}^7\text{Be}@C_{60}$ complex formation, although C-Be bond length would be 3.54 Angstrom since ${}^7\text{Be}$ is expected to be at the center of fullerene C_{60} cage, however at that position, ${}^7\text{Be}$ is equidistant from all 60 carbon ions and is held there by sixty C-Be bonds. So even if each bond is weak, there are sixty such bonds holding the beryllium ion.

In summary, we have found experimentally that the decay rate of exohedral ${}^7\text{Be}-C_{60}$ complex is equal to that of ${}^7\text{Be}$ implanted in Au within 0.2%. A radiochemical analysis of the irradiated sample shows that only 5.6% of the implanted ${}^7\text{Be}$ ions form endohedral ${}^7\text{Be}@C_{60}$ complexes and the remaining 94.4% of the ${}^7\text{Be}$ ions form exohedral ${}^7\text{Be}-C_{60}$ complexes. The measured decay rate of endohedral ${}^7\text{Be}@C_{60}$ complex is in agreement with recent accurate

measurement of Ohtsuki et al. [19]. It is interesting to note that the half-life of endohedral ${}^7\text{Be}@C_{60}$ complex is shorter than that of the exohedral complex by more than 1%. Our TB-LMTO analysis shows that for endohedral ${}^7\text{Be}@C_{60}$ complex, ${}^7\text{Be}$ ion should go to the center of C_{60} cage. For exohedral ${}^7\text{Be}-C_{60}$ complex, we expect that ${}^7\text{Be}$ should go to one of the faces of face-centered cubic C_{60} lattice forming exohedral complex with C-Be bond length ≈ 2 Angstrom.

We acknowledge useful discussion with R. Vandenbosch (University of Washington, USA), Ove Jepsen (Max Planck Institute, Germany) and J. Lu (Peking University, Beijing, China), G. P. Das (IACS, Kolkata, India) and L. M. Ramaniah (Bhabha Atomic Research Centre, Mumbai, India) and A. Mookerjee (S. N. Bose Centre for basic sciences, Kolkata, India).

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