

Molecular orbital calculations of beryllium insertion in C_n fullerene cages: $Be@C_n$ ($n=20, 60, 70, 80$) by nuclear recoil after particle capture

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The molecular structure and some properties of $Be@C_n$ ($n=20, 60, 70, 80$) endohedral metallofullerenes were analyzed using the HyperChem 7.0. Computational Chemistry Model Building Program. The results were in agreement with previous calculations using the ab initio method based on an all-electron mixed-basis approach within the framework of the local-density approximation. In the case of 7Be , the ion is inside the fullerene cage and tries to make an electronic connection with a six-membered ring of the fullerene cage in order to improve its atomic orbital distribution in the valence layer. Due to the ion radius value of only 0.45 Å and electronic capture decay, 7Be appears to emerge as an ideal tool for studying radionuclide half-life variation in different hosts.

Introduction

The fullerenes are a recently discovered class of chemical compounds. Originally searched in interstellar dust, they were synthesized, isolated, and characterized in chemical and physical terms during the 1990s. Made of sp^2 hybridized carbon atoms, they are oystalline allotropes of carbon, as are diamond (sp^3 hybridization) and graphite (sp^2 hybridization). Characteristic of a fullerene is its delocalized electron cloud shared by all of the carbon atom constituents. In this case, the four electrons ($2s^2 2p^2$) of the L-valence shell are redistributed into three hybrid sp^2 orbitals with trigonal symmetry, which give rise to the bonds among the carbon atoms, and a nonparticipating p-type orbital (perpendicular to the hybrid orbital plane) that is involved in the electronic cloud thus delocalized and shared by every atom. Fullerene molecules (Fig. 1) reach high degrees of symmetry, with maximum delocalization across all atoms in the molecule.

If a fullerene occurs as a negative ion with various charge (-1, -2, -3), the additional electrons are distributed almost equally to all carbon atoms. In these conditions, charge distribution per carbon atom is -2/20 for C_{20} , -2/60 for C_{60} , -2/70 for C_{70} , -2/80 for C_{80} , etc. Through synthesis from graphite, the four fullerenes mentioned above are the most abundantly produced of all fullerenes, which makes them quite important in practice.

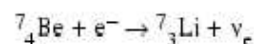
Trapping is the physico chemical phenomenon by which a positive ion is encapsulated inside an existing fullerene. The ion, which may e.g. be alkali or beryllium, has a shorter radius than that of the pentagonal and hexagonal rings of the fullerene cage structure. It enters the molecule through a six-atom ring, the area of which is larger than that of the pentagonal arrangement, and remains inside at a certain distance

from the center of the molecule, not far from the ring through which it has gone in.

C_{60} is the most representative of the fullerenes which accounts for its widespread theoretical and practical use in the making of ${}^7Be@C_{60}$ and other related compounds based on alkali metals.^{1–3}

It is made of 12 rings of five and 20 rings of six carbon atoms, as shown in Fig. 1. The C_{20} fullerene consists only of rings of five carbon atoms.

Related to the ion part, 7Be is the first radionuclide in the periodic system of the elements to possess excess protons in its nucleus. This makes it liable to capture electrons from its own shells, a process which gives rise to a stable nuclide and the release of a neutrino:



There is an 80.6% probability that the electron capture should result directly in the nucleus of 7_3Li and a 10.4% probability that it should first lead to a metastable level from which the nucleus is de-excited to 7_3Li through the release of a 0.477 MeV gamma-quantum. The above reaction takes place either way.⁴

In the case of a beryllium atom $K(1s^2), L(2s^2, 2p^0)$, the capture may involve an electron on the K shell (s-type orbitals) or L shell (s-type orbitals, since the p-type orbitals are vacant).

The theoretical ratio of the decay constant for the L-shell electron capture to the constant for K-shell electron capture is $[\lambda_L/\lambda_K]_{th} = 0.125$.⁵ Similar ratios for the other nuclides (${}^{36}Cl, {}^{37}Ar, {}^{51}Cr, {}^{54}Mn, {}^{55}Fe, {}^{57}Co, {}^{58}Co, {}^{65}Zn, {}^{71}Ge, {}^{79}Kr$) that are liable to undergo electron capture were experimentally determined and found to be very close to 0.125, actually ranging from 0.103 ± 0.003 for ${}^{37}Ar$ to 0.119 ± 0.007 for ${}^{58}Co$. Unlike the beryllium atom, these nuclides are located in the periodic system in such way that their K and L shells are inner shells and have nothing to do with the outer valence shells that

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engage in chemical interactions with other surrounding atoms.

In these conditions, the ^7Be isotope provides the opportunity for a firsthand study of electron capture from the L shell which is also a valence shell. Moreover, the beryllium ion Be^{2+} , in which the L shell is vacant ($1s^2, 2s^0, 2p^0$), makes it possible to study the behavior under of K-shell electrons capture. Nuclear emission in this case is limited to the electronic neutrino, which is hard to track or monitor, and 0.477 MeV gamma-quantum, which has been experimentally detected in the study of ^7Be decay. Neither characteristic X-rays nor Auger electrons occur in this process, since they would occur as a result of electron vacancies occupied by higher shell electrons that are not present in this case.

As a characteristic of such transitions, the radioactive decay constant depends slightly on external conditions, namely on the nature of the chemical bond which has a decisive influence on electron cloud density. In our case, the radioactive decay constant is influenced by the nature of the chemical bond, that is to say, by the type of chemical compound in which beryllium enters. This makes ^7Be atoms and especially their two-charge positive ions quite interesting to study. The decay constant change is physically reflected in a half-life increase or decrease, an effect that was predicted as early as 1947^{6,7} and was experimentally studied during the following years.⁸⁻¹⁴ As far as ^7Be was concerned, experiments showed that its decay constant in beryllium fluoride (BeF_2) and beryllium oxide was lower by 0.070% and 0.010%, respectively, than in metallic beryllium. In an attempt to detect an increase in this effect, subsequent studies² determined ^7Be half-life in various other chemical combinations. The highest effect, higher by one order of magnitude than all other effects observed, was found in the compound Be-fullerene C_{60} : $\Delta\lambda = -0.835\%$ ($\Delta\lambda, \% = [100 \times (\lambda_{\text{compound}} - \lambda_{\text{Be-beryllium}})] / \lambda_{\text{Be-beryllium}}$). This is due to the chemical nature of fullerenes and the type of bonds they can establish with other chemical elements, which have a positive influence on the decay-related properties of ^7Be .

The next nuclide after ^7Be that can undergo radioactive decay, though without the benefit of a special structure such as beryllium, is ^{36}Cl . With a radius of 1.80 Å, it will be impossible for the chlorine ion to penetrate into the fullerene even through the broader six carbon-atom ring. This seems to single out $^7\text{Be}^{2+}$ as the one opportunity for studying half-life variation by fullerene trapping.

Without a positive ion alternative for modifying half-lives, one can still try by modelling to vary $\Delta\lambda$ by using a different fullerene as trapper.

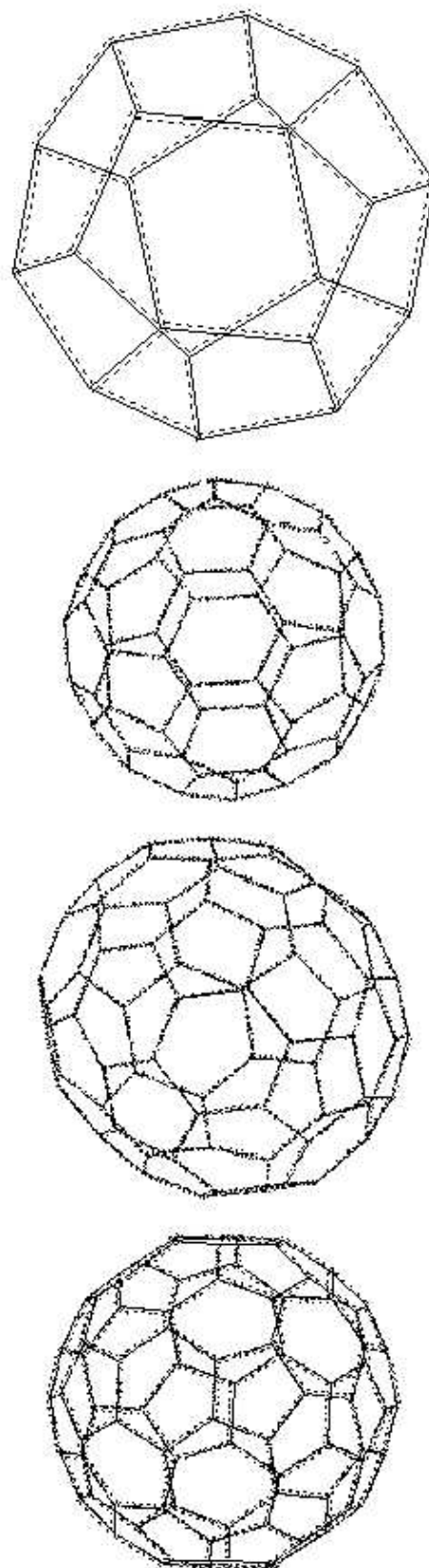


Fig. 1. Structures of fullerenes C_{20} , C_{60} , C_{70} , and C_{80}

Methods

Chemical elements were first inserted into fullerenes as argon atoms were trapped inside the C_{60} fullerene by neutron irradiation in a 1995 experiment.¹⁵ Endohedral radiofullerenes were subsequently obtained through nuclear recoil implosion.^{16–18} For example, ${}^7\text{Be}@C_{60}$ was formed by using nuclear recoil to introduce ${}^7\text{Be}$ with two positive charges into a fullerene ion-molecule. The nuclear reactions used to this end were ${}^7\text{Li}(p,n){}^7\text{Be}$ and ${}^{12}\text{C}(\gamma,an){}^7\text{Be}$. In the former, a homogeneous blend of purified fullerene and lithium carbonate was bombarded with 12 MeV protons for 2 hours at a current of 2 μA . In the second reaction, a purified fullerene sample was wrapped in aluminum foil and exposed to direct irradiation in a quartz tube. In this geometry, the sample was subjected to bremsstrahlung radiation with $E_{\text{max}} = 50$ MeV from a Pt sample that was itself under bombardment for 12 hours by a 300 MeV electron flux at 120 μA .^{1,2}

After irradiation, both fullerene samples were dissolved in carbon disulfide and filtered through a Millipore filter to remove insoluble by-products and lithium compounds. Once the solvent had evaporated, the soluble fraction was dissolved again in, toluene:hexane (7:3), and injected into an HPLC column. The collected fractions were checked for the radioisotope ${}^7\text{Be}$ by measuring the gamma-spectra with a germanium detector coupled to a multichannel analyzer. The detector had 1.5 keV resolution energy in FWHM for the characteristic 477 keV beryllium photopeak. The calculated half-lives for ${}^7\text{Be}@C_{60}$ and beryllium inserted into a metallic beryllium matrix were 52.68 ± 0.05 days and 53.12 ± 0.005 days, respectively. According to these values, the endohedral compound's time was shorter by 0.835%. The result reflected the difference in wave functions between the beryllium ion inside the compound and the beryllium atom inside the metallic beryllium matrix.²

The reaction was first studied by computational chemistry using an ab initio method for dynamic simulation.¹ This helped to predict the structure and characteristics of the resulting compound as well as the reaction mechanism and optimum velocity of the beryllium particle. It was calculated that if a beryllium ion ${}^7\text{Be}^{2+}$ with 5 eV kinetic energy hit perpendicularly at the center of a six-carbon-atom ring of C_{60}^{2-} , it would have easily penetrated the fullerene molecule and become trapped at ~ 1.0 Å depth from the fullerene cage center, right behind the ring by which it entered. The penetration was due to be so smooth because the beryllium ion radius is much shorter than that of the carbon atom ring (the ratio is $0.45/1.23 = 0.365$). The study also indicated that a beryllium ion of similar kinetic energy hitting a C–C bond would have warped the molecule, while an ion of higher kinetic energy

would have destroyed the molecule no matter where it would have hit. The experiments confirmed these results, as the fullerene molecule was to a great extent destroyed until the beryllium ions lost part of their kinetic energy through recoil and came close to ~ 5 eV, an energy at which collisions with the fullerene molecules led to their trapping instead of their destruction.¹

The Japanese authors underscored the need for a more detailed theoretical study of the structure and properties of ${}^7\text{Be}@C_{60}$. Their ab initio calculation is based on all-electron mixed-basis approach within framework of the local-density approximation.¹ The method of simulation employed is the same as a previous work concerning the stability and reactivity of C_{60} and the Li insertion into C_{60} .¹⁹ The authors put one C_{60} molecule and one Be atom in a supercell with zero and 5 eV initial velocities for C_{60} and Be, respectively. They performed six Steepest-Descent iterations between two adjacent updates of atomic positions in order to converge the electronic states, and chose $\Delta t = 4$ a.u. ~ 0.1 fs as the basic time step. For rescaling velocity and assuming a Fermi-Dirac distribution of electronic states, the simulation temperature of the whole system was set to be $T = 1000$ K.

In this order it could help to show in detail the way in which the electronic density of beryllium changes depending on the type of fullerene C_n ($n = 20, 60, 70, 80$) that does the trapping. Ultimately, such a study could show whether there can be any other fullerene that would even more sharply modify the half-life of the ${}^7\text{Be}$ nuclide. Conversely, it could help determine whether another nuclide capable of electronic capture would be able to substitute for beryllium in the endohedral compounds and increase the gap between that nuclide's decay constant inside the fullerene and its commonly accepted decay value.

We simulated the molecules by computational chemistry and studied their properties, taking into account the values we obtained by optimizing towards a geometry of minimum potential energy. Some new aspects of the properties on which we focused included: distances between the nuclide and certain atoms in the molecular complex (fullerene); initial partial charge of particles in the molecular system (endohedral compound); final partial charge (electrostatic potential) of the nuclide particle following optimization; post-optimization electronic density in the valence shell of the divalent ${}^7\text{Be}$ ion, and the energy binding atoms in the molecular system.

The following steps were necessary in the computations: "building" of $\text{Be}@C_n$ ($n = 20, 60, 70, 80$) structure by insertion of the ${}^7\text{Be}$ ion in the plane of the six (five for C_{20}) membered ring of the fullerene; use "Restraints" option for the distance between the beryllium ion and the same six (five)-membered ring

toward the cage center; geometry optimization using MM⁺; Polak-Ribière optimizer, RMS (Gradient) of kcal/mol·Å; single point calculations; geometry optimization using semiempirical AM1 method; Polak-Ribière optimizer, RMS (Gradient) of 0.1 kcal/mol·Å (then 0.01 kcal/mol·Å), accelerated convergence, singlet state, RHF, total charge zero, spin multiplicity of one; single point calculations; calculating vibrations and performing a vibrational analysis (all normal modes of vibration must have only positive values for a molecule reaching minima on EPS).

Results and discussion

Given the unique chemical structure of the C₆₀ molecule the electronic density inside it considerably affects the density of contact electrons surrounding the ⁷Be nucleus. Studying the chemical behavior of the beryllium-fullerene compound by computational chemistry therefore appears to open some interesting prospects on reducing half-lives of the radionuclides.

Firstly we calculated the electron densities in the valence shell orbitals of ⁷Be²⁺ [1s², 2s⁰ 2p⁰]. Initial electron density in valence shell $D_{in}=0 e^-$ and of the fullerene²⁻ carbon atoms that carry out the trapping. The fullerene C₂₀ [1s², 2sp²(3e⁻) 2p(1e⁻) and -2/20 e⁻ of shared electron cloud; Initial electron density in valence shell $D_{in}=4.100 e^-$] is seen to have the highest electron density in carbon atom valence shell compared to C₆₀ [1s², 2sp²(3e⁻) 2p(1e⁻) and -2/60 e⁻ of shared electron cloud. Initial electron density in valence shell $D_{in}=4.033 e^-$], C₇₀ [1s², 2sp²(3e⁻) 2p(1e⁻) and -2/70 e⁻ of shared electron cloud. Initial electron density in valence shell $D_{in}=4.029 e^-$] or C₈₀ [1s², 2sp²(3e⁻) 2p(1e⁻) and -2/80 e⁻ of shared electron cloud. Initial electron density in valence shell $D_{in}=4.025 e^-$], but the trapping area for the beryllium ion is small (radius of ring circumscribed to 5-atom ring is 0.97 Å) compared with the six-carbon-atom areas of 1.23 Å in fullerenes C₆₀, C₇₀, or C₈₀.

The beryllium ion has a radius as short as 0.45 Å, but has to overcome the molecular forces in the C₆₀ structure. Therefore, the larger the carbon ring area, the better odds it has to trap the ion. ⁷Be@C₆₀ is a stable chemical compound that was experimentally obtained through the trapping of positively (+2) charged ions of the ⁷Be radionuclide by negative (-2) ions of the fullerene C₆₀¹⁻³. The physico chemical properties of the newly developed substance, ⁷Be@C₆₀, reflected the special properties of the original components as shown in Fig. 2.

To this end, we used molecular mechanics (MM⁺) and semi-empirical (AM1) calculations in order to estimate the mechanical properties of molecules such as ⁷Be@C₂₀, ⁷Be@C₆₀, ⁷Be@C₇₀ and ⁷Be@C₈₀ (column 1), and then optimized these structures to predict some of their molecular properties, as we seen in Table 1. The objective in these calculations was to optimize the structures of the endohedral compounds every 0.5 Å as the ⁷Be ion traveled inside the fullerene cage after trapping ("restraint" condition).

In our initial system, the beryllium ion charge was +2.000 and the charge of the fullerene molecule was -2/n (where n=20, 60, 70, 80). The final partial charge of the ⁷Be ion, as calculated by our program, is given in column 4, while column 5 shows the resulting electron density in the valence shell orbitals, as calculated by subtraction.

In column 2 we entered the real final distances (close to the multiples of 0.5 for which we did out calculation) at which the molecular system reached minimum energy on the potential energy map. Values shown in bold characters are those of endohedral compounds in which the trapped ⁷Be ion assumed central position inside the fullerene molecule, and the other values correspond to the global minimum binding energy of the systems (column 3). Underscored values refer to the situation in which maximum electron density was reached in the valence shell orbitals of the trapped metallic ion.

Beryllium trapping by the fullerenes C₂₀, C₆₀, C₇₀, and C₈₀ led to energetically stable structures.

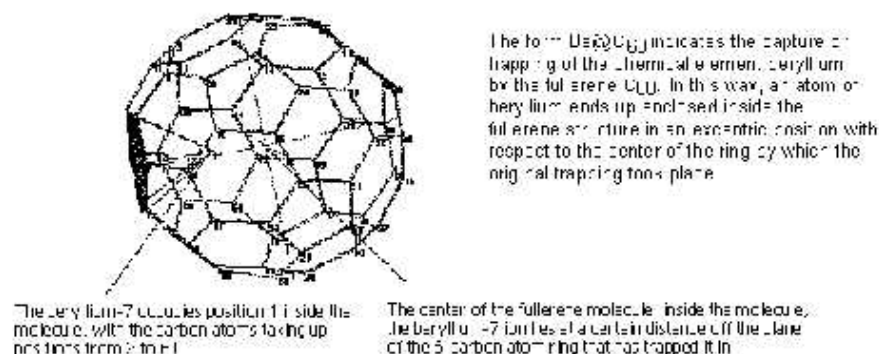


Fig. 2. Structure of ⁷Be@C₆₀.

Table 1. Calculated molecular properties of ${}^7\text{Be}@C_{20}$, ${}^7\text{Be}@C_{60}$, ${}^7\text{Be}@C_{70}$ and ${}^7\text{Be}@C_{80}$

Compound (1)	Distance from carbon ring to ${}^7\text{Be}$, Å (2)	Binding energy, kcal/mol (3)	Beryllium charge, Mulliken units (4)	${}^7\text{Be}$ electron density after trapping, D_{in} (5)
${}^7\text{Be}@C_{20}$	1.70	-2336.66	+0.98	1.02
${}^7\text{Be}@C_{60}$	2.00	-9186.31	-0.24	2.24
${}^7\text{Be}@C_{70}$ with trapping through a six-atom ring close to the shorter axis	3.25	-9213.63	-0.07	2.07
${}^7\text{Be}@C_{70}$ with trapping through a six-atom ring close to the longer axis	1.66	-10789.85	+1.02	0.98
	3.28	-10783.67	-0.04	2.04
${}^7\text{Be}@C_{80}$	1.99	-10784.25	+1.04	0.96
	3.76	-10784.18	-0.04	2.04
	1.62	-12415.27	+0.98	1.12
	3.87	-12417.27	-0.02	2.02

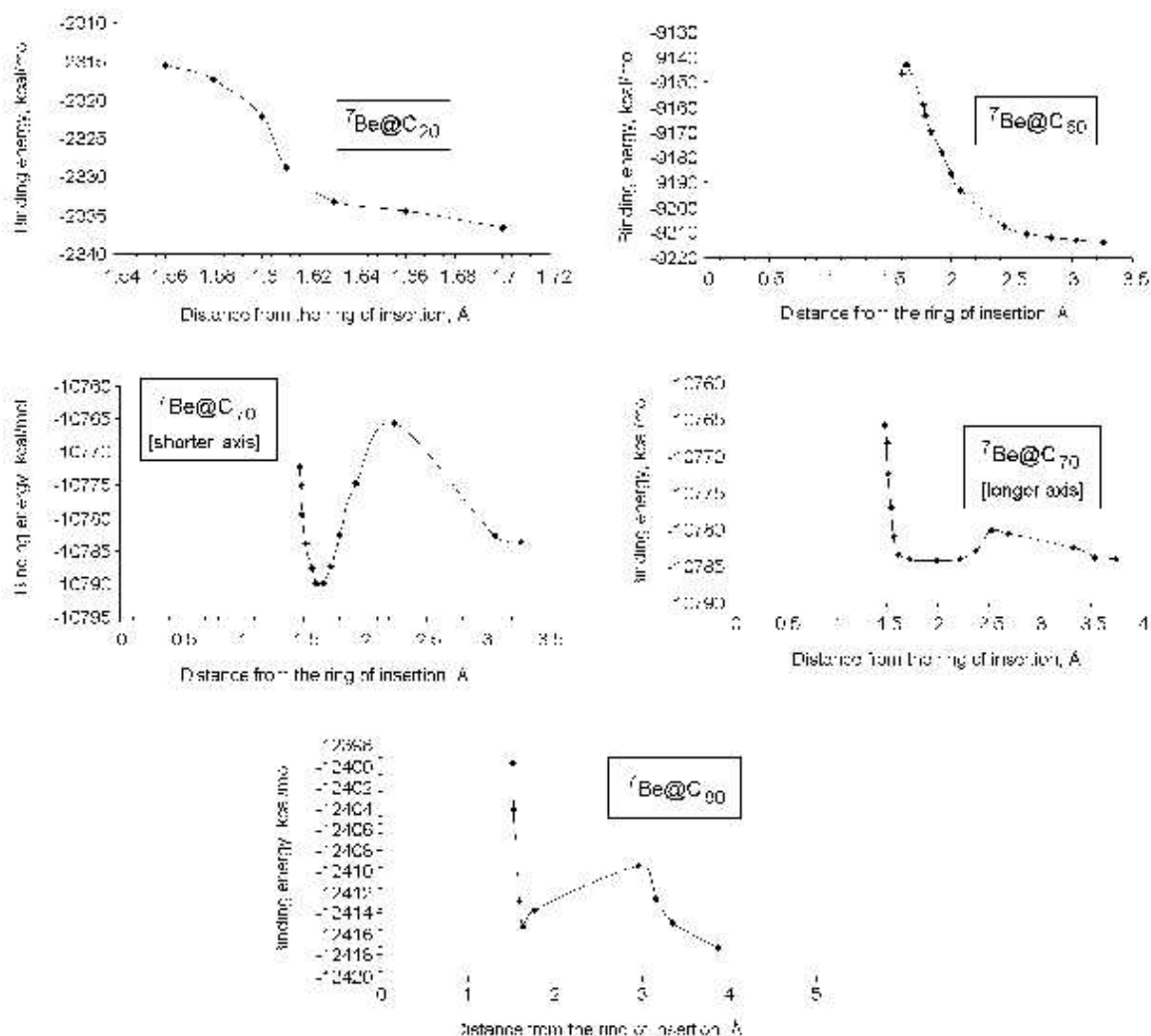


Fig. 3. Optimized structures as derived from the binding energy – distance dependence

For spin multiplicity of one, the highest energy stability in every compound series was found where the ${}^7\text{Be}$ ion resided at the center of the fullerene, except of ${}^7\text{Be}@C_{70}$ with trapping through a six-atom ring close to the shorter axis (Fig. 3).

Figure 3 proves that ${}^7\text{Be}@C_{60}$ is energetically the most stable structure. In the case of ${}^7\text{Be}@C_{60}$, earlier theoretical study as well as the experiments indicated that the ${}^7\text{Be}$ ion was ideally positioned inside the cage at about 1 Å depth from the fullerene cage center, right

behind the ring by which it entered.¹ Roughly, the same value was found for ${}^7\text{Be}@C_{60}$ (1.25 Å). For larger ring fullerenes the distances are: 1.62 Å for ${}^7\text{Be}@C_{70}$ (with trapping through a six-atom ring close to the shorter axis), 1.77 Å for ${}^7\text{Be}@C_{70}$ (with trapping through a six-atom ring close to the longer axis), and 2.25 Å for ${}^7\text{Be}@C_{80}$.

Once the beryllium ion had been trapped, the electron density in the L shell indicated that at least one electron was gained through optimum positioning in terms of the shared electron cloud of the fullerene molecule (Fig. 4).

The beryllium ion in ${}^7\text{Be}@C_{60}$ gained the two electrons it needed to become an atom and was even able to collect more than two electrons in the L shell through sharing of the delocalized fullerene electrons.

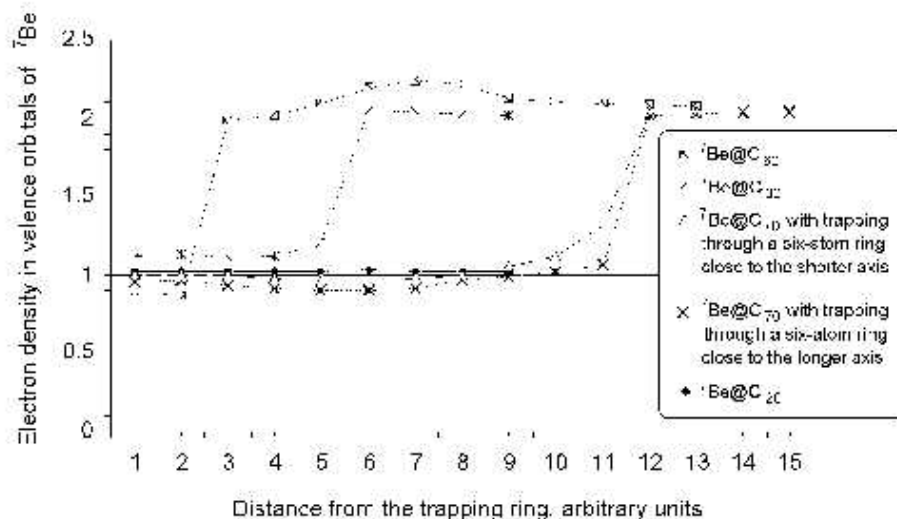


Fig. 4. Electron density distribution in ${}^7\text{Be}$ ion after trapping

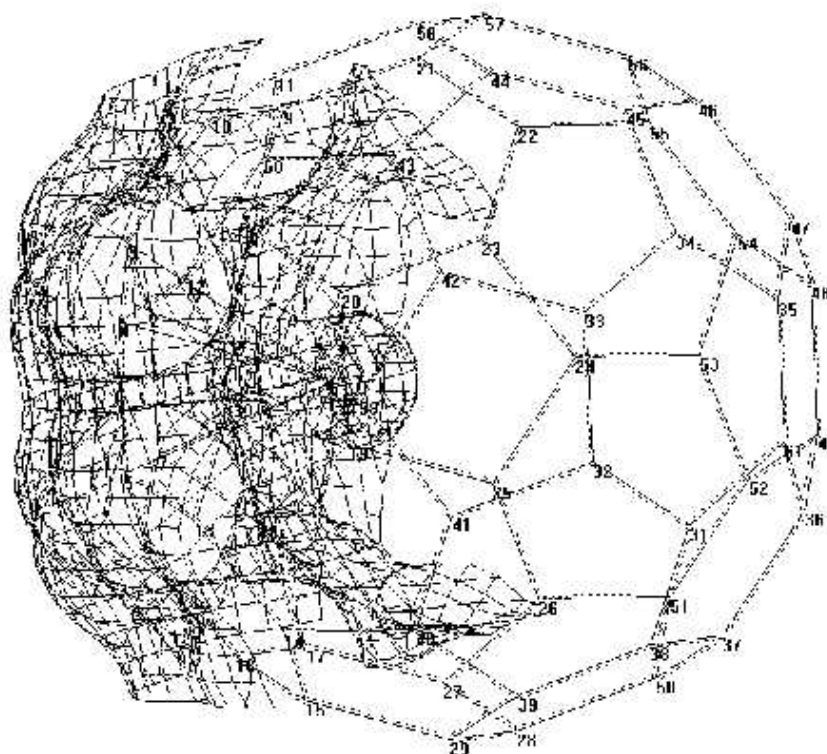


Fig. 5. 3D molecular orbital isosurface of the ${}^7\text{Be}@C_{60}$ with ${}^7\text{Be}$ ion near to the six trapping membered ring

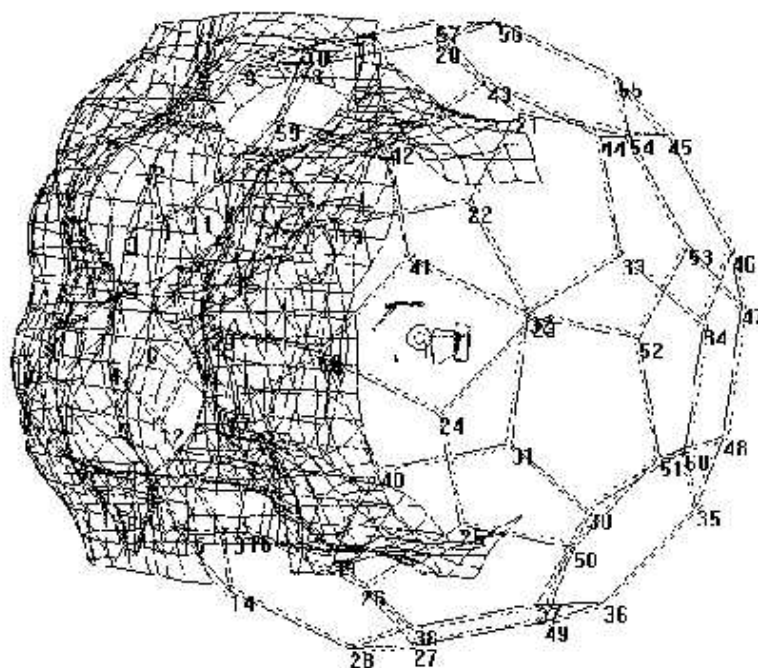


Fig. 6. 3D molecular orbital isosurface of the ${}^7\text{Be}@C_{60}$ with ${}^7\text{Be}$ ion located at the center of the fullerene cage

This arrangement of the structure provides a singular opportunity for beryllium to regain the two electrons it lost by ionization and get in contact with the delocalized shared electron cloud of fullerene C_{60} , that can increase its negative charge (the charge per atom changes from +2 to -0.240). An increased likelihood of capturing an electron from the K shell or L shell (where they are now in excess) also increases the probability of the nuclear phenomenon that is physically expressed on the statistic level by the half-life of a radioactive compound, which in our case is ${}^7\text{Be}@C_{60}$.

In graphical terms, this singular position corresponds to an optimum probability density of the electron cloud shared by a ring of sp^2 hybridized carbon atoms (Fig. 5).

When placed at the center of the fullerene C_{60} cage, the beryllium ion is isolated from the maximum density area of the shared electron cloud. Beryllium gets back its two lost electrons but nothing more than that (Fig. 6).

Conclusions

The divalent ${}^7\text{Be}$ cation proves to be a unique example for studying the variation of nuclear half-life of a radionuclide on inclusion into a fullerene cage.

Trapping of ${}^7\text{Be}^{2+}$ into C_{20} , C_{60} , C_{70} , and C_{80} fullerenes yields stable structures. For spin multiplicity of 1, calculations show that the global energetic minimum is attained for the central position except for ${}^7\text{Be}@C_{70}$. After trapping, the ${}^7\text{Be}$ cation occupies a position at distances varying between 1.25 \AA for

${}^7\text{Be}@C_{60}$ and 2.25 \AA for ${}^7\text{Be}@C_{80}$ from the center of the endohedrally filled cage. This corresponds to the maximal electronic density of orbitals after trapping. Among all studied compounds, ${}^7\text{Be}@C_{60}$ possesses the most stable structure that can be formed along the axis that goes from the cage center to the center of the ring closest to the trapped ion.

The value of the partial electrical charge (-0.24 Mulliken units) for the ${}^7\text{Be}$ ion positioned at 1.25 \AA from the cage center proves that there is an excess of electrons on the L-shell of the cation (i.e., a charge of -2.24 instead of -2) and this causes an increase of the probability of electron capture resulting in a decrease of the half-life of ${}^7\text{Be}$.

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