EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Letter of Intent to the ISOLDE and Neutron Time-of-Flight Committee

PAC study of the static and dynamic aspects of an atom inside a fullerene cage

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Abstract

We intend to encage two types of probes, metallic and nonmetallic atoms, in C60 in different experiments aiming to study the interaction and biding of such atoms inside the cages. To study these interactions we will use TDPAC, a nuclear probe technique that relies on the interaction of the nuclear quadrupole moment with the electric field gradient (EFG) produced by the surrounding electrons. The interpretation of the results will be done via theoretical calculations using, e.g., density functional theory for different configuration models. Such type of information would be of great help to understand the mechanism of endofullerene formation, which in turn would tell the route for the synthesis of the required endofullerene in significant quantities for applications. The present Letter-of-Intent aims at understanding procedures for implementing a detailed program of research.

Requested shifts: 3 shifts, (split into 3 runs over 1 year)

Introduction and Motivation

After the discovery of fullerene [1] compounds in this group which received much attention in basic research and in applications are the endofullerenes. The behavior of an atom or a cluster of atoms inside the fullerene cage makes such compounds suitable for various applications in the area of superconductivity, lasers, and ferroelectric materials [2]. A very promising application of these compounds lies in its medical use [3]. An optimistic conjecture has been made to use endofullerenes for the storage of nuclear waste by entrapping the radioactive atoms inside the cage. The self-healing property of C-C bonds is helpful in preserving the cage even if C-C bonds are broken by the radiation from radioactive atoms inside the cage. Besides the applications mentioned above, basic research interest is enormous as far as the chemical bonding of the atom inside the cage is concerned. This is the most important aspect in the study of endofullerenes.

The most well known fullerene, C_{60}, has three degenerate lowest unoccupied molecular orbitals (LUMOs), energetically slightly above the highest occupied molecular orbitals (HOMOs) [4]. These can accommodate up to six electrons. A trivalent metal ion contributing three electrons to make LUMOs half-filled stabilizes the endofullerene. However, since the inner side of the cage is electrostatically slightly positively charged as the π-electrons of the sp^2-carbon atoms are bulged outside, a negatively charged ion is expected to be stabilized inside the cage. The energy consideration due to electron transfer between the entrapped atom and the cage is the decisive factor in the stabilization of the endofullerenes.

The laser ablation or the arc discharge from the metal doped graphite electrode produces the endofullerene in situ. In this process the thermodynamics decides the formation of the endfullerene. However, in the case of the post-insertion using ion implantation into the pre-existing fullerene, the atom that once enters the cage has no chance to come out. So it is only the barrier that decides the formation of the endofullerene. Once the atom enters the cage the question remains how it behaves inside the cage. An EPR study [5] indicates that while a nitrogen atom inside the C_{60} cage does not interact with the carbon atoms and remains in the central position of the cage, Cu in Cu@C_{60} occupies a well defined (minimum potential) position inside the cage. This indicates that there is a bond of the Cu atom with C atoms. An NMR study [6] and the MEM/Rietveld method [7] for imaging of diffraction data indicates that the metal atoms inside the cage rotate. A small rotational barrier in such cases can help to control the rotation by temperature. This property of the endofullerenes can be used to develop interesting molecular devices. It is important to know the states of the atom inside the fullerene cage in terms of its position in the cage, charge states, dynamics etc. These parameters would be of great help to understand the mechanism of endofullerene formation which in turn would tell the route for the synthesis of the required endofullerene in significant quantities for the applications mentioned above.

TDPAC, a nuclear probe technique, relies on the interaction of the nuclear quadrupole moment with the electric field gradient (EFG) produced by the surrounding electrons. The angular correlation between γ-rays emitted in a cascade is exploited to obtain information on the electron distribution through the measurement of the EFG. The EFG and its asymmetry are the fingerprints of the electronic state of the probe atom. One thus can identify the position of the atom inside the fullerene cage with the support of theoretical calculations using e.g. density functional theory. In case there is rotation or grazing movement of the probe inside the cage, it will show up as a time dependent perturbation of the angular correlation.

Proposal summary

We intend to encage two different types of probes, i.e. metallic and nonmetallic atoms, in C_{60} in different experiments. The probes are

(i) Metallic : ^{111m}Cd and ^{199m}Hg

(ii) Nonmetallic : ^{77}Br and ^{80m}Br

The choice of TDPAC isotopes is made on the following basis: to start with, probes with isomeric decays should be chosen because they guarantee that apart from recoil there are no complications due to transmutation. Such short-lived isotopes are produced at ISOLDE. ^{111m}Cd and ^{199m}Hg are suitable isotopes with convenient nuclear properties which are widely used at ISOLDE. In the case of Br we are in the position to compare the result for the isomeric decay of ^{80m}Br with those of ^{77}Se, the daughter of ^{77}Br. It is anticipated that the results will be rather different.

The C_{60} target with a thickness of ~200nm on 1 mil Al-foil would be produced and transported from Kolkata, India. A fluence of approximately 10^{11} is required to get a significant quantity of endofullerenes for coincidence counting. The implantation of the ions in the energy range from 30-60 keV followed by chemical separation [8] will be carried out to get radio-chemically pure endofullerenes. Radioactive atoms other than those accommodated inside the cage will be removed by chemical separation. The radiochemistry group at Kolkata has ample experience with the preparation of endofullerenes, PAC-spectroscopy, and ab-initio calculations of EFGs. The liquid sample obtained after chemical separation is then dried on an Al-foil for PAC counting either through γ-e or γ-γ coincidence with spectrometers existing at ISOLDE. The other authors have long-standing expertise with short-lived radionuclides produced at ISOLDE and PAC-spectrometers. If successful, temperature dependent studies will follow which could reveal dynamic aspects of the probe inside the cage.

Summary of requested shifts:

We estimate that **three parasitic shifts** would be required to test the feasibility of the approach, two to be used during Hg and Cd beam times, testing metallic probes, the other for working with the Se and Br nuclear probes, obtained on the same beam time.

References:

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Appendix

DESCRIPTION OF THE PROPOSED EXPERIMENT

The experimental setup comprises: *(name the fixed-ISOLDE installations, as well as flexible elements of the experiment)*

Part of the	Availability	Design and manufacturing
SSP-GLM chamber	☒ Existing	☒ To be used without any modification
Existing equipment on the solid state labs in building 115 - 6 detector PAC standard setups - annealing furnaces - glove boxes	☒ Existing	☒ To be used without any modification ☐ To be modified
	☐ New	☐ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing

HAZARDS GENERATED BY THE EXPERIMENT

(if using fixed installation) Hazards named in the document relevant for the fixed SSP-GLM chamber and building 115 installations.

Additional hazards:

Hazards	*SSP-GLM*	*Building 115*	*[Part 3 of the experiment/equipment]*
Thermodynamic and fluidic			
Pressure	[pressure][Bar], [volume][l]		
Vacuum	10-6 mbar at SSP chamber 10 during collections		
Temperature	295 K room temperature collections		
Heat transfer	-		
Thermal properties of materials	-		
Cryogenic fluid		Liquid nitrogen, 1 Bar, few litres used during the PAC measurements on appropriate dewar	
Electrical and electromagnetic			
Electricity	[voltage] [V], [current][A]		
Static electricity			
Magnetic field	[magnetic field] [T]		
Batteries	☐		
Capacitors	☐		

Ionizing radiation			
Target material	[material]		
Beam particle type (e, p, ions, etc)			
Beam intensity			
Beam energy			
Cooling liquids	[liquid]		
Gases	[gas]		
Calibration sources:	☐		
• Open source	☒ Produced at ISOLDE: 199mHg 111mCd 77Br 80mBr	Sources to be measured at 115	
• Sealed source	☒	22Na sources provided by RP services at CERN, used at 115	
• Isotope	199mHg(42m) 111mCd (48m) 77Br (57h) 80mBr (4.4h)		
• Activity	199mHg < 3e7 Bq 111mCd < 3e7 Bq 77Br < 3.5e5 Bq 80mBr < 4.5e6 Bq		
Use of activated material:	none		
• Description	☐		
• Dose rate on contact and in 10 cm distance	[dose][mSV]		
• Isotope			
• Activity			
Non-ionizing radiation			
Laser	none		
UV light	none		
Microwaves (300MHz-30 GHz)	none		
Radiofrequency (1-300MHz)	none		
Chemical			
Toxic	[chemical agent], [quantity]		
Harmful		Toluene (ICSC: 0078) and hydrochloric acid (ICSC: 0163) , in quantities less than few centilitres per chemical. We will use toluene and hydrochloric acid for solvent extraction to separate the endofullerene from the radioactivity attached exohedrally with fullerene on ventilated fume hood on building 115. The respective ICSC forms have been printed and will be handled during preparation and experiments.	
CMR (carcinogens, mutagens and substances toxic to reproduction)	[chemical agent], [quantity]		
Corrosive	[chemical agent], [quantity]		

Irritant	[chemical agent], [quantity]		
Flammable	[chemical agent], [quantity]		
Oxidizing	[chemical agent], [quantity]		
Explosiveness	[chemical agent], [quantity]		
Asphyxiant	[chemical agent], [quantity]		
Dangerous for the environment	[chemical agent], [quantity]		
Mechanical			
Physical impact or mechanical energy (moving parts)	[none]		
Mechanical properties (Sharp, rough, slippery)	[none]		
Vibration	[none]		
Vehicles and Means of Transport	[none]		
Noise			
Frequency	[frequency],[Hz] Ambient noise at the ISOLDE Hall, building 170		
Intensity	Ambient noise at the ISOLDE Hall, building 170		
Physical			
Confined spaces	[none]		
High workplaces	[none]		
Access to high workplaces	[none]		
Obstructions in passageways	[none]		
Manual handling	All samples and sample holders are manually handled either by long tweezers to insert and extract the sample holder into and out of the SSP implantation chamber at GLM, or when manipulating the samples and sample holders inside glove boxes or fume houses on building 115 r-007	All samples and sample holders are manually handled either by long tweezers to insert and extract the sample holder into and out of the SSP implantation chamber at GLM, or when manipulating the samples and sample holders inside glove boxes or fume houses on building 115 r-007	
Poor ergonomics	[none]		

0.1 Hazard identification

3.2 Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): *(make a rough estimate of the total power consumption of the additional equipment used in the experiment)*

There is no additional equipment with relevant power consumption on these small-scale experiments.