The Bio-Nano-ECRIS project:
a new ECR ion source at Toyo University to produce endohedral fullerenes

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Takashi Uchida[1]

K. Tanaka[1,2], H. Minezaki[1], M. Muramatsu[1,3], S. Biri[4],
T. Asaji[2], A. Kitagawa[3], Y. Kato[5], Y. Yoshida[1]

[1]Bio-Nano Electronics Research Centre, Toyo University
[2]Tateyama Machine Co., Ltd.
[3]National Institute of Radiological Sciences (NIRS)
[4]Institute of Nuclear Research (ATOMKI)
[5]Osaka University

Outline

- Introduction
  - Endohedral fullerenes
  - Fullerenes in electron cyclotron resonance (ECR) plasma
- Design aspect of the Bio-Nano-ECRIS apparatus
  - Concept of the Bio-nano ECRIS apparatus
  - Overview
  - Magnetic system
- Initial experiments
  - Production and extraction of ions of fullerenes and carbons-loss fullerenes
  - Formation and extraction of fullerene and N_2 mixture plasma (synthesis of NC_n or $N@C_n$)
- Summary & Future plan

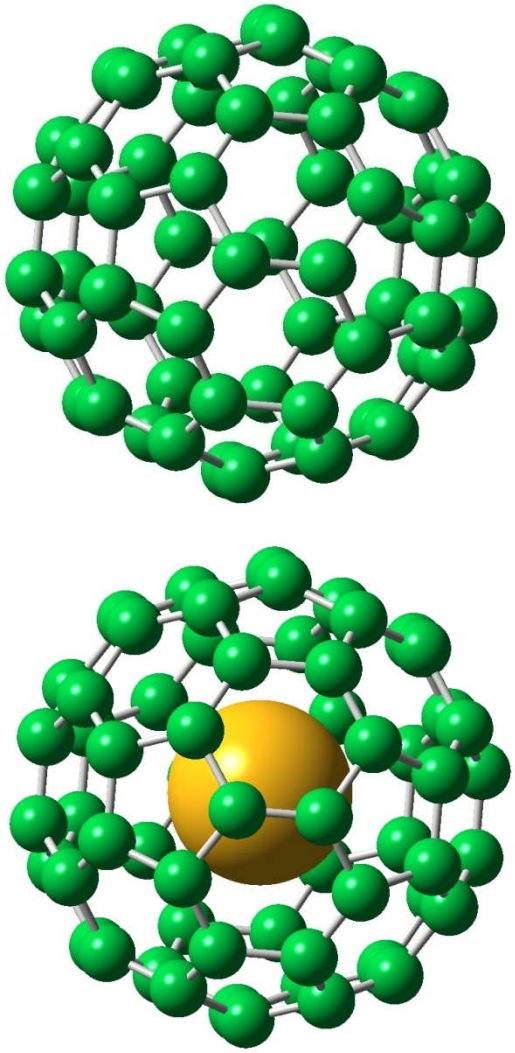
Introduction

◆ Endohedral fullerene

◆Fullerenes have a unique type of inner empty space with their unusual cage-like structures. Atoms may reside in this space and form endohedral fullerenes.

◆Endohedral fullerenes have novel physical and chemical properties that are very important for their potential applications such as magnetic resonance imaging agents, biological tracing agents, organic ferromagnets and superconductors etc.

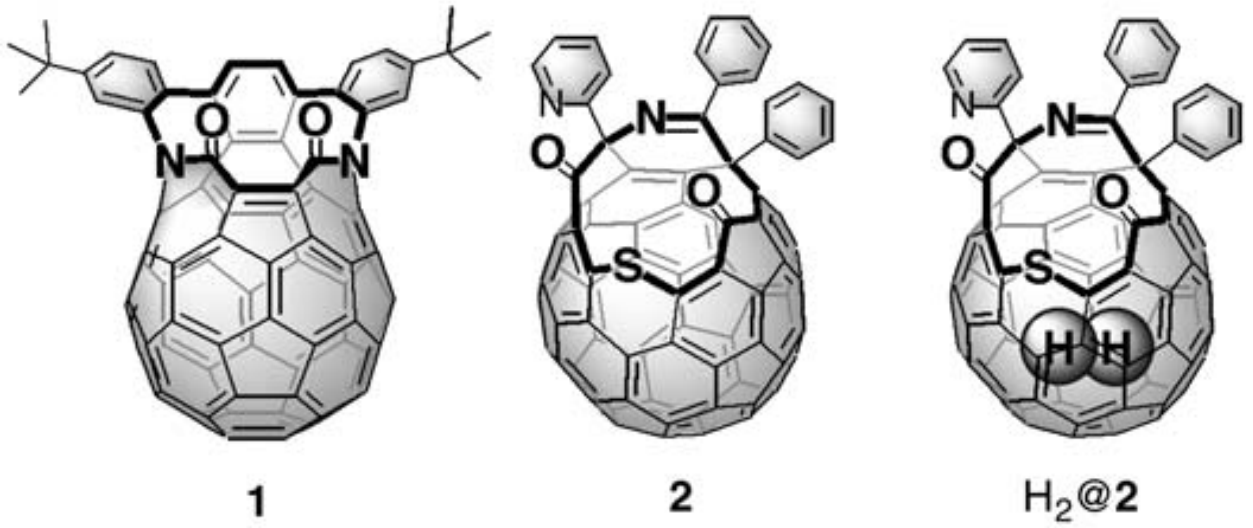
◆Endohedral fullerenes are generally produced by an arc discharge, a laser vaporization and a chemical processing methods.



Introduction

- $H_2@C_{60}$ synthesis by “molecular surgery” method

  [K. Komatsu et al., Science 307 238-240 (2005).]



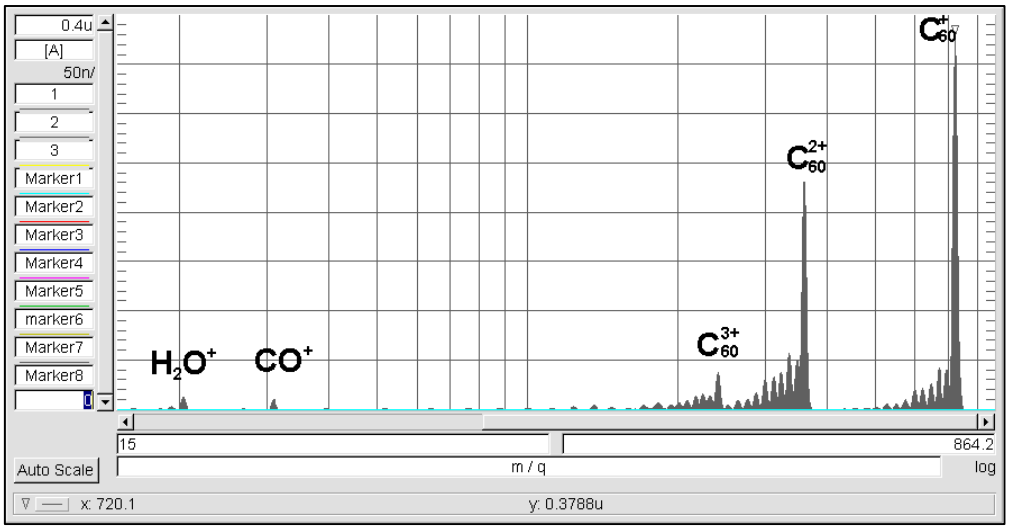
Open-cage fullerenes, which have a large orifice, are effective for the encapsulation of atoms.

Introduction

◆Fullerenes in an ECR plasma

[1] S. Biri et al., Rev Sci Instrum 73, 881 (2002).
[2] S. Biri et al., Rev Sci Instrum 77, 03A314 (2006).

Ionization and fragmentation of fullerenes



C_{60} ion beam spectrum

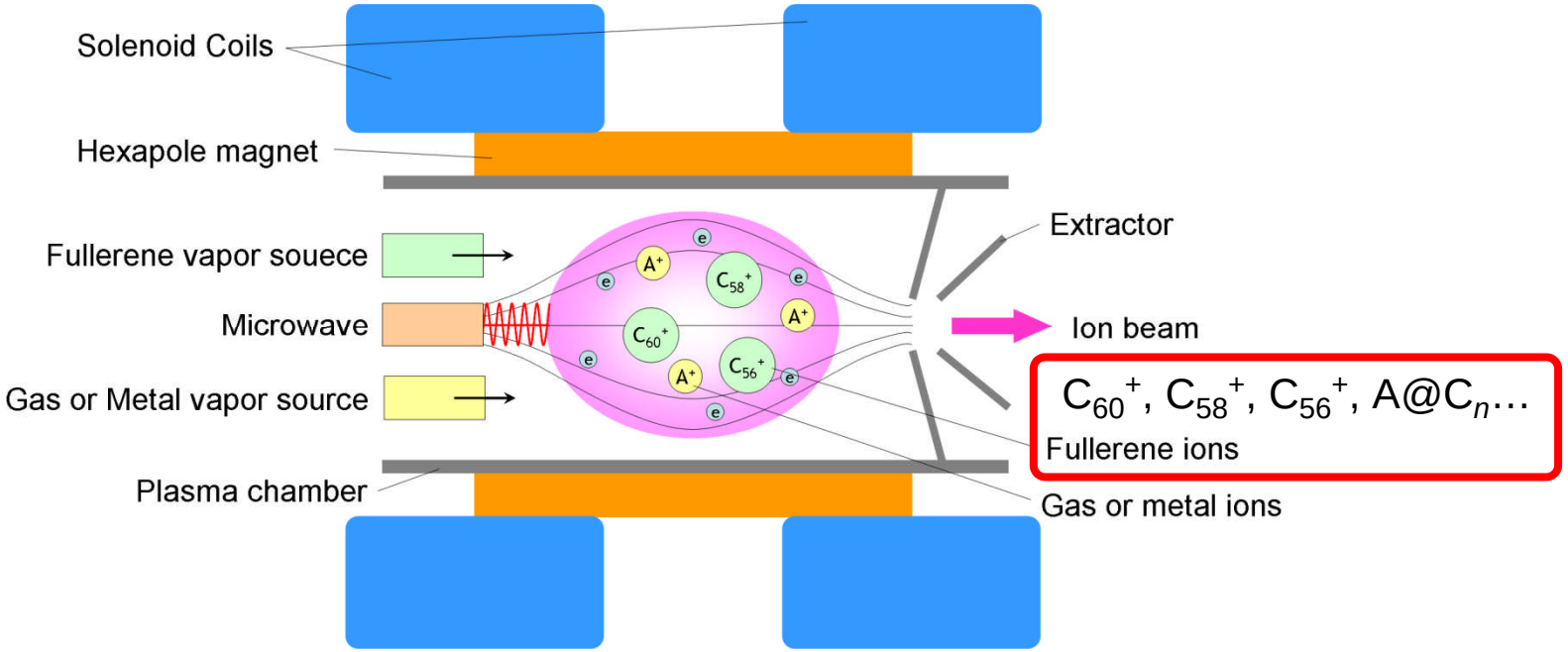
$$C_{60-2n}^{q+}$$
$$(C_{60}^{+}, C_{58}^{+}, C_{56}^{+},\ldots,$$
$$C_{60}^{2+}, C_{58}^{2+},\ldots, C_{60}^{3+},\ldots)$$

Carbons-loss fullerenes might have an orifice, even though such structure may be unstable and transient.

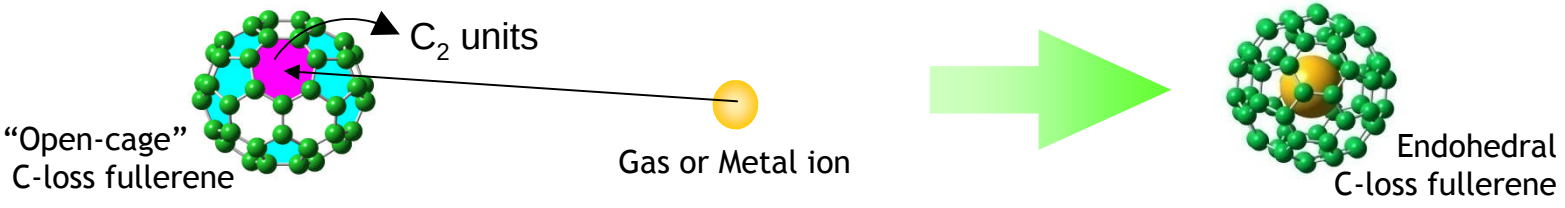
→ Carbons-loss fullerenes might be effective for the production of endohedral fullerenes.

Introduction

- Endohedral fullerenes production in the mixture plasma of fullerenes and gas or metal



Simultaneous processes of carbons-loss fullerene formation and collision reaction of the carbons-loss fullerenes with gas or metal ions



Introduction

- Possible effectiveness of ECRIS for the endohedral fullerenes production
  - Long confinement time of ions
    - → High Collision probability of fullerene ions and gas or metal ions
  - High ionization efficiency
    - → Low feed consumption
  - Low-pressure plasma
    - → Low impurity density

BUT,

There in no ECRIS, which is specialized for the generation of fullerene plasma and the synthesis of endohedral fullerenes.

Design concept of the Bio-Nano-ECRIS apparatus

Endohedral fullerene synthesis (we aim Fe@C_n synthesis)

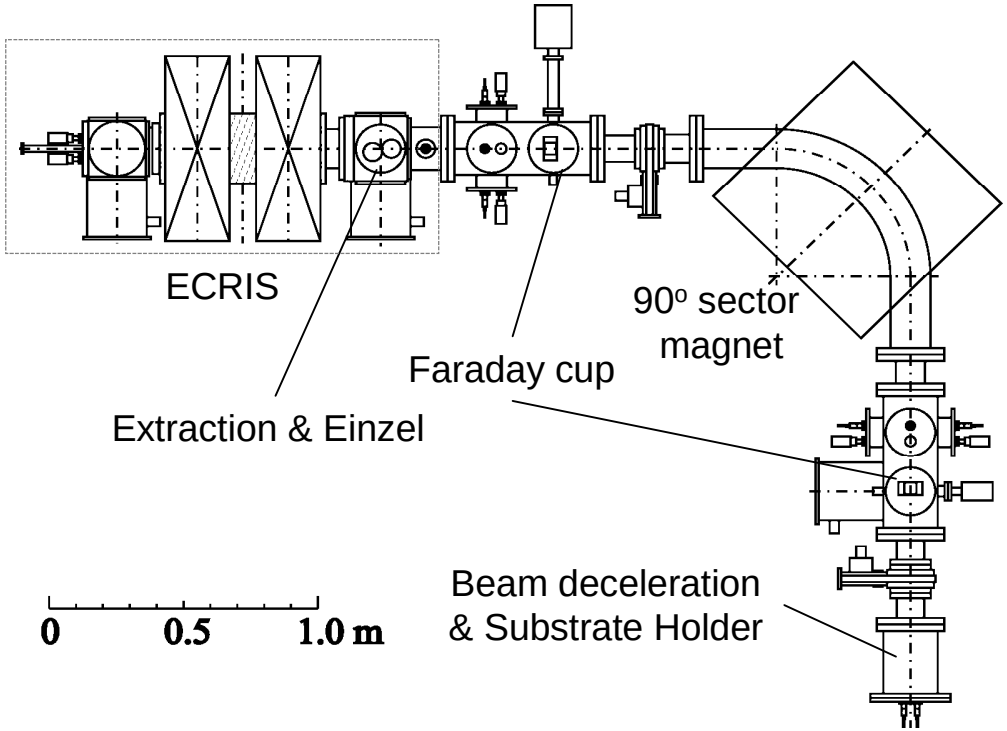
Production of low-charged large-mass plasma and beam!!

- Several evaporation sources (fullerene vapor and Fe vapor,……)
- Large plasma chamber to reduce the wall loss of low-charged large-mass ions and to mount evaporation sources
- Relatively weak magnetic field in order to reduce the synthesis of high-charged ions
- Low extraction voltage and large sector magnet to analyze the ion beam with high mass-to-charge ratio
- Beam deceleration system and substrate holder to produce the deposition

Primary differences between Bio-Nano-ECRIS and general ECRIS for multiply charged ions production

	Bio-Nano-ECRIS	General ECRIS for multiply charged ions
Extraction voltage	Low	High
Effect of confinement	Ion-ion Collision	Ion-electron Collision
Evaporation source	Several sources (fullerene, Fe, …)	No source

Bio-Nano-ECRIS apparatus

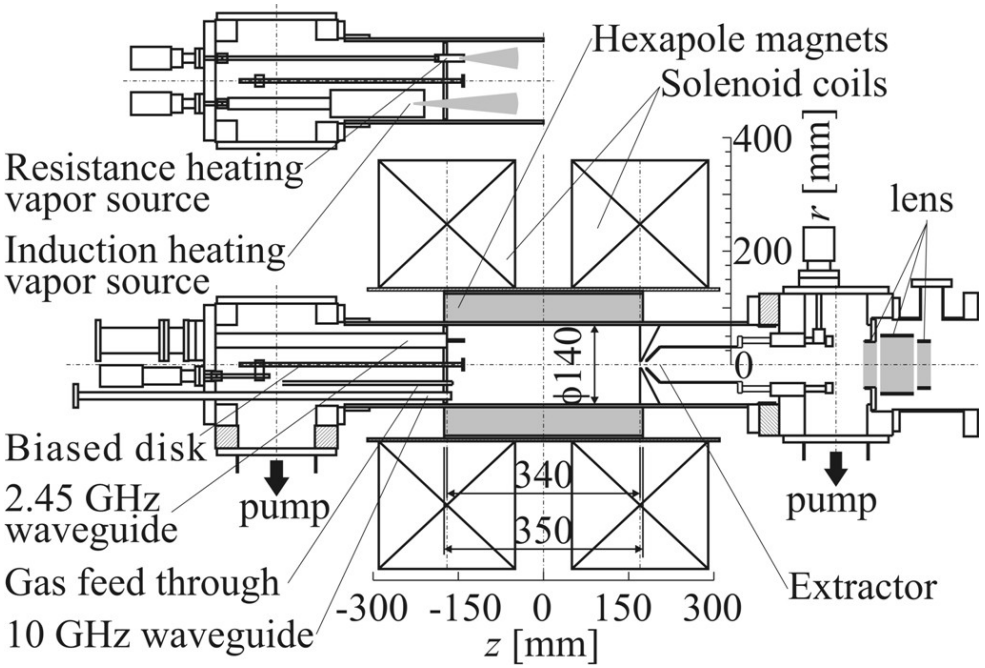


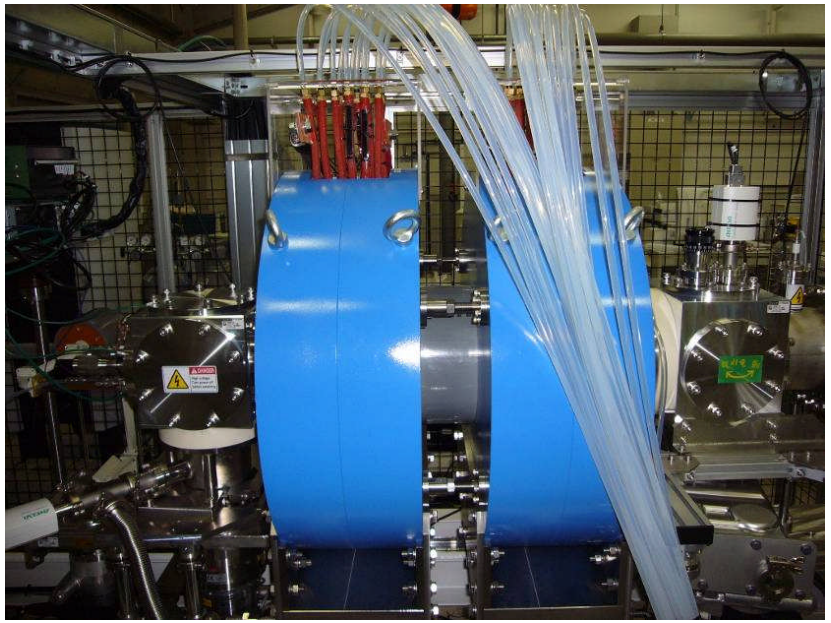


Extraction gap	1 – 6 cm
Extraction voltage	0.5 – 5 kV
Analyzing magnet	Solenoid coil, 90° sector, r = 50 cm
Magnetic field strength	0 – 0.8 T

Deceleration voltage	0 – 5 kV
Vacuum system	Turbo molecular pump (450 l/sec × 3)

The ECRIS

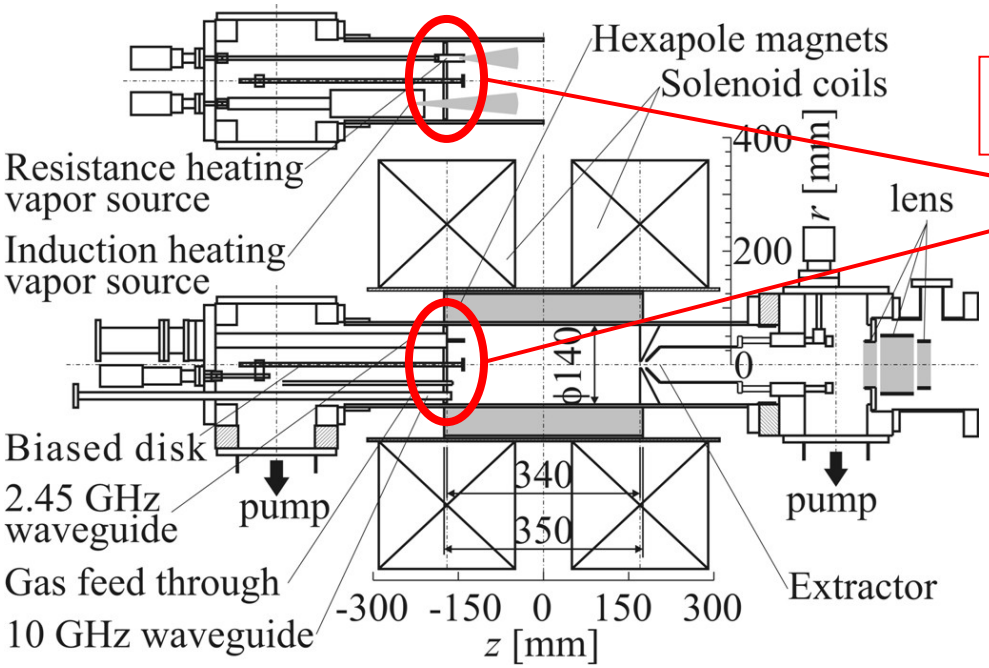


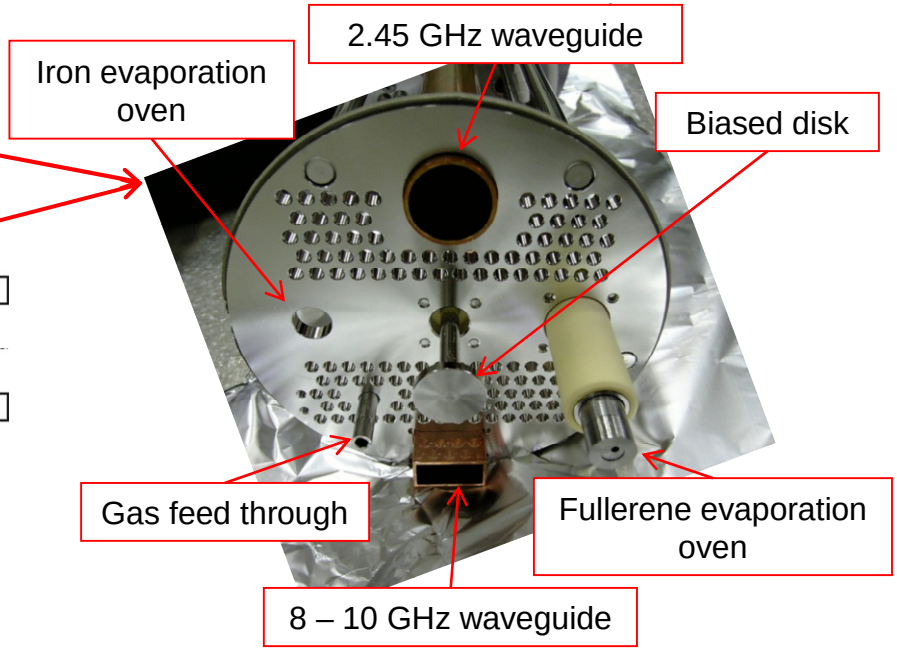


Mirror magnets	Solenoid coils
Axial magnetic induction peak (500 A)	0.442 T
Minimum field strength (500 A)	0.165 T
Mirror ratio (500A)	2.68
Hexapole Magnet	Nd-Fe-B
Maximum radial magnetic induction in chamber	0.72 T

Microwave (1)	TWT amplifier
Frequency (1)	8 – 10 GHz
Microwave (2)	Magnetron
Frequency (2)	2.45 GHz
Plasma chamber diameter	14 cm
Plasma chamber length	34 cm
Fullerene evaporation	Resistance heating oven
Temperature (normal use)	400 – 500 °C

The ECRIS

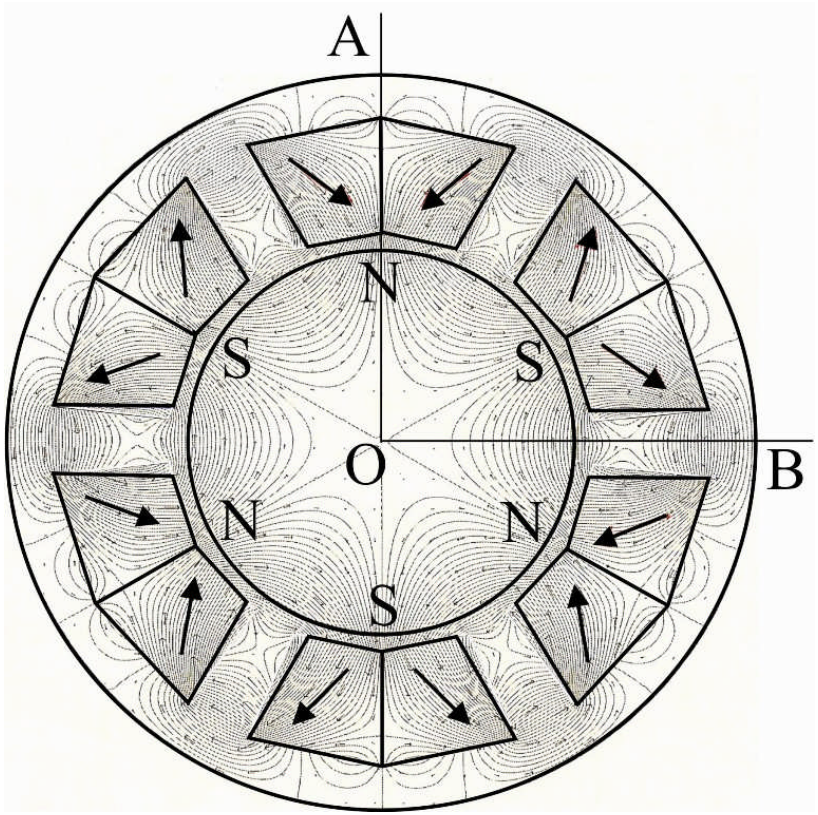


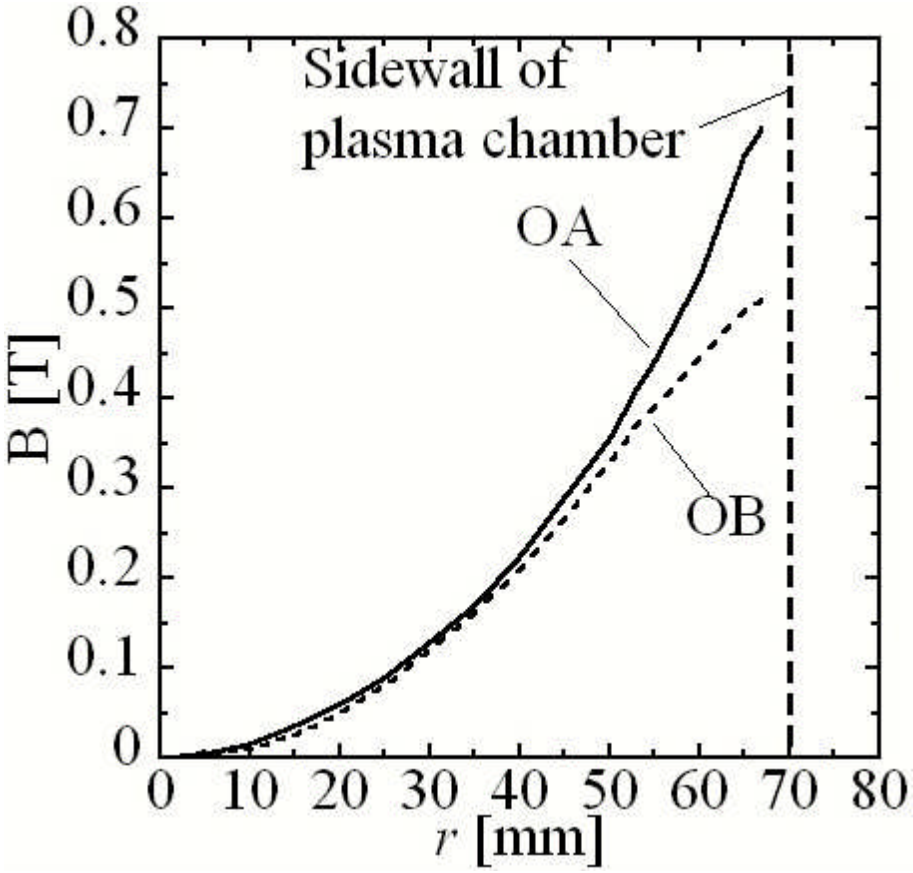


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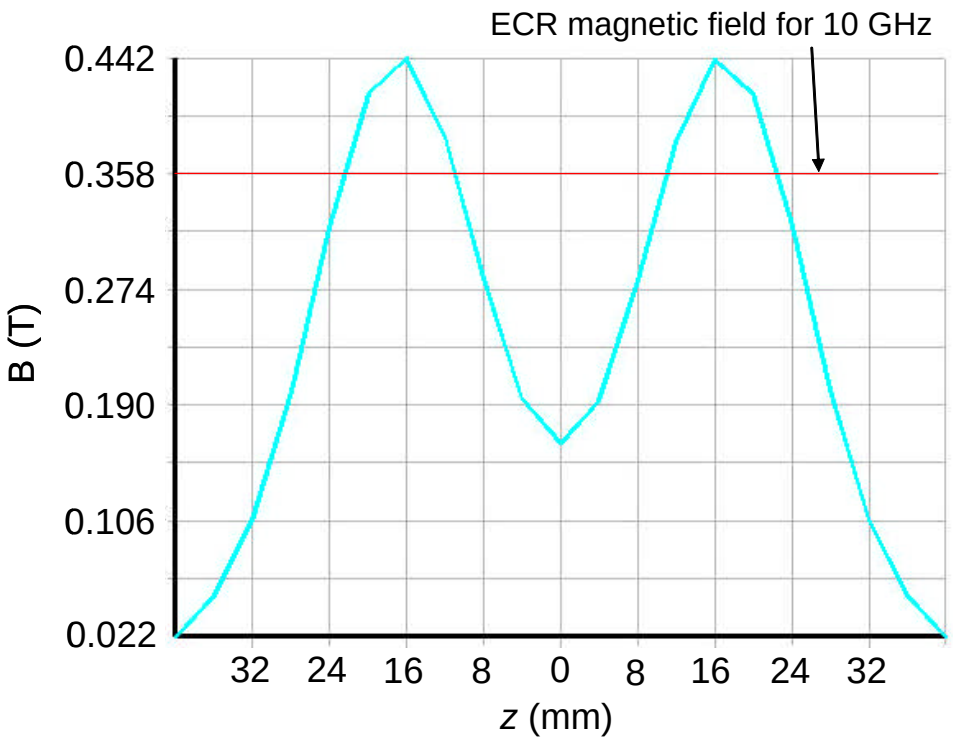
Magnetic field of the Hexapole magnet

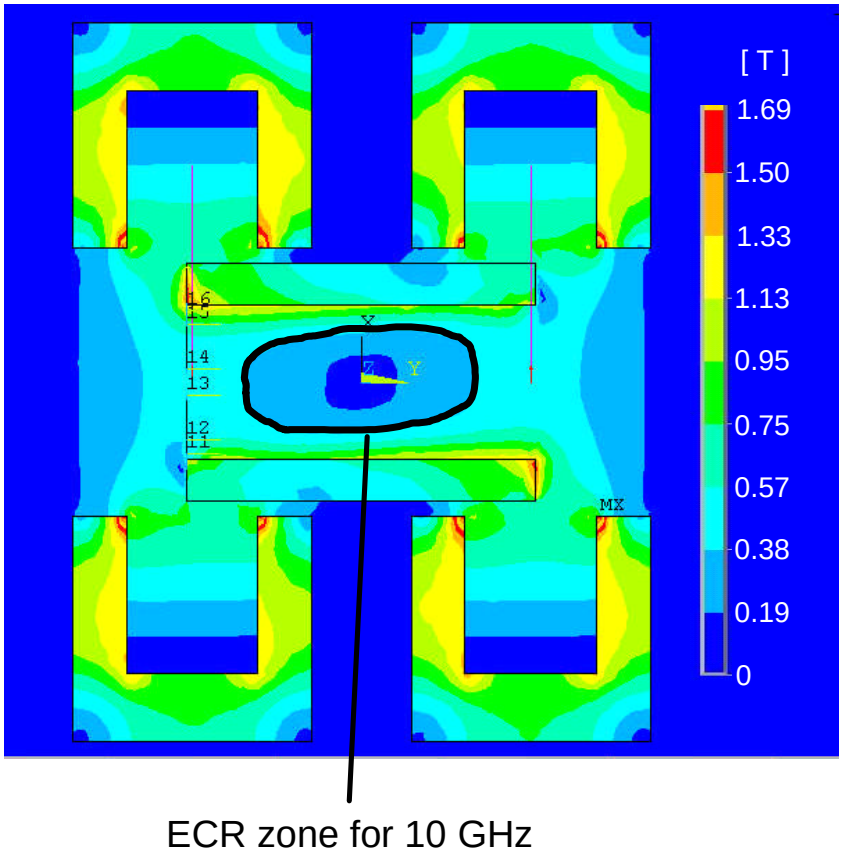




◆Maximum radial magnetic induction in chamber : 0.72 Tesla

Magnetic field of the mirror coils (500 A)



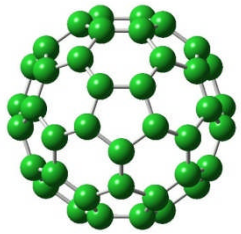


◆Field strength along the chamber axis (500 A), maximum: 0.442 Tesla
minimum : 0.165 Tesla

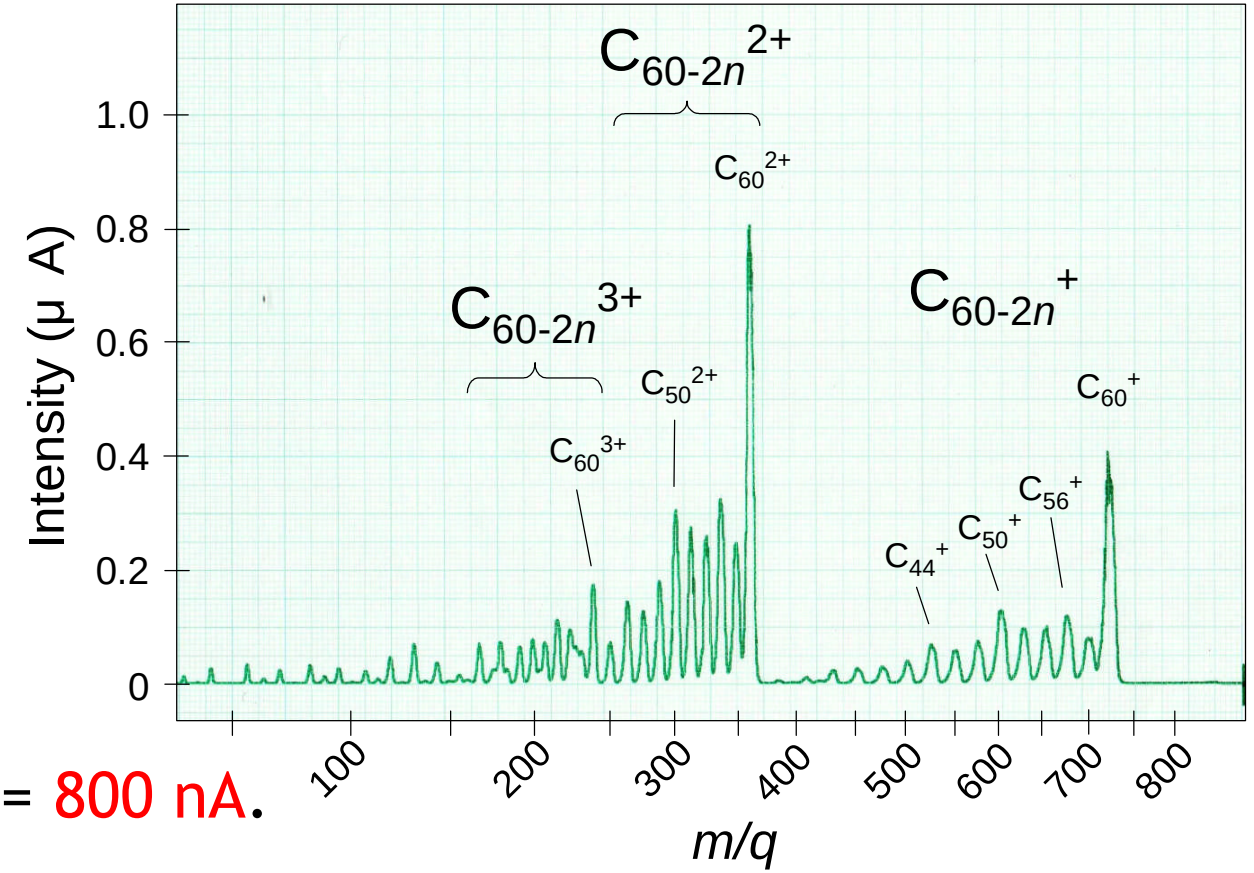
◆ECR zone (500 A, 10GHz), diameter : 10 cm
length : 23 cm

Fullerene ion beam spectra

C_{60}



- Pure C_{60} powder (99.5%)
- T_{oven} = 430 ºC
- $P_{chamber}$ = 5 × 10^{-5} Pa
- Microwave
  - frequency = 9.75 GHz
  - power = 5 W
- Mirror coil current = 500 A

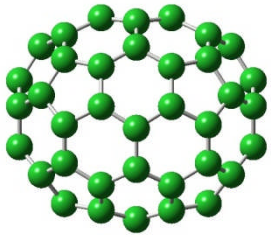


I_{C60+} = 400 nA, I_{C60}^{2+} = 800 nA.

Very clear fullerene spectrum was obtained using a new ECRIS apparatus.
The C_{60} ion beam consists of ions of C_{60} and carbons-loss C_{60}.
Multi-charged species are also observed.

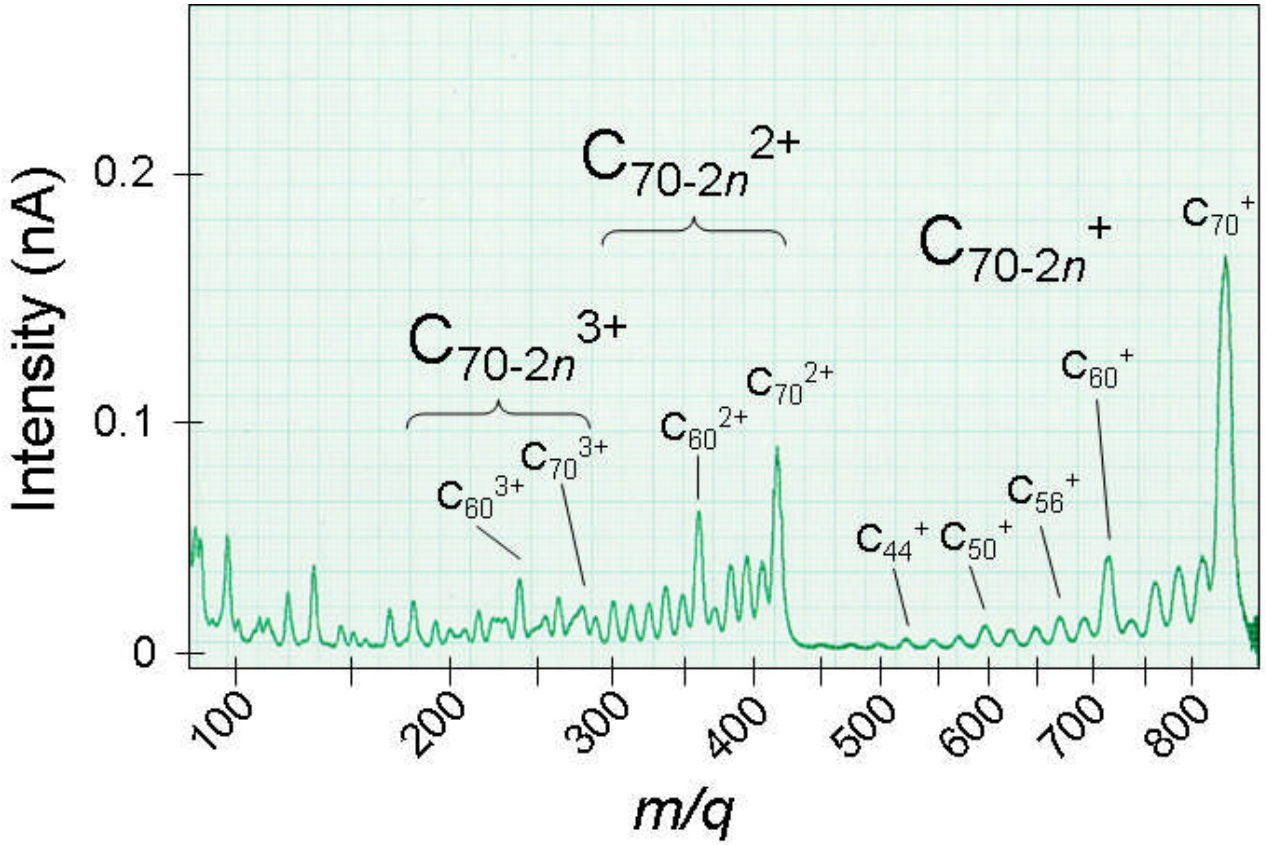
Fullerene ion beam spectra

C_{70}



- Pure C_{70} powder (98%)
- T_{oven} = 430 °C
- $P_{chamber}$ = 6 × 10^{-5} Pa
- Microwave
  - frequency = 9.75 GHz
  - power = 10 W
- Mirror coil current = 500 A

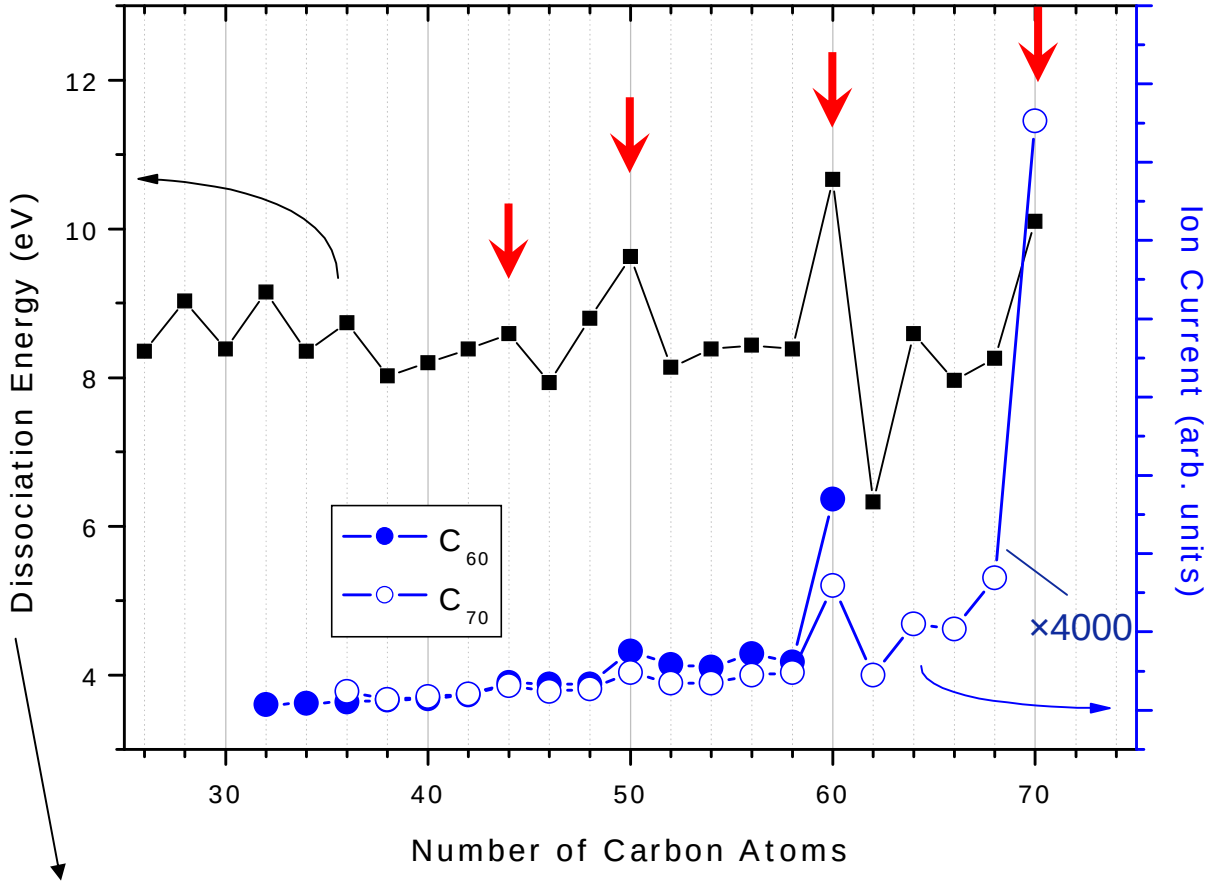
I_{C70+} = 0.2 nA



Very clear spectrum was also obtained for C_{70} source.
The C_{70} plasma consists of ions of C_{70} and carbons-loss C_{70}.
Multi-charged species are also observed.

General characteristics of fullerene ion beam spectra

◆ Comparison of C_n ion current with dissociation energy



C_{70}, C_{60}, C_{50}, C_{44}

Stable!

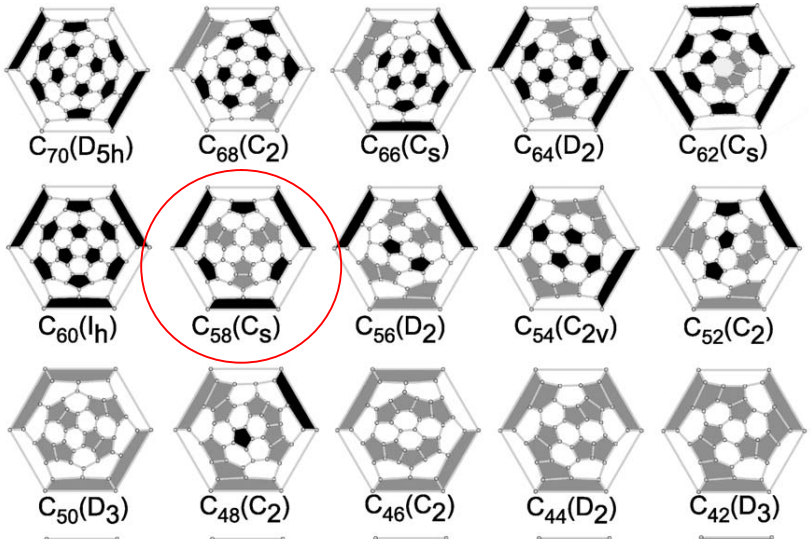
High ion current

Calculated Value from [3].

[3] S. Díaz-Tendero et al., Int. J. Mass Spectrom. 250, 133-141 (2006).

Structure of carbons-loss fullerenes

Structure of the most stable isomer for C_n [3]



No orifice
(<7-membered ring)

But,
for C_{58}, the structure including 7-membered ring is possible.

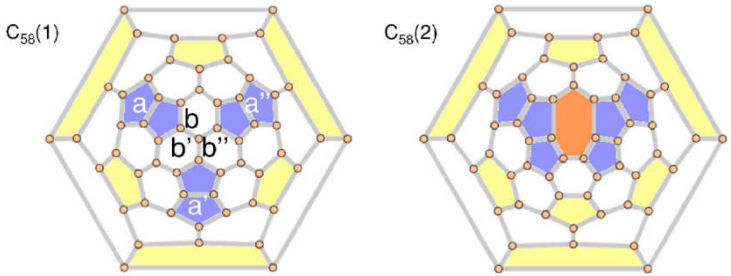
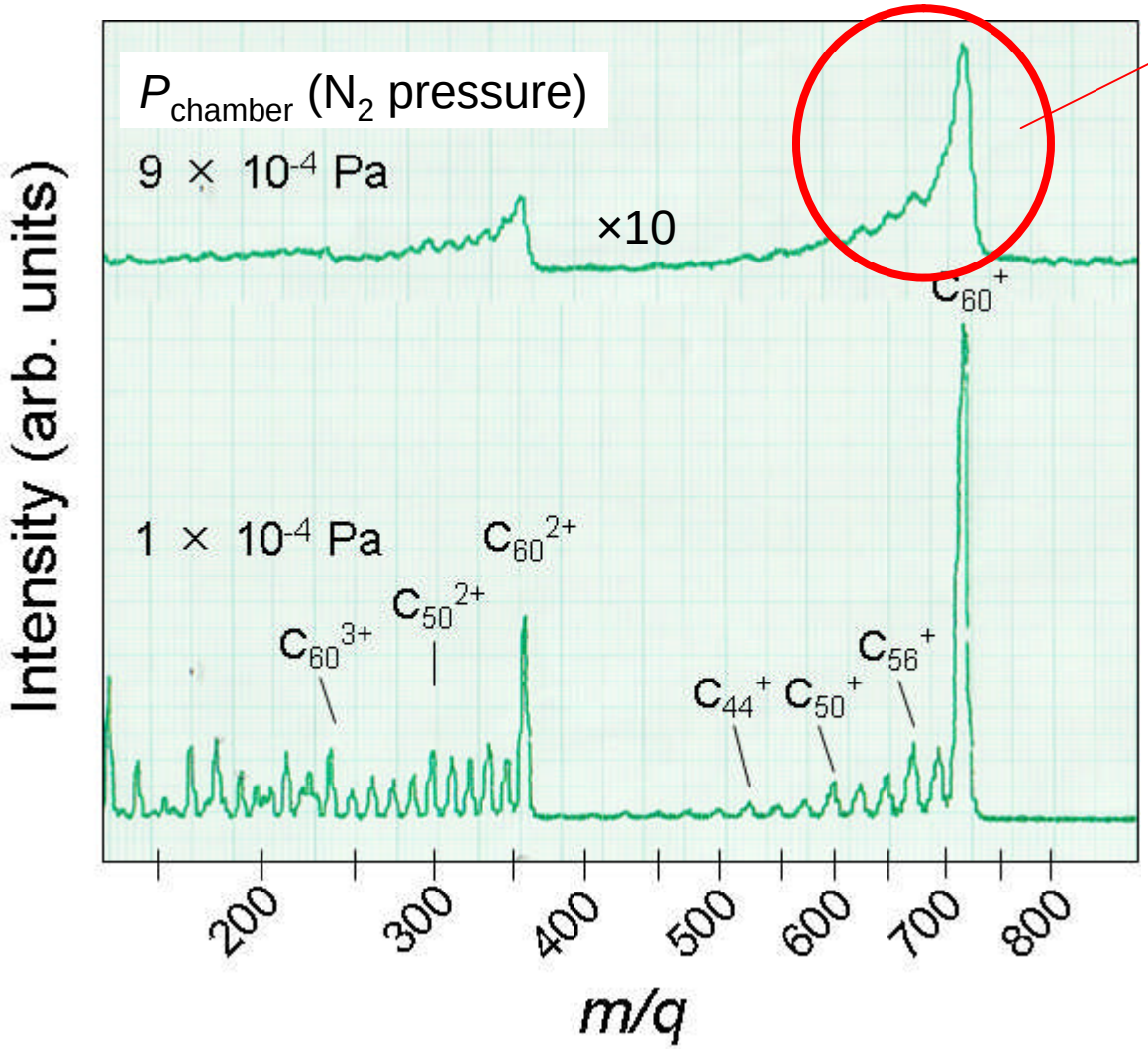


Figure from [4]

[3] S. Díaz-Tendero et al., Int. J. Mass Spectrom. 250, 133 (2006).
[4] S. Díaz-Tendero et al., J. Chem Phys. 123, 184306 (2005).

Formation and extraction of fullerene and N_2 mixture plasma



Significant broadening

Complex feature of:

C_{60} = 720, $N + C_{60}$ = 734

C_{58} = 696, $N + C_{58}$ = 710

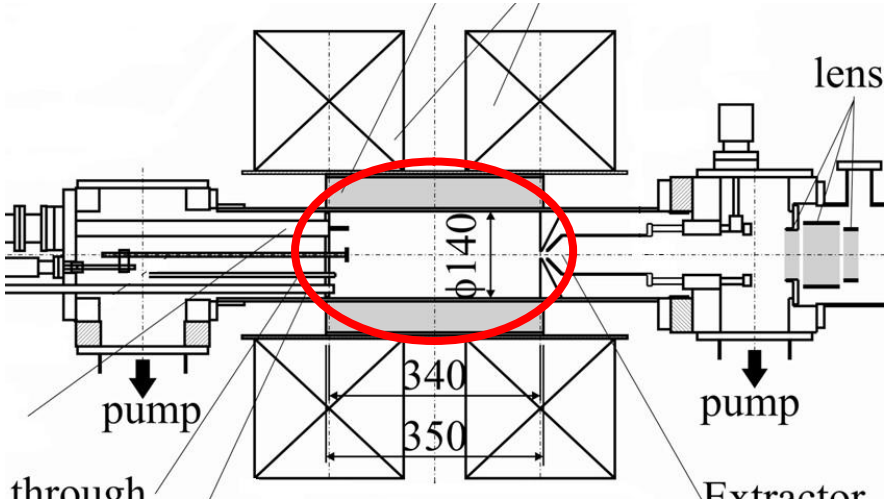
C_{56} = 672, $N + C_{56}$ = 686

NC_n ($N@C_n$)??

Beam deposition and characterization of the deposit are needed.

→ Future work

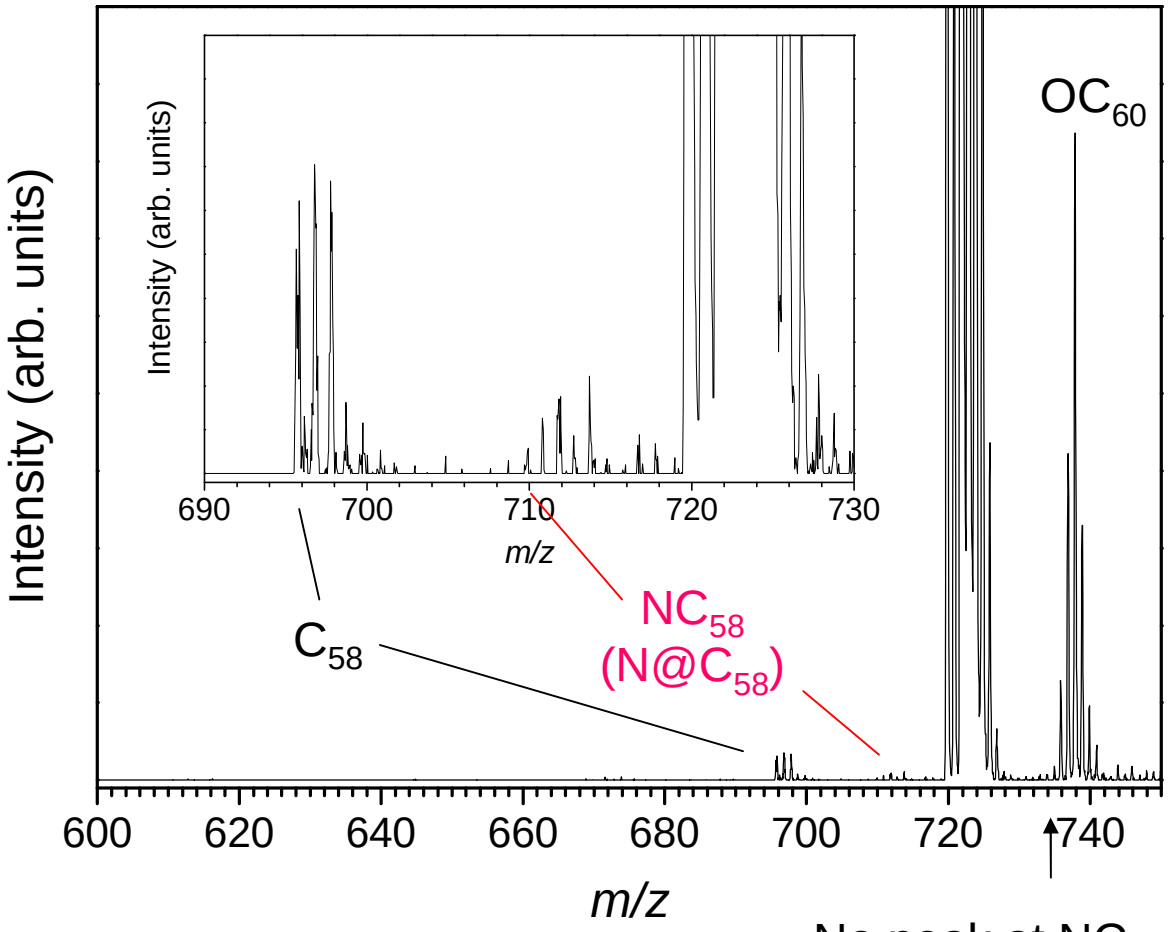
Deposit in the plasma chamber







MALDI-TOF mass spectrum of deposit in the plasma chamber



$N + C_{60} = 734$

$C_{60} = 720$

$N + C_{58} = 710$

$C_{58} = 696$

No peak at $NC_{60} = 734$

The peak of $NC_{58} = 710$ is observed!

Summary & Future plan

We have developed a new ECRIS apparatus for the synthesis of endohedral fullerenes.

- Fullerene (C_{60} and C_{70}) ions beam spectra were successfully obtained, and specific C-loss fullerene ions are separable.
- High beam intensity was obtained for C_{60}; I_{C60}^{+} = 400 nA, I_{C60}^{2+} = 800 nA.
- NC_n, in particular NC_{58} (and/or $N@C_{58}$) are produced in the mixture plasma of C_{60} and N_2.

Future work

- Separation and collection of NC_n.
- Mechanisms of carbons-loss fullerenes formation and encapsulation of atom in carbons-loss fullerenes.
- Fe ion formation and encapsulation in carbons-loss fullerenes

Acknowledgements

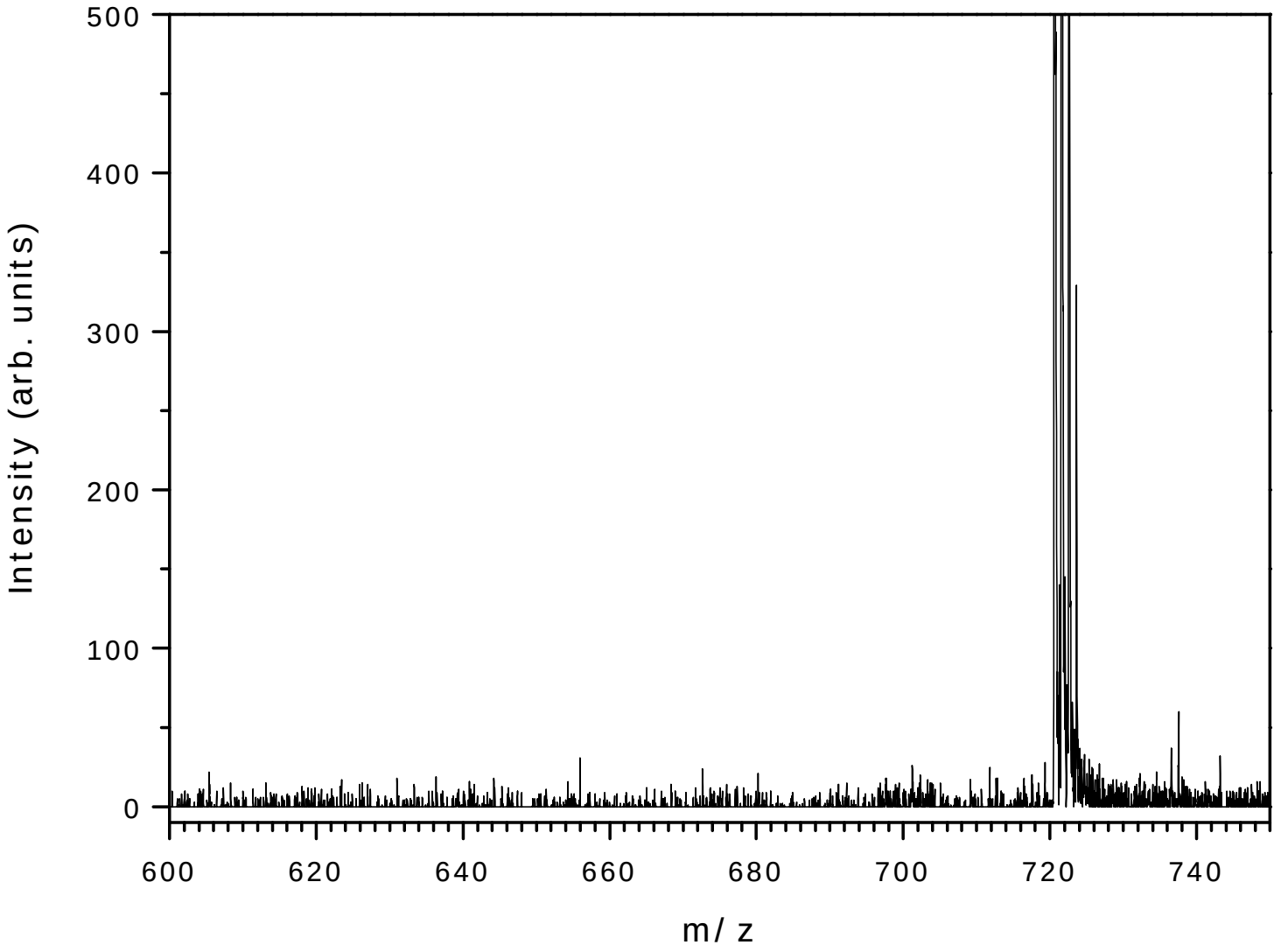
- We would like to thank Dr. Fukuda and Mr. Kurosu for MALDI-TOF-MS measurements.

- Part of this study has been supported by a Grant for the 21st Century Center of Excellence Program since 2003 and a Grant for the High-Tech Research Center Fund since 2006.

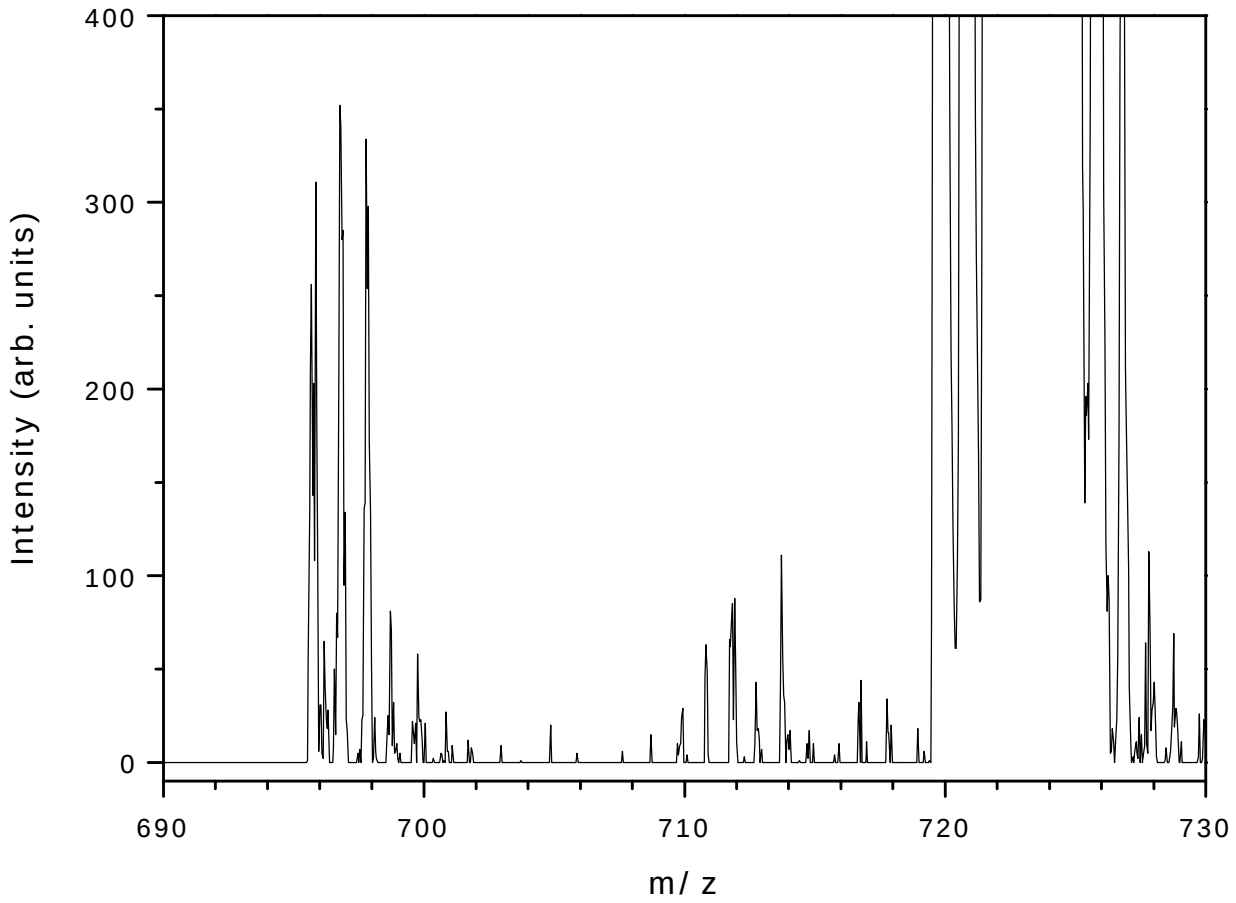
  Both funds were organized by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Thank you for your attention!

MALDI-TOF mass spectrum of pure C_{60} powder



MALDI-TOF mass spectrum of deposit in the plasma chamber



MALDI-TOF mass spectrum of deposit in the plasma chamber

