STORAGE OF BIO-MOLECULAR IONS IN AN ELECTROSTATIC STORAGE RING

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Abstract

The cooler ring TARN II, which had been used to study the recombination of atomic and molecular ions with electrons since the late 1980s, was shut down in 1999 along with the closing of the Tanashi branch of KEK. To replace TARN II, a new electrostatic storage ring was built and a beam was first stored in May 2000 at the Tsukuba site of KEK. The ring has a circumference of 8 m and can store light-to-heavy ions with an E/q of up to 30 keV. Light ions are produced with an electron cyclotron resonance ion source, while bio-molecular ions are produced with an electrospray ion source. The measured 1/e-lifetimes of stored single-charge ions injected from the ECR ion source are from 11 to 50 s. On the other hand, ions from the electrospray ion source have lifetimes from 12 to 20 s. In order to study electron-ion collisions, a compact electron beam target has been designed, which will be installed in a straight section of the ring.

1 INTRODUCTION

Since the late 1980s, many storage rings with electron coolers have been operational, some of which have been used for studying atomic physics. For atomic physics using these cooler rings, many new phenomena were found, especially concerning the dissociative recombination of molecular ions with electrons [1]. The object of the present research is being directed to heavier molecular ions. One of the difficulties in studying low-charge and heavy molecular ions with the usual magnetic storage rings is the increasing magnetic rigidity with ion mass (m), because the magnetic rigidity is proportional to $\sqrt{mE/q}$. Here, E and q are the ion energy and charge, respectively. An electrostatic storage ring is more suitable for such ions because the electrostatic rigidity is proportional to E/q and is independent of the ion mass at a given energy. There are also many advantages of electrostatic storage rings, such as compactness, ease of construction and good reproducibility. The ring is expected to be very useful for the research of atomic and molecular science in the future. Pioneering work for the electrostatic storage ring was performed by S.P.Møller (the ring ELISA in Aarhus [2]), where spherical deflectors were used to balance the horizontal and vertical focusing forces in the deflectors. This focusing resulted in very narrow waists in the middle of the deflectors. However, it was observed that the beam lifetime decreased greatly with increasing beam intensity [3]. In order to avoid such a difficulty, we designed a ring using cylindrical deflectors instead of spherical deflectors [4]. The lattices using the cylindrical deflectors allow both solutions, with and without waists, in the middle of the deflectors.

It is very attractive to expand the research object from light molecular ions mainly studied so far to heavy macro-molecular ions. In order to study the feasibility of the storage of bio-molecular ions in the ring, an elecrospray ion source accompanied by an ion trap was constructed.

An electron-beam target is indispensable for studying electron-ion collisions. In magnetic storage rings, electron coolers have been used to compress the phase space occupied by beams and at the same time as an electron target for electron-ion collision research. On the other hand, in the electrostatic ring, the electron cooling device can function mainly as an electron-beam target except light-ion beams, because the ion velocity is not necessarily high enough to cool the heavy-ion beams in the longitudinal directions. An electron-beam target which is a compact electron cooler has been designed.

In this paper, we report on the design of the ring and the results of beam tests for the light ions and bio-molecular ions produced by an electron cyclotron resonance (ECR) ion source and an electrospray ion (ESI) source, respectively.

2 LAYOUT OF THE EQUIPMENT

The layout of the ion-sources, the beam-injection system and the storage ring is shown in Fig. 1. Light atomic and molecular ions are produced in a compact ECR ion source [5] with an acceleration voltage of 20 kV, and are injected into a beam-analyzing dipole magnet. A momentum-analyzed beam is then injected into the ring through a matching section consisting of an electrostatic quadrupole triplet. On the other hand, bio-molecular ions with an energy of 30 keV/q are produced by the ESI source and injected into the ring after being bunched and mass-analyzed. The mass analyzer consists of a spherical deflector, a sextupole magnet and a dipole magnet which also serves to analyze the momentum of ion-beams from the ECR source. The ECR and ESI sources can be used alternatively without breaking the vacuum in the merging section.

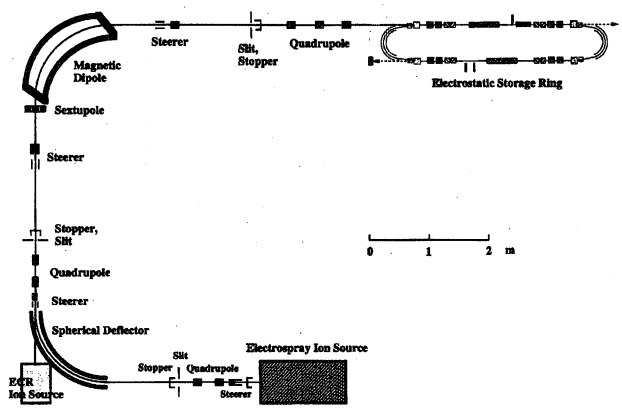

Figure 1. Entire layout of the ion sources, the mass spectrometer and the electrostatic storage ring.

3 ELECTROSPRAY ION SOURCE

A schematic drawing of the ESI source and an ion trap is shown in Fig. 2. The ESI source (JEOL, model API15, Japan) was installed on a high-voltage terminal. A sample solution at flow rates of about 5 *μl/m* enters the ESI source chamber through a stainless-steel capillary. The capillary is electrically biased at a few kilovolts relative to a counter electrode. The resulting field at the capillary tip charges the surface of the emerging liquid, dispersing it by Coulomb forces into a fine spray of charge droplets. Driven by the electric field, the droplets move towards the counter electrode. A flow of nitrogen gas at a flow rate of about 5 *l/m* assists to nebulize the solution and hasten evaporation of the solvent from each droplet, decreasing its diameter as it drifts towards the orifice of the counter electrode. Consequently, the charge density on the droplet surface increases until the Coulomb repulsion exceeds the surface tension, resulting in producing charged daughter droplets and ions by Coulomb explosion. The desolvating plate, heated at a temperature of about 200 °C, helps to dry the solvent. A syringe pump controls the flow of the solution, typically a water-methanol mixture, containing the sample.

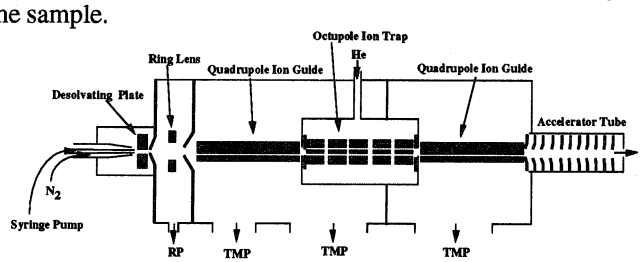

Figure 2. Schematic drawing of the electrospray ion source, ion guides and an ion trap.

Ions created by the ESI source are then conveyed to the entrance of a linear octupole RF ion-trap having an inscribed radius of 4 *mm* and a length of 15 *cm* by way of a quadruple RF ion-guide, as shown in Fig. 2. The ion-trap accumulates ions initially, and then ejects the trapped ions quickly in order to transfer them to the storage ring as a bunch. Trap electrodes composed of 8 rods of 3 *mm* in diameter are electrically isolated into five pieces, in order to independently apply a DC voltage superimposed on the RF voltage to each electrode. This makes it possible to form an axial confinement field during accumulation, and also to form an axial gradient field during ejection, in collaboration with the entrance and exit electrodes. The ions trapped into the potential well are thermalized through collisions with He gas fed into the trap at a flow rate of about 0.1 cc/m. After accumulation for a period of a few seconds, ions are released by abruptly changing each DC bias with a switching time of about 0.4 μs and transferred to another quadrupole RF ion-guide with a drift length of 14 cm. The thus-obtained bunched beam is then accelerated up to 30 keV/charge by an accelerator tube. The trap and guides are operated at a frequency of 1 MHz and a voltage of 60-500 V_{pp}.

The ion source is evacuated by a 500 *l/m* rotary pump and a 210 *l/s* turbo-molecular pump. Furthermore, two 500 *l/s* turbo molecular pumps are added to evacuate the ion guide and trap region. The typical vacuum at the second ion guide is about 1×10^{-6} Torr. The entire system is installed on a high voltage terminal and controlled by fiber optical links.

The ion trap and the beam bunching system dramatically increased the pulse beam current. A picture of the ESI source is shown in Fig. 3.

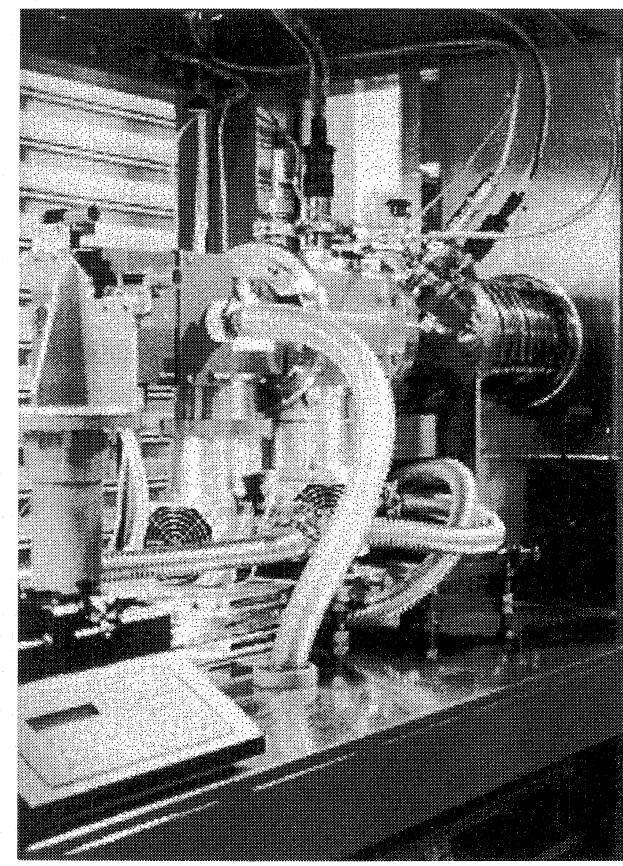

Figure 3 . Photograph of the electrospray ion source.

4 MASS SPECTROMETER

In order to mass-analyze macro-molecular ions from the ESI source, a mass spectrometer was designed while aiming at a mass resolution of 5000. The spectrometer is composed of a spherical deflector with a bending radius of 119 *cm* and a homogeneous field dipole magnet with a bending radius of 120 *cm* and an entrance and exit angle of 26.5°, as shown in Fig. 1. This constitutes a double-focusing mass-analyzing system where the final image is independent of both the velocity and the direction spread among the ions emerging from the object slit. A sextupole magnet was installed in front of the dipole magnet, which helps to compensate for the second-order aberration. The magnet was also used to momentum-analyze ions from the ECR source.

The vacuum pressure at the ion source is high, while it has to be extremely low in the storage ring. A high vacuum was attained by a differential pumping system. The typical vacuum pressure in the ion source is 1×10^{-6} Torr, while the vacuum in the ring is 3×10^{-11} Torr with beam loading.

5 ELECTROSTATIC STORAGE RING

The layout and a picture of the ring are shown in Figs. 4 and 5, respectively and the main parameters are listed in Table 1. A race-track lattice consists of two 160° deflectors, four 10° deflectors, which allow beam injection and extraction, and four quadrupole doublets. For the 160° deflectors, a cylindrical shape has been adopted. In this ring, there are four types of stable regions with and without waists of the beam envelope in the middle of the deflectors.

The type of beam injection is single-turn injection. During injection, the high voltage for the first 10° deflector is turned off, and after filling the beam in the ring it is turned on. The rising and falling times of the high voltage power supplies used in the injection are about 0.1 μs, which is sufficiently short compared with the circulation time of ions (for example, 17 μs for 20-keV O^+)

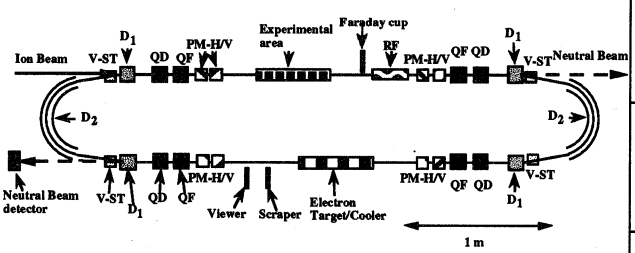

Figure 4. Layout of the electrostatic storage ring. D_1 and D_2 indicate 10° and 160° deflectors, QF and QD the horizontally focusing and defocusing electrostatic quadrupoles, PM-H and PM-V the horizontal and vertical position monitors, RF the drift-tube RF system and V-ST the vertical steerer.

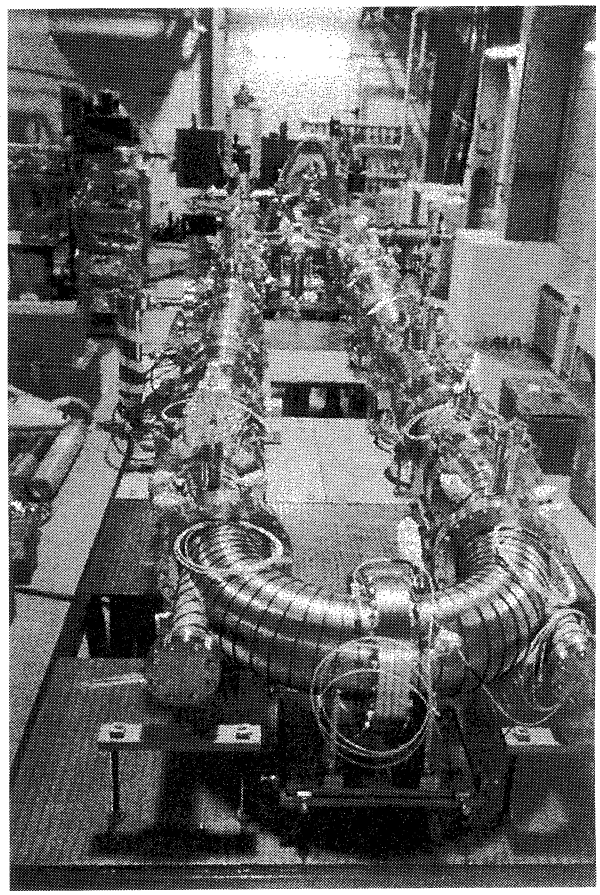

Figure 5. Photograph of the electrostatic storage ring.

Table 1. Design parameters for the electrostatic storage ring

Maximum energy	30 keV/charge
Circumference	8.136 m
Revolution time	14 μs (O^+, 30 keV)
160° cylindrical deflectors	
Central radius	250 mm
Gap	30 mm
Nominal voltage	± 3.6 kV
10° parallel plate deflectors	
Gap	60 mm
Length	92 mm
Nominal voltage	± 2.6 kV
Quadrupoles	
Inscribed radius	25 mm
Length	100 mm
Nominal voltage	± 0.75 kV
RF	
Drift tube length	203 mm
Voltage	<10 V

The beam can be bunched with an RF electrode consisting of a 20-cm long drift tube which is driven directly by an RF signal generator. The bunched beam is used for monitoring the intensity of the circulating beam current and for measuring the beam position..

Several kinds of beam diagnostic elements are installed in the straight sections, as shown in Fig. 4. The injected beam profile is observed destructively with a viewer. The injected beam current is accurately measured by a Faraday cup equipped with an electron suppressor. Four horizontal and vertical electrostatic position monitors provide position information concerning bunched beams nondestructively. A beam scraper defines the maximum beam size both horizontally and vertically, which can also be used for the beam position and profile measurements.

A vacuum pumping system is composed of four ion pumps and six titanium sublimation pumps. The entire ring is bakeable at a temperature of less than 300 °C. The vacuum pressure of the ring is on the order of 10^{-11} Torr.

A neutral beam produced by collisions with the residual gas is measured by a micro-channel plate with a phosphor anode (32 mm in diameter) installed in a vacuum extension 1.25-m downstream of the 10° deflector, as shown in Fig. 4. The count rate of the neutral beam is proportional to the number of stored ions at a constant residual-gas pressure, which gives exact information about the beam lifetime. Furthermore, a projection of the circulating beam can be observed from the neutral beam profile on the phosphor screen. The position and size of the neutral beam profile are useful for adjusting the ring parameters.

6 STORAGE OF ATOMIC AND MOLECULAR IONS

The 20-keV beams from the ECR ion source were momentum-analyzed (typical momentum resolution: $\Delta p/p \sim 10^{-3}$) and injected into the ring after being chopped. The injected beam size observed by the viewer is about 5 mm in diameter.

The change in the number of stored atomic ions with time is expressed by $N = N_0 \exp(-t/\tau)$, where τ is the lifetime. If the ring is operated at a stable working point, the finite lifetime of ions in the ring is mainly determined by interactions with the residual gas. First, ion beams are multiply scattered by the Coulomb field of the residual gas. The ions of which direction of motion exceed an acceptance angle of the ring are lost. The 1/e lifetime, (τ_{MS}), for losses due to multiple scattering is proportional to Θ_{max}^2, where Θ_{max} is a maximum acceptance angle [6]. Second, ions which change their charge state by capturing or stripping electrons deviate from the central orbit and are lost. The lifetimes by capture, (τ_{cap}), and stripping, (τ_{strip}), can be expressed by the cross sections (σ_{cap} and σ_{strip}) as $\tau_{cap} = 1/\rho v \sigma_{cap}$ and $\tau_{strip} = 1/\rho v \sigma_{strip}$, respectively. The cross sections for the residual gas interactions of atomic ions are almost energy-independent at these low energies. Therefore, the lifetimes increase with a decrease in the ion velocity. Unlike in the case of multiple scattering, the lifetimes due to the charge-changing process do not depend on the acceptance angle. The entire lifetime (τ) is related to the lifetimes due to multiple scattering, and those due to capture and stripping by $1/\tau = 1/\tau_{MS} + 1/\tau_{cap} + 1/\tau_{strip}$.

We studied the characteristics of a stored beam at a working point in the four stable regions for 20-keV O^+. The lifetimes depend greatly on the working points. The difference in the lifetimes has been deduced to come from the difference in the multiple-scattering lifetimes, which depend on the maximum acceptance angle. In fact the working point giving the longest lifetime has the largest acceptance angle among the four stable regions.

The dependence of the coasting-beam lifetime on the injected beam current was measured for a 20-keV O^+ beam. At low currents, beams decay almost exponentially with a lifetime of about 12 s, while at higher currents, the beams decay faster initially. The lifetime does not depend much on the intensity at a current of less than about 100 nA, which corresponds to 1×10^7 injected particles. This current is tolerable for practical use, like in atomic collision experiments. A rapid decrease in the beam intensity observed at high currents, which does not obey an exponential decay law, seems to be caused by intra-beam scattering, which is the scattering between beam particles. In the ELISA ring in Aarhus, spherical deflectors were recently replaced by cylindrical deflectors, and a similar lifetime dependence on beam intensity has been reported [7].

So far, we have stored atomic and molecular ions of N^+, O^+, Ne^+, Ar^+, Xe^+, N_2^+, NO^+, O_2^+, and H_2O^+ at 20 keV. These ions are stored at the same voltages for the deflectors and quadrupoles. The decays of the beam intensity for atomic ions are shown in Fig. 6.

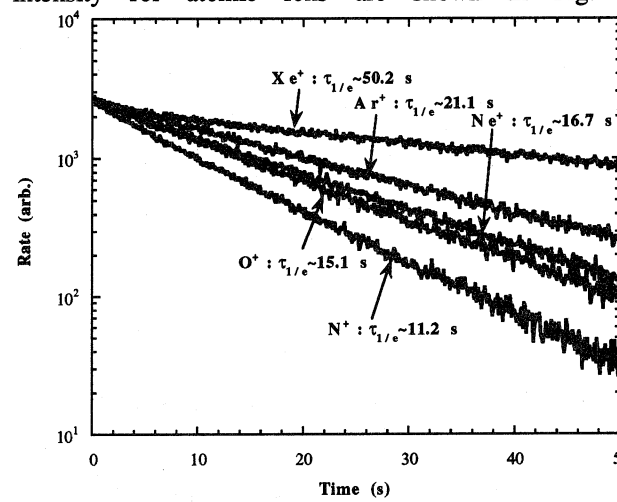

Figure 6. Time dependence of the neutral beam production rate for 20-keV atomic ions at an injected current of 10~20 nA. The vacuum pressure was about 3×10^{-11} Torr. The decay curves are arbitrarily scaled in magnitude to facilitate a comparison [4].

The lifetimes increase with the mass numbers (A). This is partly due to the fact that the lifetimes (τ_{MS}, τ_{cap} and τ_{strip}) are all proportional to $\sqrt{A}$ for a fixed energy, although they also depend on the cross sections.

7 STORAGE OF BIO-MOLECULAR IONS

The ions from the ESI source were accumulated in the trap for a period of a few seconds. The ions were then ejected in a bunch and accelerated to an energy of 20 keV/charge. After being mass-analyzed, the ions were injected into the ring. Figure 7 shows the neutral particle production rate as a function of the storage time for the singly and multiply charged positive ions of the arginine dimer, reserpine, angiotensin, insulin chain B and insulin from bovine pancreas. As can be seen in the figure, the beams have lifetimes of 12 s - 20 s, which are surprisingly long because large bio-molecules have usually been assumed to be fragile, resulting in a short surviving time in collisions with residual gas. The cross sections for the collision with residual gas deduced from the beam lifetime are on the order of 10^{-15} cm^2.

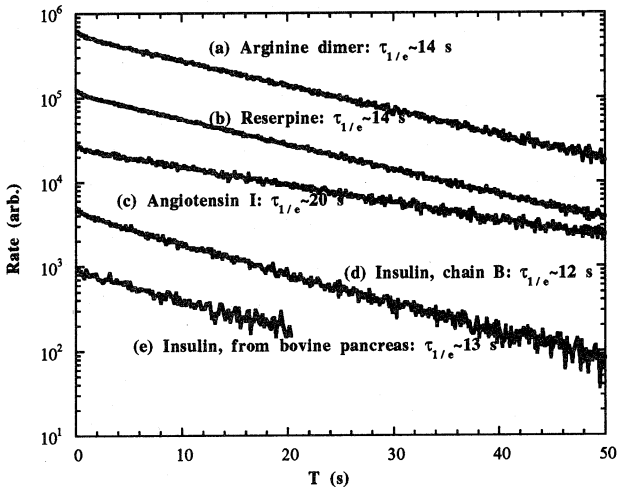

Figure 7. Time dependence of the neutral beam production rates for 20-keV/charge bio-molecular ions: (a) arginine dimer (charge, 1+; M.W.,~331), (b) reserpine (1+; ~609), (c) angiotensin (1+; ~1298), (d) insulin chain B (3+, ~3499) and (e) insulin from bovine pancreas (5+; ~5738). The 1/e lifetimes are indicated in the figure. The vacuum pressure was about 4×10^{-11} Torr. The decay curves are arbitrarily scaled in magnitude to facilitate a comparison.

8 DESIGN OF AN ELECTRON BEAM TARGET

The electron beam target can also function as a beam cooler as well as an electron target for light ions [8]. The structure is almost the same as the adiabatic-expansion-type electron cooling device [9]. Electrons are emitted from a thermo-cathode with a diameter of 5 mm (3.5 mm) and guided in a uniform solenoid field after acceleration and expansion by a factor of 16 (32). The main design parameters are: interaction length, 20 cm; electron beam diameter at the interaction region, 20 mm; maximum energy, 100 eV; maximum current, 2 mA; maximum solenoid field at the gun, 1 kG and maximum solenoid field at the interaction region, 100 G. This will be installed in one of the straight sections of the ring (see Fig. 4). Steering of the ion beam at the toroidal field is corrected by a pair of electrostatic horizontal steerers at the entrance and the exit of the electron beam device.

9 CONCLUSION

It was shown that an electrostatic storage ring can be used to store atomic and molecular ions, including bio-molecular ions, at sufficiently long lifetimes with moderate intensities. The lifetimes are long enough to cool vibrationally excited ions for those molecules with dipole moments. The ring can store ion beams independent of their masses. Therefore, it is especially suitable for studying macromolecules, like bio-molecular ions. If we introduce electrons into the ring, they can open up a way to conduct research on atomic collisions. Thus, the ring is very attractive for studying chemistry and biology as well as physics.

10 ACKNOWLEDGMENTS

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11 REFERENCES

[1] T.Tanabe et al., Phys. Rev. Lett. 70 (1993) 422.
[2] S.P.Møller, Nucl. Instr. and Meth. A 394 (1997) 281.
[3] S.P.Møller, U.V. Pedersen, Proceedings of the 1999 Particle Accelerator Conference, New York, 1999, p. 2295.
[4] T.Tanabe, K.Chida, K.Noda, I.Watanabe, Nucl. Instr. and Meth. (2001), in press.
[5] M.Sekiguchi, H.Matsushita, I.Jonoshita, M.Kabasawa, Rev. Sci. Instrum. 69 (1998) 837.
[6] D.Habs et al., Nucl. Instr. and Meth. B43 (1989) 390.
[7] S.P.Møller, P.Bowe, J.S.Nielsen, U.V.Pedersen, Proceedings of the 7th European Particle Accelerator Conference, EPAC2000, Vienna, 2000, p. 788.
[8] E.Syresin, private communications.
[9] T.Tanabe et al., Nucl. Instr. and Meth. A441 (2000) 326.