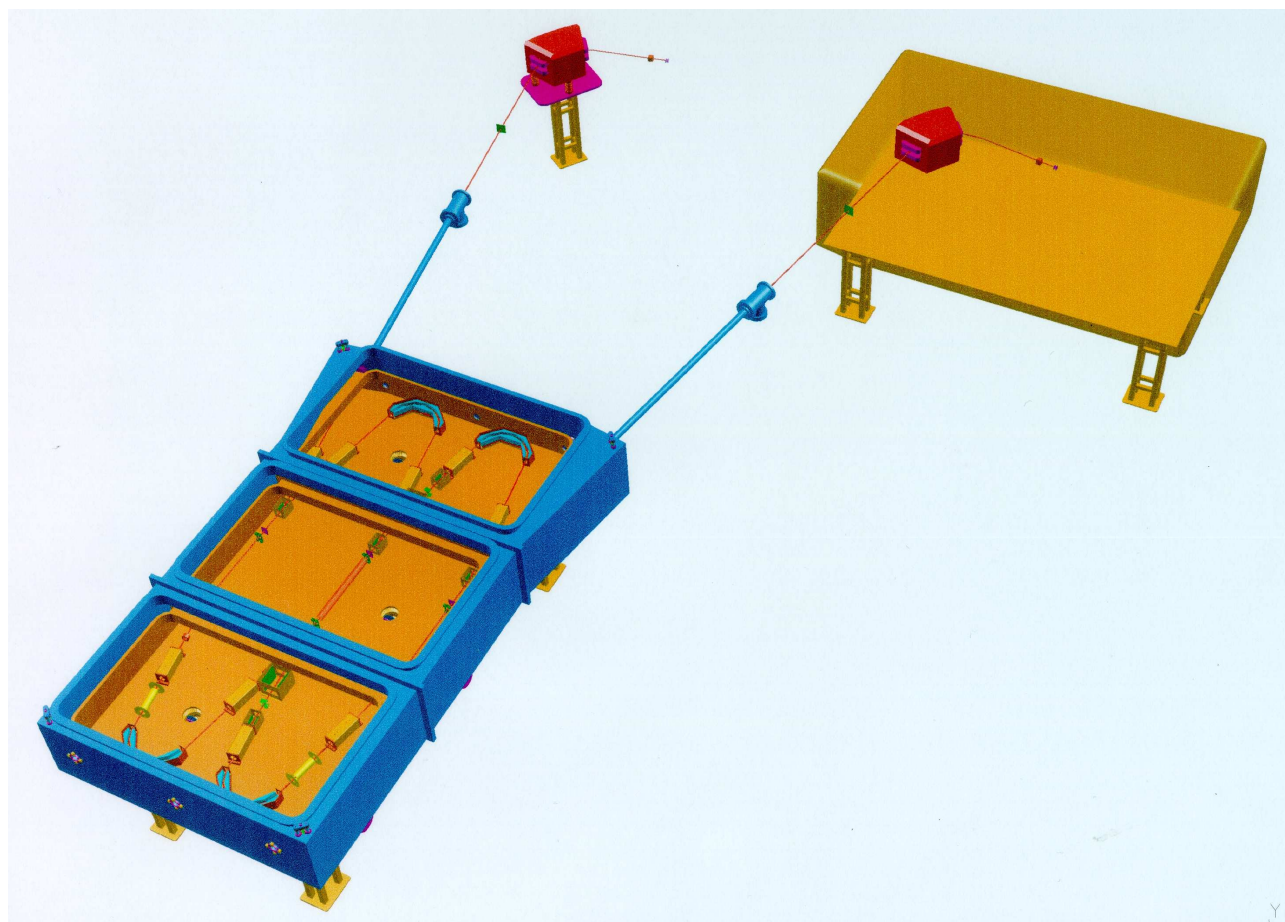


# The DESIREE project at MSL

Report from the 2002 design study

Updated 27 March 2003



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Report from the 2002 design study, 1 October 2002 updated 27 March 2003)

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## ***Summary of the design study***

*A design study of an electrostatic accelerator DESIREE – Double ElectroStatic Ion Ring ExpERiment – has shown that the construction of a double ring structure for merging positive and negative ions is feasible. The accelerator system can be cooled down to a temperature of around 15K. A scientific program and some experiments as well as technical details of the design are presented in this report. Work until end of March 2003 is included. The cost for the system is estimated to 25.2 MSEK (cost for personnel with salary from the MSL running budget is not included). The major parts of the investments will be needed in the second year of the project and commissioning is planned for the end of the third.*

## ***Introduction***

An application for a grant of 23 075 kSEK for designing and construction of a compact double electrostatic storage ring at the Manne Siegbahn Laboratory in Stockholm was sent to the Swedish Research Council in the spring 2001.

The review of the application was positive and a grant of 1 025 kSEK was given for a design study during 2002, while a decision about the full application was postponed until autumn 2002. The applicants, prof. Örjan Skeppstedt, doc K-G. Rensfelt and doc. Håkan Danared, MSL, were asked by the Research Council to submit a report about the design study on 1 October 2002 at the latest. The design work has continued also after the delivery of the report and the work until end of March 2003 is accounted for in this report.

## ***Overview of the project***

### **The DESIREE design-study group**

The work with development of the DESIREE project during 2002 is done by a design-study group from MSL and from Fysikum at Stockholm University. The team has established several contacts with scientists and experts from other institutions.

The scientific motivations for the project has developed with significant new and more concrete plans, although the main structure in the proposed scientific program in last year's VR-application is maintained. The work with the development of the scientific program for DESIREE is coordinated by doc. Henning Schmidt assisted by dr. Jens Jensen, both from Fysikum, SU. They have been in close contacts with the scientists, who were active in formulating the scientific motivations presented in the 2001 application. (prof. Mats Larsson, prof. Henrik Cederquist, doc. Tony Hansson, prof. Sven Mannervik, doc. Peter van der Meulen, doc. Peder Royen, doc. Henning Schmidt, SU and prof. Jan Pettersson, Chalmers/Göteborg University). Important new aspects on the experimental program on biomolecules have been contributed by prof. Roman A. Zubarev, Dept. of Material Science, Uppsala University and prof. Einar Uggerud, Dept. of Chemistry, University of Oslo.

A machine-design group, lead by doc. K-G Rensfelt, MSL works with a study of the DESIREE project. The group consists of accelerator physicists from MSL, doc. K-G Rensfelt, doc Håkan Danared, dr. Leif Liljeby, dr. Ansgar Simonsson, and a research engineer from MSL (vacuum expert etc.), mr. Lars Bagge. A mechanical constructor and draughtsman (CAD-work) from Fysikum, mr Kjell Schmidt, has been linked to the project. The coordinator for the work with the scientific program, Doc Henning Schmidt and dr Jens Jensen takes part in the work of the machine-design group in order to ensure close links between the scientific and technical aspects of the

project. Miss Marie Andersson is doing her diploma work (“fysikerlinjen”, SU) on ion-optics calculations for DESIREE with doc. Håkan Danared as principal supervisor.

The scientific program and the design of the DESIREE facility have developed in parallel in an iterative interplay between future users and the machine design group. The users supply the new ideas and request new options to be available, while the design group with its practical and economical responsibilities helps to find practical solutions and when necessary to define where the limits of feasibility lie.

## **Scientific motivations and experiments**

Here some of the important scientific motivations and some proposed experiments at DESIREE are outlined. Detailed descriptions are given below in the section “Experimental projects at the DESIREE facility”, in which a rather broad scientific programme at the new facility is described.

### *Merged beam experiments*

The most important unique feature of DESIREE is the possibility to perform merged-beams experiments with positive and negative ions that are stored and cooled to low temperatures, around 15K, by temperature equilibrium with the surroundings.

Examples of research utilizing these features are:

Mutual neutralization in fundamental systems (atomic and molecular)

Mutual neutralization in astrophysical plasmas

Mutual neutralization in atmospherical ion chemistry

Studies of “Electron Capture Dissociation”-like processes and the physics in biomolecules after electron capture

One basic idea of this type of research program is the possibility to study selectively such collisions in which the negative ion is assumed to provide an electron for collision with a positive ion, while the remaining neutral atom acts as a spectator. Compared to today’s research on electron-ion collisions at ion-storage rings, DESIREE will give the unique additional possibility to study temperature dependence of the processes down to temperatures in the 15K region, where vibrational excitations of molecules are excluded and only few rotational levels are populated.

In other studies with merging negative and positive ions, however, the presence of the negative ion as an entity – and not only providing an electron - in the collisions is a new key parameter. Such research is of relevance e.g. for the understanding of processes in astrophysical plasmas, where molecular anions provide parts of the negative charge in addition to electrons and accordingly play an important role for interstellar chemistry. DESIREE gives optimal conditions for such studies as the low temperature and the excellent vacuum simulates the interstellar environment, where the processes take place.

### *Single-ring experiments*

DESIREE offers new possibilities also for single-ring experiments.

#### Life-time measurements

The ultra-cool environment and extreme vacuum together with the absence of magnetic fields offer ideal conditions for lifetime measurements of metastable negative ions.

#### Atomic and molecular laser spectroscopy

An electrostatic ring is an ideal combination of a single-pass set-up for high spectral resolution and a storage ring for long observation. The conditions for studies of lifetimes of atomic metastable ions

with the same technique for Fast Ion Beam LASer Spectroscopy (FIBLAS), that has been developed at CRYRING, are excellent at DESIREE. Due to the small dimensions, the efficiency for laser excitations as well as for passive fluorescence detection will be very high.

For molecular laser spectroscopy, the cold environment and ultra-high vacuum of DESIREE will offer excellent conditions. Molecules can be cooled so only a few rotational levels are populated and the vacuum conditions provide an almost background free environment for e.g. photodissociation experiments.

### Experiments on biomolecules

Again the cooling feature of DESIREE will provide new experimental possibilities. As example, ion mobility determination can be used for selecting ions of a specific structure (e.g. degree of folding/unfolding). When transferred to the cold DESIREE environment, the ions will be 'frozen' in their state of conformation and experiment can be performed on molecular ions – as e.g. proteins with well defined 3-dimensional structures.

### Highlights of proposed experiments:

Out of the section 'Experimental projects at the DESIREE facility' we select here two examples with high scientific potential:

The diffuse interstellar absorption bands are features in the visible and near-infrared observed as absorption in the diffuse interstellar clouds. This environment is highly interesting as the primary synthesis of small polyatomic molecules is considered to take place there. It is speculated that anions of carbon chains or hydrocarbons may be responsible for these bands. In DESIREE, two projects are proposed which relate to this problem. Firstly it is possible to perform molecular spectroscopy with vibrationally relaxed species, and secondly, if anions are shown to be present in the interstellar clouds, it is of high interest to investigate their influence on the interstellar ion chemistry through collisions with the most abundant positive ions studied in merged beams of positive/negative ions.

To extract information on the amino acid residue sequence and the three-dimensional structure of proteins in mass spectrometry, it is necessary to break up the molecule in fragments. This is traditionally done in collisions with neutral gases, but through the process of electron capture dissociation (ECD) free electrons have the ability of introducing cleavage of bonds usually not affected in gas collisions [R. A. Zubarev et al., J. Am. Chem. Soc. 120, 3265 (1998)]. While proven effective in practical application, the detailed mechanism of ECD is not known at present. As described in more detail below, we expect to be able to shed light on this problem by investigations of the ECD-like process of mutual neutralization between protonated biomolecules and low electron affinity anions in low relative energy merged-beams collisions.

### Initial experiments

The conceptually simplest experiments conceivable in storage rings are lifetime determinations of metastable ions.

The cold environment and extreme vacuum expected in DESIREE will offer ideal conditions for a high precision experiment to improve the accuracy of the life time of the most fundamental negative ion, He<sup>-</sup>. Also lifetimes of other negative ions could be studied at an early stage after commissioning of the system.

Another early type of experiment could be studies of lifetimes of metastable atomic levels using the laser-based techniques with laser probing and optical pumping, that have been developed at CRYRING by Mannervik et al.

A third early type of lifetime measurements that could be performed are experiments on lifetimes of larger molecular ions as fullerenes and biomolecules as amino acids.

## **The DESIREE accelerator system**

A view of the DESIREE accelerator system, as outlined in the design study, is shown on the cover page of this report. A short overview of the system is presented in this section. A more detailed description is given in the section “Technical details of the DESIREE facility” below.

The scientific demands of performing merged beam collisions of positive and negative ions and of storing molecular ions with low internal rotational-vibrational excitation has led to the design of a double ring structure encompassed in a double wall tank. The accelerator structure and the inner aluminium wall can be cooled down to around 15K by use of a cryogenerator. The outer wall at room temperature is made of ordinary steel. The space between the walls will be filled with superinsulation and includes an intermediate temperature shield.

All experiments which need to, or can, be performed at low temperature will benefit from the fact that a temperature around 15K inherently guarantees an excellent vacuum. However, due to requirements of some of the proposed experiments and for flexibility for future demands, provisions have been made also for running experiments at room temperature.

Each ring will have one straight section for injection of ions and one common straight section allowing for merging of circulating positively and negatively charged beams in the two rings. All straight sections will be provided with ports for experimental set-ups (detectors, lasers etc.) in both directions. The cool down time will make exchange of equipment inside the inner tank time consuming. Therefore some general purpose detectors will be positioned after the merger section to be used by all experimental groups.

The energies of the circulating ions are set by the injection energies defined by the voltages on the high voltages platforms of the injectors for the two rings. The maximum voltages of the two platforms will be 25 kV and 100 kV respectively.

The condition that the velocities should be the same in merged-beam experiments implies that the energy ratio must be the same as the mass ratio of the ions in the two rings. The rings will have small RF systems to allow bunching of the beams and they will have the same circumference, 9,2 m, to allow the beams in the two rings to be in phase. The rings will have the same voltage specifications although the ion optics elements of each ring will not be located in the same positions due to differences in the beam paths for the two beams in the merging section and the injection straight sections.

All ion-optic elements of the rings and of the transport lines from the injectors to the rings will be purely electrostatic. The only magnetic elements will be analysing magnets after the ion sources in the injector systems. The magnet of the high energy injector will allow transmission of singly charged ions of masses up to  $10^5$  Da at 2 keV total energy.

The scientific potential of DESIREE requires a versatile supply of ions. A number of ion sources for singly charged light ions are available today at MSL for CRYRING experiments. These should be possible to use also at DESIREE. Three new and dedicated ion sources are proposed to be included in the project: A source for negatively charged ions, an electrospray source, mainly for biomolecular ions and a small ECR source for higher charge states and large currents of low charge state ions.

## **Time schedule**

The status of the design work is such that a period of one year will be required for optimising the overall design and details of the different parts of the system. This means that the main part of the investment money is needed during the second year after decision on funding. Assuming the resources discussed below it is estimated that first injection of a beam into DESIREE at room temperature could be possible during the middle of the third year and at 15 K half a year later. The time schedule is discussed in some more details below in the section “Technical design”

## **Manpower**

Extra personnel, outside the MSL ordinary staff, needed to construct DESIREE is dependent on the development of the normal running budget for the laboratory. It should be emphasized that the construction and later running of the system is very much dependent on the competence and knowledge of persons in the staff of MSL. The possibility to share staff between the running of CRYRING and the construction and later on the running of DESIREE is very cost effective.

The staff needed to construct DESIREE is estimated to consist of 1.5 accelerator physicist/project manager, 2.5 mechanical engineer and 2 electronic/engineer in average for 3 years, starting after ending the design study. Besides the work of these persons it is anticipated that some 1150 mandays for mechanical manufacturing and some 135 mandays have to be bought from other university departments and from industry.

## **Cost estimates**

### *The construction of DESIREE*

In the “Technical design” section a total cost estimate of 25.2 MSEK for the construction of DESIREE during the three year period is presented. This amount assumes that MSL will contribute with experienced manpower corresponding 6.8 MSEK and that the overall infrastructure of MSL can be used.

In table 1 of the “Technical design section” a break-down of the cost estimates is presented. Besides the personnel cost, the major areas of expenditures are injectors (6,8 MSEK), the two rings (7.1 MSEK) and HV Power supplies (4.1 MSEK).

As already mentioned, three ion sources are included in the project to ensure possibilities for a versatile ion-production program for the facility. As also was mentioned earlier, a general purpose detector system to be positioned inside the tank of the system is included in the project costs.

### *The running of DESIREE*

The running of the DESIREE facility should not be very complicated. It is assumed that about 1.5 to 2 full time equivalent staff members from MSL should be needed. Again it should be emphasized that this estimate assumes that the infrastructure of MSL is available and the competence needed can be spread over the MSL staff. The operating of DESIREE outside normal working hours should be possible to coordinate with the operation of the CRYRING facility and should not require extra staff.

## **DESIREE users**

The DESIREE facility will offer new exciting research possibilities. A number of leaders (from Stockholm and Gothenburg mainly) for existing projects at CRYRING have been strongly involved in the working out of the scientific program at DESIREE. These scientists have strong contacts with most of the user groups at CRYRING and it is natural to assume that the existing CRYRING community will be the base for the first years use of DESIREE.

The complementary features of CRYRING – with e.g. the unique electron cooler/target – and DESIREE – with e.g. its unique low temperature environment for accelerators – facilities will be of strong scientific value for the user groups. With the two facilities available, one can anticipate somewhat longer experiment periods for the projects run at the facilities than what is currently scheduled at the CRYRING facility. Many of the projects should certainly benefit from that.

The research program at DESIREE has its base in the science and technique developed at CRYRING and other storage ring facilities. There is however a new element of research with biomolecules that has a potential to attract new users from other fields than the atomic and molecular fields of the present user community at CRYRING. It should, however, be realized that it takes rather long time for new users, who have no experience of accelerator based research, to initiate and also to participate in research at an accelerator. The physicists, who are used to this type of research, have to form the bridges to new groups of users in a process that has to take some time, when the facility begins to work. The field of synchrotron radiation science is an example on such development.

We are, however, very satisfied that a new group from Uppsala with prof. Roman A. Zubarev as leader has taken very active part in the formulation of the scientific program for DESIREE. Prof. Zubarev has a very good experience from the biophysics field, where he has worked in a strong scientific environment in Odense, Denmark and also in USA. The Odense group is well known for work in “physics oriented” biophysics e.g. massspectrometry of biomolecules and dissociative recombination of biomolecules.

MSL with Fysikum at SU as partner is a member of the EU-network LEIF (Low Energy Ion beam Facilities). This network is now planning to approach the 6:th framework program with an application of support from the the so-called Integrated Infrastructure Initiatives (I<sup>3</sup>), which combine Transnational Research Access, Research and Technical Development and Networking elements of the 5:th framework. In the discussions within the LEIF community, the DESIREE project has been considered to be an important new component of the collaboration and it can be expected that groups from the LEIF network will form a very interesting new user community for research at DESIREE.

# *Scientific programme at the DESIREE facility.*

## **Introduction**

Here we present the status of the scientific program for the DESIREE project. Some aspects are similar to the program of last year's original proposal, but many significant new and more concrete plans are also included.

While the original idea to initiate the DESIREE project obviously had its background in ideas for future experiments, the development of the design work has also had strong impact on the formulation of the present scientific program. This program and the design have developed in parallel in an iterative interplay between the future users and the machine design group. The users supply the new ideas and request new options to be available, while the design group with its practical and economical responsibilities helps to find practical solutions and when necessary to define the limits of feasibility.

This text is organized in order of increasing complexity both in the systems studied and in the experimental technique. We start by discussing experiments on atomic and small molecular ions in first single-ring and later merged-beams configuration. In the present context we define 'small molecules' to be any molecule besides those of biological interest. Thus  $C_{60}$  will be included among the small molecules even though it is heavier than the smallest biomolecules (single amino acids). Then we move on to discuss the larger molecules of biological interest. This order of the material does not mean that the biological systems are considered to be less important. On the contrary the studies of peptides, proteins, and perhaps even DNA made possible by the high upper mass limit of the electrostatic system remain the primary motivation for the present project.

## **Experiments with atomic and small molecular ions**

### *Single-Ring Experiments*

#### Lifetime measurements of metastable ions.

The conceptually simplest experiment that is conceivable in a storage ring is the lifetime determination of an intrinsically unstable species. Metastable negative atomic ions that decay via autodetachment on a  $\mu\text{s}$  or  $\text{ms}$  time scale are among the simplest such systems. The negative ions are stored in the ring and as they decay with a time-independent decay rate the number of stored ions will decrease exponentially. The detachment process itself delivers a sensitive tool for a relative measurement of the number of stored ions as the neutral atoms produced in the process leave the ring and can be detected. Any metastable negative ion can be studied with this technique, but here we limit ourselves to one example: The most fundamental metastable negative ion  $\text{He}^-(1s2s2p\ ^4P_{3/2})$  was studied as one of the first experiments at the ASTRID storage ring in Århus [T. Andersen et al. Phys. Rev. A, **47**, 890 (1993)], and constituted a great improvement over earlier lifetime determinations for this ion. However, the accuracy was limited to about 5% by two systematic effects: The dipole magnets mixed the  $J=5/2$  with the much shorter lived  $J=3/2$  fine structure level, and the thermal radiation from the 300 K vacuum chamber walls acted to decrease the measured lifetime by photodetaching the excess electron bound by only 77 meV with respect to the neutral  $\text{He}(1s2s\ ^3S_1)$  state. This situation has been somewhat improved by the use of electrostatic storage devices (storage ring ELISA, Århus [U. V. Pedersen et al, Phys. Rev. A, **64**, 012503 (2001)] and electrostatic trap, Weizmann Institute, Israel [A. Wolf, et al. Rev. A, **59**, 267 (1999)]), but the uncertainties are still a few per cent (and presently not overlapping). The very cold environment and extreme ultra-high vacuum expected in DESIREE will together with the absence of magnetic fields offer ideal conditions for a high-precision (few per mille uncertainty) benchmark

experiment on this fundamental system, where the prospects for future theoretical work of similar accuracy are best.

When applying this technique to larger systems such as fullerenes, more subtle effects come into play and much more information can be extracted. Due to the high number of internal degrees of freedom sufficient energy is stored in the molecule to make spontaneous fragmentation or electron emission possible even for intrinsically stable systems at modest temperatures. When initially hot molecules are stored the decay curve is not exponential, but rather scales with time as  $1/t$ . The reason for this deviation from the usual exponential decay law is that the hotter molecules has a higher fragmentation probability than the colder ones, so that the distribution of temperatures and thus mean fragmentation probability changes with time. At ASTRID and ELISA in Århus this statistical decay has been investigated for e.g. negative fullerene ions ( $C_{60}^-$ ,  $C_{70}^-$ , etc...) [see e.g. J. U. Andersen et al., Phys. Rev. A, **65**, 053202]. Here we want to apply this technique in the studies of multiply charged positive fullerenes ( $C_{60}^{q+}$ ,  $q=2-5$ ) that can be produced in the ECR ion source [R. Völpel et al., Phys. Rev. Lett. **71**, 3439 (1993); H. Cederquist et al. Phys. Rev. A. **63**, 025201 (2001)]. These systems are known to fragment spontaneously on a ms or  $\mu$ s time scale when produced hot, whereas the presence of a truly stable ground state remains an open question. Even at room temperature several eV of internal energy is stored in the molecule and observation of spontaneous fission does not rule out the presence of a stable ground state. Allowing the molecular ions to cool down to the 15 K range proposed for DESIREE will make the determination of the upper charge limit for truly stable fullerenes possible.

#### Laser spectroscopy of atomic ions

The decay of the metastable systems discussed in the previous sub-section leads to a change in the charge and/or mass so that the ions are no longer stored. In the present sub-section we discuss metastable states of positive atomic ions, the path of which are not affected by the decay to a lower energy level. Therefore more sophisticated techniques are required to extract the lifetimes of these metastable states.

About five years ago a new application of Fast Ion Beam LAser Spectroscopy (FIBLAS) was introduced at CRYRING by Mannervik *et al.* The technique has been developed to a very competitive method for studies of lifetimes of metastable levels. Lifetimes from 10 ms to 1 s have been measured with accuracies down to 1 %. So far, two laser-based techniques have been utilized: laser probing and optical pumping. Both methods take advantage of the selectivity and resolution achieved in collinear laser spectroscopy [S. Mannervik et al., Phys. Rev. Lett.,**83**, 698 (1999)].

An electrostatic storage ring is an ideal combination of a single-pass set-up for high spectral resolution and a storage ring for long observation. In such a ring it will be possible to take advantage of the credits of both methods. The limiting factor in the spectral resolution will be the Doppler broadening, which can be kept as low as about 50 MHz with the well stabilized high voltage supply for the ion source platform. With such conditions, high-resolution spectroscopy should be feasible in the same fashion as in single pass experiments. Isotope shifts have been accurately measured in single-pass by switching the isotope separator between the different isotopes. In an electrostatic storage ring it will be possible to store the different isotopes (or a selected number of isotopes as well as a specific combination). The ring is only energy selective and the ring itself will guarantee that the same kinetic energy is maintained for the isotopes. Laser spectroscopy would here be directly applicable to perform very accurate measurements of isotope shifts. There might also be situations where it would be desirable to store different elements simultaneously at the same energy in order to perform relative measurements of spectroscopic quantities.

In DESIREE measurements of metastable lifetimes can be performed in a similar fashion as have been done in CRYRING. In fact, the conditions for such measurements should be considerably better in such a small ring. Due to the smaller dimensions, the efficiency for laser excitation as well as for passive fluorescence detection will be about ten times higher. The smaller dimensions allow for lifetime measurements of much shorter lifetimes in the  $\mu$ s region. For studies of magnetic

mixing of states due to fine structure and hyperfine structure interaction an electrostatic ring is better since interfering external magnetic fields are avoided. This also allows for selective studies of magnetic effects by applying magnetic probe fields.

More generally, a small storage ring of this kind is better suited for preparation of the beam in specific states by the use of optical pumping, laser excitation, radio-frequency excitation, field quenching etc. Such preparation may open new possibilities for advanced selective studies.

#### Laser spectroscopy of molecular ions

Whereas the FIBLAS technique for *atomic* ions rely on detection of fluorescence, spectroscopy of *molecular* ions more often rely on the detection of fragments (atomic or molecular, neutral or charged) arising from the breakup of the parent molecular ion induced by absorption of a photon. Thus, the molecular ion is photo-excited from a bound level to either an unbound level residing in the nuclear continuum or to a quasibound level, which is coupled to the continuum. In either case, the molecule breaks up and one or several of the resulting fragments are detected. The technique was developed in the late 1970s at linear single-pass accelerators [J. P. Moseley, Adv. Chem. Phys., 40, 245 (1983)], and has been applied, although not extensively, also at ion storage rings [U. Hechtfisher et al., Phys. Rev. Lett. **80**, 2809 (1998)].

In the single-pass version of molecular ion spectroscopy, the ions often occupy a broad distribution of vibrational-rotational levels, because the molecular ions are produced hot in the ion source and have little probability to relax to the ground vibrational level in the short time scale of the experiment. The single most important feature of DESIREE in this context is to allow not only vibrational but also rotational cooling. With the proposed temperature range around 15 K, only a few rotational levels are populated. The second most important point is the excellent expected vacuum conditions. In experiments relying on photodissociation for the detection of photon absorption, collision with rest gas molecules leading to molecular breakup is the most significant background process, but bearing the expected extreme vacuum conditions in mind, this contribution will not be significant.

A very interesting prospect for molecular absorption spectroscopy is to consider anions possibly responsible for the hitherto not definitely identified diffuse interstellar absorption bands. These features in the visible and near infrared are observed when light from distant sources pass through diffuse interstellar clouds on their way to Earth. Both Polycyclic Aromatic Hydrocarbon anions [A. Léger and L. d'Hendecourt, Astron. and Astroph. **146**, 81 (1985)] as well as negatively charged carbon chains [Tulej et al., Astrophys. J, **506**, L69 (1998)] have been put forward as candidates for these features, but completely convincing evidence has not yet been provided. The extreme vacuum and low temperature of DESIREE will make it possible to study these molecular anions in very low vibronic states and thereby mimic the conditions in the interstellar medium. The experimental technique will be similar to that of Tulej et al with two laser beams, one of which is scanned over the absorption features, while the other (e. g. the 3<sup>rd</sup> harmonic of a Nd: YAG) is used to selectively photodetach the excited molecular ions to produce a detectable neutral product.

A new form of molecular laser spectroscopy applicable to larger molecules (e.g. fullerenes) has been developed in Århus at the ASTRID and ELISA storage rings. As discussed earlier (sec. "Single-Ring experiments") hot negative fullerenes may spontaneously emit their excess electron and become neutral. However, the probability for this to happen depends very strongly on the internal temperature of the anion. Because of the very fast coupling between the electronic and vibrational degrees of freedom the molecules can be heated up to temperatures corresponding to the absorption of several photons from a single ns-duration laser pulse. The increase in the electron detachment rate as a function of the applied laser wavelength gives the desired absorption spectrum. [K. Hansen et al, Eur. Phys. J. D, **9**, 351 (1999)]. Very recently this technique was also applied to study biomolecular ions in ELISA [S. B. Nielsen et al., Phys. Rev. Lett., **87**, 228102 (2001)]. It is particularly motivated to apply this technique in DESIREE for systems where the low initial temperature is important.

## Merged-beams experiments

The possibility to perform merged-beams experiments with positive and negative ions that are stored and cooled to low temperatures by temperature equilibrium with the surroundings is the most clearly unique feature of the present project. In the following sub-sections we discuss this technique and a number of different possibilities for positive/negative ion collision studies at the low relative energies offered by the merged-beams configuration. The use of the merged-beams technique in studies of biomolecules is discussed below.

### General considerations on count rates and background in merged-beams experiments

The level of detail of the present document is not aimed at providing count rate estimates of every proposed experiment. It appears, however, relevant to present this for one example of merged-beams experiment, as it is not entirely obvious that the stored ion beams can be made sufficiently dense to obtain a reasonable signal in this configuration.

The count rate in a merged-beams experiment is given by:

$$R = \frac{I^+ I^-}{e^2} \frac{v_{\text{rel}}}{v^+ v^-} \frac{L \sigma}{A_{\text{max}}}, \quad (\text{eq.1})$$

where  $I^{+/-}$  are the positive/negative ion currents,  $v^{+/-}$  the positive/negative ion velocities,  $v_{\text{rel}}$  the relative velocity,  $L$  (=80 cm) the length of the interaction region,  $\sigma$  the cross section of the process under investigation,  $A_{\text{max}}$  the larger of the two cross sectional beam areas, and  $e$  the elementary charge.

As an example we consider the mutual neutralization process in  $\text{H}^- - \text{H}_2^+$  collision, which is discussed in more detail in the following sub-section. With 10 keV  $\text{H}^-$  and 20.5 keV  $\text{H}_2^+$ , the energy in the relative motion will be only about 1 eV<sup>1</sup>. For  $\sigma$  we take the value that follows from the electron-transfer distance from a classical over-barrier estimate (see "Mutual neutralization in fundamental systems") and find  $\sigma = \pi(13.5 a_0)^2 = 1.6 \times 10^{-14} \text{ cm}^2$ .  $A_{\text{max}}$  we set to  $1 \text{ cm}^2$  and finally we assume modest values of the ion currents for these simple ions by setting  $I^+ = I^- = 100 \text{ nA}$ . Inserting these parameters in eq. 1 yields a rate of  $44 \text{ s}^{-1}$ . To find a background rate for comparison, we need to make an assumption concerning the density of residual gas. It is expected that a similar vacuum to that of CRYRING ( $10^{-12} \text{ mbar}$ ) can be obtained in DESIREE at room temperature and that the cooling to 15 K will result in a reduction of the *density* by about a factor of ten (the *pressure* is reduced by a larger factor, but here the density is the relevant entity). At the present energies the cross sections for loss of an electron from  $\text{H}^-$  and capture of an electron to  $\text{H}_2^+$  will both be about the geometrical cross sections for contact between two  $1 \text{ \AA}$  diameter objects. (We set  $\sigma^{1-0} = \sigma^{-1-0} = 2 \times 10^{-16} \text{ cm}^2$ ). With an interaction length of 80 cm and two 100 nA beams this yields a background of  $48 \text{ s}^{-1}$ . So signal and background are about equal, but the fact that *two* neutrals can be detected from a mutual neutralization process whereas only one fast neutral particle is produced in background events gives the possibility of reducing the background by more than a factor of thousand! Please note that the present example gives a conservative estimate of  $R$  combining high velocity with modest currents (cf. eq. 1).

### Mutual neutralization in fundamental systems

One of the most successful applications of CRYRING and the other similar-sized heavy-ion storage rings in Århus and Heidelberg during their first decade of operation has been and still is the investigation of recombination between small molecular ions and free electrons [M. Larsson (1997) *Annu. Rev. Phys. Chem.* **48**, 151 and references therein]. Here we consider the mutual neutralization between small molecules and negative atomic ions, which is related to the molecular recombination in a manner described in the following.

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<sup>1</sup> This *kinematical compression* is a trivial consequence of the quadratic dependence of the kinetic energy on the velocity and here it has the consequence that the practically attainable lowest collision velocities will depend on the transverse velocity spreads and will be determined by the alignment and focusing of the two ion beams.

As an example we consider the simple system  $H^- + H_2^+$  and consider whether the molecule will dissociate after electron transfer from the negative ion or not. As the distance between the two collision partners decrease, the potential barrier that prevents the excess electron from  $H^-$  from jumping to the energetically more favourable positive molecular ion will decrease in height. According to a simple classical over-the-barrier estimate the barrier height will vanish at a distance as large as 13.5 a.u. The electron will be released from the negative ion to form an excited state of the neutral  $H_2$  molecule closely inside this critical distance. This excited state belongs to the Rydberg series, which converges to the  $1s\sigma_g$  ground state of the  $H_2^+$  molecular ion. The corresponding potential energy curve crosses that of the doubly excited  $(2p\sigma_u)^2 \ ^1\Sigma_g^+$  resonance state and pre-dissociation along this path is possible. On the other hand, the crossing of these two  $H_2$  potential energy curves occurs at an internuclear distance exceeding the classical outer turning point of the lowest vibrational level of the Rydberg state. This means that the predissociation will rely on tunneling through a barrier and thus the rate will be dramatically reduced. As a consequence the usually much slower process of radiative stabilization may become competitive, in which case the formation of neutral molecules will be an important channel. In the related molecular recombination process, dissociation has almost unit probability. For that process the dominant channel is one where the doubly excited resonant state is formed directly in the capture process. By replacing  $H^-$  with other negative ions with varying electron affinities, we can choose which levels to form after the initial capture process and thus study the pre-dissociation versus radiative stabilization for different Rydberg levels, and may view such a series of measurements as an extension of the dissociative recombination studies of this molecular ion to *negative* electron energies. A consequence of the large projectile-target distance at the time of electron transfer is that for a large majority of the mutual neutralization events the impact parameter is much larger than the  $H_2$  internuclear distance. This supports the assumption that the remaining neutral atom plays no role after providing the active electron.

The multihit microchannel-plate detector with its capability of determining arrival times and positions of several particles from the same collision event will (besides acting to suppress the background as described in the previous sub-section) allow detailed analysis of the kinetic energy released in the event of dissociation of the neutral molecule. The kinetic energy release will in that case reveal the energetic position of the intermediate state of the neutral molecule populated in the initial electron transfer process.

#### Mutual neutralization in astrophysical plasmas

The formation of polyatomic ions in the interstellar medium is considered to be through chemistry involving ionized species. The degree of ionization in the interstellar clouds is determined by a balance between ionization by cosmic radiation and neutralization processes. In the gas phase two such processes exist: Electron-ion recombination and positive/negative ion mutual neutralization. One of the primary motivations for the studies at CRYRING of dissociative recombination for astrophysically abundant cations (e.g.  $H_2^+$  ( $HD^+$ ),  $H_3^+$ ,  $OH^+$ ,  $H_3O^+$ ,  $CO^+$ ,  $HCO^+$ ,  $CH_2^+$ ,  $CH_3^+$ , and  $CH_5^+$  [M. Larsson (1997) *Annu. Rev. Phys. Chem.* **48**, 151 and references therein]) has been the role of this process in interstellar chemistry in regions where the negative charge is primarily in the form of free electrons [A. Dalgarno, *Astro. Lett. Comm.*, **26**, 153 (1988)].

As discussed in "Laser spectroscopy of molecular ions" above it is speculated that anions of carbon chain molecules [Tulej et al., *Astrophys. J.*, **506**, L69 (1998)] or polycyclic aromatic hydrocarbons [A. Léger and L. d'Hendecourt, *Astron. and Astroph.* **146**, 81 (1985); M. K. Crawford, A. G. G. M. Tielens, and L. J. Allamandola, *Astroph. J.*, **293**, L45 (1985)] may be present in diffuse interstellar clouds and be responsible for the diffuse interstellar absorption bands. If present in the amounts required to explain the observed absorption, it is possible that the negative charge is more often in the form of anions than free electrons. In such an environment the role of mutual neutralization in the ion chemistry is more important than dissociative recombination and the possibility offered by DESIREE to study these processes highly relevant to this field [A. Dalgarno, Private comm. (2001) and in 'Proc. Of the 1999 conf. On Dissociative Recombination', eds. M. Larsson, J. B. A. Mitchell, and I. F. Schneider (2000)].

## Role of mutual neutralization in atmospheric ion chemistry

Ions are formed in the terrestrial atmosphere by the action of UV radiation, cosmic rays and radioactive emanation. Below an altitude of 70 km in the atmosphere mutual neutralization in positive/negative ion-ion collisions is the major loss process for charged particles. The details of these collision processes are at present largely unknown.

The nature of the ambient ions in the atmosphere has been established using ground-based and balloon-borne mass spectrometry in the troposphere and stratosphere, and using rockets and satellites in the upper atmospheric regions. Below about 90 km, molecular ions dominate the ion population and the ions become increasingly complex with decreasing altitude. At low altitudes the dominant charged species are polyatomic cluster ions, such as  $\text{H}^+(\text{H}_2\text{O})_n(\text{NH}_3)_m$ ,  $\text{NO}_3^-(\text{HNO}_3)_n$  and  $\text{HSO}_4^-(\text{HNO}_3)_m$ .

The ion chemistry is dominated by switching and proton transfer reactions involving chemically active minority species. The initial positive ions are the products of the ionization of the major neutral molecules, i.e.  $\text{N}^+$ ,  $\text{N}^{2+}$ ,  $\text{O}^+$  and  $\text{O}^{2+}$ . The primary ions react efficiently with ambient  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and are converted into  $\text{H}^+(\text{H}_2\text{O})_n$ . The water cluster ions continue to react with minority species that exist in the atmosphere, and are converted into complex cluster ions of the type  $\text{H}^+(\text{H}_2\text{O})_n(\text{bases})_m$  (bases =  $\text{NH}_3$ ,  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{OH}$ , etc.).

In parallel with the positive ion processes, a rich negative ion chemistry develops from the primary negative ions  $\text{O}^{2-}$  and  $\text{O}^-$ . In the upper atmosphere, free electrons are the dominating negatively charged particles. However, in the lower regions attachment rates are sufficiently fast that the negative charge is primarily in the form of anions. The primary anions are converted into the stable ion  $\text{NO}_3^-$ , and consecutive reactions produce ions like  $\text{NO}_3^-(\text{H}_2\text{O})_n(\text{acid})_m$  with acids  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ .

Other minor constituents of the atmosphere, including organic species, could also be involved in the positive and negative ion chemistry. It should be noted that pollutants of anthropogenic origin including  $\text{NH}_3$ ,  $\text{NO}_x$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  have a particularly strong influence on the ion chemistry.

A major challenge of atmospheric ion chemistry is to identify the routes to the observed ions and to quantitatively explain their relative concentrations. The details of the ion processes are determined by binding energies of clusters, temperature in accordance with thermodynamic constraints, and relative concentrations in atmospheric air. Of particular importance are the ion removal processes. The gas phase destruction process for stratospheric and tropospheric cluster ions is known to be dominated by mutual neutralization. However, little is known about the rates for these reactions, and the products formed are at present a matter of speculation. It is likely that considerable fragmentation will occur, producing the individual composite molecules. Partial coalescence may also occur depending on the size and stability of the cluster ions involved. The resulting highly polarized neutral products may act as nucleation sites for other molecules, leading to the production of aerosols. Ion-induced nucleation has recently been suggested as an important route to formation of new aerosol particles in the atmosphere.

Only two specific binary cluster-cluster reaction rates have been reported, as deduced from Flowing Afterglow Langmuir Probe (FALP) measurements [D. Smith, M. J. Church, and T. M. Miller, *J. Chem. Phys.* 68 (1978) 1224], [D. Smith and N.G. Adams "Studies of Ion-Ion Recombination Using Flowing Afterglow Plasmas. In *Physics of Ion-Ion and Electron-Ion Collisions*; NATO ASI Ser. B83; Brouillard and McGowan, Eds.; Plenum: New York, 1983]. We are aware of one previous study using merged cluster ion beams. Plastridge et al. [B. Plastridge, M. H. Cohen, K. A. Cowen, D. A. Wood, and J. V. Coe, *J. Phys. Chem.* 99 (1995) 118] measured relative rate constants for the reaction  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n + \text{OH}^-(\text{H}_2\text{O})_m$  ( $m, n = 0-3$ ). The neutralization reaction mechanism changed dramatically with clustering, which was interpreted as a change from electron transfer to proton transfer with increasing cluster size.

## Collisions involving fullerenes

Since 1994 investigations of  $C_{60}$  and other fullerene molecules have been carried out at MSL. These studies have been keV collisions with highly charged ions as projectiles and the carbon molecules as target [see e.g. S. H. Schwartz, et al. Phys. Rev. A. 63, 013201 (2001)]. By coincident detection of the projectile final charge state and intact or fragmented  $C_{60}$  ions the short-time stability of these systems has been investigated. One serious concern in these experiments is the high temperature of the target molecules, which are brought into the gas phase through evaporation in an oven at a temperature of 500-600 °C thus carrying up to 10 eV of internal energy already prior to the collision. With DESIREE it is possible to perform similar collision experiments between highly charged ions from the ECR ion source stored in one ring and cold negative fullerenes ( $C_{60}^-$ ) stored in the other ring to investigate these systems in an initially cold state.

With DESIREE collisions between negatively and positively charged fullerenes at low relative energies will become possible. A first collision system could be  $C_{60}^+ - C_{60}^-$ , which is discussed in detail in last year's application. For these large molecules the transfer can be described classically when considering the molecules as small metal spheres [H. Zettergren et al., Phys. Rev. A, 66, 032710 (2002)]. Mutual neutralization will therefore be well described, by assuming it to occur with unit probability when the distance between the two molecules becomes less than the critical distance of about 10 Å. The more interesting question for this system is the formation of bound states, of which three different categories exist: Cage fusion to form neutral  $C_{120}$  molecules takes place at small impact parameters and relatively high relative energies of the order of 50 eV [F. Rohmund et al, Phys. Rev. Lett., 76, 3289 (1996)]. Formation of dimers of two neutral  $C_{60}$  molecules bound by van der Waals forces expected to occur at lower energies and for impact parameters less than the critical distance for electron transfer. Finally for impact parameters exceeding the critical distance and very low (sub eV) relative energies the formation of bound states of  $C_{60}^+ - C_{60}^-$  complexes is expected [O. Knospe and R. Schmidt, Z. Phys. D, 37, 85 (1996)].

In the framework of the LEIF (Low Energy Ion-beam Facilities) EU network experiments have been performed at CEA, Grenoble and at GANIL, Caen on keV collisions between multiply charged and neutral fullerenes [H. Cederquist et al. Phys. Rev. A. 63, 025201 (2001)]. These experiments shed light on the electrical properties of fullerene materials including the technologically promising nanotubes [J. Li, C. Papadopoulos, and J. Xu, Nature 402, 253 (1999)]. It is, however, questioned to which extent the conclusions from these rather energetic collisions between hot projectile fullerenes and hot target fullerenes can be transferred to the low temperature material properties. In DESIREE we can perform low-energy collisions between internally cold fullerenes and thus attain a situation much closer to material science conditions but still in the gas phase.

## **Experiments with Biomolecules**

The development of the electrospray technique for production of ions for mass spectrometry has been an important ingredient in the revolution in biochemistry and biotechnology over the past decade. The potential contributions to this field from a project like the present one is to investigate mechanisms in e.g. the fragmentation induced to obtain sequencing information in mass spectrometry. In the ElectroSpray Ion source (ESI) ions of biomolecules representing a very broad mass spectrum from the smallest amino acids to almost macroscopical DNA can be produced. Positively charged molecular ions produced with this technique are in general protonated versions of the neutral molecules. To get a high number of ions for injection into the storage ring, the ions from the ESI are guided by an octupole beam guide to an accumulation trap where they are trapped and cooled in a buffer gas. This same technique is being successfully used at ELISA.

Depending on the specific circumstances during the protonation process a protein ion may emerge in its natural folded 3D shape or it may have partially un-folded. The physical and chemical properties can be distinctly different for such different conformers of the protein even though the mass and charge are the same. To distinguish and select among different conformers ion mobility

experiments is a common tool. The protein ions are passed through a gas and their loss of kinetic energy is taken as a measure of their physical extension and thus reveals the degree of folding/unfolding. Ion mobility determination may be used to selectively inject into DESIREE only ions of a specific structure. When transferred to the cold DESIREE environment the ions will be 'frozen' in their state of confirmation, and we will thus attain the unique capability to perform experiments on protein ions with well-defined three-dimensional structures.

The DESIREE will be well suited for studies of the heavy biomolecules because that unlike the magnetic storage rings the electrostatic configuration does not put any practical upper limit on the mass. In practice the upper mass limit is determined by the analyzing magnet at the high-voltage platform and will be about 100 kDa (1 Da=1 atomic mass unit) for singly charged ions.

#### *Single-Ring experiments on biomolecules*

At the ELISA ring activities in the studies of biomolecular ions have commenced. The statistical  $1/t$  decays discussed for hot fullerene ions in sec "Lifetime measurements of metastable ions" above have been measured for a range of amino acids and the role of radiative cooling by infrared active vibrations has been investigated [J. U. Andersen et al 'Statistical  $1/t$  decay of collisionally excited amino acids and quenching by radiative cooling.', to be published]. Further a similar 'absorption spectroscopy via heating' method as that described for fullerenes above has been applied in absorption spectroscopy of the active chromophore of the so-called green fluorescent protein [S. B. Nielsen et al., Phys. Rev. Lett., 87, 228102 (2001)]. A specific point of discussion in the above reference was the question of the influence on the absorption features of the chromophore by the surrounding protein in its so-called  $\beta$ -can structure. With the possibility discussed above to select the conformer prior to injection and to keep this 'frozen' structure in the cold ring, measurements of absorption features of this specific chromophore or other similar 'protein-wrapped' structures can be performed for more or less un-folded conformers of the protein. This way more detailed information on the influence of the 'wrapping' protein material on the properties of the inner parts can be extracted.

#### *Merged-beams experiments on biomolecules*

Recently the process of Electron Capture Dissociation (ECD, Zubarev et al., J. Am. Chem. Soc. 120, 3265 (1998)) has been introduced as an efficient tool in mass spectrometry and sequencing of proteins and determination of their post-translational modifications. In ECD, a free electron is captured and the excess energy released when the electron gets bound is eventually dissipated in a fragmentation of the larger structure. Unlike fragmentation in collisions with heavier objects, which generally leads to cleavage of the weakest bond, the ECD process may lead to cleavages at other stronger bonds, such as the backbone N-C $\alpha$  bond and S-S bond. This way more detailed structural information can be extracted from the mass spectra. More importantly, this fragmentation appears to be acting "soft", that is cleavage of strong bonds does not affect much more labile bonds, if present. This way, positions of even very labile post-translational modifications can be determined [Mirgorodskaya et al., Anal. Chem. 71, 4431 (1999)].

While ECD is gaining popularity in mass spectrometry, there are still several open questions concerning the detailed mechanism of the process, in particular the question of the ergodicity/non-ergodicity of the process. In an ergodic process the excess energy is distributed randomly among all the degrees of freedom and fragmentation takes place when this randomized process leaves sufficient energy in one vibrational mode for that particular bond to break (a mechanism similar to nuclear  $\alpha$ -decay). The extreme case of a non-ergodic process would be a direct Dissociative Recombination process (known from studies of smaller molecules at CRYRING and other heavy-ion storage rings) in which the electron is captured into a doubly excited anti-bonding electronic state and immediate fragmentation takes place. A third way in which the ECD process is often viewed is to consider the captured electron to be bound to an excess proton of the positively charged biomolecule. The hydrogen atom formed this way is then set free and will because of its radical nature engage in a chemical reaction leading to fragmentation.

A key to a more detailed understanding of the process may be to determine the relative velocity dependence of the total ECD reaction cross section (as an example the direct Dissociative Recombination at a di-sulfide bond is expected to show a maximum at around 0.6 eV relative energy). Inside the plasma of a Fourier transform mass spectrometer, the relative velocity is not a well-controlled parameter and it is therefore of interest to perform collision experiments at a well-defined relative velocity in a beam-target experiment. This should lead not only to a better understanding of the ECD process but also to the optimization of the experimental parameters in analytical applications, and possibly to discovery of new fragmentation effects.

The very lightest amino acids (e.g. glycine and alanine) with masses below 100 amu are accessible for Dissociative Recombination studies in a merged-beams electron-ion experiment in the electron cooler of the heavy-ion storage ring CRYRING, similar to DR experiments on other small molecules performed so far. (A proposal to perform such studies has been submitted to the CRYRING Program Advisory Committee - CPAC). The main interest is, however, not so much in dissociating the amino acids but to study the fragmentation of larger structures into their constituents and in particular to investigate the ECD mechanism for small chains of amino acid residues (peptides and small proteins) in the mass range of 100-1000 amu and heavier. For these species merged-beams electron-ion experiments are not possible because the low maximum velocities in the magnetic confinement storage ring will require electron beams of sub-eV for velocity matching, which is not practical.

With a stationary electron target inside DESIREE it will be possible to perform e<sup>-</sup>-ion collisions and thus study ECD processes in amino acid based complexes of, in principle, any mass. Because of the very large mass difference of electrons and heavy molecules the range of relative velocities, which may be obtained by changing the energy of the stored positive ion beam, is relatively limited. With 100 keV as maximum energy in the ring center-of-mass electron energies exceeding 1 eV will only be available for ions with masses below 50 amu. With a sufficiently cold electron target this may be of interest for studies of light biomolecules at low relative velocities.

An apparently much more attractive idea is to make use of the unique double-ring structure of DESIREE, where we envision collision studies in which an electron is transferred from a negative ion stored in one of the rings to a positive (bio-) molecule stored in the other ring. By proper choice of anion, systems can be found where this negative ion only acts as a donor of the electron. This way we can then effectively perform electron collision experiments. An intriguing point in this context is the fact that as the electron is initially bound it will be possible to access states that are lying lower in energy than the states one can access with free electrons even at 0 eV relative energy. By tuning the relative energies of the two ion beams it is further possible to vary the relative energies exactly as in an electron-ion merged-beams experiment. The only difference being that the condition of equal velocities does not correspond to 0 eV electron energy, but to a negative energy determined by the electron affinity of the anion (see the discussion of merged-beams experiments for small molecules 2.2.a). It is the underlying assumption that whatever the exact ECD mechanism is, the interesting physics takes place after the electron is captured and is not strongly influenced by the nature of the capture process. It will be an obvious starting point to demonstrate first that ECD-like processes do in fact take place even when the electron is provided by a negative ion and to further establish to which extent the choice of negative ion affects the experimental results. A strength of this new technique is that any relative electron energy from 0 eV to around 50 eV can be obtained even for very heavy and slow ions by proper choice of the energy and mass of the anion. For low relative energies one will choose a heavy anion, whereas for high relative energies H<sup>-</sup> with up to 100 keV is available. As argued above it is to be expected that some information on the ECD mechanism can be extracted from a measurement of the total cross section as a function of the energy. More advanced measurements with coincident detection of charged and neutral fragments, which will give insight in the fragmentation, will be a logical next step.

In particular in high relative velocity collisions one may worry about the role of the fast projectile after the 'electron delivery'. However, the large electron transfer distances involved will allow for mutual neutralization events with rather large impact parameters so that these fast neutrals will pass

at a safe distance. Experimentally such large-impact parameter events are identified by the direct detection of the fast neutral projectile at a well-defined time before the arrival of the neutral biomolecule (or fragments of it) and at a position on the detector corresponding to a small scattering angle and thus a 'soft' collision.

Another current issue in ECD research is the observation of electron capture without dissociation in e.g. multiply protonated ubiquitin (a protein consisting of a single chain of 76 amino acid residues forming a specific three dimensional structure) [Zubarev et al *Anal. Chem.* 72, 563 (2000)]. This is explained by assuming that though strong bonds in the chain are broken, the weaker bonds responsible for the 3D structure can keep the complex together. Additional vibrational excitation dissociates the weak bonding and separates the fragments, the masses of which are indicative of the 3D structure, since only bonds not participating in weak bonding are broken in ECD. Therefore, ECD of large proteins can give valuable information of their gas-phase 3D structure. However, the excess of energy in ECD should be minimal to prevent the structure from premature unfolding. The possibility offered by the merged-beams technique to bring in free electrons at negative energy is highly attractive for 3D structure studies as well as for further investigations of the ECD process.

A completely different category of merged-beams experiments involving biomolecules also considered are collisions between highly charged atomic ions produced in the ECR source and negatively charged biomolecules. The highly charged ion is able to remove tens of electrons from the biomolecule and thereby induce a Coulombic explosion, which can lead to different fragmentation patterns than those known from collisions with neutrals or from ECD. If such studies turn out successful, one can speculate in a future role for highly charged ions in biomolecular mass spectrometry.

## **Concluding remarks**

The DESIREE facility is planned as a user's facility to which detailed proposals for experiments are to be submitted. This is the same construction as for the CRYRING facility, and it is to be expected that (as in the case of CRYRING) the actual experimental program will develop into something rather different from the initial intentions and that the truly brilliant experimental results will emerge in fields not even considered from the outset. It is, however, very satisfactory to be able to present as broad an ensemble of possible interesting experimental programs as the present one to already at this early stage be able to ensure a large scientific output from this project.

# ***Technical design***

## **Introduction**

The proposal to construct a double electrostatic ring possible to cool to around 15 K is further studied by a group of potential users and MSL personnel. The different parts of the scientific programme and their consequences for the technical design of the machine are investigated. In this iterative process new ideas are continuously coming up and an overall design that can be the base for detailed construction work is not yet settled. However the major parameters of the systems are chosen and the updated design can be used for an improved estimate of costs, need for personnel resources and time needed to achieve the project. The presentation below will not describe the project in details but rather discuss the items that represent new ideas and are essential for the performance of the project

## **General parameters**

The two basic ideas that make DESIREE differ from other electrostatic ring projects are the double ring structure for merged beams and the possibility to cool the whole internal structure of the rings down to about 15 K. From an optimisation between the scientific interest and the technical and economic feasibility the basic parameters and also details have been deduced.

The energies of the circulating ions are set by the injection energy, the voltage of the injector platform although minor changes of the energy can be done with the small RF systems intended for bunched beam experiments. The condition that the velocities should be the same in merged beams give that the energy ratio must be the same as the mass ratio. The following parameters have been settled:

Injector voltage 1:  $U_1$   $-25 \text{ kV} < U_1 < 25 \text{ kV}$

Injector voltage 2:  $U_2$   $-100 \text{ kV} < U_2 < 100 \text{ kV}$

Voltages with absolute values at least down to 5 kV can be used. To achieve the merging conditions the ions in the two rings will have opposite signs. Ring 1 (25 kV injection voltage) will be constructed with the same voltage specifications as ring 2 (100 kV injection energy). The maximum mass ratios in merged beam experiments will be at least 20 for singly charged ions. The heavier ion will be stored in ring 2.

## **Injectors and injection lines**

The design of the injectors is straightforward and well known to the MSL staff. Three systems with acceleration voltage ranging from 50 kV to 300 kV have been constructed and are presently in operation or will be taken in operation at MSL.

In injector 2 the analysing system is placed on the 100 kV platform with the ion source on another platform up to 30 kV higher. The analysing magnet will have a bending power of about 2 Tm in which can bend close to 100000 Da singly charged ions at 2 keV total energy. Typical resolving power will be around 1000 but depends on the emittance and energy spread of the ion source used, of the intensity needed, and of course of the design of the system.

Injector 1 will have the analysing magnet on ground. An extra power supply will extract the ions to separate the source extraction voltage and the acceleration voltage. The injector platforms will be prepared for easy exchange of ion sources of different kinds as discussed below. The magnets in the drawings are not shown to scale.

The stability and ripple of the acceleration voltage will directly give the energy spread in the rings. The power supplies will therefore have a voltage stability of  $1 \cdot 10^{-5}$ .

The transfer lines are equipped only with electrostatic elements. The injection is made at an angle of 10 deg to the injection straight sections. In this way the prolongation in both directions of the straight sections (6 ports) are freely available for experiments.

## Ion sources

The production of ions of different kinds will be an essential part of the project as it is for CRYRING. It will also be a major part of the running costs. Standard ion sources for singly charged light ions would be available within the laboratory. Three new and dedicated ion sources are proposed to be included in the project:

- One negative, because in all merged-beam experiments one of the beams has to be negative ions.
- One electrospray ion source to produce mainly ions of biomolecules
- One small ECR source for higher charge states and large currents of low charge state ions.

## The rings

### *Beam optical considerations*

Methods for systematic investigation of storage rings using electrostatic elements is not developed to the same level of sophistication as for rings with magnetic elements. In the application 2001 the proposed lattices were based on first order calculations, symmetry arguments and experience. The continued studies have aimed at checking the influence of the difference in merger straight section and the injection straight section for ring 2 (high energy ring) or/and of the local velocity modification in the merger section. The conclusion from first order matrix analysis is that with four-quadrupole families (instead of two in the symmetric case) it is possible to find stable solutions with the lattices shown in fig 1. With the voltage of the drift tube in the merger section up to one third of the injection voltage of ring 1 stable solutions can still be found.

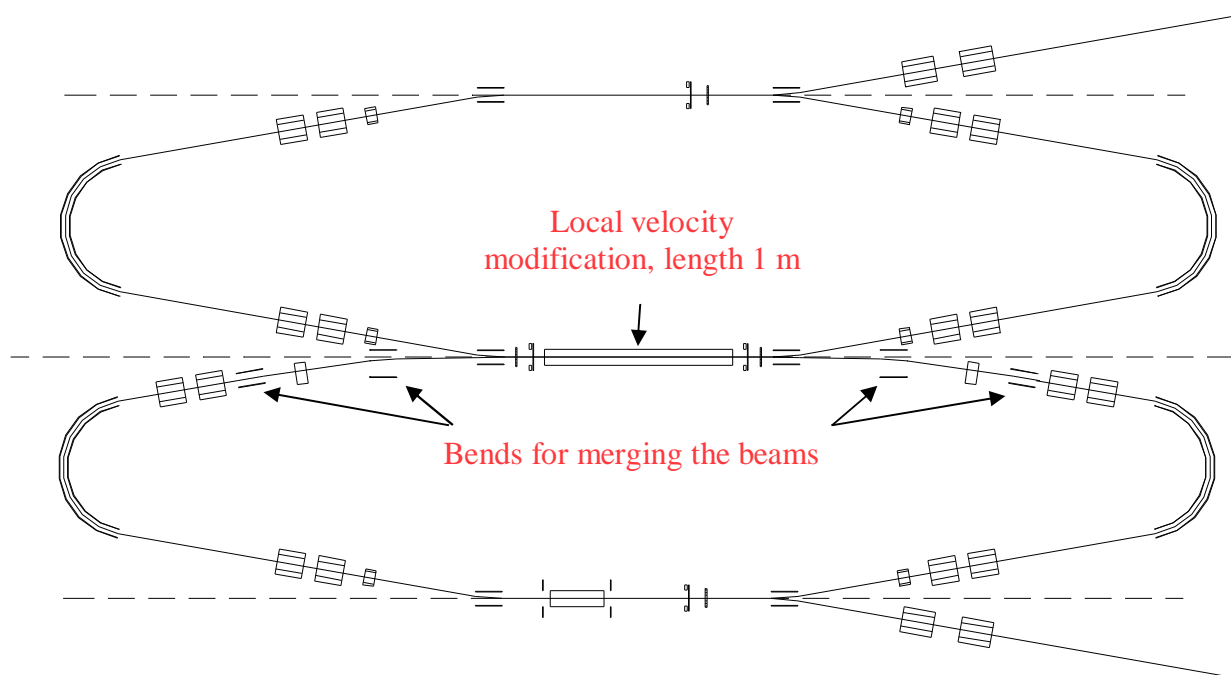


Figure 1. Lattice of ring 1 (above) and ring 2 (below) of DESIREE

The conditions set by the experimental programme can be fulfilled. Both rings will have the same circumference, 9.2 m, to allow bunched beams in the two rings to be in phase. The beam in the merger section can be close to parallel or focused by choosing the appropriate working point (quadrupole settings). Future crossed beam experiments, gas target and electron target need a good focused circulating beam. That can be achieved at the middle of the injection straight sections in both rings.

The extension of the calculation to higher orders, necessary for detailed optimisation of the lattices, is complicated and calls for computer programme development. Therefore we will directly go to ray tracing using the electric fields calculated from the mechanical shape and voltage of the elements. This is very time consuming and can only be done as final check of selected configurations. A model of the proposed lattice of ring 1 is set up using the program SIMION. The beam has recently been traced for 76 500 turns at one working point without any sign of growing. The number of turns was limited by computer time (8.5 h). The simulations will continue using a faster computer. The agreement with the first order calculations is good.

A scheme to inject via one ring into the other is considered. It will facilitate the choice of ion source and means that single ring experiments can be run in either ring without preferences.

### *Cryogenic considerations*

One of the very unique features of this project is the cooling of both the rings down to about 15 K. The direct advantage for the experiments is described above but an improved vacuum will also be an indirect gain as discussed below. This idea is unique which makes the technical challenge very interesting.

The linear dimension of the rings will change in the order of per mille, which means several mm in both horizontal directions, between room temperature and 15 K. The transport of heat via radiation is too slow to be practical in the foreseen applications. All electrodes must consequently have good heat conduction to the structure and at the same time be electrically insulated.

### *Mechanical design*

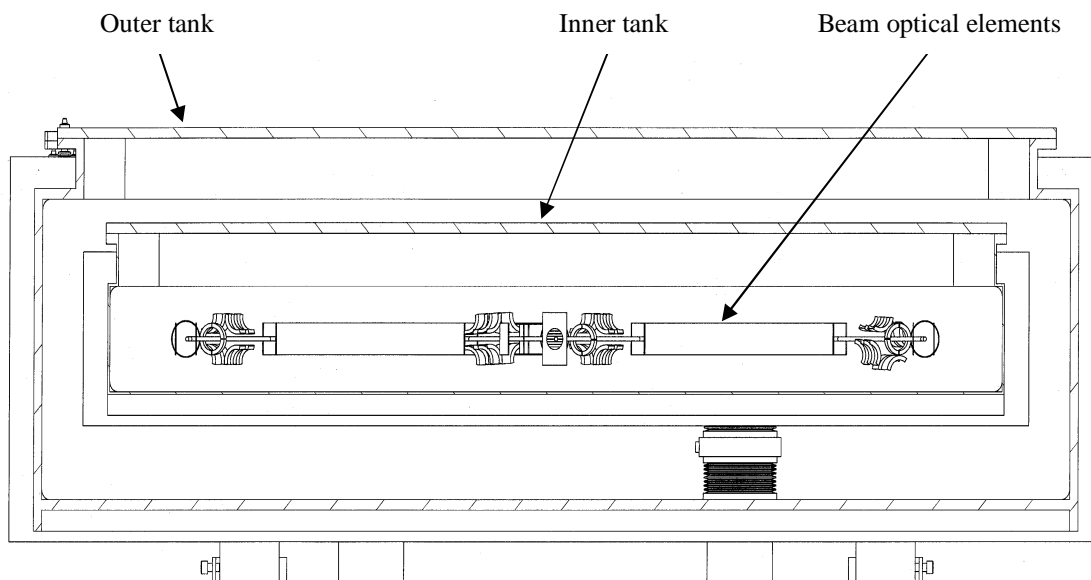
All the beam optical elements of the rings will be mounted on a structure of aluminium to which the cold heads of the cryogenerators are connected. An inner tank, also made of aluminium mainly for vacuum technical reasons, will surround it. At a distance about 100 mm further out there will be an outer tank made of ordinary steel. The space between the tanks will be filled with super insulation and include one intermediate temperature shield. The inner tank will be supported in the four corners by four stainless steel rods, easily adjustable from outside.

A vertical cross section of DESIREE is shown in figure 2. The tanks and beam optical elements are shown but not the Al structure, super insulation or intermediate screen.

All connections between the rings and outer room will be made downwards. The rings will be accessible through lids upwards.

The beam optical elements and inner tank will be connected to the cooled aluminium structure with good heat conduction so can reach the operation temperature of 10-20 K all of it as fast as possible. The intermediate shield will be connected to the intermediate stage of the cryogenerator ( 70 K).. At some position where the heat load might be high the shield can be cooled by LN<sub>2</sub> precooling.

The top and the bottom will be reinforced with beams to make them withstand the air pressure with only minor bending. The beams are not shown in the drawings. The tanks will be divided in three parts each, for reasons of transportation.



**Figure 2 Cross section of DESIREE through the middle of the straight sections.**

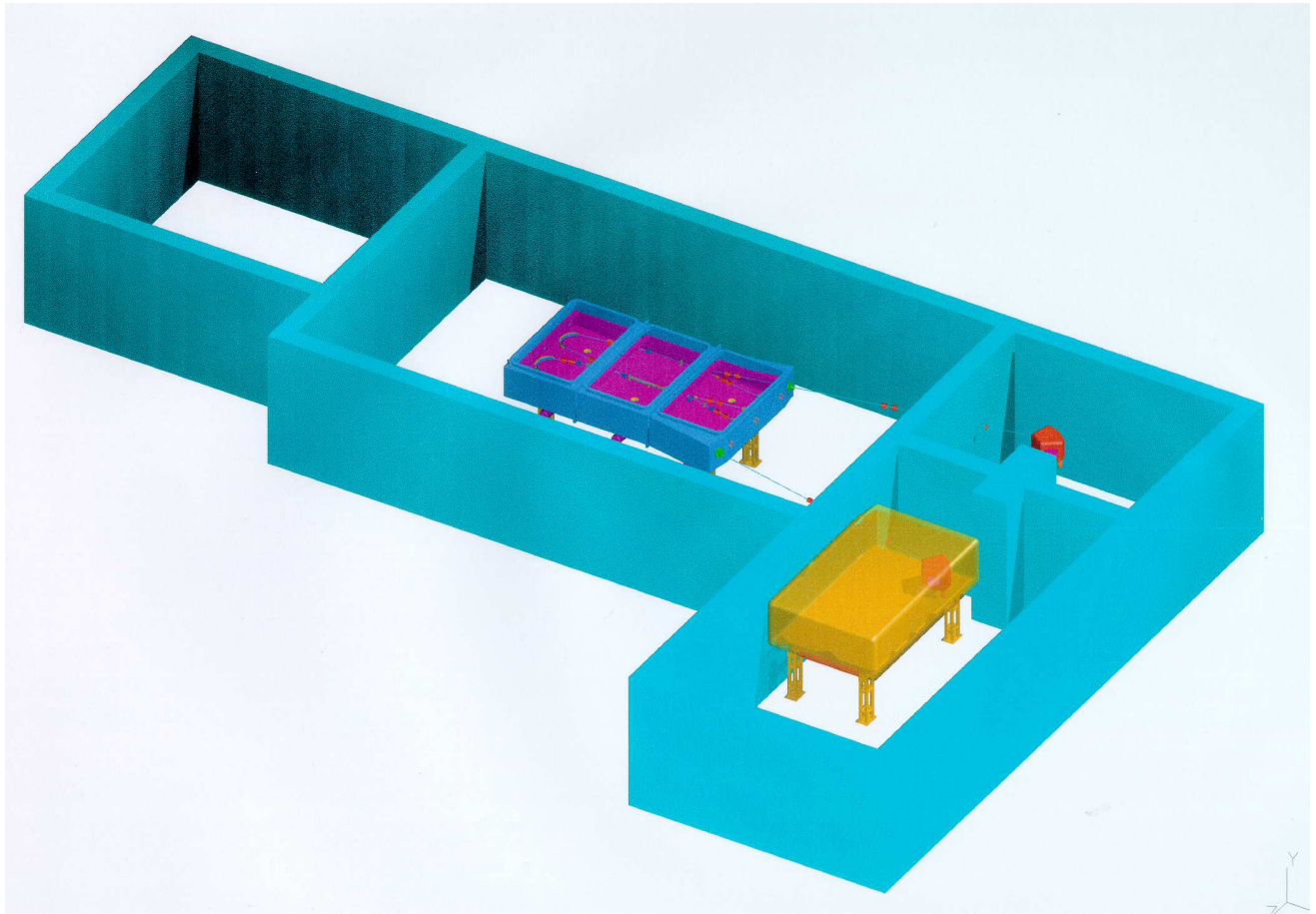
### *Vacuum*

The rest gas pressure is a crucial parameter in most experiments planned for DESIREE as for other storage rings. At 15 K all the walls will cryopump most molecules so it will not be a problem to achieve an excellent vacuum. All experiments that not have to avoid cold surroundings could benefit from that. However some of the experimental programmes proposed should be run at higher temperatures, even above room temperature. It is a complication to operate at temperatures where the system must be baked to get acceptable vacuum condition. Available super insulation does not withstand temperatures much above 150 °C. The DESIREE can be operated at room temperature with vacuum comparable to CRYRING a few times  $10^{-12}$  Torr. The choice of aluminium as main construction material will give as low diffusion after baking at 150 °C as would stainless steel after baking at 300 °C. The pumping will be done with turbo pumps, already needed for the pump down, and NEG strips. The inner tank will be cooled during activation of the NEG strips.

The use of ordinary steel for the outer tank will help to shield the rings from magnetic fields, which will improve the low energy properties of the machine.

### **Premises**

Four adjacent rooms in the basement of the building where MSL moved in during September 2002 are reserved for the DESIREE facility. A surface physics laboratory earlier occupied them, which is now moving out and the rooms are to be renovated. After that the systems for air cooling, electric power, water-cooling and compressed air must be installed.



**Figure 3. DESIREE in the planned premises at MSL.**

## **Cost estimate**

Table 1 presents a summary of the cost estimate of the DESIREE project. The numbers are summed from much more detailed tables where all foreseen parts are listed. Some of the subsystems are well known and the cost can be estimated to a fairly high degree of accuracy, some are more difficult to estimate. The accuracy down to unity SEK is kept in the table and the item unforeseen is added at the end to avoid overestimation of the uncertainty.

### *Comments*

The injectors and injector lines comprise well known techniques. The efforts in design and money will be put on stable acceleration voltage, a powerful bending magnet on injector 2, optimal choice of ion sources and effective pumping on the platforms. The investment cost and later running cost can be reduced using the resources of CRYRING.

The cost of the two vacuum tanks is not only significant but also the most uncertain until it is finally designed. The vacuum, (6 turbo pumps with valves bellows and vacumeters) and cryo equipment (cryo generators, super insulation and temperature measurements) are on the other hand commercially available standard products. The cost is based on offered prices.

The diagnostics (strip detectors, faraday cups both in injection lines and in the rings) is based on equipment developed at MSL and is not available commercially.

The exchange of equipment inside the inner tank like detectors will be time consuming. Therefore some detectors will be positioned after the merger section to be used by all experimental groups. They will be position sensitive channel plates with phosphor screen anodes. The light from the

phosphor screen is observed through view ports to give time and position information by an optical system the most expensive parts of which are: image intensifier, CCD camera, frame grabber and photomultiplier tube.

The prices of power supplies are offered ones.

The cost for the control system is very low because it will be an extension of a new system being installed at CRYRING this year. The staffs needed to construct DESIREE are estimated to be 1.5 accelerator physicist/project manager, 2.5 mechanical engineers and 2 electronic engineers in average for 3 years, starting after ending the design study. The mechanical manufacturing is estimated to 1148 mandays and for manufacturing of electronic equipment is estimated to 135 mandays. The numbers in the table is calculated using 400 SEK/h. This is not possible to produce within the MSL staff. The personnel cost of MSL would need another 5. MSEK in total for the three years when constructing DESIREE in order to keep the activities at CRYRING at a reasonable level.

## **Time schedule**

An accurate and reliable time schedule can be done only when the technical design of the project is decided to some detail and the available resources are known. The different parts of DESIREE, as listed in table 1, have been analysed based on the design presented in this report. When the design study is completed and the project is funded a period of one year is foreseen for optimising the overall design and finalising the detailed designed of the different parts of the system. The overall time schedule will be defined by the series: -final overall design – detailed construction of tanks – purchase of tanks – mounting of tanks – mounting of structure and beam optical elements - mounting of cryogenic and vacuum equipment – commissioning. Assuming the resources discussed above it is estimated that first injection of a beam into DESIREE at room temperature could be possible in the middle of the third year after start of the project and at 15 K half a year later. A time schedule based on the assumption made in this report and with the project start date set to 1 September 2003 is presented below. Only the time defining subsystems are included.

## Summary of estimated costs

| DESIREE  |  | Summary of costs            |                   |
|--|--|-----------------------------|-------------------|
| Subsystem  |  | Comment                     | Cost, SEK         |
| <b>Total</b>                                     |  |                             | <b>25 198 635</b> |
| <i>1 Injectors, injection lines</i>              |  |                             | <i>6 812 400</i>  |
| 1 Injector 1                                     |  | Accelerating voltage 25 kV  | 872 100           |
| 2 Injector 2                                     |  | Accelerating voltage 100 kV | 1 342 300         |
| 3 Ion sources                                    |  |                             | 3 309 000         |
| 1 Negative IS                                    |  |                             | 255 000           |
| 2 Electrospray                                   |  | components                  | 400 000           |
| 3 ECR  |  | Mikrogan                    | 2 654 000         |
| 4 Injlinje 1                                     |  |                             | 560 500           |
| 5 Injlinje 2                                     |  |                             | 728 500           |
| <i>2 Rings</i>                                   |  |                             | <i>7 050 000</i>  |
| 1 outer tank                                     |  | Steel                       | 500 000           |
| 2 inner tank                                     |  | Aluminium                   | 1 276 000         |
| 3 structure                                      |  | Aluminium                   | 150 000           |
| 4 Ion optical elements                           |  |                             | 695 000           |
| 5 Vacuum equipment                               |  |                             | 1 779 000         |
| 6 Cryo equipment                                 |  |                             | 915 000           |
| 7 Diagnostics in the rings                       |  |                             | 685 000           |
| 8 Detectors inside the tank                      |  |                             | 1 050 000         |
| <i>3 Power supplies HV</i>                       |  |                             | <i>4 100 000</i>  |
| <i>4 Control system ao</i>                       |  |                             | <i>400 700</i>    |
| <i>5 Other costs</i>                             |  |                             | <i>200 000</i>    |
| 1 Travel, visits..                               |  |                             | 200 000           |
| <i>6 Project premises</i>                        |  |                             | <i>530 000</i>    |
| 1 Renovation by AH                               |  |                             |                   |
| 2 Overhead crane                                 |  |                             | 100 000           |
| 3 Ventilation/air condition                      |  |                             | 250 000           |
| 4 Electric power installations                   |  |                             | 50 000            |
| 5 Water cooling, compressed air                  |  |                             | 80 000            |
| 6 Desks, cupboards, shelves...                   |  |                             | 50 000            |
| <i>7 Personnel</i>                               |  |                             | <i>4 905 600</i>  |
| Management, calculations, constructions mounting |  |                             | 7 600 000         |
| Manufacturing, mech.                             |  |                             | 3 673 600         |
| Manufacturing, electronics                       |  |                             | 432 000           |
| MSL contribution                                 |  |                             | -6 800 000        |
| <i>9 Unforeseen</i>                              |  | <i>5%</i>                   | <i>1 199 935</i>  |

Table 1. Summary of estimated costs for DESIREE.

# Time schedule for time defining subprojects.

This time schedule assumes full funding and project start 1 September 2003.

