Ion trajectory simulations for the design of a compact electrostatic ion storage ring: the Mini-Ring.

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Introduction

The Mini-Ring is an electrostatic ion storage Ring that has been developed since year 2007 [1]. The purpose of this storage ring is to study delayed relaxation processes in complex cationic molecules. Our first investigations have been concerning the PAH (Polycyclic Aromatic Hydrocarbons) family of molecules that have astrophysical relevance. Those PAHs are presently the best candidates to explain the astrophysical observation of far infra-red bands attributed to C-C or C-H vibration modes and DIBS (diffused interstellar Bands) in the interstellar medium or diffuse clouds [2]. The stability of those PAHs under strong X or UV radiations is still a matter of debate. It is commonly thought that excited molecules with an internal energy E_i possibly relax by electron emission if E_i exceeds the ionization potential, by unimolecular dissociation if E_i exceeds the dissociation energy or by infra-red light emission corresponding to transition between vibration levels. However, it has been proposed in 1997 that PAHs molecules can dissipate a high amount of excitation energy via delayed fluorescence emission, due to the so-called Poincaré or recurrent fluorescence [3, 4]. With the Mini-Ring, we have evidenced that this latter process is dominant in the case of Anthracene and Napthtalene cations with E_i in the range of 6 to 10 eV [5].

In complex molecules such as PAHs, all these physical processes, may occur in typical time scales ranging from several microseconds to seconds [5]. In order to study their typical time scale and branching ratios, it is necessary to perform observations on long time ranges and consequently to store the molecules. Electrostatic storage rings present the advantage to have storage conditions that are independent on the mass of the molecule, no remanent magnetic fields, low electric power consumption compared to magnetic rings, compact design of electrodes that can be of any useful shape.

In the present paper, we will develop some basic concepts concerning ion trajectory simulations that have been perfomed with the SIMION 8.01 software in order to optimize the geometry of the Mini-Ring and determine some of its ion optics properties like stable trajectory diagram or acceptance. We will also discuss about the Kinetic Energy Release (KER) measurements that have been performed and compared with ion trajectory simulations.

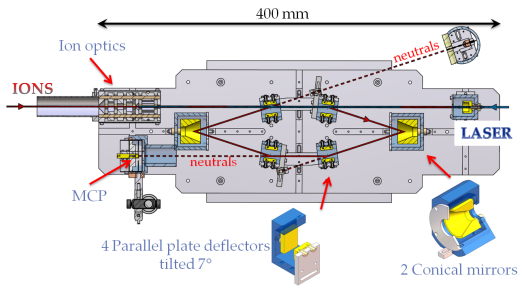

FIGURE 1 – Schematic view of the Mini-Ring. The deflectors and conical mirror design are shown in insets. PSD stands for Position Sensitive Detector, composed of 2 multichannel plates and a résistive anode

The basic concepts of the Mini-Ring

The concept of the design of the Mini-Ring originates from the Electrostatic Ion Beam Traps (EIBT) that have developed since the mid-1990's. Those EIBT themselves are based on an analogy with optical laser cavities. It is well known that optical cavities composed of 2 spherical mirrors are stable, i.e., can store a light beam almost for ever, if the focal length f of the mirrors fullfills the following inequality,

$$\frac{L}{4} \leq f < \infty, \tag{1}$$

where L is the length of the cavity. In EIBT, the focal length is simply controlled by a voltage on an electrode, or more precisely for a given geometry of the mirrors by the ratio $\xi = \frac{qV}{E_k}$, where q is the ion charge, V the voltage of the focusing electrode and E_k the ion kinetic energy. A very simple EIBT, composed of only 3 electrodes has been successfully developed in Stockholm. The mirrors are electrodes with a conical shape.This shape ensures that at the ion turning point, the shape of the equipotential surface is almost spherical. Hence, as we wanted a very compact design for the Mini-Ring, with as few electrodes as possible, our basic concept is an off-axis injection of the ion beam to conical shaped electrodes. In order to do so, we placed 4 parallel plate

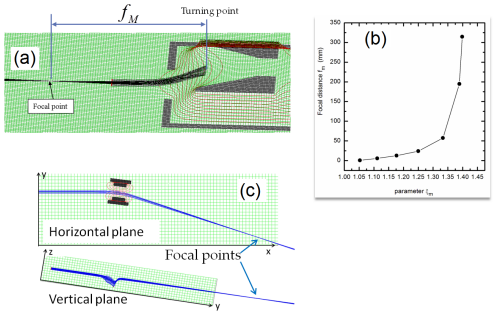

FIGURE 2 – (a) : simulation of the focal point for the conical mirror. (b) Simultated focal distance of the conical mirrors as a function of the corresponding $\xi_m = qV_m/E_k$ parameter.

(c) Simulation of the focusing properties of the deflectors. For a given deflection angle of about 17°, there is a strong focusing effet in the horizontal plane perpendicular to the electrodes, and a weak focusing effect in the vertical plane, paralel to the electrodes.

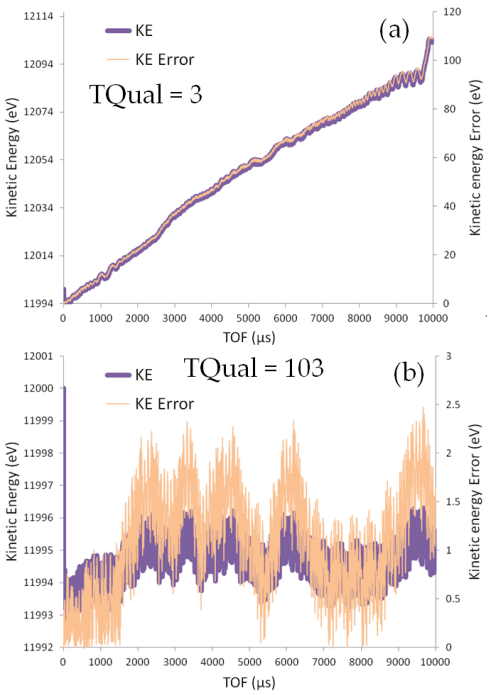

FIGURE 3 – Evolution of the ion kinetic energy KE) and of the ion kinetic energy error (KE Error) as a function of the time of flight for $TQual = 3$ (a) and for $TQual = 103$ (b).

deflectors in between the conical mirrors as shown in Fig. 1.

The focusing properties of the deflectors and the conical mirrors can be simulated in SIMION simply by launching parallel beam toward them and determine at which position the outgoing beam is crossing (Fig. 2).

For the conical mirror, the focal length can be precisely defined as the distance between the turning point of the trajectory (the position of this point is also slightly changing as a function of the voltage) and the position of the focal point (Fig. 2a). Although, it would be probably rather easy to use advanced programming to vary the conical electrode voltage and determine the focal distance, it has not been used to obtain the points of Fig. 2b. Fig. 2b shows that the focal distance f_m increase sharply with increasing ξ_m parameter (label m stands for "mirror") with a vertical asymptote at $\xi_m = 1.4$. For $\xi_m > 1.4$ the conical mirror become defocussing and ion storage is impossible. Nonetheless, there is a rather broad ξ_m range, and consequently a broad voltage range, where the conditions of inequalities 1 are fulfilled.

For the deflectors, at a given deflection angle of about 17°, there is a strong focusing effect in the horizontal plane perpendicular to the electrodes, and a weak focusing effect in the vertical plane, parallel to the electrodes (see Fig. 2c).

Actually, the ion trajectory through half of the Mini-Ring, e.g. through deflector D2, conical mirror C1 and deflector D3 is similar to light passing through 2 converging lenses, being reflected by a plane mirror and passing again through the 2 lenses. The difficulty in order to push further the optical analogy arises from the fact that the focus distance of the deflector is not the same in the horizontal plane and in the vertical plane.

Ion trajectory simulations

Let's discuss some of the difficulties we are facing when trying to simulate ion trajectory in a storage ring like this. Firstly, the design of the electrodes of the Mini-Ring, especially the design of the deflectors lead to important effects of the fringing fields. Hence, it is necessary to define potential arrays (PA) whose size exceeds largely the size of the electrodes. as a consequence, it happened to be difficult to define a PA for each deflector and conical mirror and assemble them in the Ion Optical work Bench (IOB) because the overlapping and continuity conditions between the different PAs could hardly be solved. We preferred to draw the whole ring in a single PA# file. In order to save memory, computing time, etc., we have taken advantage of symmetries to draw $1/8^{th}$ of the Mini-Ring and use X, Y, Z planar symmetries. Later on, using a better computer, we verified that drawing the whole Mini-Ring without symmetries did not change significantly the outcomes of the simulations.

Another issue when simulating any ion storage device is the minimum time of flight (TOF) to reach in order to state that a trajectory is stable. The corollary of this question is the computation time. In this work, we considered as stable , a trajectory that leads to a storage time of at least $10ms$. The computation times for a single trajectory (with standard PC equipped with Intel Core i7 CPU cadenced at 2.67 GHz with 4.00 Go RAM) were about $16s$ and $46s$ for the standard quality factor $TQual = 3$ and for $TQual = 103$, respectively.

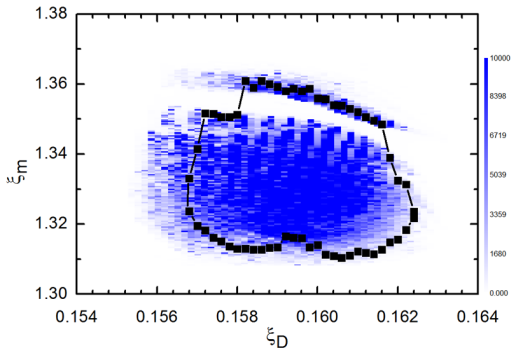

FIGURE 4 – Stability diagram computed with Lua code. Black squares linked with black line : limit curve of the stable region (SR) computed with a dichotomy algorithm. Blue square : Time of flight computed for each couple (ξ_D, ξ_m), and ξ_D and ξ_m scanned with fixed steps

The computation quality factor TQual is also an issue. It is actually stated in the SIMION manual that $TQual = 103$ is the minimum required value when trajectories have velocity reversals. Since there are many of those velocity reversals in the Mini-Ring trajectories, we could not afford to reduce TQual under 103 in order to save computation time. This issue is clearly evidenced in Fig. 3. With $TQual = 3$, the initial kinetic energy (KE) of 12 keV is increased by about 120 eV after a TOF of 10 ms (about 1% relative error), whereas with $TQual = 103$ the KE error is oscillatory and remain below 3 eV ($< 0.03\%$), which is acceptable.

The last issue that could be discussed is intra-beam ion-ion interactions, also referred as Coulomb repulsion. Since in reality we are limited to very low beam intensities to avoid any possible detector saturation, we consider that this issue should have very limited consequences in the experiment.

In order to determine the acceptable ranges for the voltages V_D and V_m to be applied on the deflectors and the conical mirrors and consequently for their respective ξ_D and ξ_m parameters, we have implemented a Lua code. By scanning V_D and V_m with fixed steps and plot in a 3D map the TOF as a function of V_D and V_m, we would in principle be able to define a region of stable trajectories, so called Stability Region (SR). However, this method would not be optimum regarding computation time. Indeed, long trajectory computation times occur when storage conditions are fulfilled inside the SR whereas the computation time is very short for V_D and V_m outside the SR. A more efficient way would be to search only for the limits of the SR, computing as few stable trajectories as possible. To do so, the Lua code scans V_D and searches for the lower and upper limits of the SR using a dichotomy algorithm. Hence, it is expected that the SR fits inside the area delimited by the black squares of Fig. 4. Nevertheless, more recently with a better computer and also a slightly different positioning of the deflectors and conical mirrors (the tilt angle of 7° was not included in the previous calculation and the deflection angle was slightly smaller by about 0.2°), we have computed the whole stability diagram (more than 48 hours computation time). Surprisingly, it showed the existence of a gap between two stable regions that has not been found with the previous method. More investigations concerning the combined focusing properties of the conical mirrors and the deflectors would be needed in order to explain this gap.

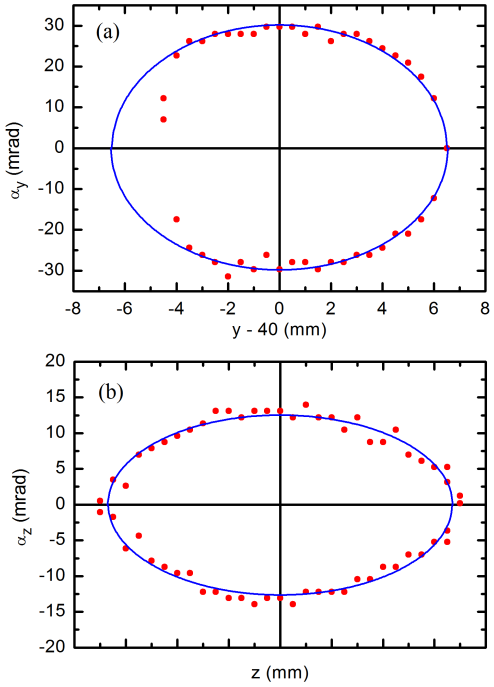

FIGURE 5 – Phase space diagrams computed with a dichotomy algorithm to search for the limit of the stable trajectories as a functions of the angles α_y and α_z.

The same dichotomy method was used to determine the maximum emittance of a beam that can be stored in the Mini-Ring. More precisely, we have constructed phase space diagrams by scanning the y or z coordinate with steps of 0.5 mm and seaching the limit angles α_y and α_z such that the trajectory remains stable for at least 10 ms. The area delimited by the blue curve is expected to correspond to the maximum emittance of a beam that can be stored int the Mini-Ring.

Geometry optimization

In order to test different geometrical configurations, we have used the batch mode operation of SIMION with a Lua code. This code implements the geometry file using a variable to translate the deflectors perpendicularly to conical mirrors symmetry axis, thus changing the injection angle to the conical mirrors. The algorithm of the Lua code is quite simple : create a geometry file, i.e., Mini-Ring.gem, the use the $gem2PA$ SIMION function to create Mini-Ring.PA# file, then use the SIMION $refine$ function to obtain the Mini-Ring.PA0 (and also the PAs for each electrode), create an appropriate Mini-Ring.fly2 file, i.e., a single tra-

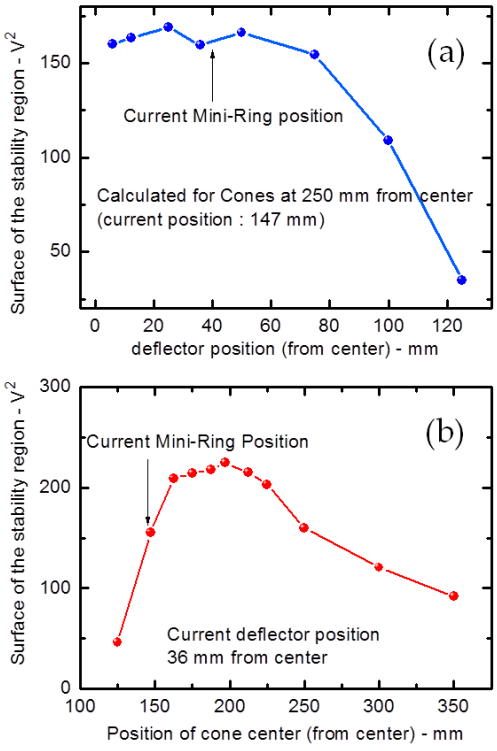

FIGURE 6 – Area of the stability diagram when changing the geometry of the Mini-Ring by (a) translating the deflectors perpendicularly to the symmetry axis of the conical mirrors and (b) translating the conical mirrors along their symmetry axis.(Lines are to guide the eye)

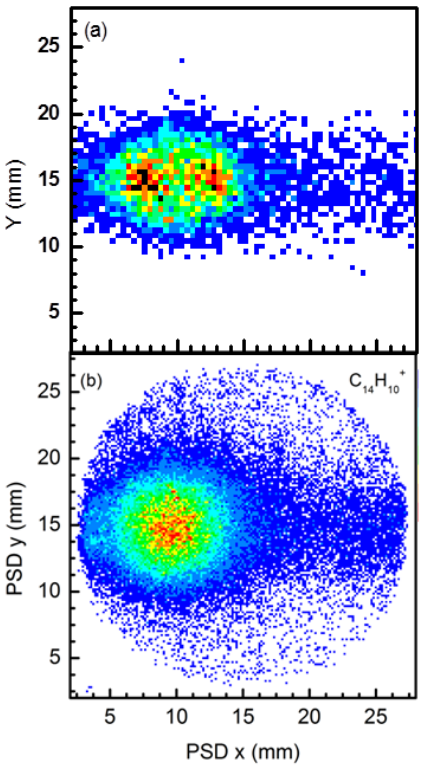

FIGURE 7 – (a) : SIMION simulation of the position of the neutral on the PSD for a KER of 0.5 eV. (b) experimental result recorded for the unimolecular dissociation of anthracene $C_{14}H_{10}^{+} \rightarrow C_{12}H_{8}^{+} + C_2H_2$

jectory with a non centered initial position ($x = 0$, $y = 40.5$, $z = 0.5$, $\alpha_y = 0$ and $\alpha_z = 0$) well inside the expected acceptance and calculate the stability diagram with the dichotomy method as described above. Then the code loops in order to change the geometry variables in fixed steps. A criterion for optimizing the geometry may be to maximize the area of the SR. Hence a convergence procedure could be used instead of fixed steps. However, since we did not expect any sharp geometry optimum as shown in Fig. 6, we considered it unnecessary. In Fig. 6a, there is a rather sharp decrease of the area of the SR when the position of the deflectors is at more than 70 mm from the Mini-Ring axis. This corresponds to deflection angles larger than 18° for which we could verify that the storage condition of Eq. 1 is not fulfilled anymore.

For a fixed position of the deflectors, we used the same algorithm to study the effect of a translation of the conical mirrors along their axis of symmetry. Fig. 6b shows that an optimum position of the cone exists in order to maximize the area of the SR. This is due to the fact that, on one hand, at short distance, the deflection angle becomes too large and, on the other hand, at long distance the Eq. 1 becomes less easy to fulfill for the conical mirrors. Indeed, if the distance between the conical mirrors is increased, the focal distance of the mirrors must be increased too and we rapidly approach the critical part of the curve of Fig. 2b, where a small change of ξ_m corresponds to a huge change of f_m. Despite the existence of this "optimum" value, we have chosen a distance such that it is a bit more critical to find stable trajectories (indicated by an arrow on Fig. 6b. The main reason is that when studying unimolecular dissociations such as the hydrogen loss from anthracene cations $C_{14}H_{10}^{+}$, it is mandatory that the daughter ion $C_{14}H_{9}^{+}$cannot remain stored on a stable trajectory.

Unimolecular dissociation and Kinetic Energy Release (KER)

As mentioned above, unimolecular dissociation of PAHs cations is one of the important issues addressed by our experiments with the Mini-Ring. Supposing that we can store at $t = 0$ an ensemble of molecular cations all with the same internal energy above its dissociation energy, unimolecular dissociation will occur with a typical lifetime τ that can be estimated for instance with an Arrhenius law or the RRKM model. In this case, we expect the number of stored ions to decrease with an exponential decay law $N(t) = N_0 exp(-t/\tau)$ and we would like to record the time and the position of the emitted neutrals on the PSD, just like in the real experiment. The example code 1 shows the corresponding Lua code corresponding to the segment *other_action* of the Lua file associated with the cor-

responding IOB file. Firstly, the fragmentation time, denoted by $Frag\_time$ has to be computed such that it is randomly chosen with an exponential distribution with a lifetime τ with the mathematical expression $Frag\_time = \tau * ln(1/rand)$, where $rand$ is a random number between 0 and 1. Secondly, we have to implement the fragmentation when the TOF is greater than the $Frag\_time$, the SIMION's variables ion_mass and ion_charge are set to the mass of the fragment and to zero respectively. Thirdly, the KER is leading to an additional velocity whose direction is randomly determined in spherical coordinates. Fig. 7(a) displays the spot size resulting from the simulation of the unimolcular dissociation $C_{14}H_{10}^{+} \rightarrow C_{12}H_{8}^{+} + C_2H_2$ with a KER of 0.5 eV. The spot corresponds to the position of the emitted neutral C_2H_2 on the PSD for about 1000 ion trajectories with initial position and angle randomly chosen with gaussian distributions of 1 mm and 0.6° full width at half maximum, respectively. The simulation matches quite well with the experimental result shown in Fig. 7(b), although the simulated spot of Fig. 7a is slightly broader indicating that the measured KER is slightly smaller than 0.5 eV.

conclusion

We have shown along this paper some examples of the simulation work performed with SIMION in relation with the development of a new electrostatic ion storage rinf, the Mini-Ring. We have pointed out the importance of computing accurately the velocity reversals. We have shown how to reduce the computation time by avoiding to simulate too many stable trajectories and we have employed the batch mode of SIMION to perform some geometry optimizations. More work could have been done especially in order to simulate non perfect machining and positioning of the electrodes. Indeed, in the real world, although it is rather easy to find good storage conditions, it happens that different voltages need to be applied on each of the deflector and on each of the cones. Nonetheless, ion trajectory simulations were absolutely essential in order to design such a non-conventional electrostatic ion storage ring.

Références

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LUA Code

example code 1

```
function segment.other_actions()

   if ion_time_of_flight==ion_time_step then
   -- Calculate the value of Frag_Time
     Frag_Time = Frag_LifeTime*ln(1/simion.rand())

   end

  if ion_time_of_flight == Frag_Time then
    ion_mass = max (1,ion_mass-Delta_M) -- change ion_mass
        ion_charge = 0 -- change ion charge

        ion_color = 7

        -- Define the velocity of the fragment
        -- according to the KER entered by the user

        local Frag_ke = Delta_Ec
        -- velocity of the fragment
        local speed = ke_to_speed(Frag_ke,ion_mass)
        -- Direction phi of emission randomly chosen
        local phi = 2* math.pi*simion.rand()
        -- Direction theta of emission randomly chosen
        local theta = math.pi*simion.rand()
        ion_vz_mm = ion_vz_mm + speed * cos(theta)
        -- new values of speed
        ion_vx_mm = ion_vx_mm + speed * sin(theta)* cos(phi)
        ion_vy_mm = ion_vy_mm + speed * sin(theta)* sin(phi)
        mark()
        beep()



end
```