

Design of a Quadrupole Mass Spectrometer for the Characterization on Europa's Atmosphere

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By

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The Designated Project Committee Approves the Project Titled

DESIGN OF A QUADRUPOLE MASS SPECTROMETER FOR THE
CHARACTERIZATION OF EUROPA'S ATMOSPHERE

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ABSTRACT

DESIGN OF A QUADRUPOLE MASS SPECTROMETER FOR THE CHARACTERIZATION OF EUROPA'S ATMOSPHERE

by Jorge I. Cortés

A quadrupole mass spectrometer was designed with the ability to characterize the tenuous atmosphere of Jupiter's moon, Europa. As a constraint, this instrument was to fit within a 3U cubesat chassis without sacrificing measurement resolution and accuracy. Ion trajectories are studied through simulations carried out in the numerical computing programming language, MATLAB and the finite element analysis simulation software, COMSOL Multiphysics. Optimal mission parameters are then implemented in an instrument design that was built, tested, and validated.

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CHAPTER ONE

INTRODUCTION

1.1 Motivation and Approach

The main motivation behind this project is the spirit of discovery and exploration. Space exploration is and will always be a domain of endless possibilities. It is with great motivation that I embark on this journey; a journey that will hopefully bring about insight towards methodologies used in discovering, exploring, and characterizing strange, yet oddly familiar worlds. The following encapsulates the project statement and approach.

Quadrupole mass spectrometers are scientific instruments used in mass spectrometry, an analytical technique that uses the mass-to-charge ratio of an ion in order to identify its abundance within a given sample. These types of instruments are used prevalently within the aerospace field where the main applications are in the study of planetary atmospheres and in monitoring the air quality during manned space missions; the first of which will be dealt with in this project.

In order to gain insight towards design parameters, a study will first be conducted in modeling ion trajectories as they traverse a quadrupole mass spectrometer. Equations of motion will be derived and simulations will be conducted. Once done, the design iteration process will begin with the goal of restricting the size to a 3U cubesat module (30x10x10 cm) without affecting measurement resolution and accuracy. A prototype of the quadrupole mass spectrometer will then be build in order to validate the design process.

CHAPTER TWO

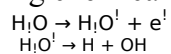
LITERATURE REVIEW

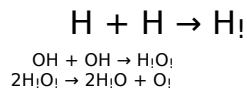
2.1 Introduction to Literature Review

The following literature review will cover different articles concerning Europa's atmosphere, its surface composition, the Jovian magnetosphere, and the use of quadrupole mass spectrometers.

2.2 Europa's Atmosphere

The existence of atmospheres on the Galilean satellites of Jupiter was first postulated circa 1970 by Steklov and Ioffe [1]. They developed a methodology where, considering the absence of strong gas sources, upper limits were obtained for gas densities in the predicted atmospheres of Io, Europa, and Callisto. Although fairly convincing, a better case was presented by Johnson et al. (1982) where high-energy ions and particles ejected from the Jovian magnetosphere cause a process known as radiolysis on Europa's surface. Radiolysis is a chemical process where the dissociation of molecules occurs via nuclear radiation. Given the known existence of Europa's top mantle composed of water ice, an O₂ atmosphere was predicted due to the radiolytic decomposition of the icy surface through the bombardment of magnetospheric plasma [2]. During this process, the following chemical reactions occur:





it should be noted that the first reaction occurs due to water ice molecules being hit with high energy ions and particles. From here it is clear that radiolysis results in the production of H₂ molecules, O₂ molecules, and left over H₂O molecules. Considering the gaseous phase of these molecules and Europa's gravitational effect on them, the H₂ molecules are expected to drift away and escape relatively easily. On the other hand, the heavier O₂ and H₂O molecules would stay behind. From here it is easy to imagine the existence of an oxygen rich atmosphere.

The O₂ atmosphere was later detected and confirmed through observations made by the Hubble Space Telescope. Through the emissions of atomic oxygen at 1304 and 1356 Å it was deduced that a tenuous O₂ atmosphere exists and that emissions come from electron impact dissociation of O₂ as opposed to electron impact excitation of atomic oxygen. Additionally, through their observations and analysis, Hall et al were able to calculate the surface pressure produced by the oxygen atmosphere; approximately 10⁻¹¹ that of the Earth's atmosphere at sea level [3].

2.3 Europa's Surface Composition

The main interest behind the exploration of Europa is the possibility of a vast liquid water ocean beneath the icy shell. This harbors so much interest due to the high

viability of organic life existing there. Although data regarding the surface or crustal composition is limited, the sputtered atmospheric constituents and near-infrared reflectance spectra of surface regions give a lot to study [4]. This data was gathered through the Galileo NIMS investigation. The Near Infrared Mapping Spectrometer (NIMS) instrument had four main objectives when it was deployed on board the Galileo Orbiter [5]:

1. Map the distribution of surface minerals on the Galilean satellites at spatial resolutions of 5-30 km.
2. Identify the phases and mixtures present thereon
3. Correlate observed mineralogical distributions with the geomorphology observed with the solid-state imaging (SSI) system.
4. Determine cloud morphology of the Jovian atmosphere and its structure over a wide range of phase angles.

The data collected during the orbit of the Galileo spacecraft about Jupiter indicates that there are regions on Europa's surface that demonstrate "distorted H₂O vibrational overtone bands in the 1.5 and 2.0 μm region". This is particularly interesting because it indicates that these regions contain "highly concentrated solvated contaminants" [4]. In order to understand the significance of this, one must first understand the term 'solvated'. Based off of the definition provided by the International Union of Pure and Applied Chemistry (IUPAC), solvation is the process via which a solute and a solvent become stabilized. An example of this can be "the ionic groups of an ion-exchange resin" [6]. This is a very strong indicator of radiolysis occurring on Europa's surface. Although it

had been stated before, the process of high-energy particles disassociating surface molecules was never proven to actually occur on Europa's surface. The data provided by the NIMS instrument proved to be invaluable in advancing theorized models of Europa's atmosphere and surface composition. Based off of analysis carried out, the data provided by the NIMS instrument can be interpreted one of two ways; either these regions are composed of hydrated salt minerals or of sulfuric acid. Both hypotheses are highly plausible. The hydrated salt minerals point towards a liquid ocean beneath the mantle of ice. An ocean would explain the presence of minerals and salts on Europa's surface. During the formation of Europa, its core would have incorporated any material that could be found in the surroundings. From previous studies, it is known that Europa's core is mostly composed of silicates. If an ocean does indeed exist within Europa, the combination of tidal heating and surface erosion could bring silicates along with other minerals to the surface. These would then be encapsulated within the icy surface. Through the process of radiolysis, as previously described, this silicates and minerals would disassociate and create regions as found.

Moreover, if upon further studies these regions prove to be composed of sulfuric acid, this would be easily explained by Io's volcanic activity. Io, another of Jupiter's moons, has been observed to have high volcanic activity on its surface. The plumes erupting from Io's surface are mainly composed of sulfur (S) and sulfur dioxide (SO₂). Given the proximity between Io and Europa, the content ejected by Io could reach Europa and interact with its surface.

2.4 Jovian Magnetosphere

Jupiter's magnetosphere is massive, approximately 20,000 times stronger than Earth's magnetosphere. It is easily the solar system's largest and this can be attributed to the large amount of metallic hydrogen within Jupiter. Io, Europa, Ganymede, and Callisto are fully embedded within the Jovian magnetosphere.

2.6 Mass Spectrometry

Mass spectrometry is a broad subject that has been heavily developed since it was first introduced. At its best, this analytical technique only requires "a few nanomoles of sample to obtain characteristic information regarding the structure and molecular weight of the analyte." [8] What makes this a powerful technique is that, theoretically, each compound produces a unique mass spectrum; thus, this can be used in identifying the different compounds that make up an atmosphere. All mass spectrometers work in the following way: a sample vapor is introduced into the instrument where ionization occurs. During this process, the sample vapor absorbs copious amounts of energy until decomposition occurs. Once this occurs, the sample decomposes into uni-molecular samples with unique mass-to-charge ratios. From here, a specific type of mass analysis occurs depending on the type of mass spectrometer being used. The instrument then records the data and produces a mass spectrum similar to the one shown below.

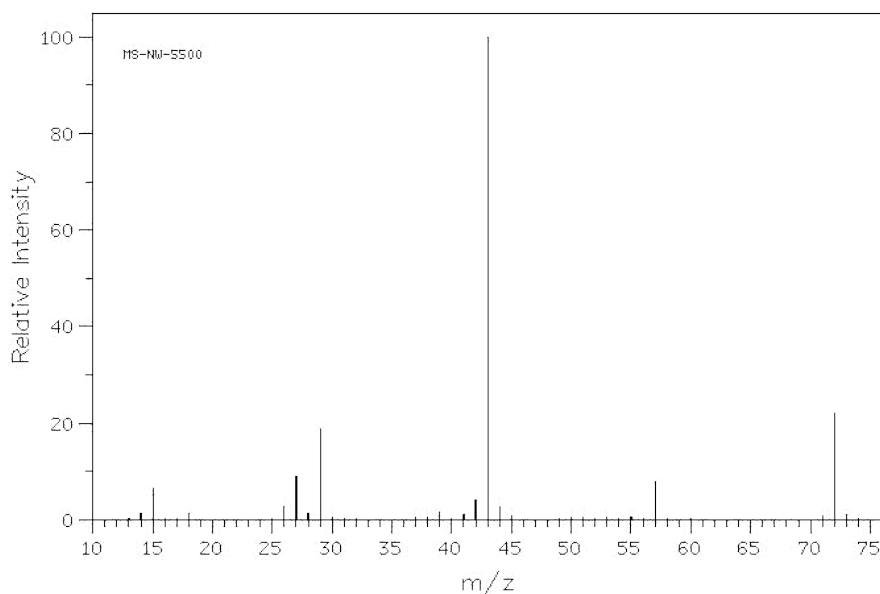


Figure 1: Sample Mass Spectrum Plot

Each peak corresponds to a specific molecular sample. The x-axis displays mass-to-charge ratio in increasing order and the y-axis depicts a relative intensity factor in increasing order. The highest peak, known as the base peak, is used as a reference to normalize the relative abundances of all the other ions present in the disassociated sample.

2.6.1 Quadrupole Mass Spectrometers

Quadrupole mass spectrometers are a specific type of mass spectrometer that are nonmagnetic and “employ a combination of direct-current (DC) and radio-frequency (RF) potentials as mass filters” [8]. This combination of DC and RF potentials ensures that only a predetermined molecular sample of a specific mass-to-charge ratio traverses the length of the instrument without oscillating out of control. All other samples oscillate out of control as the travel through the filter and eventually “crash” into one of the

electrodes. Because these instruments are used in characterizing the composition of samples, it would be a very poor design if only identification of one mass-to-charge ratio could be achieved per instrument. Therefore, these instruments run sweeps of different DC and RF potentials in order to identify distinct mass-to-charge ratios.

This instrument is composed of four parallel cylindrical rods, known as the quadrupole rods, arranged in a symmetrical fashion. Opposing rods are “connected together electrically and to RF and DC voltage generators” [8]. A schematic of the instrument and the quadrupole rod arrangement may be seen below.

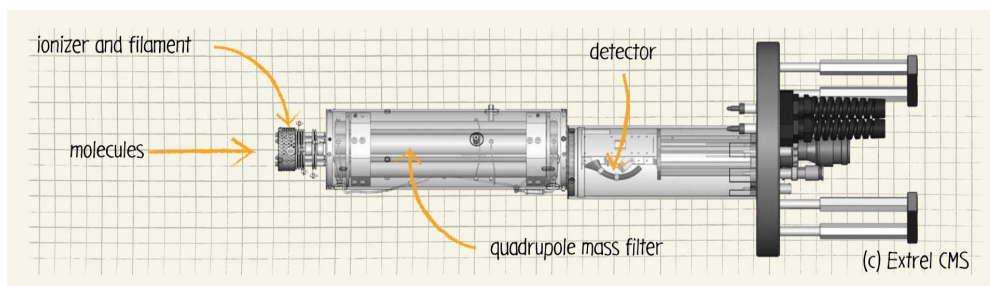


Figure 2: Quadrupole Mass Spectrometer

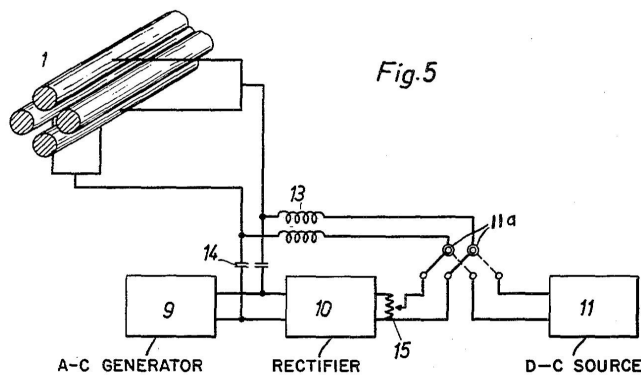


Figure 3: Quadrupole Rod Arrangement

CHAPTER THREE

THEORY

3.3 Ion Trajectories Within a Quadrupole Field

The following is mostly a summary of the derivations found within Dawson's *Quadrupole Mass Spectrometry and Its Applications*.

The electric field generated by the quadrupole rods is as follows:

$$E = -\lambda(x^2 + y^2) - \gamma z^2 - E_0 t$$

It should be noted that there exists a linear dependence on the co-ordinate position. From the equation, λ , σ , and γ are weighting constants and E_0 is "a position-independent factor which may be a function of time" [9]. Because the field is uncoupled in all three directions, the analysis of ion motion becomes quite trivial. Of course, this is assuming a perfect electric field.

Let us now consider the motion of an ion within this field. Depending on the ion's initial position, the force acting upon it varies. The further the ion is displaced from the origin, the more it experiences the effects of the force, eE . If we allow the field to follow restraints imposed by Laplace's equation, the following can be achieved.

$$\nabla^2 \phi = 0$$

$$= \quad ; \quad = -2$$

To better comprehend the values assumed by λ , σ , and γ , the electric potentials should be solved for. Given that $\frac{d^2}{dx^2} = 1$, an integral may be carried out that would yield the following.

If we allow λ to equal $-\sigma$ and γ to equal 0 as it was previously stated, then the z term from the previous equation drops out and the expression becomes as seen below.

$$\dots \left(\dots \right)^{-1}$$

As is analogous with potential flow theory pertaining to a fluid, this represents a field composed of equipotential lines as is shown in the figure 4.

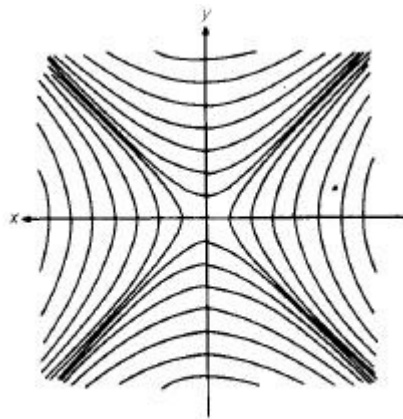


Figure 4: Equipotential Lines for a Quadrupole Field

Four hyperbolic cylinders produce these sets of equipotential lines, where adjacent electrodes are oppositely charged. This is portrayed in figure 5.

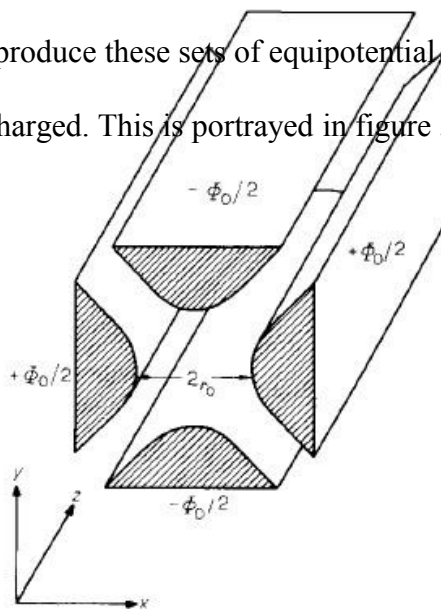


Figure 5: Hyperbolic Cylinder Arrangement

As seen above, the minimum distance between opposite electrodes is assigned the term, $2r_0$. With $\lambda = -1/r_0^2$ the electric potential between the rods is given by the expression below.

$$\phi = \frac{V_0}{2} \left(\frac{x^2}{r_0^2} - \frac{y^2}{r_0^2} \right)$$

From here expression for the electric field in the x and y direction can be obtained.

$$E_x = -\frac{\partial \phi}{\partial x} = -\frac{V_0}{r_0^2} x$$
$$E_y = -\frac{\partial \phi}{\partial y} = \frac{V_0}{r_0^2} y$$

Attention is now turned towards obtaining the equations of motion. Let us start our motion analysis as with any other; considering Newton's Law.

From the Lorentz Force, we have the equation below; where e is the electric charge.

$$\vec{F} = e[\vec{E} + \vec{v} \times \vec{B}]$$

This gives us the force due to an electric and magnetic field. We are only concerned with the force due to an electric field since quadrupole mass spectrometers are nonmagnetic instruments; therefore, our force equation becomes the below expression.

We can thus rewrite Newton's Second Law as:

Utilizing the expressions formerly obtained describing the electric field in the x and y direction, the equations of ion motion become:

$$m \ddot{x} = -e \left(\frac{\partial \phi}{\partial x} \right) = 0$$

$$m \ddot{y} = -e \left(\frac{\partial \phi}{\partial y} \right) = 0$$

Let us say ϕ_0 is constant and define the term A as seen below.

The equations of motion are simplified to those seen here.

These are second order ordinary differential equations with the following solutions.

$$x = A \sin \sqrt{\omega} t + B \cos \sqrt{\omega} t$$

$$= \frac{1}{2} \sqrt{\frac{2}{1-\cos^2 \theta}} + \frac{1}{2} \sqrt{\frac{2}{1+\cos^2 \theta}}$$

The solution for $x(t)$ yields simple harmonic motion within the x-z plane; $y(t)$ yields a “defocusing” within the y-z plane.

The term φ_0 is not constant however. Instead, it is (usually) a periodic function as follows:

$$\varphi_0 = \left(- \cos \theta \right)$$

Therefore the equations of motion become:

$$+ \left(\frac{1}{2} \right) \left(- \cos \theta = 0 \right)$$

$$- \left(\frac{1}{2} \right) \left(\cos \theta = 0 \right)$$

Let us now turn our attention to Hill's Differential Equation:

$$y'' + Q(y) = 0$$

The function $f(t)$ is periodic and as can be seen above, the equations of motion fit this general form. Let us define the following terms in order to simplify analysis

$$\frac{1}{2} \left(\frac{1}{1-\cos^2 \theta} + \frac{1}{1+\cos^2 \theta} \right) = \frac{2}{1-\cos^2 \theta}$$

We can now define our equation of motion as follows, where u can represent either x or

y .

$$y'' + (1 - 2 \cos^2 \theta) y = 0$$

This is now in the form of a Mathieu Equation in canonical form; a special case of Hill's

Differential Equation. Solutions to the Mathieu Equation are well known where the

solution form of the above case is seen below. This is depicted as a stability diagram shown in figure 6.

$$= \sum_{n=-\infty}^{\infty} \dots = \sum_{n=-\infty}^{\infty} \dots$$

Stable regions for ions with specific mass-to-charge ratios can be obtained based off of the Mathieu stability diagram, where a specific D.C. and R.F. voltage will yield sustained oscillations as the ion traverses the instrument.

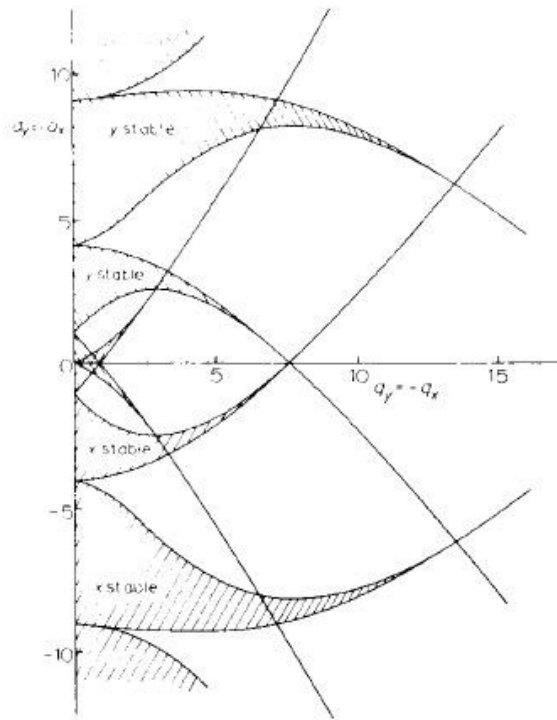


Figure 6: Mathieu Stability Equation

CHAPTER FOUR

SIMULATIONS OF ION TRAJECTORIES WITHIN A QUADRUPOLE MASS SPECTROMETER

4.1 2D Simulations Using MATLAB

As a preliminary study, the equations of motion were modeled in MATLAB's Simulink toolbox. The block diagram for the motion of an ion within the X-Z plane of the instrument is seen below in figure 7.

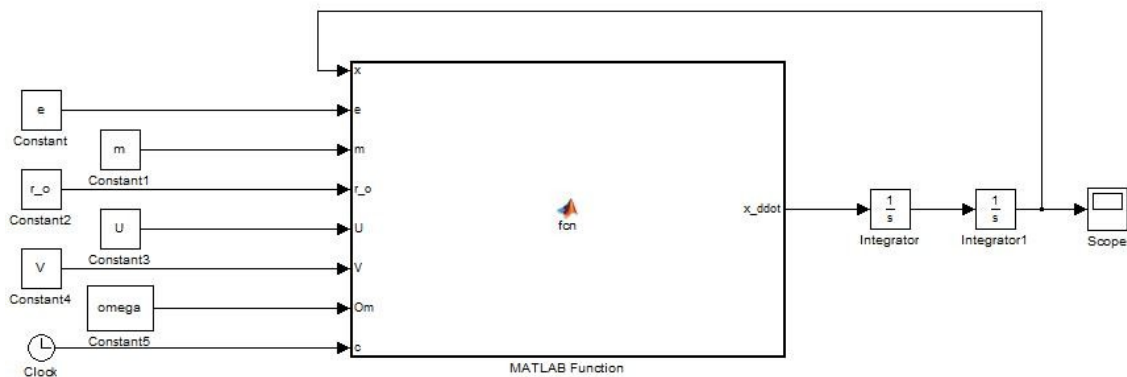


Figure 7: Simulink Block Diagram for Mathieu Equation

These 2D simulations will be expanded later. Trials will be re-done and benchmarked against published data in order to validate the modeled equations. The results shown below are for an atomic mass of 16 and 32. The inscribed radius, r_o , was set as 0.005 mm and the voltage potentials were chosen to favor the ion of 16 amu. As can be seen from figure 8 and 9, the ion of 16 amu has oscillations bounded well within the 0.005 mm

radius of the instrument while the ion of 32 amu oscillates well outside the boundary set by the inscribed radius.

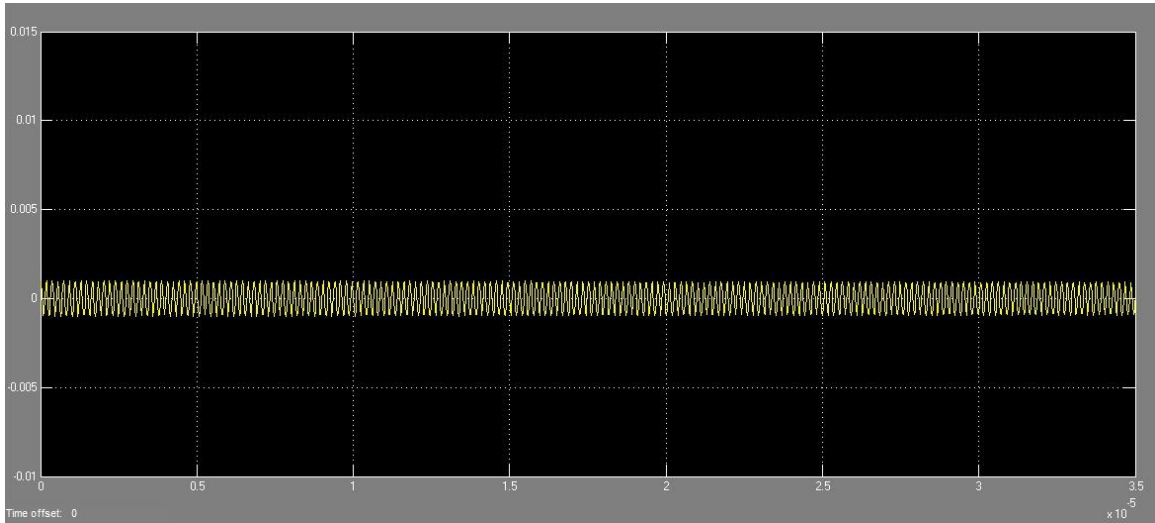


Figure 8: Ion Oscillations Contained Within Instrument X-Z Plane

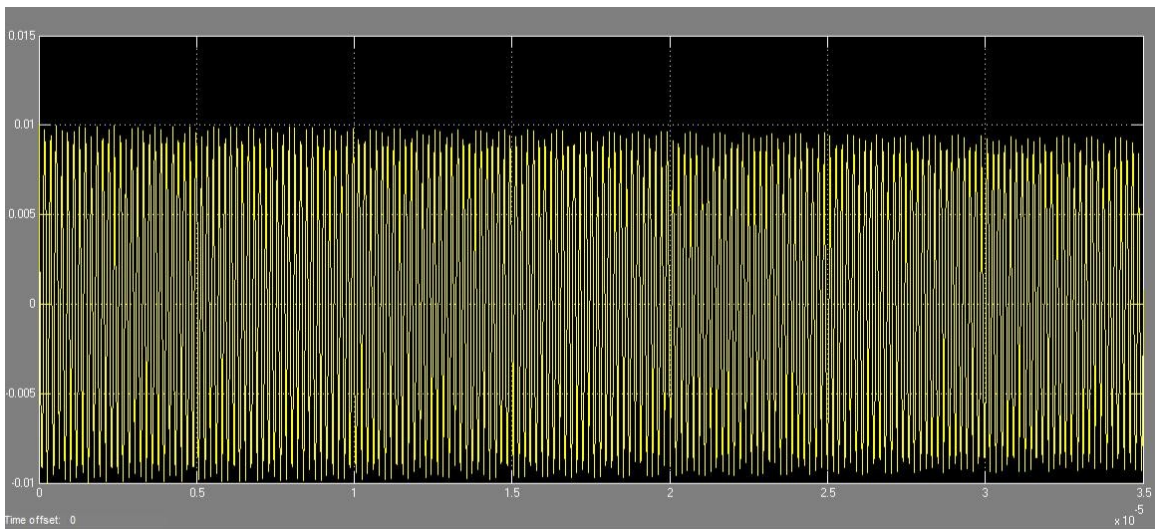


Figure 9: Ion Oscillations Not Contained Within Instrument X-Z Plane

4.2 3D Simulations Using COMSOL Multiphysics

Simulations within COMSOL are run with the parameters shown in figure 10 and the results can be seen in the following figures. As with the 2D simulations, more cases will be ran in order to conduct a parametric study and compare with published data.

Parameters			
Name	Expression	Value	Description
re	2.768[mm]	0.002768 m	Rod radius
r0	re/1.147	0.0024133 m	Inscribed radius
rsrc	0.75[mm]	7.5E-4 m	Source radius
rcase	4*re	0.011072 m	Case radius
Lquad	127[mm]	0.127 m	Quadrupole length
a	0.05	0.05	Mathieu coefficient
q	0.7	0.7	Mathieu coefficient
f	4[MHz]	4E6 Hz	Frequency
omega	2*pi*f	2.5133E7 Hz	Angular frequency
mi	40[amu]	6.6422E-26 kg	Ion mass
Vac	$q*mi*omega^2*r0^2/(4*e_const)$	266.88 V	AC voltage
Udc	$a*mi*omega^2*r0^2/(8*e_const)$	9.5316 V	DC voltage
A	2[V]	2 V	Accelerating voltage
vx0	$sqrt(2*e_const*A/mi)$	3106.2 m/s	Initial x velocity

Figure 10: Parameters Used for 3D Simulations

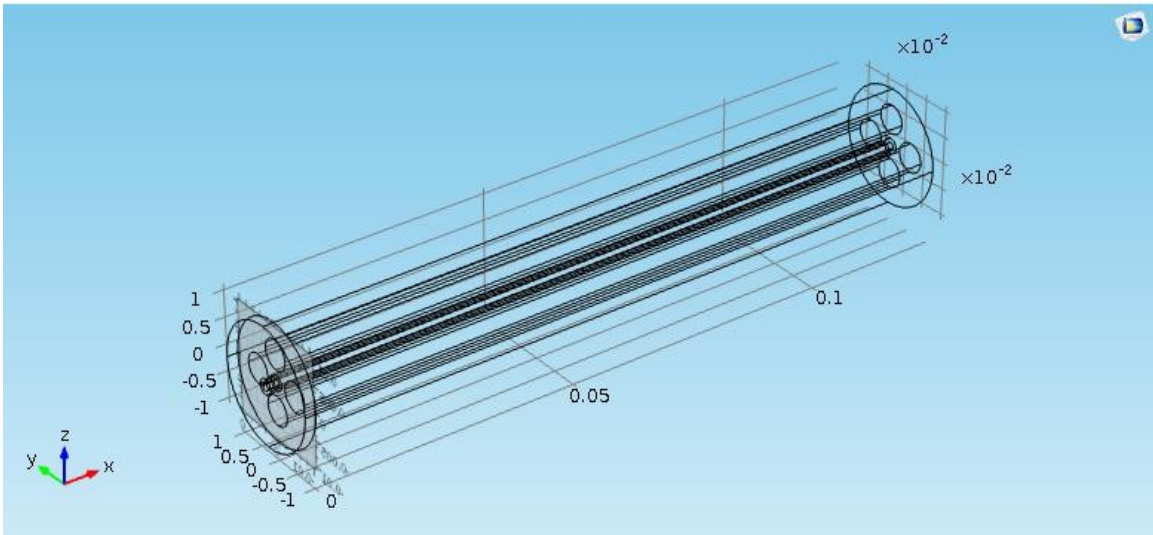


Figure 11: Quadrupole Geometry in COMSOL

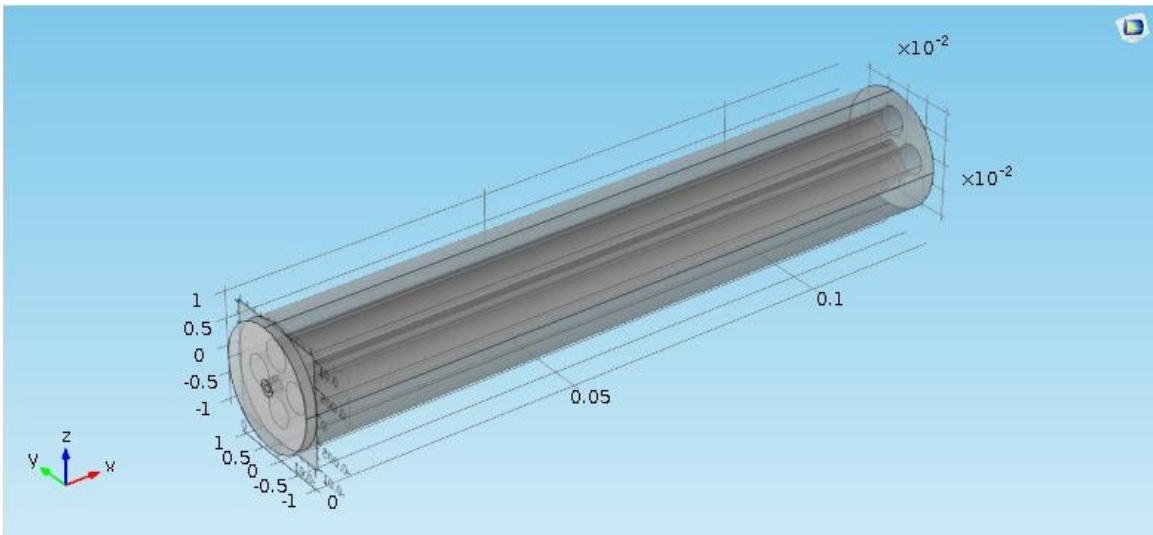


Figure 12: Quadrupole Model in COMSOL

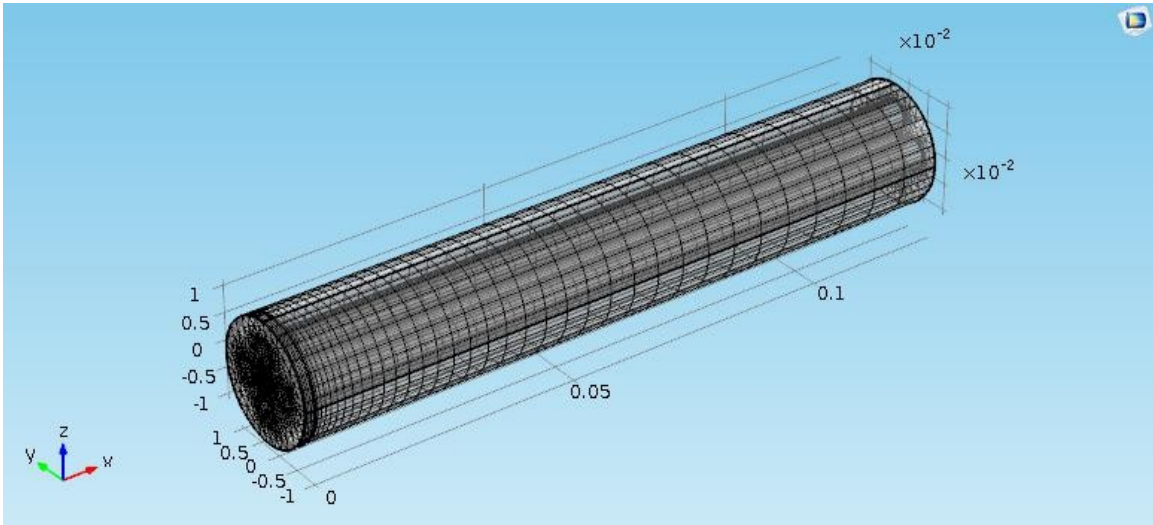


Figure 13: Mesh for Simulations

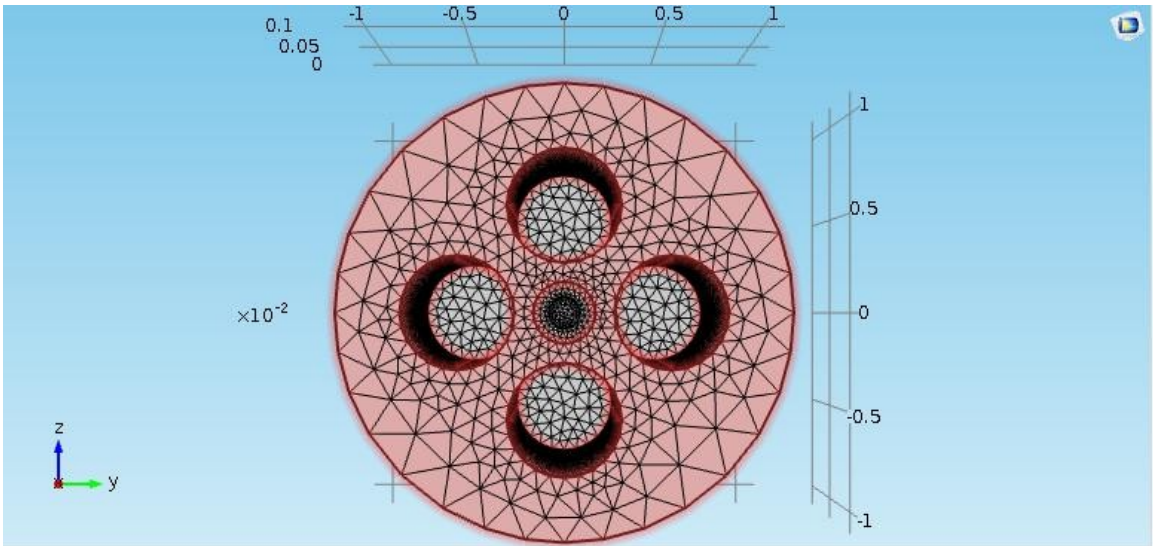


Figure 14: Free Triangular Mesh

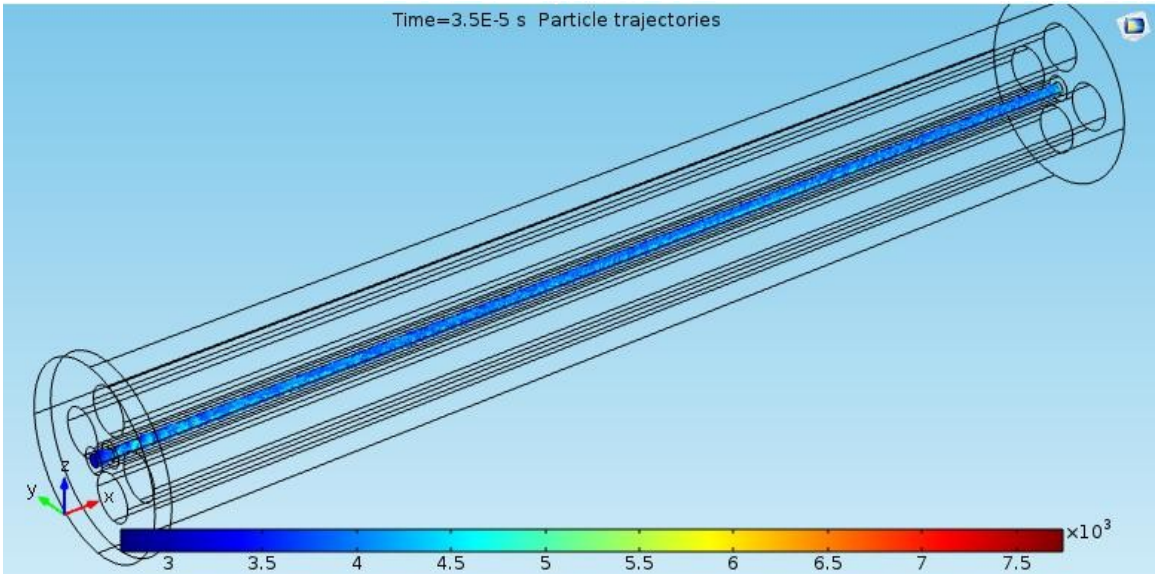


Figure 15: Ion Trajectories

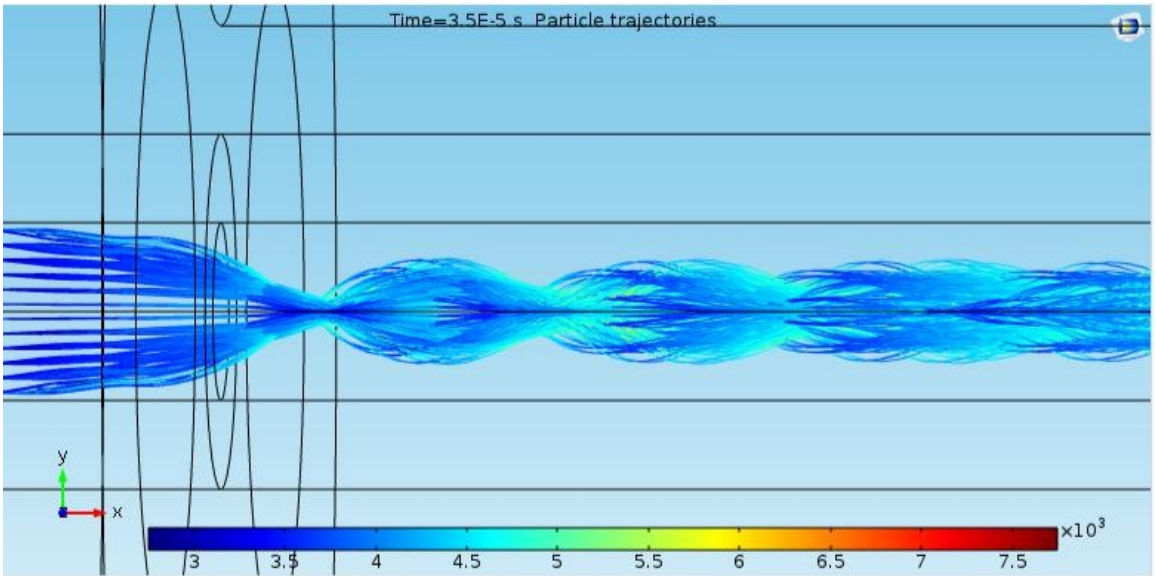


Figure 16: Close-up of Ion Trajectories

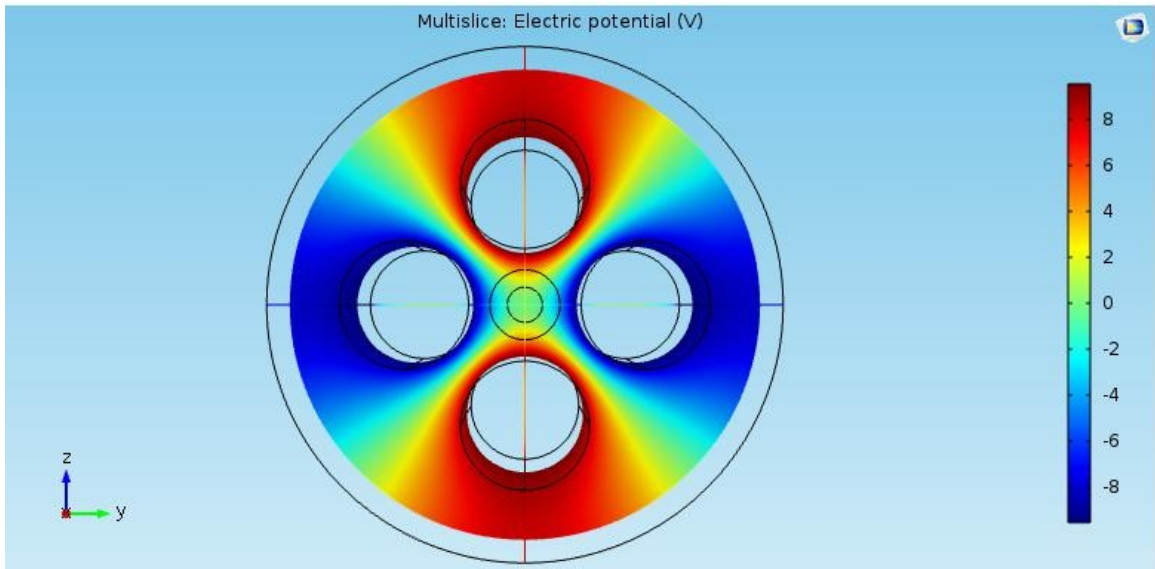


Figure 17: Electric Potential Generated by Quadrupole

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