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Electrospray Ionization Applied to C60 and Carbon Nanotubes

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Abstract

An apparatus has been developed with the intent to produce beams consisting of C_{60} and Single Walled Carbon Nanotubes (SWCNTs) by using Electrospray Ionization. Although Electrospray Ionization is commonly used for producing beams of large biomolecules, this technique has not been attempted before for producing Fullerene beams.

Through the process of Electrospray Ionization, beams consisting of C_{60} and Single Walled Carbon Nanotubes (SWCNTs) can be obtained and measured using electrometers. Utilizing these measurements various alterations have been done to maximize the intensity of these beams. Many more minor and major additions are planned to improve the sensitivity of measurements as well as the consistency of spray producible through this apparatus. The major improvement planned is the addition of a magnetic field sufficient to bend the beam in such a way as to separate a certain mass to charge ratio of particles.

Introduction

SWCNTs are one atom thick tubes of carbon with diameters on the nanometer scale[1]. These tubes have incredible electrical properties that give them great potential to be used in nanotechnology as well as optics. Currently the means to study these tubes is limited to studying them in solution or attached to some surface. This experiment uses the method of Electrospray Ionization to pose a possible means by which to study SWCNTs outside of solution and being attached to other materials.

Electrospray Ionization is a method usually used to study biomolecules. The process of Electrospray ionization is done through first dissolving the molecule, or in the case of this experiment, nanotubes, into solution. Microliters per minute of this solution are transported using a fused silica capillary which is connected to a needle with a voltage of a few kV applied to it biased either positive or negative. This charge then builds up on the solution inside the needle until the repulsion between charges overcomes the surface tension of the solution causing the solution at the tip of the needle to blow off a small amount of its mass in the form of droplets with a large amount of charge on them. This process continues in the droplets until the all that is left is the nanotube carrying charge which then enters the apparatus[2].

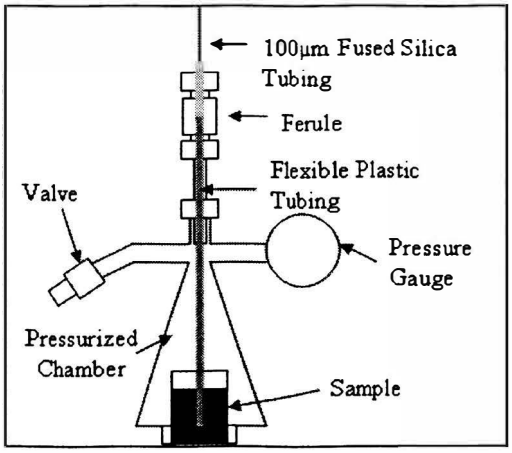
The goals of this experiment are to dissolve nanotubes in solution, construct an electrospray apparatus, and collect data regarding the mass to charge ratio of the particles detected.

Obtaining a Spray

In order for the Electrospray Ionization process to work, a method of supplying microliters per minute of the sample to a high voltage needle is needed. Various different methods were discussed including a method that uses the pull of gravity to draw the solution down a tube to the needle, a method involving a stepping motor to push the solution through a tube towards the needle, and a method that uses pressure to force liquid through a tube out of the needle.

The method involving gravity does not give a steady current flow while the equipment for a stepping motor is not readily available. The method chosen was applying pressure to a chamber to force the liquid out of a container, through a tube and towards the needle.

Figure 1



The chosen technique works based on the fact that the overall pressure of the gas in the chamber will not change as a certain amount of liquid travels out through the plastic tube. A pressure gauge was added to allow monitoring of the pressure in the chamber. The gauge also allowed for a determination between too much pressure and not enough, a crucial distinction as too much pressure requires a higher voltage to produce a spray, but too little pressure does not supply sufficient solution. Flow rates for a range of pressures were measured. For the desired rate, the typical pressures used were between 2-5 psi. From this chamber the solution travels through a fused silica tubing to the input needle on the apparatus.

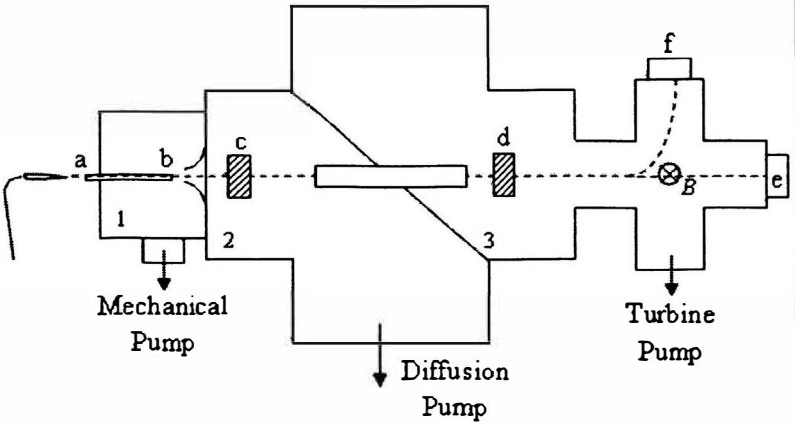
Path of the Beam

The first part of the beam is produced at the end of the needle. At this point, the solution is subjected to a voltage between 2.5-3 kV, depending on pressure and solution turning it into a spray through the process described above. This spray is then attracted (by the voltage difference at the front plate surrounding the input capillary as well as the pressure difference between atmosphere and the 300 mTorr in the first chamber) into the capillary and into the first chamber of the apparatus. Tests were done using two variables, length and inside diameter, to better conclude which would be preferred for the pressure desired in chamber one.

To exit the first chamber the beam passes through a cone which has a small entrance hole. The purpose of the cone is to reject particles that are not traveling in a generally straight direction. The shape of the cone prevents particles with obscured paths from recoiling back into the path of those that are traveling through the cone. This allows for a more defined spray going into the second chamber. Directly after the cone there is a small grid. The grid is held at ground so as to draw the charged particles through the cone and into the second chamber.

After entering the second chamber, the beam goes through an aperture. The purpose of this aperture will be discussed during the topic of maximizing the beam. Inside the second chamber there is a pressure of approximately 10^{-5}Torr achieved through a diffusion pump. This causes a pressure difference that also helps to draw particles in from the first chamber. From the second chamber the particles flow through a transmitting tube into the third chamber.

Figure 2



This diagram of the Electrospray Ionization apparatus shows (a) the input from the needle into the capillary, (b) the transfer from the capillary to the cone, (c & d) the apertures that refine the beam, and (e & f) the detectors. The different vacuum chambers are represented by (1) 300mTorr, (2) 10^{-5} Torr, and (3) which is approximately the same pressure as (2). Chamber (3) also has an area magnetized to alter the beam and bend it toward detector (f). Detector (e) is used when the magnetic field is not used.

In the third chamber the spray travels through a second aperture. After passing through this aperture, the spray then travels to the end of the apparatus where it is measured by the detector. Inside the third chamber the pressure is usually lower than in the second chamber (10^{-6}Torr), as a turbo pump is used to pump the third chamber.

Maximizing Beam and Enhancing Detection

One of the main problems presented in this experiment is that of refining the spray of particles into more of a beam, thus allowing more of our sample to reach the detector. Areas we looked into refining include where the input needle aligns with the input capillary, the alignment between the input capillary and the cone, voltage across the input capillary and cone, voltage across the apertures, and ways to test if each step has been maximized.

The first step in maximizing the beam was to align the input needle and input capillary. In order to do this a system was devised that allowed the needle to be positioned in one spot, yet minor adjustments could be made to better align it. This came in the form of a triangular piece with a hole in the middle for the needle. Once in the hole, the triangular piece is attached to the apparatus via three screws, which can be tightened or loosened to improve the alignment. The beam was detected after traveling through the capillary and the needle was adjusted until a maximum detection was obtained.

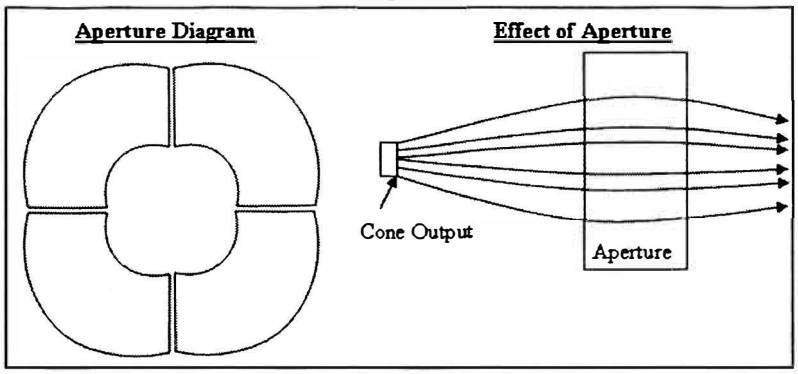
The second part of enhancing the quality of the beam was to align the input capillary with the cone. This has been a difficult task to accomplish due in most part to being unable to visually see the alignment. A couple of approaches have been made. The first approach is similar to above, where the capillary is adjusted on a three screw system until a maximum detection is obtained. Unfortunately, the closest detector is the one at the far end of the apparatus. This makes it hard to ensure that the beam is really being maximized. An attempt was made to detect the beam on the grid, but due to the limited interaction between the grid and beam, this methods has proven challenging. The second approach was to observe the pressure in the second chamber. The principle behind this is that when the capillary and the cone are best aligned, the pressure in the second chamber will increase. This was very difficult as pressure changes were small and hard to detect. This is not the ideal means by which to align the two openings, although it is effective for an approximate alignment.

The next step in enhancing the quality of the beam is to apply a voltage across the capillary and the cone. The principle behind this is if the positively charge particles travel

through a positively charged tube, they will be repelled from the sides, rather than attracted to them, resulting in fewer particles attaching themselves to the inside of the capillary and more reaching the other side. One problem resulting from this addition to the experiment is the fact that if too high a voltage is applied to the capillary there is a discharge on the inside of the chamber. This is undesired as it alters the received data and in severe cases could even lead to damaging the electrometers. Because of this the voltage applied was limited to between 100V and 400V.

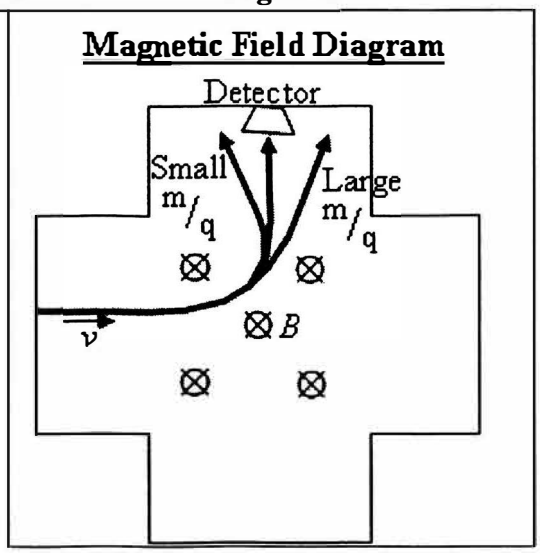
The next step is applying a voltage to the apertures in order to focus and refine the beam. The apertures themselves consist of 4 plates with voltage across them. The voltages are either positive or negative to effectively adjust the beam and to focus it. This was adjusted by first applying a similar voltage across all four plates until the beam was maximized. This gave a reference voltage. Next, three of the plates were held at this reference voltage while the fourth had varying voltages applied to it, both positive and negative, until the beam was again maximized. This was done to all four plates and allowed a good representation of the voltage strength that needed to be applied to each in order for the beam to be oriented in the proper direction. The end result is four similar plates with varying positive voltages in the first aperture. The second aperture was found to not yield any better results with either positive or negative voltages, so it is held at ground potential.

Figure 3



The next element of the apparatus is refining what is received in the detector. The goal of this is to use an electromagnet to select out a certain mass to charge ratio of particles. The way this works is through the force equation $F=q(vxB)$. The incident particles travel through a magnetic field and are bent upwards towards a detector. The velocity of each particle is dependent on the mass in such a way that it will be bent more with lower mass. If the particle has a higher charge then it will be affected by the magnetic field more strongly causing it to bend more. Unfortunately at this time this idea has not been successfully tested. One major issue is that the current size of the magnetic field is too small to bend the beam due to the size of the particles being tested. A solution to this problem is adding more turns in the electromagnets so as to provide a higher magnetic field to bend the beam sufficiently.

Figure 4



Detection

The present method for detecting the beam is by measuring the charges attached to the particles being sprayed. Because the particles have charges on them, they are effectively ions and the ion current they produce can be measured via electrometers. In the beginning two electrometers were used to detect the amount of transmittance at two different stages very close to the beginning, the idea being that we would be able to tell the ratio of transmittance from one point to the next. After moving the detection to the back of the apparatus only one electrometer is needed and thus only one was used. At the end, a detector capable of counting each ion of the beam was installed in chamber three. This gave much more sensitivity and allowed investigation on how the focus and steering voltages helped or hurt the beam intensity.

Various Samples Tested

This experiment has been done with various different samples. They include alcohol, a C_{60}-toluene-alcohol mixture, and SWCNT dissolved in sulfuric acid (H_2SO_4). The most widely used was alcohol since it was easily obtained, cheap, and caused little problems with clogging of the fused silica and needle. Alcohol was used primarily as a test subject to ensure that the apparatus itself was functioning. The C_{60} mixture was used as well to obtain to test the capabilities of the apparatus.

C_{60}, or buckyballs, are carbon atoms arranged in the shape of a sphere that resembles a soccer ball. The first attempt to spray C_{60} in toluene was unsuccessful as sufficient voltage could not be applied to the needle without resulting in a large discharge. An attempt was then made to add alcohol to the solution, since alcohol was known to spray. This showed an improvement and alcohol was added until a steady spray could be obtained. However, when excessive voltage is applied to this mixture, violent discharges are obtained.

SWCNTs are hard to dissolve in solution. Unlike C_{60} nanotubes cannot be dissolved in toluene. Research conducted on methods to submerse SWCNTs in solution revealed various different techniques, but most involved wrapping them with other molecules, such as gum arabic[3]. This is extremely undesired as it would alter data obtained at the detectors, since the nanotubes would have aggregates attached. The SWCNTs were dissolved in several substances in hopes to make a solution of nanotubes. These substances include alcohol, toluene, water, and sulfuric acid (H_2SO_4). Of these substances only sulfuric acid was successful in suspending the SWCNTs. This is the solution that was tested in the apparatus.

Successful tests of both the C_{60} and SWCNT mixtures have been achieved. The SWCNT sprays the easiest with the least likelihood of discharge. At this point it is difficult to state one particular reading as the basis for our measurements as obtaining a stable beam current has been very problematic to achieve. However, many different improvements and alterations are planned for the apparatus itself so as to insure that a stable current is achieved.

Future Goals and Improvements

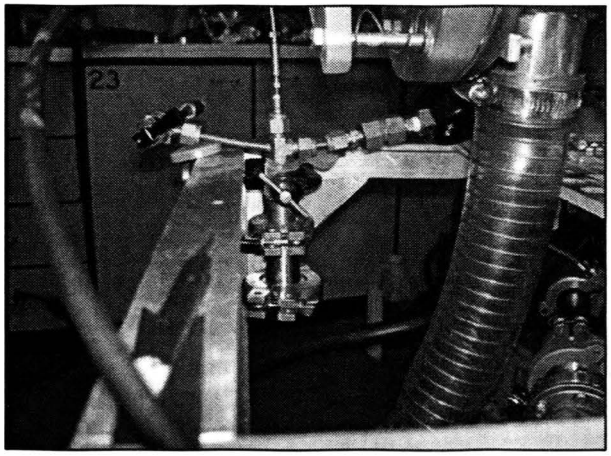
This apparatus is constantly going through changes. These include things from minor alterations to increase our ability to align different components, to major changes that allow us to better define what we are detecting.

Some of the minor changes that are planned for the apparatus include a method that better aligns the needle and capillary. Currently, the method for alignment is not entirely sturdy, thus the alignment needs to be altered periodically as it can be bumped or nudged out of place easily. A desired alteration includes the needle being attached to the same plate as the capillary so that should one move, the other maintains the same orientation to it as before. Another improvement includes the alignment between the capillary and the cone. Methods for this are currently being looked into. Another improvement being made is one that allows detecting just past the cone. This would allow alignment between the cone and capillary to be made much more easily further allowing the bigger changes to take place.

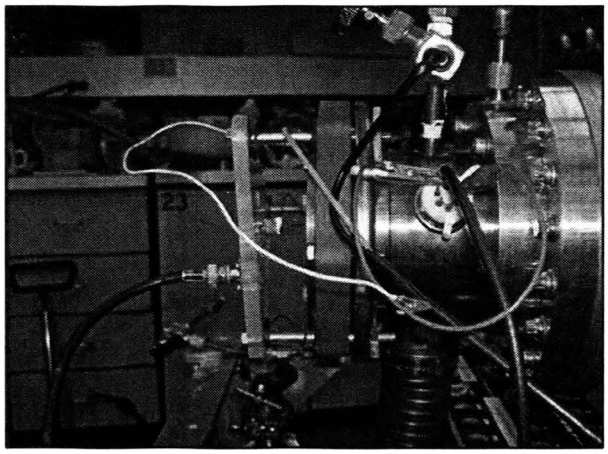
Due to the fact that the electromagnet did not work previously, it is of big importance that a solution be developed. One solution that has been presented is increasing the number of turns of wire to increase the overall magnetic field. This would cause the particles to go through a much smaller radius and reach the detector.

Photographs of the Electrospray Ionization Apparatus

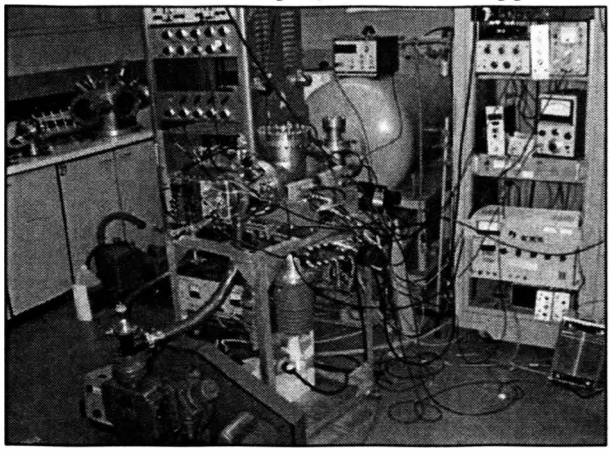
Pressurized Input Chamber



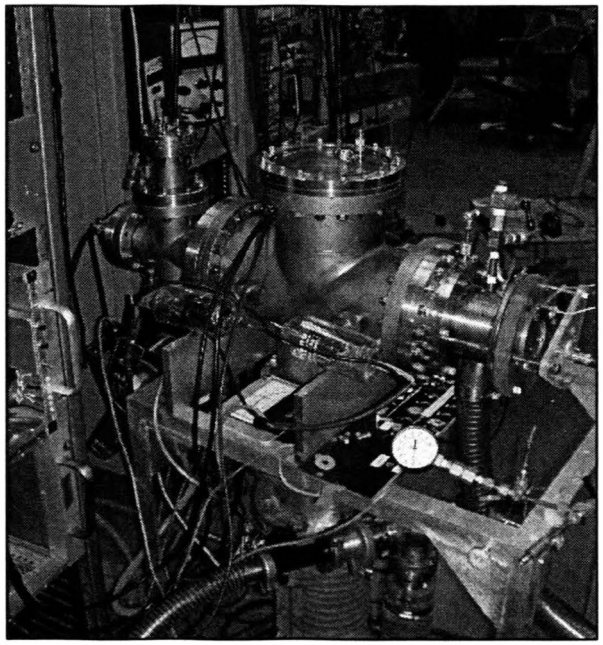
Input Needle and Alignment Mechanism



Front View: Electrospray Ionization Apparatus



Rear View: Electrospray Ionization Apparatus



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(2)"What Is Electrospray." NewObjective.com. 2004. New Objective. June 2006 <http://www.newobjective.com/electrospray/index.html>.

(3)Bandyopadhyaya, Rajdip, Einat Nativ-Roth, Oren Regev, and Rachel Yerushalmi-Rozen. "Stabilization of Individual Carbon Nanotubes in Aqueous Solutions." Nano Letters 2(2002): 25-28.

Stadler, Frank Louis. "Electrospray Ionization Source for the Deposition of Large Molecules and Clusters." (2004)
(This resource was used to observe an example of a successfully completed Electrospray Ionization apparatus so as to gain an idea of how to approach the experiment)