Design of a High Temperature Supersonic Expansion Source

by

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I. Introduction

In the McCall Lab, our goal is to obtain the first rotationally cold gas phase spectrum of C_{60}^+. Our interest in these molecules stems from the notion that they are possible diffuse interstellar band (DIB) carriers. The DIBs were first discovered in 1922[1]. Since that time no one has been able to identify the molecular carriers of any of these bands, and some believe it to be the longest standing mystery of spectroscopy. Although two of these bands have been identified as due to C_{60}^+[3], this identification is questionable because the supporting laboratory data was from Ne matrix studies[4]. The data show spectra of C_{60}^+ in Ne and Ar matrices, and it is explicitly stated in this paper that these results cannot be used for DIB identification because of the uncertain shifts associated with matrix spectra. This obstacle is overcome by using the matrix data as a loose guide in our line search. With a reliable rotationally cold gas phase spectrum it will be possible to definitively prove or disprove the claim that C_{60}^+ is a DIB carrier.

This thesis is an overview of the work carried out in the development of a high temperature, supersonic discharge source for the C_{60}^+ experiment. Previous source designs are outlined, and the advantages of the source design currently in use for this experiment will be discussed in detail.

II. Source Design

a. Requirements

In order to obtain a rotationally cold vapor phase spectrum of C_{60}^+, it was first necessary to create rotationally cold C_{60}^+. The first step in this process involves subliming C_{60}. This is done by heating a pellet of C_{60} to a temperature greater than 500˚ C, at which point a sufficient vapor pressure is achieved to do spectroscopy. Since a positive cation is desired, an electron is stripped from the C_{60} molecule using a high voltage discharge. Once C_{60}^+ vapor is obtained, it is necessary to cool it to interstellar temperatures (~20K). This is accomplished through the use of a supersonic expansion. Henceforth, the heating device will be referred to as the oven, and the discharge/expansion device will be referred to as the source. All sources are built upon the same basic conflat (CF) substrate. This substrate is a standard 1-1/3” CF blank (Lesker part number F0133X000N) with counter-bored screw holes as shown in figure 1a-b. All figures are 2x scale unless otherwise noted.

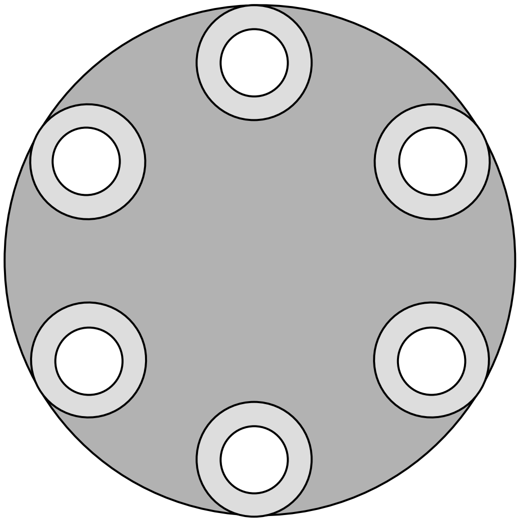


Figure 1a


Figure 1b

b. Slit source

The original source as seen in figure 2 was a slit source design. The advantages of a slit source over more traditional pinhole expansion sources are threefold. The first advantage is that a slit expands almost exclusively along the slit axis. This not only increases path length, but also increases the column density along the expansion plane. Second, the number density falls off linearly, 1/R, with a slit compared with the quadratic, $1/R^2$, pinhole expansion and so there are a higher number of cold ions to be probed at a given distance from the source. Third, the slit source is able to provide more in plane collision partners. This collimates expanding particles so that their velocity is focused perpendicular to the beam axis. Doppler widths can be compressed by a factor of 5-20[5].

In the first attempt to strike a plasma with this source, titanium jaws with a ~30º angle were used. The jaws had a spacing of 25 micrometers. The insulator material was 1mm thick Cogetherm. When voltage was applied, the screws holding the jaws in place (point c) began to arc to the jaws themselves. A purple coloration was noticed, which was later identified as an N_2 plasma. An increase in backing pressure caused more arcing. The initial design called for the screws that mount the jaws to be at ground, and for the jaws to be at a higher potential. The proximity of these parts made arcing very difficult to eliminate

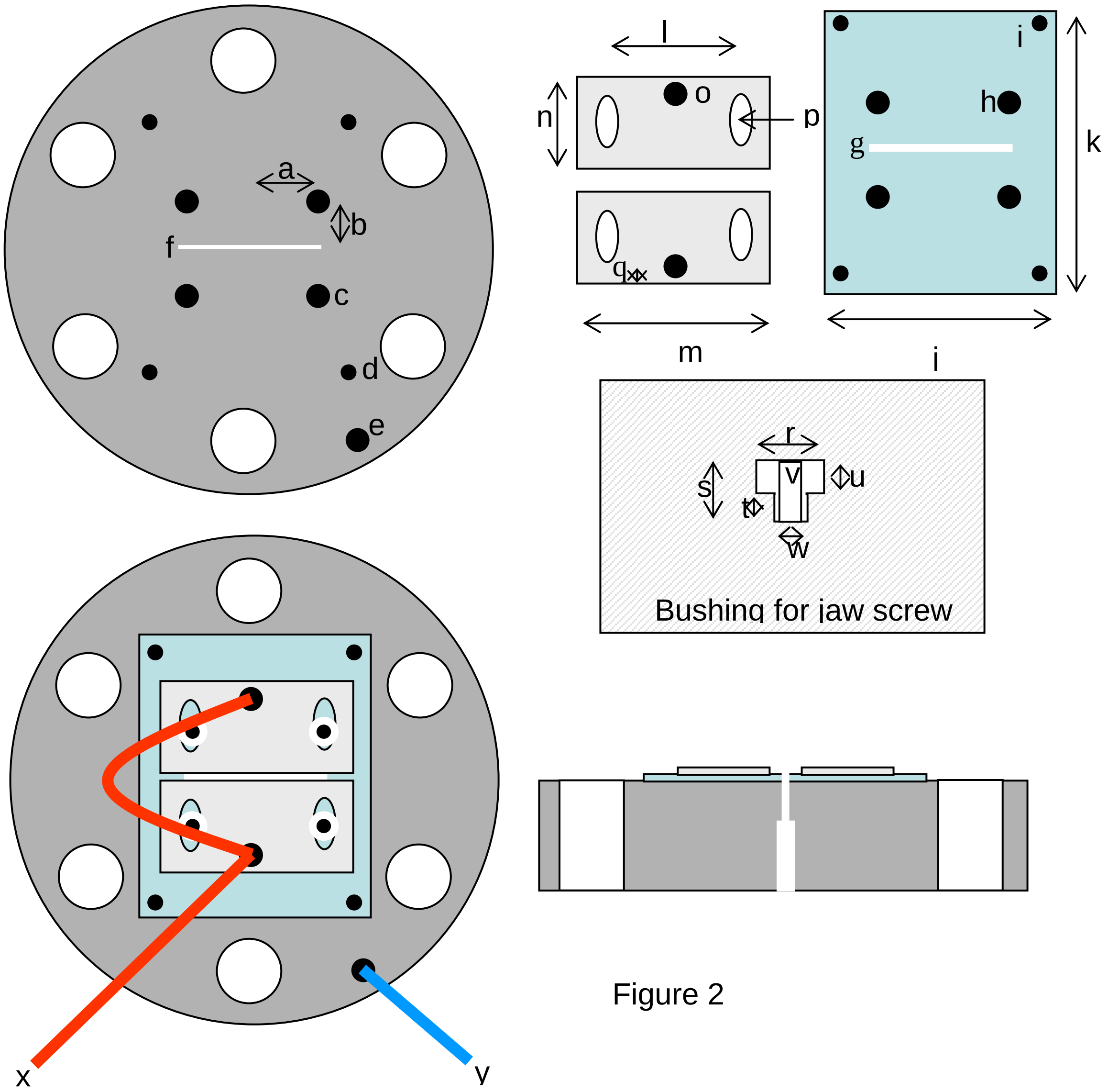


Figure 2

a	0.18”
b	0.125”
c	0-80 tapped
d	sized for Teflon pin
e	0-80 tapped
f	0.004” x 0.394”
g	0.012”
h	0.094”
i	0.63”
j	sized for Teflon pin
k	0.77”
l	0.36”
m	0.529”
n	0.25”
o	0-80 tapped through
p	0-80 clearance±0.004” travel
q	0.063”
r	0.185”
s	0.074”
t	0.037”
u	0.037”
v	0-80 clearance
w	0.094”
x	hot lead, negative
y	ground lead

One possible fix was to use non-conductive screws. Nylon screws were too flexible, and could only be tightened so far before the screw would stop turning, and the head would twist. Ceramic screws were deemed to be too fragile. Since non-conductive screws did not seem to work, attempts were made to stop the arcing by covering the jaws with electrical tape. The arcing persisted, and the tape peeled off. On the same line of thought, the screw heads were covered with a more resilient non-conductive material. The first attempt was Apiezon Q putty. The arcing continued, and turned a greenish orange color. “Shooting stars” were also seen emanating from the discharge, which were most likely bits of Q burning off. As before, an increase in gas pressure correlated with an increased arcing.

After taking the source apart, it was noted that the bushings were too short. The jaws had arced to the screws. The next bushings (figure 3) were designed to be a bit taller, and had the screw heads countersunk. This alleviated the screw arcing problem, but the jaws continued to arc to the conflat. Doubling the spacer thickness and altering ballast resistance yielded the same results.

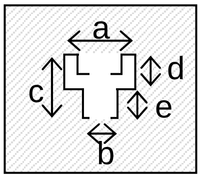


Figure 3

a	0.185”
b	0.094”
c	0.169
d	0.092”
e	0.077”

The next approach was to double the slit width to 50 micrometers. With this configuration a jet was struck. Current did not seem to have an effect, but the shape of the supersonic expansion could be varied by changing the chamber pressure. The jet was uneven due to jaw unevenness. This issue could not be resolved, and work began on a simpler pinhole source.

c. Early Pinhole

All of the early pinholes relied on face seals to attach the various source components. These designs were bulky, and overly complicated. None of them ever really worked because the various layers would arc together due to internal leaks. These designs will not be discussed in detail here because no valuable information was ascertained from these trials, but the final version did lead to the next phase of source design and is therefore shown in Figures 4a-d. In the trials, it was decided that glue was needed to obtain a good seal between the components, and so subsequent source designs utilized this option.

d. High Pinhole

As a proof of concept (i.e. our problems all stem from the fact that a good face seal cannot be made between the source pieces), a source was glued together entirely with Torr-Seal (Figure 5a-b). This source produced the first supersonic jet.

Several different gasket materials were then tried between the pieces of a figure 4 type source. A Viton O-ring was able to provide a good seal between the conflat and bottom spacer, but this is not practical for high temperature applications. Aluminum foil (~15mil) made a decent seal, and copper (2mil) made an even better seal. The main problem with using copper is that it is not very robust, and the gaskets charred/disintegrated very quickly. The next attempt was a gasket made from alumina paper (Cotronics ceramic paper trial kit). The 1/32” thick paper compressed well, and made a decent seal. When the Cotronics 901A hardener was applied, compression was greatly reduced, and the seal leaked. Where gaskets had failed, it was felt that an adhesive seal might work.

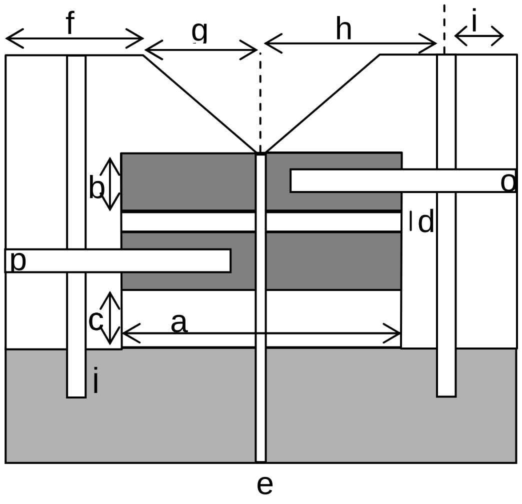


Figure 4a

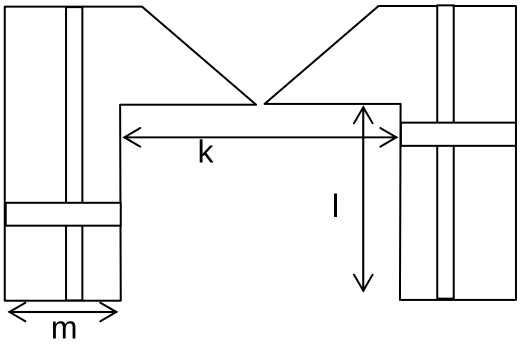


Figure 4b

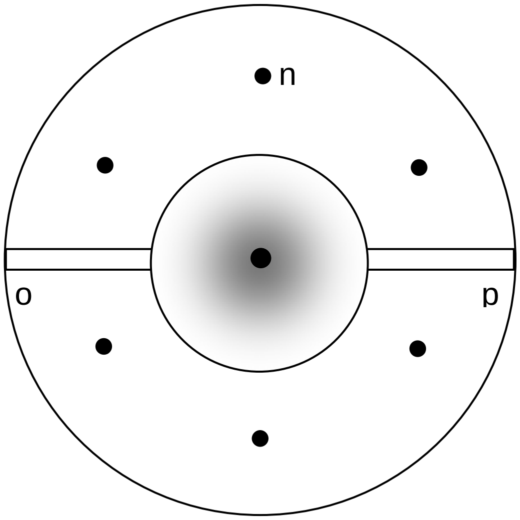


Figure 4c

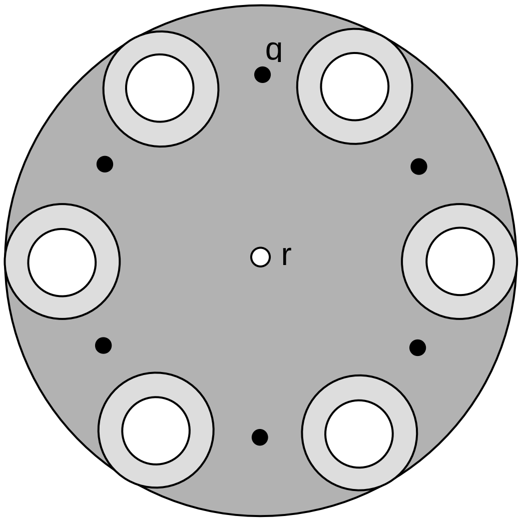


Figure 4d

a	0.79”	g	0.283”	m	0.265”
b	0.15” SS	h	0.474”	n	0-80 clearance
c	0.15” alumina	i	0.191”	o	0-80 clearance, 0.263” from top
d	0.05” alumina	j	0-80 tapped	p	0-80 clearance, 0.463” from top
e	.02” pinhole	k	0.8”	q	0-80 tapped
f	0.382”	l	0.58”	r	0.02” pinhole

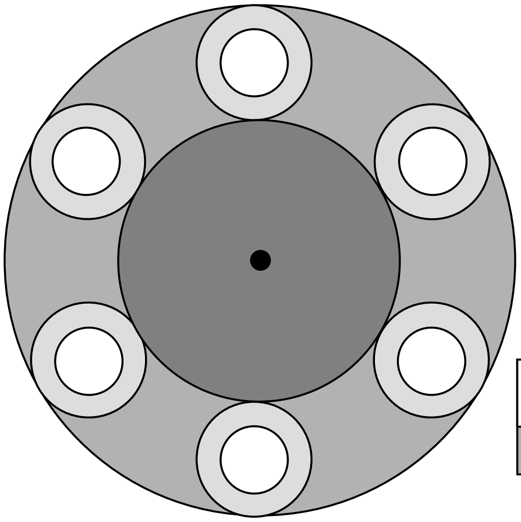


Figure 5a

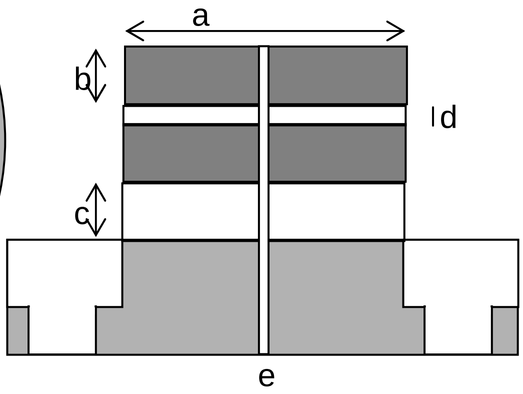


Figure 5b

a	0.79”
b	0.15” SS
c	0.15” alumina
d	0.05” alumina
e	.02” pinhole

A 970N kit for electrical and structural applications from Cotronics was obtained. It contained 7 different adhesive products. 950 Metallic Aluminum is electrically conductive. This property is not desirable when trying to induce a voltage separation and was used in a spectacularly unsuccessful fashion. 7030 High Strength was the next option, but it expanded greatly as it set. 907GF dried to a crumbly state, which was not vacuum tight. The 901 Fiber Based Alumina and 919 Electrically Resistant adhesives were not vacuum tight. The 940 Fast Setting Ceramic did not adhere well to stainless steel or alumina. This only left the 989 General Purpose Alumina adhesive. This glue worked very well. It is non-conductive, heat tolerant, and forms a vacuum tight seal. From this point onwards 989 General Purpose adhesive was used exclusively except for a brief period when 989FS, a fast setting version, was used. The consistency of the fast set was a bit more watery making it easier to apply, but overall it lacked the structural integrity desired.

Sources were glued together as seen in figures 5a-b. Relatively thick layers of glue were applied between layers, and then the layers were squeezed together. There were two major problems with this, the first being that glue would enter the pinhole. The second was that it was difficult to keep the pinhole aligned through the various layers. Wires or needles of similar diameter to the pinhole were used to keep the channel clear/aligned during the gluing process. After the glue set, the excess was removed from the channel using a drill bit in a pin vise.

As time went on it was noticed that it was quite difficult to glue the large electrodes in place; excess glue would get stuck in the screw heads along the conflat. A new source was devised as seen in Figures 6a-b. Two major changes were made. The first change was the reduction in the diameter of the electrode and spacer. As long as the pinhole is not altered, the outer dimensions are unimportant. The second change was to remove the bottom spacer and electrode. This is possible because the conflat is attached to the oven, which is in turn attached to the chamber, which is grounded. This causes the conflat to act in an identical manner as the bottom electrode. The only reason that this bottom electrode and spacer ever existed is that it was originally uncertain which polarity of high voltage should be used. A positive voltage was attempted, but a successful discharge never struck. A negative voltage was shown to work with the Torr-sealed source, and this is what was used from that point on.

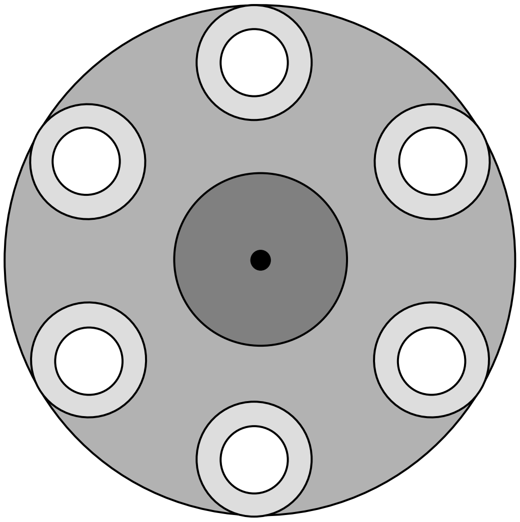


Figure 6a

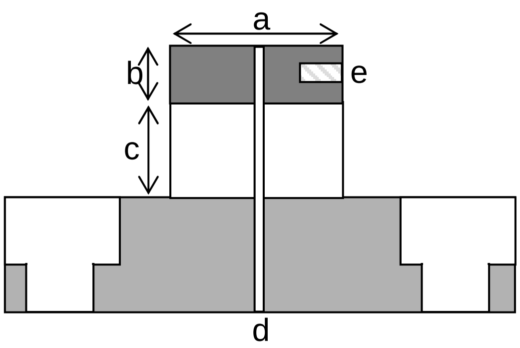


Figure 6b

a	0.45”
b	0.15” SS
c	0.25” alumina
d	0.02” pinhole
e	0-80 tapped

Though much success was met with these glued sources, several problems still arose. The first, and perhaps most major problem, is that the glue being used was shaken, and not stirred. This meant that the glue was not properly mixed, and its integrity had been compromised. The glue’s quality also deteriorated over time due to solvent evaporation. The solution to this was to separate a newly opened tub of glue into smaller containers. This minimized surface area and exposure time of each portion. A second problem is that small parasitic volumes were present between layers. This enabled plasma to enter the volume and burn its way out of the source between layers. The problem was solved with a combination of compression and proper stirring techniques. Shaking and whipping air into the glue were found to be major causes of bubbles in the glue. The final problems were, as before, keeping the pinhole aligned and clear of glue.

e. Late Pinhole

The alignment problem was an increasing frustration with the experiment, as the source lifetimes were on the order of days, and so it was decided that something needed to be done to make the process easier. The solution was to make a source that slotted together like Lego™ blocks. The design can be seen in Figures 7a-b.

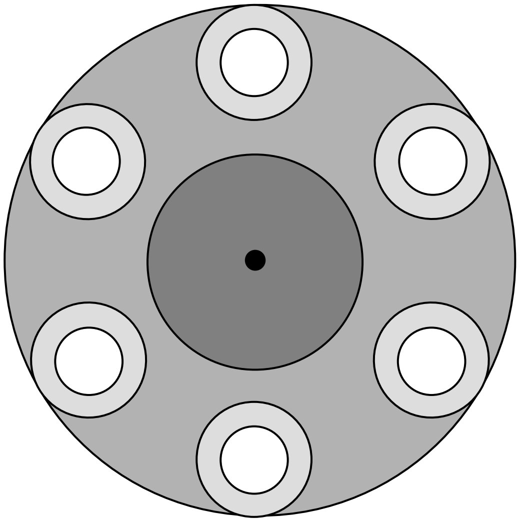


Figure 7a

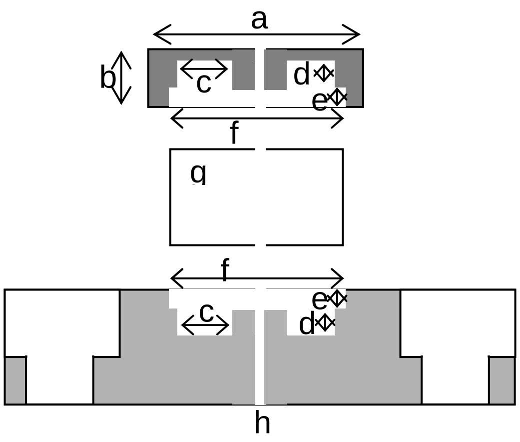


Figure 7b

a	0.551”
b	0.15” SS
c	0.145”
d	0.07”
e	0.05”
f	0.451”
g	0.19” thick Macor, 0.045” OD
h	0.05” pinhole

This design holds a threefold advantage over its predecessor. The first advantage is that the channel is always aligned. The second advantage is that the glue is mostly confined to the grooves cut into the conflat/electrode. The third is that this design is more structurally sound. This design worked quite well. Sources lasted for such an extended period of time that lifecycle problems became visible. Over time the small pinholes in the electrode had a tendency to be eaten away by the plasma in a trumpet shape as seen in Figure 8. The second lifecycle problem came only after heating the oven. Because of the insulating alumina layer, a temperature gradient was created across the source. C_{60} vaporized in the oven began to condense in the source, and would eventually plug the pinhole. The initial solution was to widen the pinhole in the electrode as seen in Figure 9. This prevented the electrode from forming the bugle shape, and perhaps altering the supersonic expansion. Though it helped, this did not solve the clogging problem. The solution was to ensure that the source was as warm, if not warmer, than the oven itself.

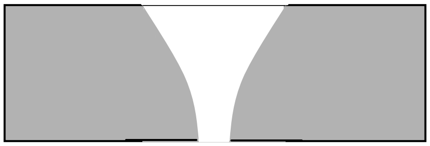


Figure 8

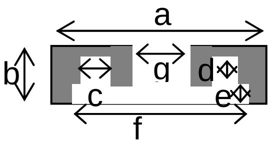


Figure 9

a	0.551” SS
b	0.15”
c	0.08”
d	0.07”
e	0.05”
f	0.451”
g	0.15”

f. Renaissance Pinhole

The Lego™ pinhole design worked well, but the sources, as all sources do, eventually succumbed to small pockets of plasma eating between the layers of the source (on the order of days as opposed to hours with older designs). A radical new design was proposed, as can be seen in Figures 10a-b. In this design the pinhole is determined solely by the conflat. This means that pressure does not build behind the pieces of the source. This results in a much more robust piece of equipment, but at some cost. This design does not seem to cool quite as well as older sources, but it is able to do a fair job as is shown in the heating section.

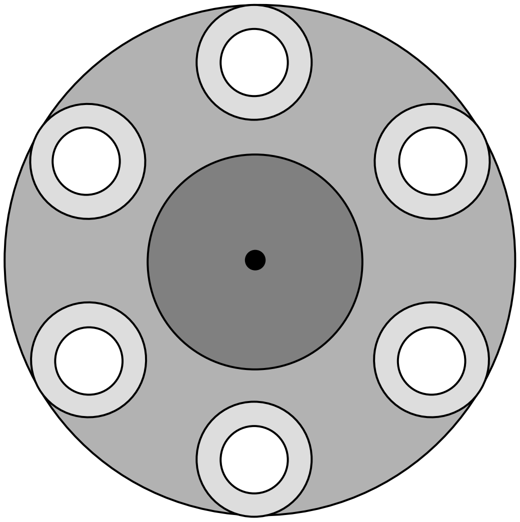


Figure 10a

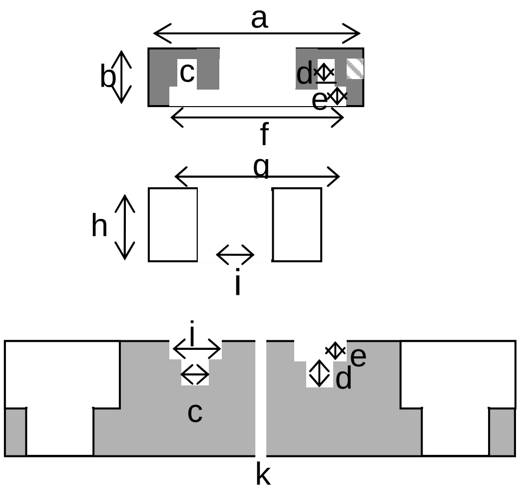


Figure 10b

a	0.551” SS	g	0.450”
b	0.15”	h	0.19” alumina
c	0.05”	i	0.25”
d	0.07”	j	0.101”
e	0.05”	k	0.030” pinhole
f	0.451”		

III. Heating

a. Oven

Along with creating supersonically cooled plasma, heating the oven was another major issue. The original design can be seen in Figure 11. The oven is made of stainless steel. Though copper may seem to be a better material due to its superior thermal conduction, copper is also more reactive and less resilient to high temperatures. The gas line (a in Figure 11) is ¼” stainless with a Swagelok fitting into the back of the oven. Upon contemplation, it was thought that this design would not transfer enough heat to the gas, so 1/8” copper tubing was wrapped around the outside of the oven. The first heating method involved cartridge heaters (Omega product number CIR-2047/120).

Originally, these heaters were press fit into the holes (c in figure 11), but after the first attempt to use the heaters in atmosphere they became stuck, and so the holes were drilled out to be clearance holes. When placed in vacuum, the lead wire insulation on the junction to the heater consistently blew up and the heaters shorted. This is because in a vacuum, the only paths of heat transfer are direct contact and radiation. The back of the heaters (where the wires come out) are not in thermal contact with anything, and hot spots build up. These hot spots eventually create such a thermal gradient with the rest of the heater that they blow out. This shorts the heater and renders it useless.

Since UHV rated cartridge heaters are cost prohibitive, halogen light bulbs (Bright Effects Model #LBPQ150T4/JCD) were chosen as a source of radiative heat. The selected bulbs were 150 Watt. They were attached to a variac, and simply slipped into the holes previously occupied by the cartridge heaters. With this setup, a maximum temperature of ~ 610˚C was achieved. This was an acceptable solution, but over time the copper tubing coiled around the oven lost its strength, and began to break. It became impossible to attach new tubing around the oven, and a new design was necessary.

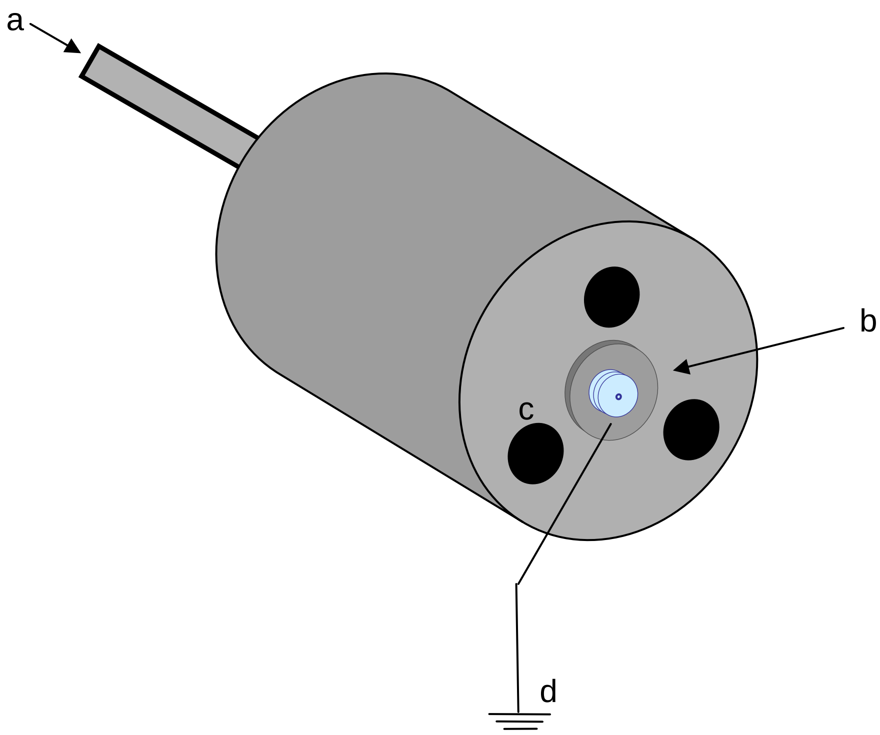


Figure 11, not scaled

a	Gas flow into oven
b	Source
c	Clearance holes for cartridge heaters
d	Ground attachment

The solution can be seen in figure 12. An in-line heater was developed to preheat the gas before it enters the oven. The device is nothing more than flex copper wrapped around a ½" ID stainless steel pipe. This was attempted without the pipe, but it was found that the pipe was needed prevent hot spots from localizing around the bulbs. With this device temperatures of ~660˚ C are achievable. A higher temperature can probably be attained by increasing the in-line voltage, but it is not worth the risks associated with rupturing the gas line.

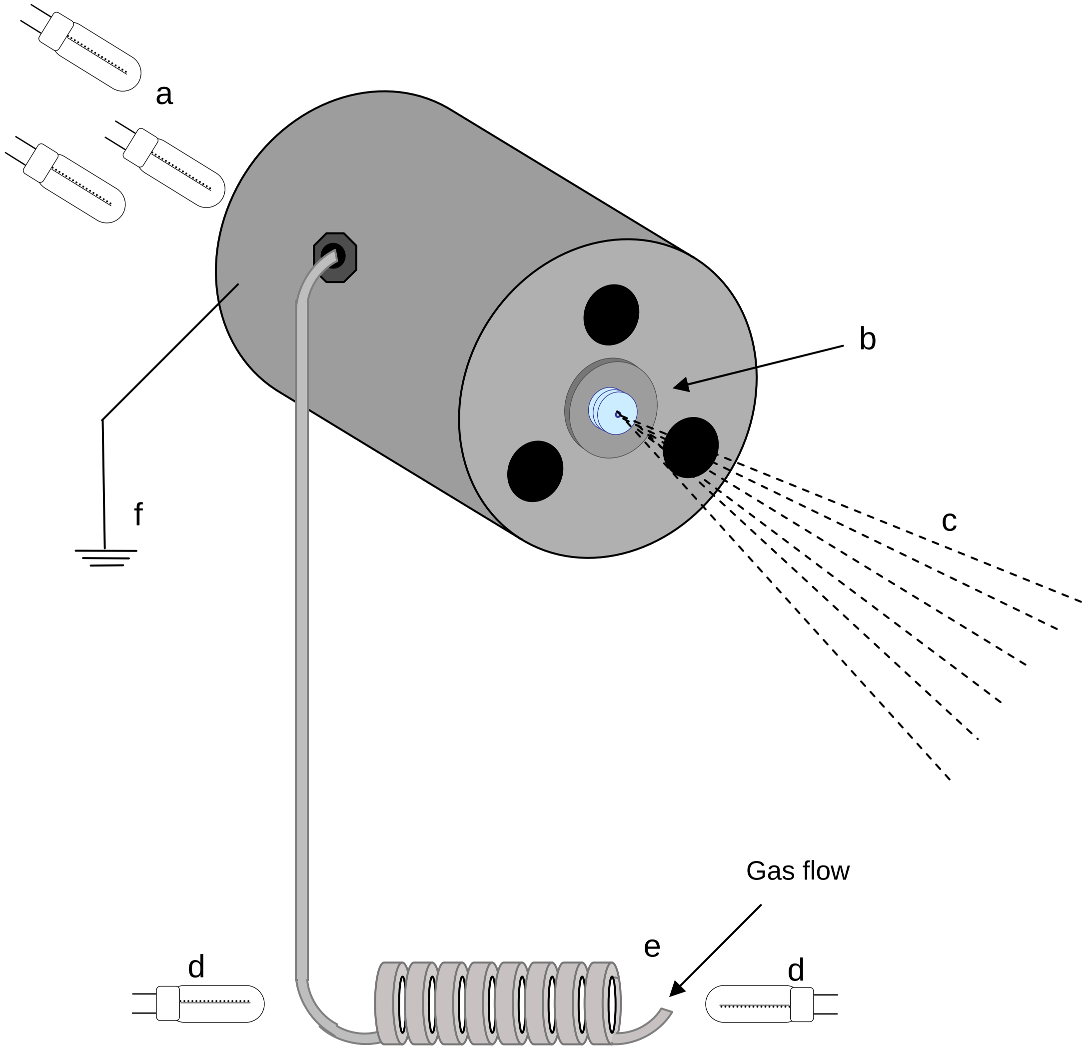


Figure 12, not scaled

a	150 Watt bulbs
b	Source
c	Supersonic Expansion
d	100 Watt bulbs
e	In-line heater
f	Ground attachment

As described previously in the source section, the pinhole clogged when C_{60} crystallized on the inside of the source. The simplest solution was to heat the source so that it was as hot, if not hotter, than the oven itself. To accomplish this, a 35 Watt halogen spotlight was aimed at the front of the source.

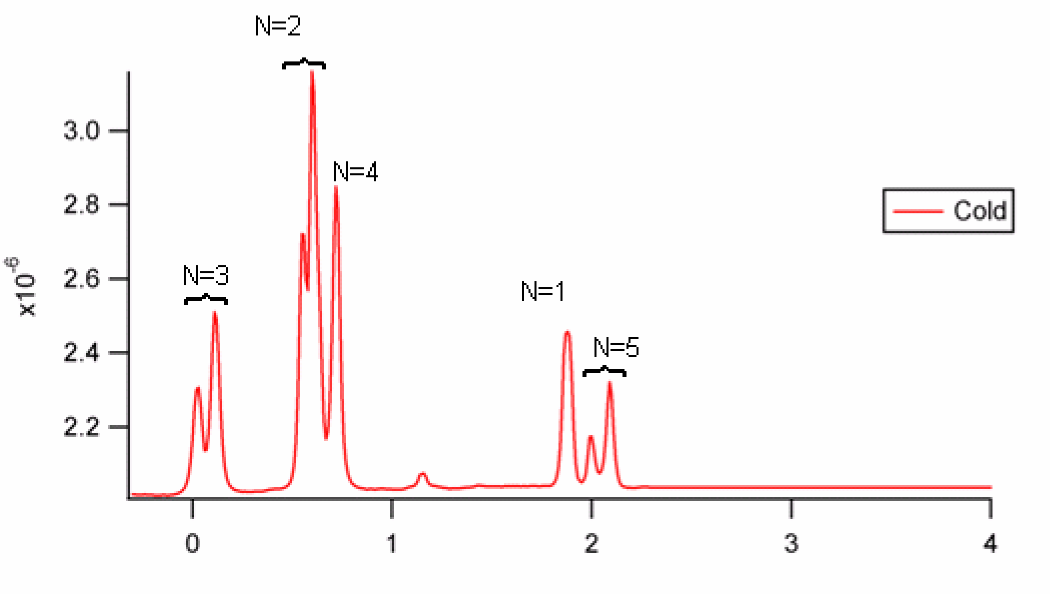
b. Sample

The sample that we introduce was originally a cylindrical pellet with a ¼” radius. With its limited surface area and aerodynamic shape, this form did not allow an acceptable amount C_{60} to sublime. The pellets were broken into jagged pieces to increase surface contact with the heated carrier gas. To ensure that the pieces/powder stayed together they were incased in a fine copper mesh with an outer diameter roughly the size of the oven cavity. This caused the gas to flow entirely through the sample, and we were left with an adequate amount of C_{60} vapor.

c. Rotational Temperatures

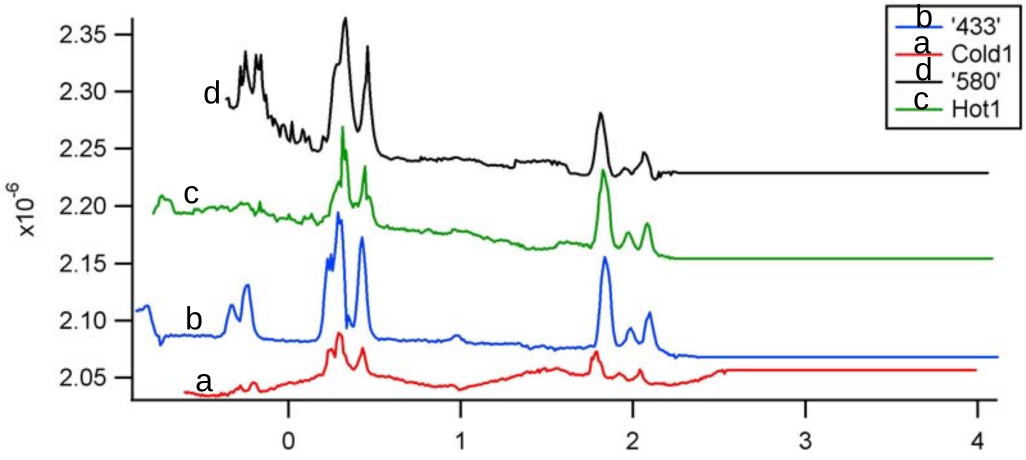
Heating the sample to 650˚ C is necessary to complete the experiment, but counter to the goal of achieving rotationally cold molecules. Molecules are re-cooled through the use of a supersonic expansion, but cooling efficiency must be balanced with other factors such as sample density. As a reference, a set of N_2^+ lines as seen in Figure 13. The relative intensities of the lines can be used to determine the rotational temperature. As a rule even states should always be more populated than odd states. This is due to nuclear spin coupling in the even states. In cold spectra, lower N states should be more intense than higher N states.

Figure 14 shows a few spectra taken with the high pinhole source. It can be seen that as sample temperature increases, the ratios $N_{=2}$:$N_{=4}$ and $N_{=1}$:$N_{=5}$ are nearly constant. This proves that we are able to produce cold ions with elevated source temperatures. Figure 15 contains spectra obtained with the renaissance pinhole source. It is clear that this design does not cool as efficiently as its predecessor. It is thought that this source does not cool as well because a plasma is formed after the jet is expanding, rather than before it expands.



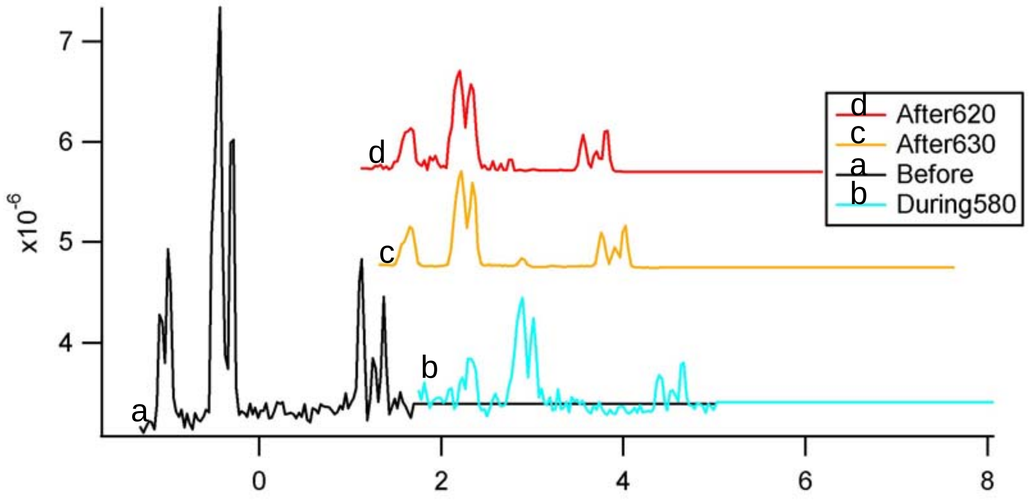
High Pinhole Source
Rotational temperature ~22 K
Source gas room temperature

Figure 13



High Pinhole Source
Rotational temperature ~25 K
Source gas temperature indicated on graph, cold is room temperature, hot is 610K

Figure 14



Renaissance Pinhole Source
Rotational Temperature
a ~25K
b-d ~ 35K
Source gas temperature indicated on graph, Before is before heating is applied

Figure 15

IV. Conductance

When working with any vacuum system, it is necessary to calculate the conductance of the system, or the ability of matter to flow through the system. A high conductance system can pass more matter per second than a low conductance system. A few of the basic equations can be seen in Figure 16. Conductance calculations can get quite in depth, but I will only cover the essential equations and approximations needed to set up the vacuum system needed to handle the gas load of a supersonic expansion source as described in this paper.

When doing these calculations, it is first necessary to find out what the throughput (matter/second) of your system is. In the case of a supersonic expansion source, the throughput is defined by the amount of gas entering the pinhole. Next, the desired chamber pressure must be found that produces the desired expansion profile[6]. Combining these two factors into equation d yields the effective pumping speed required to evacuate the chamber to the specified pressure with the specified flow of gas. Since the pipes offer resistance to the flow of gas, it is necessary to factor in conductive losses. With equation f, one can calculate the actual pumping speed the vacuum pump would need to handle the load.

The conductance of a length of pipe can be calculated as seen in equation g. Conductance is additive, so the conductance of each element can be added together to yield the total conductance of a system. Besides straight lengths of pipe, any alteration to the pipe will cause a conductance loss. Each alteration is given a Moody friction factor, which determines the equivalent length. The friction factor is determined by the shape of the pipe alteration as seen in formulas n,o. Exit loss happens ever time a pipe flows into an area of random conductance, such as a bend or reducer. Entrance loss occurs when flow goes from an area of random conductance into a straight section of pipe. Correct use of entrance and exit loss can be seen in Figure 17.

a	Q	=	Throughput (Torr*L/s)	
b	Q	~	$15.7*P_0(\text{Torr})*d^2(\text{cm})$	Air through an aperture
c	Q	~	$45*P_0(\text{Torr})*d^2(\text{cm})$	He through an aperture
d	P_{Chamber}	=	$Q / S_{\text{effective}}$ (Torr)	Chamber pressure
e	S	=	Pumping speed (L/s)	
f	$S_{\text{effective}}^{-1}$	=	$S^{-1} + C^{-1}$	
g	C	=	$182(\text{L/s})*D^4*P_{\text{avg}}(\text{Torr})/L(\text{cm})$	Conductance
h	$L_{\text{equivalent}}$	=	$k*D/f$	L_{eq} (cm), D is diameter pipe (cm)
i	f	=	$64/Re$	Moody friction factor
j	Re	=	$8*Q/D$	Reynolds number, air, 20˚ C
k	Re	=	$1.13*Q/D$	He, 20˚ C
l	$L_{\text{equivalent}}$	~	$Re*D/64$	Exit loss
m		~	$12.5*D$	Entrance los, 90˚ Elbow
n	k	=	0.78	Pipe extending into chamber
o		=	0.5	Pipe flush with chamber

Figure 16

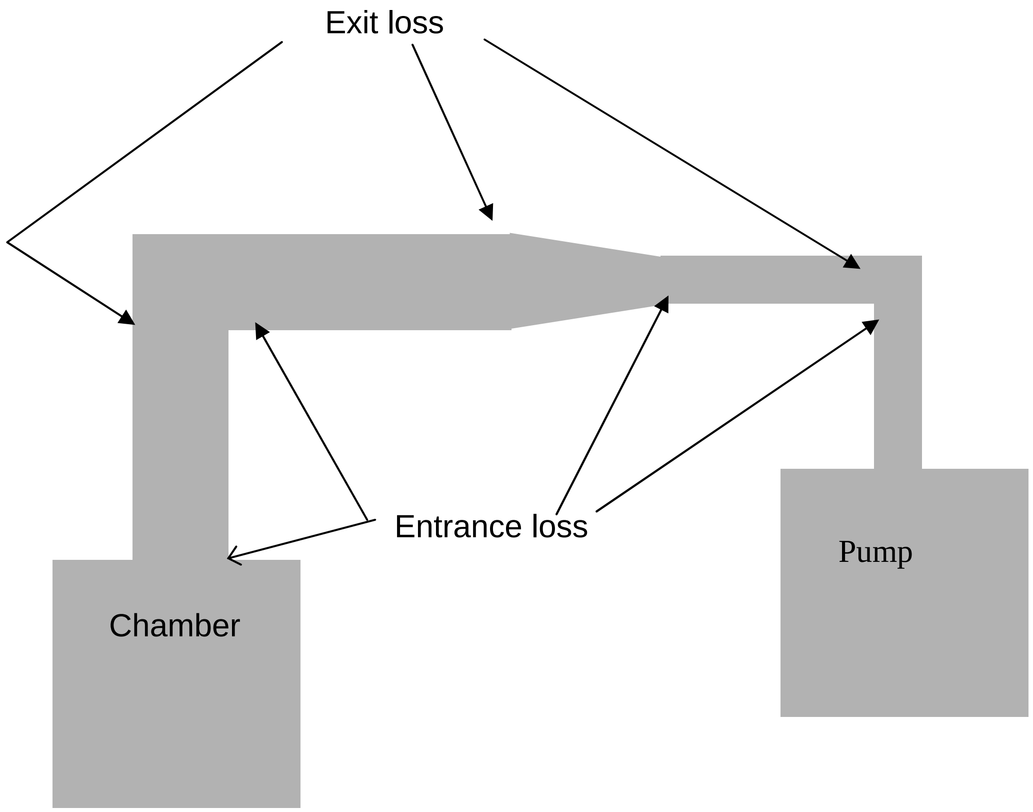


Figure 17

V. Conclusion

A description of the design/troubleshooting of a cw-supersonic expansion source has been presented. The final design discussed has been applied successfully to N_2^+, and it is felt that success will be met with the heated source to obtain a rotationally cold C_{60}^+ spectrum in the near future.

VI. References

[1] M. L. Heger, Lick Observatory Bulletin 337, 141 (1922)
[2] Jan Fulara and Jacek Krelowski, New Astronomy Reviews, **44** (10), 581 (2000)
[3] B. H. Foing and P. Ehrenfreund, Nature, **369**, 296 (1994)
[4] J. Fulara, M. Jakobi, and J. P. Maier, Chem. Phys. Lett., **211**, 227 (1993)
[5] S. Davis, D. T. Anderson, G. Duxbury, and D. J. Nesbitt, J. Chem. Phys., 107 (15), 5661 (1997)
[6] R. Campargue, J. Phys. Chem., **88**, 4466 (1984)