Production of Anthracene ($C_{14}H_{10}$) Clusters using Cold Aerodynamic Source (CAS) and Verification of the Products via Time of Flight Spectroscopy

Saloan Algharbi
Department of Physics
Lund University-Sweden
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Master’s Thesis

Saloan Algharbi

Supervisor:

Dr. Klavs Hansen
Department of Physics
University of Gothenburg

Department of Physics
Lund University-Sweden
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Dedication and Acknowledgements

I have lovingly dedicate this thesis to the first teachers in my life, my parents "Dr. Adnan Algharbi & Suhiel Alameen", to my wife "Halah" who supported me on each step of the way and sure there is no doubt in my mind that without her continued support and counsel I could not have completed this process, to my brother "Snan and his family" and sister "Solafa and her family".

I would like to express my deep thanks and gratitude to my supervisor Dr. Klavs Hansen for his help and guidance to perform my thesis work and special thanks to the colleagues Sasa Vuckovic from University of Gothenburg, Naseem Salim and Aymen Qatamin from Lund University for helping and advising me during this work. Finally, I am grateful to my friend Sinan Harb, for his effort of language issues.
Abstract

Molecular cluster is a nanoparticle that is defined as an agglomerate of few up to $10^{6-7}$ of molecules (corresponding to 1-100 nm in size) that can be manipulated by the cluster beams. Molecular cluster properties typically lie between the individual molecule and bulk matter properties.

This work describes the employment of the Cold Aerodynamic Source (CAS) to produce a narrow, collimated and isolated beam of molecular clusters in gas phase and to prepare it for the spectroscopic studies. CAS was constructed in the University of Gothenburg in Sweden by Sasa Vuckovic as part of his PhD thesis to produce different types of cluster beams.

CAS consists of an aggregation chamber, an aerodynamic lens system and an expansion chamber. The presence of helium carrier gas, which is mixed with the gas of the anthracene ($C_{14}H_{10}$) (produced by resistive heating of the solid anthracene) at low operating pressure that reaches 10 mbar, induces the anthracene molecules to bind together through lowering their internal energy as well as preventing them from sticking to the walls of the source and producing different sizes of anthracene clusters. The 10 mbar inlet pressure for the gas mixture (anthracene clusters - helium) enters the aerodynamic lens system (ALS) consisting of five thin orifices allowing specific sizes of anthracene clusters ($C_{14}H_{10}$)$_n$ to focus near the symmetry axis of the device. A highly collimated beam of anthracene clusters for a spectroscopic study was prepared through expanding the gas mixture through the nozzle into an evacuated chamber. The helium gas was skimmed from the beam by a skimmer, which is located at 5mm apart from the nozzle.

The simulation software "FLUENT 6.2.22" has been utilized to examine the ALS performance and showed that particles with sizes below 30 nm could be focused.

Time of flight mass spectrometry (TOFMS) has been used in this work to characterize the beam through identifying the beam components according to their times of the flight which were absolutely proportional to the square root of their mass-to-charge ratio.
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Chapter 1

1.1 Introduction

In the mid of 1980s, K. Eric Drexler took an interest in emerging technologies and their consequences for the future. In 1986, he introduced a nanotechnology term to describe the accuracy of the molecular manufacturing systems and their applications in the field of scientific research. Nanotechnology includes manufacturing machines and mechanisms with a nanoscale of unit length, known as a nanometer. A nanometer is $10^{-9}$ m, equivalent to three to five atoms wide. Nanotechnology’s building unit is a nanoparticle, which is defined as a small object with a size range up to 100 nm. A nanoparticle is chemically represented as a countable number of particles (from few to $10^6-7$ particles), such as atoms, molecules (homo or hetero) or even clusters (clusters of fullerene C$_{60}$) [1]. In recent years clusters have attracted a great deal of attention due to their intermediate structure and properties (chemical and physical) between molecular and bulk matter. The study of the cluster properties gives important information on chemical reactions, condensation, solvation effects and furthermore is used to model surface deposition phenomena [2]. Different types of clusters have been produced, such as metallic, semiconductors, ionic, rare gas, and molecular clusters (introduced in this work later), that are mainly classified according to the type of the particles they are formed by, and the type of intermolecular bond [2-7].

The cold aerodynamic source (CAS) that has been used in this thesis work was a new source for producing molecular clusters and was constructed at University of Gothenburg in Sweden by Sasa Vuckovic as part of his PhD thesis [24]. I have been using the CAS in this master thesis work to produce an isolated beam of anthracene (C$_{14}$H$_{10}$)$_n$ clusters in their gas phase at very low translation, rotation and vibration temperature [8, 9, 23]. The produced beam has been prepared for spectroscopic studies. Here I have performed a photoionization of the clusters with a femtosecond laser with properties of 780nm near IR, 150fs pulse duration, 500mW power and 1 kHz repetition rate. A Time of flight mass spectrometry (TOFMS) has been used in this work to identify the beam of clusters. By applying an electric field the cations are accelerated from the position of ionization (they were initially created by ionizing the anthracene cluster beam) towards the detector, which is located at the other end of the device. The TOFMS uses the mass spectrometric method to identify the time of flight of the cations and consequently their mass-to-charge ratio $\sqrt{m/q}$ . The arrival time of the heavier cations to the detector is later, since they are harder to accelerate through the TOFMS [10].
1.2 Purpose

The purpose of this work is to employ the Cold Aerodynamic Source CAS for producing a narrow, collimated molecular beam of anthracene clusters \((C_{14}H_{10})_n\) in their gas phase. The use of the liquid nitrogen cooling in the CAS allows the preparation for spectroscopic study of Van der Waals clusters under conditions of very low temperature of internal molecular translation, vibration and rotation degrees of freedom.

1.3 Anthracene \((C_{14}H_{10})\)

The anthracene molecule belongs to a chemical group known "polycyclic aromatic hydrocarbons (PAHs)" and consists of three benzene rings. Anthracene can be found naturally in the environment and can be also man-made. Anthracene is varying in colors from a colorless to a pale yellow crystal-like solid. Like the most PAH molecules, the anthracene is used to make pesticides, plastics, dyes and scintillation counters used to count the number of sparks over a period of time. In this work the anthracene material has been used as a model for producing a beam of molecular clusters by using the cold aerodynamic source CAS.

\[
\text{Figure (1.1); Anthracene chemical structure}
\]

Chapter 2

Background

This chapter will present some concepts and technologies utilized in this thesis work.

2.1 Molecular cluster

A molecular cluster is composed of an integer number of molecules in their gas phase. The dimeric nucleus of the cluster \((X_2)\) consists of two molecules held together by one or more of van der Waals and hydrogen forces. Clusters grow gradually when molecules are deposited around the nucleus, forming a quaspherical particle. Molecular clusters are mainly divided into:

- **Homo clusters**, that consist of one type of molecules such as the anthracene clusters \((C_{14}H_{10})_n\) (presented in this project).
• **Hetero clusters** that are formed by different types of molecules, such as a compound of two different molecules \((\text{CH}_3\text{OH})_n (\text{H}_2\text{O})_m\) or a molecule with rare gas \((\text{C}_{14}\text{H}_{10})_n (\text{Rg})_m\) or a molecule with ion \(\Gamma (\text{H}_2\text{O})_n\).

### 2.2 The purpose behind studying the molecular clusters

The study of molecular cluster at the recent time became of great significance, because the variation of their size (in the range of several molecules to a bulk matter) gives them different fundamental properties that lie in intermediate position between the molecule and the bulk properties. In addition, it gives important information of the nucleation and crystal growth phenomena. The molecular clusters are of interest for several reasons. First, they are applicable as models for studying some atmospheric processes occurring at the surface of water droplets such as ozone depletion, formation of acid rain and generation of pollutants. Secondly, they serve as model of the solvation process through studying the solvent influence on electronic and vibrational excited states of the solute molecule [20].

### 2.3 Intermolecular forces

Sir John Edward Lennard-Jones in 1924 proposed a Lennard-Jones potential to approximate the binding energy between two atoms or molecules depending on their separation distance. The Lennard-Jones potential, referred with the L-J potential, 12-6 potential or 6-12 potential, describes both the attractions and repulsions between particles. The Lennard-Jones potential is represented by equation (1), where the first part of the equation, \((\sigma/r)^{12}\) represents the repulsive forces while the latter part of the equation, \((\sigma/r)^6\) denotes attraction between the particles:

\[
V = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad \text{................(1)}
\]

where \(V\) is the intermolecular potential (Lennard-Jones potential) between two atoms or molecules separated by \(r\) distance, \(\varepsilon\) is the potential well depth that represents how strongly the atoms or molecules interact with each other. \(\sigma\) is the separation at which the potential is equal to zero and is referred to as the van der Waals radius (see figure 2.1) [31].
van der Waals and hydrogen bonds

Non uniform distributions and the constant movement of the electrons within the atom cause the formation of temporary dipoles in atom or molecule [31].

Different types of van der Waals and hydrogen bonds can bind the molecular clusters with a range of energies that depend on the intermolecular force that arises between the constituents of the clusters. Table (2.1) lists van der Waals and hydrogen bonds with their range of strength energies and the typical distance of each type.

<table>
<thead>
<tr>
<th>Force</th>
<th>Strength (eV)</th>
<th>Distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Waals bonds</td>
<td>0.0041 – 0.041</td>
<td>0.3 – 0.6</td>
</tr>
<tr>
<td>Hydrogen bonds</td>
<td>0.12 – 0.31</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table (2.1) shows the van der Waals and the hydrogen bonds strength with the minimum expectation distance between the molecules [31].

van der Waals bonds are mainly classified into three different types according to the molecular dipole moment of permanent, instantaneous or of induction type between the molecules. Below are different types of van der Waals bonds that might be emergence between the molecules:
2.4.1 The London dispersion interaction is named after Fritz London, who was the first that suggested this intermolecular bond. This kind of force is the weakest intermolecular force, typically corresponding to a binding energy in the range of $\leq 0.1\text{eV}$ that arises spontaneously between non-polar clusters: At some point of time an electron rich side of the molecule (delta negative $\delta^-$) attracts the electron depleted side (delta positive $\delta^+$) for the neighbor atom or molecule as shown in figure (2.2) [21].

$$V_{\text{Disp}} = -\frac{3}{2} \frac{\alpha_1 \alpha_2}{(4\pi\varepsilon_0)^2} \frac{I_1 I_2}{r^6} \left( \frac{1}{I_1} + \frac{1}{I_2} \right) \quad \cdots \quad (2)$$

where $\alpha$ is the molecule polarizability, $I$ is the ionization energy of the molecule and $r$ is the separation distance.

$\delta^-$ $\delta^-$ $\delta^-$ $\delta^+$

Electrons Nucleus

**Figure (2.2)** shows London dispersion force. Rich electron end attracts the positive end

2.4.2 Dipole-dipole interaction or Keesom interaction. The strength of this kind of interaction is in between the London dispersion force and ionic or covalent bonds. It depends on the inverse of the temperature and the sixth power of the distance between the dipoles. This kind of electrostatic interaction occurs between permanent dipoles in molecules have substantially different electronegativity such as the attraction between chloride and hydrogen atoms forming a hydrochloride molecule (see figure 2.3). The attraction energy for the dipole moments $\mu_1$ and $\mu_2$, separated by $r$ distance at $T$ temperature can be calculated by equation (3) [21]:

$$V_{DD}(r) = -\frac{1}{2} \frac{\mu_1 \mu_2}{4\pi\varepsilon_0} \left( \frac{1}{r^6} \right) \left( \frac{1}{3kT} \right) \quad \cdots \quad (3)$$

$\delta^-$ $\delta^-$ $\delta^+$ $\delta^+$

**Figure (2.3)** shows dipole-dipole interaction between two permanent dipoles of HCl molecules

2.4.3 Induction force: the non-uniform charge distribution of polar molecule induces a dipole in a neighboring molecule. The interaction energy between the permanent dipole $\mu_1$ for the first molecule and the induced dipole on the neighboring (polar or non-polar) molecule with
polarizability $\alpha_2$ at $r$ distance is given by:

$$V_{DID} (r) = -\frac{2\mu_0^2\alpha_2}{(4\pi\epsilon_0)^2 r^6} \quad \text{…………………… (4)}$$

![Diagram](image)

**Figure (2.4) shows the induction force between permanent dipole and non-polar molecules**

### 2.4.4 Hydrogen bonding

is an attractive electromagnetic interaction of a hydrogen atom that binds covalently with one electronegative atom such as O, N or F. This bond can occur between molecules (intermolecularly), or within different atoms of a single molecule (intramolecularly), as shown in figure (2.5). The strength of hydrogen bond is in range of 0.12 – 0.31eV that lies between the van der Waals and ionic or covalent bonds [31, 32].

![Diagram](image)

**Figure (2.5) shows model of hydrogen bonds between molecules of water**

### 2.5 Cluster sources

In 1956 the group of Becker et al. was among the researchers who focused on producing a highly intense molecular beam at the physics institute at the University of Marburg. They accidently produced molecular clusters for the first time as an unwanted production through their work to produce an intense molecular beam at low temperature [11]. The experimental device for producing the clusters is called a cluster source. There are several cluster sources developed for different experimental purposes. All sources should require good evacuation conditions for reducing cluster collision with surrounding molecules, thus minimizing the cluster beam
intensity. Below are listed the different cluster sources for the different purposes:

2.5.1 **Supersonic or free jet source** for generating molecular clusters of liquid metals such as mercury: The source is provided with an oven to evaporate the metals. Vapor pressure at 10 - 100 mbar is mixed with inert carrier gas at a temperature of 77 – 1500 K in order to expand the gas mixture into vacuum through a small nozzle to create a supersonic beam of molecular metal clusters [25].

2.5.2 **Gas aggregation source:** The metal vapor in this source is also generated by evaporating the material of interest into a cold inert carrier gas like helium or argon at a pressure range of 50-500 Pa, where the metal vapor condenses and creates the clusters [26].

2.5.3 **Laser vaporization source:** A pulsed source that uses an intense pulse laser (UV Nd:YAG $>10^7$ Wcm$^{-2}$) to produce small to medium size metal or semiconductor clusters (up to several hundred atoms) of materials with high boiling point not possible to evaporate with other ordinary evaporation tools. The vaporized material is introduced into cold helium gas to cool it and so induce the cluster formation [27].

2.5.4 **Ion sputtering source** for producing a beam of clusters with hundreds of atoms: The clusters are typically produced through bombarding a metal target with a high energy beam (in the range of 10 -30 keV and a current of order 10mA) of gas ions such as Xe, as shown in the figure (2.6) [28].

![Figure 2.6](image)

**Figure 2.6** shows ion-sputtering source using an ion gun to bombard gas ions to the metal target

(W. A. de Heer, The Physics of Simple Metal Clusters, Reviews of Modern Physics 65(3), (1993),

2.5.5 **Pulsed arc discharge source:** This source is somewhat similar to a laser vaporization source; the only difference is that the cluster material is vaporized with an electrical discharge. The cluster beams generated by this source are more intense than those of the laser vaporization source [29].
2.5.6 Liquid metal ion source: This source used is for producing multi-charged clusters of volatile metals. The ion source consists of a needle, wetted with liquid metal (such as indium) and heated above the melting point (156.6°C for indium). A very high electric potential is applied between the needle tip and the extractor electrode until it reaches the field $10^9$ V/m, where the surface tension force to and the field strength around the electrode will be in equilibrium and form a Taylor cone (see figure 2.7). At the tip, the atoms are ionized and accelerated out by the field that created them, forming the ionic metal clusters [30].

![Liquid metal ion source](image)

**Figure 2.7:** Liquid metal ion source (M. Tajmar and C. A. Scharlemann, Development of Electric and Chemical Microthrusters, International Journal of Aerospace Engineering, Volume 2011 (2011)).

2.5.7 Cold aerodynamic source (CAS): The CAS was used in this thesis and will be described in chapter 3 with more details. It was constructed at the University of Gothenburg in Sweden by Sasa Vuckovic as part of his PhD. thesis for generating different types of clusters. In this work, I used the CAS source for producing anthracene clusters ($C_{14}H_{10}$)$_n$. The degree of clustering in the CAS is expected to depend on several factors, such as the material vapor pressure, size of the nozzle orifice and the carrier gas temperature (i.e. high vapor pressure with low carrier gas temperature results in large cluster size) [24].

2.6 Molecular cluster formation

This section introduces the main steps of cluster formation in CAS including nucleation of clusters, cluster growth and mechanisms of cooling the clusters to stabilize them against evaporation or even fragmentation.
2.6.1 Nucleation of clusters

Vapor of the molecules of interest with high vibration energy was produced by resistive heating of the oven. In presence of cooling inert carrier gas (such as helium gas) collisions with the cluster nuclei reduce their internal energy through the heat transfer to the chamber walls.

2.6.2 Cluster growth

Growth occurs by deposition of more and more atoms/molecules to cluster nuclei to form large clusters.

- Cluster growth by deposition of one atom/molecule:
  \[ A_S + A \rightarrow A_{S+1} \]
  where \( A_S \) and \( A \) are clusters and a deposited molecule

- Fusion of clusters by two smaller clusters:
  \[ A_S + A_R \rightarrow A_{S+R} \]

Furthermore, at the growth region the new-formed clusters may be quite hot and shrink by losing atoms (evaporation) or by splitting into smaller clusters (fragmentation) meaning that there is a competition between cluster growth and decay. Thus, to overcome this and produce stable clusters one must reach a low enough temperature to suppress the cluster decay process [12].

2.7 Cooling of clusters

This section introduces the three main mechanisms of removing the excess thermal energy from the molecular cluster beam that might influence the cluster decay as mentioned in the previous section.

2.7.1 Collision cooling; Clusters cool down through their collision with another cluster monomer or with atoms of the inert carrier gas. The excess heat is removed as kinetic energy.

\[ A_S(T_1) + B(KE_i) \rightarrow A_S(T_2<T_1) + B(KE_2 KE_i) \]

where \( B \) is another atom of the A element or inert carrier gas.

2.7.2 Evaporative cooling; Clusters cool down by losing atoms as vapor through the endothermic reaction, where excitation energy is consumed through the bond dissociation.

\[ A_S(T_1) \rightarrow A_{S-1}(T_2<T_1) + A(KE_i) \]

followed by \( A_{S-1}(T_2<T_1) \rightarrow A_{S-2}(T_3<T_2) + A(KE_2) \) and so on.
2.7.3 Radiative cooling: Clusters also lose their internal energy by emitting infrared radiation. This cooling mechanism is inefficient as compared with the two types above, due to the long time scale compared with the experiment time scale [12].

\[ A_S (T_1) \rightarrow A_S (T_2 < T_1) + hv \]

2.8 Time of flight mass spectrometer (TOFMS)
In 1946 W. E. Stephens employed the first TOFMS instrument "Pulsed Mass Spectrometer with Time Dispersion"[23]. TOFMS with a pulsed ion source is widely used nowadays due to its benefits: a large mass range of particles can be investigated, the mass spectrum for extremely small ion concentrations can be generated in a few microseconds, no needs to sequentially selecting certain ions. Furthermore, the TOFMS is inexpensive and easy to construct.

2.8.1 Linear single stage acceleration time of flight mass spectrometer (LSSA-TOFMS)
The LSSA-TOFMS was constructed initially by Wiley and McLaren in 1950. The LSSA-TOFMS with an applied electric potential provides all ions with same kinetic energy despite of their different initial kinetic energies (see equation 5). Subsequently, the ions will drift freely in a field free drift region in the time-of-flight spectrometer and will be separated according to their velocities which in turn are mass dependent.

\[ E_k = qV = \frac{1}{2}mv^2 \]  

where \( q \) is the elementary charge and \( V \) is the potential gradient along the acceleration region of the TOFMS.

\[ \frac{D}{T} = \left( \frac{2qV}{m} \right)^{1/2} \]

where \( D \) is the flight distance

\[ TOF = \frac{D}{\sqrt{2V}} \sqrt{\frac{m}{q}} \]

Wiley and McLaren observed that ions of a specific mass to charge ratio reach the detector with disperse arrival times due to their different initial position. The uncertainty in the time of ion formation and their location in the extraction region result in a reduction in resolution. In 1955, Wiley and McLaren had overcome these problems; increasing the resolution by constructing a linear dual stage time of flight mass spectrometer (LDSA-TOFMS) as shown in figure (2.8) to correct for the spatial and initial kinetic energy distributions of ions [14].
2.8.2 High mass resolution in the LDSA-TOFMS

This section introduces the mechanism of the high mass resolution in the LDSA-TOFMS that was initially designed and constructed by Wiley and McLaren. The LDSA-TOFMS is composed of two main regions; the dual stage ion source, that consists of the extraction and acceleration regions which are symbolized with ER, AR and the field free flight tube symbolized by DT in figure (2.8). The repeller plate and extraction electrode grid limit the extraction region (ER) and the potentials $V_j$ and $V_2$ are applied, where $V_j > V_2$. Similarly the extraction grid and the acceleration grid ($V_j = 0$) limit the acceleration region (AR). The principle of the separation mechanism in LDSA-TOFMS is simple and can be represented as follows; the electric field applied to the ions in their various positions in the extraction region will accelerate them toward the detector with different kinetic energy, according to equation (5). Therefore, the ions upstream from the detector, referred to as an (a) particle in figure (2.10) experience a higher electric potential than those located nearby the detector, referred to as a (b) particle in Figure (2.9).

$$E_k = qV = \frac{1}{2}mv^2$$

Due to $V_a > V_b$ this leads to $Ek_a > Ek_b$ and consequently $v_a > v_b$.

In general, a high resolution is achieved by reducing the spread in arrival time at the detector for the ions with the same masses and order of ionization through adjusting both the electric potential over the ER and AR regions and the length of the field free drift tube DSF. This is illustrated in figure (2.9).
The mass resolution of TOFMS is defined as:

\[ R = \frac{m}{\Delta m} = \frac{t}{2\Delta t} \quad \cdots \cdots (7) \]

where the \( \Delta t \) term represents the Full Width at Half Maximum Height (FWHM) of the observed ion peaks and \( \Delta m \) is the mass difference for two successive ions [15].

### 2.9 Calculation of flight times in the LDSA-TOFMS

Through the description of the ion motion from the initial position \( x_o \) until it hits the detector, as shown in figure (2.10), the total time of flight \( T \) is equal to the sum of the flight time along the TOFMS three regions:

\[ T = T_{ER} + T_{AR} + T_{DT} \quad \cdots \cdots (8) \]

#### 2.9.1 Time of flight in the ER:

By applying an electric potential to the ion with zero initial velocity \( (v_o = 0) \), the ion will drift toward the end of the ER. To determine the flight time of the ion in the ER region, recall the equation of motion:

\[ s = v_o t + \frac{1}{2} \alpha t^2 \quad \cdots \cdots (9) \]
where $s$ (referred to as $x_o$ in eq. 11) represents the ion distance from its initial creating position until the end of ER region, $v_o$ is the initial ion velocity (from rest $v_o = 0$) and $a$ is the acceleration along ER that is constant and electric field dependent as shown:

$$a = \frac{F}{m} = \frac{qE}{m} = \frac{q \Delta V}{mL} \quad \text{………….. (10)}$$

By substituting all the above quantities in equation (9), one obtains the time of flight of the ion along ER region ($T_{ER}$):

$$x_o = 0 + \frac{q V_{12}}{2m ER} T_{ER}^2 \Rightarrow T_{ER} = \sqrt{\frac{2x_o m ER}{q V_{12}}} \quad \text{…….. (11)}$$

The final velocity at the end of the ER is obtained by deriving the equation of motion (eq. 9) with respect to time:

$$\frac{d}{dt} \left( v_o t + \frac{1}{2} a t^2 \right) = v_o + at \quad \text{………….. (12)}$$

$$v_{ER} = v_o + (a T_{ER}) = \frac{q V_{12}}{m ER} \sqrt{\frac{2x_o m ER}{q V_{12}}} \quad \text{…… (13) where } v_o = 0$$

$$v_{ER} = \sqrt{\frac{2x_o q V_{12}}{m ER}} \quad \text{………….. (14)}$$

**2.9.2 Time of flight in the AR:**

The final velocity of the ion at the end of AR is related to its initial velocity that is defined in equation (14):

$$v^2 = v_o^2 + 2aL \quad \text{………….. (15)} \quad \text{where } v_o = v_{ER} \text{ and } a = \frac{qV_2}{m}$$

$$V_{AR}^2 = \frac{2x_o q V_{12}}{m ER} + \frac{2q V_2 AR}{m AR} \Rightarrow V_{AR} = \sqrt{\frac{2x_o q V_{12}}{m ER} + \frac{2q V_2}{m}} \quad \text{…… (16)}$$

The time of flight along the AR is determined as a function of the initial and final velocity along AR:

$$T_{AR} = \frac{(v_{ER} - V_{AR})}{AR} \quad \text{………….. (17)}$$

$$T_{AR} = \frac{1}{AR} \left[ \sqrt{\frac{2x_o q V_{12} + 2q ER V_2}{m ER}} - \sqrt{\frac{2x_o q V_{12}}{m ER}} \right] \quad \text{………….. (18)}$$
2.9.3 Time of flight in the DT:

In this region, there is no electric field, and the ions will therefore move freely towards the MCP detector with initial velocity \( v_{AR} \). The time of flight will be the following function of \( v_{AR} \) and the free drift tube length \( DT \):

\[
T_{DT} = \frac{DT}{v_{AR}} = \frac{DT}{\sqrt{\frac{2x_o qV_{12} + 2q ER V_2}{m_{ER}}}} \quad (19)
\]

Finally, the sum of the equations 11, 18 and 19, gives the total time of flight through \( ER, AR \) and \( DT \), and that can be used to identify the initial ion position at the \( ER \), where the ion was created through the photoionization by a femtosecond laser.

\[
T = \sqrt{\frac{2x_o m_{ER}}{q V_{12}}} + \frac{1}{AR} \left[ \sqrt{\frac{2x_o qV_{12} + 2q ER V_2}{m_{ER}}} - \frac{2x_o qV_{12} + 2q ER V_2}{m_{ER}} \right] + \frac{DT}{\sqrt{\frac{2x_o qV_{12} + 2q ER V_2}{m_{ER}}}} \quad \ldots (20)
\]

By considering \( k_o = \frac{(x_o q V_{12}) + (AR q V_2)}{x_o q V_{12}} \), the Wiley-McLaren time-of-flight equation gives the following results with respect to the initial ion position and zero kinetic energy:

\[
T(Ek, x_o)_{0, x_o} = \frac{m}{2U_{\text{total}}} \left[ 2k_o^{1/2} x_o + \frac{2k_o^{1/2} AR}{k_o^{1/2} + 1} + DT \right] \quad \ldots (21)
\]

where \( U_{\text{total}} = (q \ ER \ E_{ER}) + (q \ AR \ E_{AR}) \) is the ion total kinetic energy which has been gained in the extraction and acceleration regions and which is position-dependent.

Finally, setting the Wiley-McLaren time-of-flight derivative with respect to the initial ion position to zero \( (dT/dx_o = 0) \) results in the space focusing \( D_{sf} \) equation. That gives the conditions for space focusing \( D_{sf} \) of the initial spatial distribution of ions to achieve a high mass resolution through adjusting the electric field ratio of the acceleration to extraction regions \( E_{AR}/E_{ER} \).

\[
D_{sf} = 2k_o^{3/2} x_o \left[ 1 - \frac{1}{k_o + k_o^{1/2}} \frac{AR}{x_o} \right] \quad \ldots (22)
\]
Chapter 3

Experiment Equipment

The CAS works as a source to provide clusters for the TOF mass spectrometer [13]. The experiment equipment is composed mainly of **Cold Aerodynamic Source (CAS)** and **Time of Flight Mass Spectrometer (TOFMS)**. The CAS consists of mainly three parts; **Clusters Source, Aerodynamic Lens System (ALS)** and **Acceleration chamber**, which are located respectively in **the Aggregation Chamber, Middle Chamber** and **the Expansion Chamber** (see figure 3.1). A femtosecond laser interacts with the cluster beam and ionizes the clusters after which they are extracted at the **Analysis Chamber**. This chapter will introduce a description of the design and operating mechanism of the CAS, the ionization laser and the TOFMS equipment.

![Figure 3.1: CAS scheme, showing the main chambers and their components (S. Vuckovic, thesis, to be submitted)](image)

### 3.1 Cluster source

The first step for producing the clusters lies in the source oven, where the material of interest is evaporated. The oven is located in the so-called aggregation chamber and heated by applying a current that corresponds to a specific temperature that enables atoms to escape the surface of the material.

The oven is constructed as a crucible made of **Boron Nitride (BN)** and can stand up to 500 °C. The crucible is cylindrical with 7 mm inner diameter and 11 mm length with total volume of
423mm\(^3\). The heating is provided by a resistance wire (**Nickel-Chromium Alloy**) utilized as a heater by applying a voltage. A Boron Nitride cylindrical shield envelops both the crucible and the heater coil as shown in figure 3.2.

![Isolation shield and Nickel-Chromium Alloy wire](image)

**Figure 3.2:** The CAS oven (*S. Vuckovic, thesis, to be submitted*)

The aggregation chamber is supplied also with a helium gas inlet, regulated with a flowmeter, in order to achieve a flow through the ALS. Another chamber filled with liquid nitrogen surrounds the aggregation chamber and the ALS and supplies the system with enough cooling power to support the cluster nucleation and growth.

### 3.2 Aerodynamic lens system (ALS)

The usefulness of the ALS is due to their simple mechanical parts and the ability to achieve a continuous flow of nanoparticles in range of size 3-30 nm. The source is composed of a long tube connected to the aggregation chamber and extended along the middle and expansion chambers (see figure 3.1). The ALS is composed of four main parts; **inlet orifice**, five **lenses** (thin plates), **nozzle** and **skimmer**.

The **inlet orifice** size increases the pressure of the clusters – gas mixture inside the aggregation chamber and decreases the mass flow-rate through the ALS. The first relaxation chamber (between the inlet orifice and the first lens) is 200 mm in length and 15 mm in diameter. It is four times longer than the successive relaxation chambers, in order to provide enough time for the gas mixture to slow down and fill the whole chamber and reach steady and laminar flow, where the laminar flow allows focusing the particles through the successive lenses and creation of a narrow beam. The ALS is composed by five **lenses**, made by 0.3 mm thin plates, with various aperture diameters 2.48, 2.45, 2.40, 2.33, and 2.19 mm. The lenses are separated by five spacers (of length 50 mm) giving the mixture enough time to slow down before entering the next lens [9].

The **nozzle** at the end of the source is 30 mm long with an outer diameter of 11.90 mm and an inner entrance diameter of 3 mm. Through it the clusters – helium gas expands into the expansion chamber where the pressure is on the order of \(10^{-1} - 10^{-2}\) mbar. A 1 mm skimmer is
present some 5 mm downstream from the nozzle as shown in figure (3.3), to skim the helium gas away from the cluster beam, creating an intense narrow and highly collimated beam of clusters [22].

![Figure 3.3: Aerodynamic lens system (S. Vuckovic, thesis, to be submitted)](image)

Figure (3.4) shows a blue-white beam of the anthracene deposit that appears due to a small nozzle-skimmer misalignment.

![Figure 3.4: The blue-white beam is an anthracene deposit that appears due to a small nozzle-skimmer misalignment.](image)

### 3.3 Acceleration chamber

Directly behind the skimmer the analysis chamber is equipped with a quartz crystal sensor to monitor and measure the deposition of the clusters in terms of mass per unit area. Furthermore, the analysis chamber is connected orthogonally to the Time of Flight Mass Spectrometer (TOFMS), working at high vacuum (10⁻⁷ mbar) to identify cation clusters according to their mass to charge ratio. Thus, the clusters will ionize in the TOFMS tube by the use of a femtosecond laser (780nm near infrared, 150fs pulse duration, 500mW power and 1kHz repetition rate) that is
generated by Clark-MXR and guided through the viewport of the analysis chamber at the CAS end (see figure 3.5) [18]. The ionization process of clusters in the TOFMS is optimized by moving a 50cm - focal length lens along the laser beam (in front of the viewport) to get the best focus on the cluster beam that leaves the CAS to make sure the two beams interact in the gap between the extraction and accelerating plate of the TOFMS.

![Anthracene beam spot]

**Figure 3.5:** Anthracene clusters hitting the acceleration chamber viewport

The ions created in the gap between the extraction grids are accelerated towards the MCP detector by applying high positive potential on the acceleration plates (4.0 kV and 3.0 kV) respectively. The detector is floated to large negative potential of MCP (-300 V and -2.3kV) and the setup has a resolution of $n/\Delta n \approx 200-300$ (see figure 3.6).

![Laser beam, Lens, U1, U2, Deflectors, Pump, Detector, Cluster beam]

**Figure 3.6** shows the ionization of the cluster beam with 780 nm near IR laser beam and accelerating them through the field free flight tube towards the MCP detector.
3.4 Numerical simulation of the ALS

A numerical simulation is performed to track the particle behavior through the ALS by using the software called FLUENT (version 6.2.22), designed by Wang et al. at the University of Minnesota [16]. The software is utilized to design the correct aerodynamic lens system according to the input parameter for the following categories: Gas Properties, Lens Conditions and Particle Properties.

3.4.1 Gas properties: The carrier gas main objectives are

- To carry out the excess heat and stabilize the cluster growth against the cluster decay (as mentioned in cluster growth section in chapter 2).
- To prevent the cluster sticking to the source wall.
- To guide the clusters along its flow streamline through the ALS to obtain a high focus and a collimated beam of cluster [16].

The carrier gas properties (at room temperature ~ 296 K and atmospheric pressure ~ 101 kPa) are necessary inputs for this numerical simulation and are including

- Molecular weight \((m) = 4.003 \text{ g/mol}\)
- Specific heat ratio \(\left( k \right) = \frac{c_p}{c_v} = 1.667\)
- Viscosity \(= 1.9 \times 10^{-5} \text{ Pa·s}\)
- The helium mean free path \(\left( l \right) = \frac{k_BT}{P\pi d^2} = 197 \text{ nm}\) (where \(k_B\) is the Boltzmann constant, \(T\) is the room temperature, \(P\) is the atmospheric pressure and \(d\) is the diameter of the helium atom ~ 100 pm that is 1 Å) [19].

3.4.2 Lens conditions: Five lenses (numbered from 1-5) are utilized in addition to inlet orifice (lens number 0) and the nozzle orifice (lens number 6). The input orifice is the pressure-limiting orifice and enables control of the input flow rate. Figure (3.7a) shows how the input pressure is affected by the inlet orifice size and not at all by the lens sizes. The inlet pressures chosen in these ALS calculations were \((1, 10, 20, \text{ and } 40 \text{ kPa})\) corresponding to the anthracene vapor pressure at a specific operating temperature \((T \sim 362\text{K} = 89^\circ \text{C})\) where the atoms are capable to sublime from the surface of the anthracene material of the heated source oven. The operating pressure was in range of 100 Pa in front of the nozzle and 0.1 Pa behind the nozzle.
Figure (3.7b) shows the pressure drops after each neck of the orifices. The largest pressure drop can be seen after the inlet orifice (dropping from 1 kPa down to approximately 786 Pa). The size of the inlet orifice (besides the length of the first relaxation chamber as compared with the successive lenses) is affecting the pressure drop across the whole ALS, in order to have laminar flow [Appendix B].

![Graph showing pressure drop vs. lens number](image)

**Figure 3.7a** shows the pressure affected by the inlet orifice size (by FLUENT software 6.2.22)

**Figure 3.7b** shows the pressure drop as a function of the inlet orifice size = 1.69 mm, corresponding to input pressure = 1 kPa (by FLUENT software 6.2.22)

### 3.4.3 Particle properties:

Due to the limitations of the software, which is designed for aerodynamic experiments on larger particles, it was not possible to examine particles within a size range of 3 to 30 nm that have been produced in this work (more details in chapter 4). A density of 1250 kg/m³ of anthracene molecules with range of sizes 30 - 300 nm were examined in order to study their behavior under a number of different conditions [Appendix A].

### 3.5 Relationship between the dimensionless numbers

The main objective of the aerodynamic lens design is to focus the particles on the axis of the instrument. This means obtaining maximum particle beam focusing, but also minimum particle loss and minimum pumping capacity for specific inputs (particle size range, particle density, etc.). To achieve these aims one should optimize the operating parameters (like pressure, carrier gas properties and mass flowrate) and lens construction (like number of lenses, orifice size, inner...
diameter and length of spacers between lenses). The flow through the lenses should be laminar, subsonic and continuous. Whether or not one has laminar flow depends on a dimensionless number known Reynolds number (Re) which is defined as a ratio for inertia and viscosity. Back and Roschke (1972) and Gong et al. (1996) proved that laminar flow can be achieved at low Reynolds number, that is in range of less than 200 [16].

\[ Re = \frac{4m'}{\pi \mu d_f} \leq 200 \]  

(23)

where \( m' \) is the mass flowrate, \( \mu \) and \( d_f \) are the gas viscosity and the orifice diameter.

As well as making the flow laminar through minimizing the fluid Reynolds number, the operator should provide a subsonic flow speed through the lenses. Subsonic flow speed is achieved by limiting the Mach number (the ratio of flow speed to sound speed) to be as lower than unity, to avoid the destructive influence of the shock wave on the particle focusing [Appendix B].

\[ Ma = \frac{u}{c} < 1 \]  

(24)

where \( u \) is the average of the flow velocity and \( c \) is the speed of sound in the helium gas 
\( c = \sqrt{\frac{\gamma RT}{M}} \approx 1016 \text{ m/s} \), \( \gamma \) is the helium specific heat ratio\( \approx 1.667 \), \( R \) is the universal gas constant \( \approx 8.314 \text{ J/mol·K} \) and \( M \) is the helium molecular mass \( \approx 4 \text{ g/mol} \) at room temperature \( T \approx 298 \text{ K} \).

In addition a Knudsen number is defined as the ratio of the mean free path to the lens diameter. It must be in range of less than 0.1 to produce a continuous laminar flow. This is achieved by increasing the source pressure to decrease the mean free path to be much smaller than the diameter of the lens [17].

\[ Kn = \frac{2l}{d_f} < 0.1 \]  

(25)

where \( l \) is the helium gas mean free path \( \approx 197\text{nm} \) (for 1 atm and room temperature) and \( d_f \) is the inlet orifice and lenses sizes [appendix B].

Figure (3.8) shows the sudden dropping of pressure and rise of flow velocity across each neck of a lens. The flow is subsonic \( (Ma < 1) \) through the whole ALS, except at the nozzle, where the flow speed is sonic \( (Ma \sim 1) \). Wang et al. suggested the highest \( Re \) at the nozzle to be always below 200 to ensure laminar flow, otherwise turbulence and instability could broaden the particle
beam significantly. Furthermore, they recommended the highest flow Knudsen number for the continuous flow must be smaller than 0.1. Appendix B shows that the flow Knudsen number at the nozzle in our case was in the range of 0.0125 [16].

\[ St = \frac{\tau v_c}{d_f} \]  

(26)

where \( \tau \) is the fluid relaxation time, \( v_c \) is a characteristic of flow velocity and \( d_f \) is the orifice size.

The contraction factor (\( \eta \)) of the particle trajectory is a strong function of the Stokes number and is defined as the ratio of the new particle radial location to the radial location of the fluid streamline \( \eta = \frac{r_p(\infty)}{r_o(\infty)} \), where \( r_p \) is the trajectory amplitude for the clusters of interest and \( r_o \) is the amplitude for carrier gas streamline (see figure 3.9). The relationships between Stokes number (\( St \)) and the contraction factor (\( \eta \)) for different sizes of particles can be described by:

\[ \eta = 1 - \frac{3}{4} St \left[ 1 - \frac{1}{\rho U} \left( \frac{1 + \frac{1}{3} \gamma M^2}{1 - M^2} \right) \right] \]  

(27)

Figure 3.8 shows the pressure drop and the particle velocity through the ALS, calculated (by the FLUENT software 6.2.22)

3.6 Viscous flow through single lens system

Stokes number (\( St \)) is an important quantity to identify the particles focusing through the ALS by determining their extent of deviation from the carrier gas flow streamline. Stokes number (\( St \)) is defined as the ratio of the particle stopping distance to the characteristic dimension of the inlet orifice [8].
where $\tau$ is the particle relaxation time, $\rho$ is the fluid centerline density, $U$ is the centerline velocity for the particles, $M$ the flow Mach number and $\gamma$ is the specific heat ratio.

- Very small particles have low Stokes number ($St \ll 1$) due to their low inertia, meaning that their stopping distances are much less than the orifice size or $\eta = 1$ (equivalent to $r_p(\infty) = r_o(\infty)$) as indicated by the blue line in figure (3.9).
- Large particles are characterized by large Stokes number $St >> 1$, which corresponds to the contraction factor $|\eta| > 1$ (meaning radial trajectory amplitudes much higher than that of the carrier gas streamlines). The particles are defocusing far from the axis of flow towards the negative coordinates (as indicated by the red dash line in figure 3.9).
- Intermediate particles with an optimum Stokes number $St \sim 1$, corresponding to $|\eta| < 1$ are focused near the flow axis and forming a narrow beam (as indicated by the black dashed line in figure 3.9) [8].

Best focusing is achieved for an inlet orifice size that will provide an optimum Stokes number $St_{optimum} \sim 1$, corresponding to $|\eta| < 1$ in conjunction with Reynolds number $Re \leq 200$ (to dominate the flow to be in laminar status). Nevertheless, a very small orifice size results in large fluid Reynolds and Stokes numbers that impede the focusing of the particles near the centerline and they may cause the orifice to be blocked by deposited material [16].

Figure 3.9 shows the particle focusing through single aerodynamic lens

Figure (3.10 and 3.11) show the relationship between Stokes number $St$ and the contraction factor $\eta$ through the ALS for beams of different particle sizes (300, 232.5, 165, 97.5 and 30 nm) and their focusing mechanism through the successive lenses (1-5). The focusing range is limited by the maximum size ($d_{p1} = 300\text{nm}$) and minimum size ($d_{pn} = 30\text{nm}$), such that the first lens focuses 300nm size particles, the last lens focuses 30nm size particles and lens $i$ focuses
where \( n = 5 \) (number of lenses) [16]. As shown in figures (3-10 and 3.11) the best focusing was obtained at lenses one and two (comparing with the red and black dashed lines), then gradually across the next lenses the beam is defocused due to the fact that the particle sizes chosen for this simulation (30-300nm) were larger than the current sizes produced by the source, since the software does not respond to sizes below 30nm. The limitation of 30 nm is due to fact that the software is designed for aerosol applications.

\[
d_{pi} = d_{p1} - \frac{d_{p1-dpn}}{n-1} \quad (i - 1)
\]

Figure 3.10: Stokes number for different sizes along the system (by FLUENT software 6.2.22)

Figure 3.11: Contraction factor for different sizes along the system (by FLUENT software 6.2.22)

**Chapter 4**

**Results and discussion**

**4.1 Ion spectra**

Through applying heating power to the oven, the atoms evaporate from the anthracene surface. The helium - anthracene gas mixture under an operating pressure up to 10 mbar induces the anthracene molecules to bind together to produce different sizes of anthracene clusters. Their TOF mass spectroscopy starts to appear sequentially at the other end of the device. The first peak in the TOF spectrum typically represents the lightest ion (hydrogen ion, H\(^{+}\)). Gradually when the oven temperature is increased, the heavy ionic fragments of anthracene such as CH\(^{+}\), C\(_2\)H\(_2\)^{+}, C\(_3\)H\(_3\)^{+}, etc. appear according to their mass to charge ratio (see figure 4.1.2).

To identify all the peaks of the TOF mass spectroscopy that have been obtained in this work, recall the time of flight equation with respect to the time correction under the experiment conditions (represented by the second term of equation 28). This is due to different electronic delays in the ionization and the starting pulse of the TOF acquisition system. The delay is
obtained from table (4.1.1) where assigned peaks have been listed.

\[ TOF \text{ (ns)} = 1059.6 \, m^{1/2} \text{ (a.m.u)} - 1049.5 \ldots \ldots \ldots \ldots (28) \]

The anthracene monomer molecule started to appear at a TOF≈ 13063 ns at 89°C (corresponding to heating power of 1.3 × 6 watt). At 125.3°C the dimer molecule with TOF≈ 18952ns appeared. Both the trimer with TOF≈ 23509ns and tetramer with TOF≈ 27284ns appeared at 138°C see figure 4.1.1 (a, b and c). At the temperatures 145.5-147.3°C (corresponding to heating power of 2.1×10 watt), all the rest of anthracene patterns (pentamer, hexamer and heptamer) appeared as shown in figure (4.1.2).

\[ \text{Figure 4.1.1 a,b,c and d show the source background and the emergence of anthracene patterns as a function of rising temperature.} \]
Figure 4.1.2: Anthracene TOF mass spectrum. Where the TOF is represented by 18952, 23509, 27284, 30681, 33475 and 36300 ns respectively for the molecules; dimer, trimer, tetramer, pentamer, hexamer and heptamer (are respectively proportional to factors of $\sqrt{2}, \sqrt{3}, \sqrt{4}, \sqrt{5}, \sqrt{6}$ and $\sqrt{7}$ for the TOF of the monomer molecule $\approx 13063\text{ns}$).

Figure 4.1.3: The relationship between the square root of molecules masses to their corresponding time of flight
Table 4.1.1: Time of flight for the fragments and anthracene molecule pattern corresponding to their mass to charge ratio.

<table>
<thead>
<tr>
<th>TOF/ns</th>
<th>Mass/a.m.u</th>
<th>Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>89</td>
<td>1.00728</td>
<td>H⁺</td>
</tr>
<tr>
<td>2770</td>
<td>13</td>
<td>CH⁺</td>
</tr>
<tr>
<td>4330</td>
<td>26</td>
<td>C₂H₂⁺</td>
</tr>
<tr>
<td>5550</td>
<td>39</td>
<td>C₃H₃⁺</td>
</tr>
<tr>
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<td>51</td>
<td>C₄H₄⁺</td>
</tr>
<tr>
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<td>63</td>
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<td>C₆H₆⁺</td>
</tr>
<tr>
<td>9050</td>
<td>91</td>
<td>C₇H₇⁺</td>
</tr>
<tr>
<td>9641</td>
<td>102</td>
<td>C₈H₈⁺</td>
</tr>
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<td>10300</td>
<td>115</td>
<td>C₉H₉⁺</td>
</tr>
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<tr>
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<td>C₁₂H₁₂⁺</td>
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<td>165</td>
<td>C₁₃H₁₃⁺</td>
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<tr>
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<td>178</td>
<td>C₁₄H₁₄⁺</td>
</tr>
<tr>
<td>18952</td>
<td>356</td>
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</tr>
<tr>
<td>23509</td>
<td>534</td>
<td>(C₁₄H₁₄O)₃⁺</td>
</tr>
<tr>
<td>27284</td>
<td>712</td>
<td>(C₁₄H₁₄O)₄⁺</td>
</tr>
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<td>30681</td>
<td>890</td>
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</tr>
<tr>
<td>33475</td>
<td>1068</td>
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<tr>
<td>36300</td>
<td>1246</td>
<td>(C₁₄H₁₄O)₇⁺</td>
</tr>
</tbody>
</table>

Figures (4.1.4 and 4.1.5) illustrate the anthracene peak intensity variation with temperature up to the maximum value at 147.5°C. Above this temperature, the intensity falls down due to the evaporation of all the anthracene material leaving the source empty as shown in figure (4.1.5).

**Figure 4.1.4:** Variation of the anthracene intensity with temperature.

**Figure 4.1.5:** No anthracene patterns at high enough temperature since all the anthracene evaporates and the source gets emptied.
4.2 Cluster size properties

The molecular clusters are formed with aggregates of integer number of \( N \) molecules (as mentioned in chapter 2.3 cluster formation) form as quaspherical particles with:

- Volume \( V_c = N V_m \), where \( V_m \) is the molecular volume \( V_m = \frac{m}{n} \).

- Radius \( R_c = \frac{1}{\sqrt[3]{N}} R_m \), where \( R_m \) is the anthracene molecular radius \( R_m = \frac{3M}{4\pi \rho N_A} \approx 0.38 \text{ nm} \) \( (M \text{ is mass molar, } \rho \text{ is mass density}) \).

- Surface area \( S_c = 4\pi R_c^2 = 4\pi (\frac{1}{\sqrt[3]{N}} R_m)^2 \).

Seven anthracene clusters with the radii \( R_c = N^{1/3} R_m = 0.38, 0.48, 0.55, 0.60, 0.65, 0.70 \) and \( 0.73 \text{ nm} \) respectively were produced and corresponding to surface areas \( S_c = 4\pi R_c^2 \approx 1.8, 2.9, 3.8, 4.6, 5.3, 6.0 \) and \( 6.6 \text{ nm}^2 \).

Figure 4.2 illustrates that the cluster radii \( (R_c) \), is increasing slightly with the factor of \( N^{1/3} \), while the cluster surface area \( (S_c) \) increasing with the same factor \( (N^{1/3}) \).

In addition, the fraction of the cluster component molecules found on their surface to the total number of the cluster molecules decreases with the scale \( N^{1/3} \), where \( F_s = \frac{N_s}{N} = \frac{4N^{2/3}}{N} = 4N^{-1/3} \).
Conclusion

The performance characteristics of the Cold Aerodynamic Source CAS has been described in terms of the maximum observed size of the produced anthracene clusters and the source temperature limits for their production. Seven peaks of anthracene clusters (nanoparticles) with radii 0.38, 0.48, 0.55, 0.60, 0.65, 0.70 and 0.73 nm respectively with surface areas of 1.8, 2.9, 3.8, 4.6, 5.31, 6.0 and 6.62 nm² were produced in a temperature range of 89-147.5 °C. Above that temperature all the anthracene evaporated and the source will be completely empty.

The ALS for focusing and preparing the cluster beam for the spectroscopic studies is described in terms of the Stokes, Reynolds, Mach and Knudsen numbers, and an overview of the optimum conditions was given. These include an optimum Stokes number of 1, Reynolds number below 200, Mach numbers below one (subsonic velocity) through the ALS, as well as Knudsen numbers below 0.1.

Finally, simulation software FLUENT 6.2.22 showed anthracene nanoparticles in order of size of 30 nm could be transmitted through this CAS.
**Bibliography**


## Appendix A

### Input Properties

<table>
<thead>
<tr>
<th>Gas Properties (room temperature &amp; atmospheric pressure)</th>
<th>Lens Conditions</th>
<th>Particle Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass: 4.003 g/mol</td>
<td>n (orifice): 5</td>
<td>p: 1250 kg/m³</td>
</tr>
<tr>
<td>Specific heat ratio: 1.667</td>
<td>Pressure before inlet: 1 kPa</td>
<td>dp1: 300 nm</td>
</tr>
<tr>
<td>Viscosity: 0.000019 Pa·s</td>
<td>Pressure before nozzle: 787 Pa</td>
<td>dpn: 30 nm</td>
</tr>
<tr>
<td>Mean free path: 197 nm</td>
<td>Volumetric flowrate: 0.2 slm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Operating temperature: 362 K</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Detector distance: 1000 mm</td>
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</table>
## Appendix B

### Flow Results

<table>
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<th>Lens</th>
<th>Diameter (mm)</th>
<th>P upstream (Pa)</th>
<th>ρ (kg/m³)</th>
<th>Q (cm³/s)</th>
<th>Q* 10⁻⁷ (kg/s)</th>
<th>V (m/s)</th>
<th>Mach</th>
<th>Re</th>
<th>Kn *10⁻²</th>
<th>Spacer L (mm)</th>
<th>Spacer D (mm)</th>
</tr>
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Appendix C

Particle Results

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