CHAPTER II

THE MOLECULAR BEAM MACHINE

2.1 Overview

In the present work clusters are studied free in a molecular beam [G. Scoles, 1988] [W.A. de Heer, 1993]. The experimental set up consists of a source, where clusters are formed and thermalized in helium, then they travel in vacuum and pass in between a pair of deflection plates where an inhomogeneous electric field is applied. This field produces a force that deflects the particles. Using position-sensitive time-of-flight-mass-spectrometry [W.A. de Heer, 1991a] the mass and deflections are determined simultaneously. This information, together with the speed of the beam allows us to find polarizabilities and dipole moments. As shown in the schematic diagram in figure 5 the apparatus consists of a series of vacuum chambers where clusters are created, deflected and detected. In the first chamber there is only rough vacuum (10^{-2} Torr). The pressures are progressively lower in the next chambers and the mass spectrometer is at high vacuum (10^{-9} Torr). The distance from the source to the detector is 2.51m. The experiment is pulsed. Normally the repetition rate is 20 Hz, which means that the source produces a beam of clusters every 50 ms. These clusters are deflected and detected and results are accumulated in a computer. To get good statistics the experiments last several hours with hundreds of alternations between field on and off.

2.2 Cluster Source

In our experiments we use a laser vaporization source [R.E. Smalley, 1983] like the one shown in figure 6. The sample material, usually in the shape of a rod, sits inside a cavity. A YAG laser beam (Continuum, Surelite I-20) is focused on the sample. The laser pulses have a full width at half the maximum of 6 ns and energy of 55 mJ per shot, so the instantaneous power is about 1 MW. This is enough to evaporate about 10^{13} atoms from the surface of the sample. These atoms are very hot, but at the same time as the laser pulses a valve is opened, injecting about 5×10^{-6} mol of gas in the cavity. The gas is usually helium. It cools down the atoms that then coalesce to form clusters. The cavity

has a nozzle, so the gas escapes the cavity carrying the clusters with it. Because the clusters are very small they acquire the speed of the carrier gas. At the exit of the nozzle there is a skimmer that communicates the first chamber with the second. Only the center part of the beam goes through the hole in the skimmer to the next chamber.

One very important goal in our experiments was to produce low temperatures beams to try to uncover new physics. Furthermore, keeping all other conditions equal, deflections (either magnetic or electric) are inversely proportional to the speed of the beam squared. In other words, they are inversely proportional to the temperature. Consequently a beam at 50 K will be deflected six times more than at room temperature, which translates into better accuracy in the measurements.

One first attempt to get low temperature beams was to cool down the source. The pulsed valve operated at room temperature so that the gas entered the cavity at 300 K and was cooled in the source. This scheme worked reasonably well for intermediate temperatures, in the order of 100 K, but not below. What happens is that the colder the gas is, the more difficult it is to cool it down since the heat conductivity is proportional to $T^{2/3}$ in helium [CRC Handbook, 1980, page E-3].

$$\boldsymbol{K} = 1.5\ (T / 300\ K)^{2/3}\ mW\ K^{-1}\ cm^{-1} \qquad (8)$$

Where $\boldsymbol{K}$ is the heat conductivity and T is the temperature.

A numerical calculation shows that in the case of our source, the time needed to cool the gas from room temperature to 20 K is of the order of 10 ms, while the residence time of the gas in the source is only 1 ms. To solve this problem a different source design was needed.

The improved version involves two pulsed valves. The first one operates at room temperature and injects the gas into a reservoir where it can stay for up to 50 ms. Then, after the gas is already cooled, the second pulse valve injects the gas into the source. This way we are sure that the gas is at the temperature of the source. This design required that

we had to build our own pulse valve, because there is no commercial valve available that operates at 20 K. Figure 7 shows this cryogenic source. The confirmation that this source really cools the gas down came from measurements of the speed of the beam (see below).

Both, the source and reservoir are connected to the second stage of a cold head (Sumitomo, SRDK), which reaches T= 4 K with a load of 1 W. Under operating conditions with the source in place the lowest temperature that we can get is T= 9 K.

Some important details in designing the cryogenic source include:

- Establishing a way to check alignment with the rest of the machine and make adjustments. This is important since at low temperatures the cold finger shrinks by about 2 mm. In our design there are three screws that can be tighten to adjust the position of the source which sits on a thick o-ring. And because we can remove the sample from outside we can check the alignment by looking directly through the source.

- The first chamber is at rough vacuum of 10^{-2} Torr so the heat losses due to convection are high. This problem is compounded with the fact that the gas is dumped in cycles of high instantaneous pressure. The way to solve this problem was by surrounding the second stage of the cold head and part of the source with a protective jacket that could be pumped from the next chamber, so the pressure was 10^{-4} Torr inside the jacket. The only parts of the source exposed to the pressure of the first chamber were covered with insulation for additional protection.

- The temperature is measured with a silicon diode (LakeShore, 470) that is placed in contact with the source.
- To be able to control the temperature there is a 25-ohm heater (LakeShore, CYC320) attached to the source. An external proportional, integral and derivative regulator (LakeShore, 321) controls the current.

2.3 Deflection Plates

To generate the inhomogeneous electric field we use a pair of brass plates (figure 8). One plate is grounded while the other is connected to a voltage source. We can safely apply 20 kV without electrical breakdown in the vacuum chamber. In our experiments the plates are curved, which produces a force on the particles. Flat parallel plates were used in control experiments.

The cross section of the deflection plates is depicted in figure 8(a). The gap between the plates has a minimum of 2.4 mm. The most curved side has a radius of 2.7 mm and it is 5.1 mm for the less curved side. In figure 8(b) the high voltage connection is shown, it is made by a feed-through insulator, rated for 25 kV (Kurt-Lesker, EFT). The high-voltage source (FUG, HCN 35-35000) is controlled by the data acquisition computer and switches on and off every minute. The cluster beam is collimated so that only a narrow (0.3 mm) and short (4 mm) area of the electric field is used. In the calibration of the machine the deviations of field and gradient in that region are taken into account to calculate the average electric field and gradient.

The force on a particle in a field is given by equation 9.

$$\vec{F} = -\nabla U \tag{9}$$

Where U is the potential energy. In the case of a particle with polarizability α, the energy in an electric field E is given by equation 10.

$$U = \frac{1}{2}\alpha E^2 \tag{10}$$

So the force in the x-direction acting on this particle becomes:

$$F_x = \alpha \vec{E} . \frac{\partial \vec{E}}{\partial x} \tag{11}$$

If the electric field is in the x-direction this equation can be written:

$$F_x = \alpha E_x \frac{\partial E_x}{\partial x} \tag{12}$$

In the case of a particle with a permanent dipole moment P, the energy is given by the following equation:

$$U = -\vec{P}.\vec{E} \tag{13}$$

If the electric field is in the x-direction the force will be:

$$F_x = P_x \frac{\partial E_x}{\partial x} \tag{14}$$

Where P_x is the projection of the dipole moment on the x-axis. Notice that this equation is also valid for a polarizable particle where:

$$P_x = \alpha E_x \tag{15}$$

The geometry of the trajectories and the plates is shown in figure 9. Given these parameters and using equation 14 for the force the deflection is given by the following equation:

$$d = P_x \frac{\partial E_x}{\partial x} L_1 \left(\frac{L_1}{2} + L_2 \right) \frac{1}{v^2} \frac{1}{m} \tag{16}$$

Where d is the deflection, P_x is the projection of the dipole moment (either induced or permanent) on the axis of the electric field, L_1 is the length of the electric deflection plates, L_2 is the distance between the plates and the detection region, v is the speed of the beam and m is the mass of the cluster.

Note that deflections are inversely proportional to the square of the speed. Also, if the particle studied is polarizable, P_x will be proportional to the electric field and because the derivative is also proportional to E, deflections will be quadratic with the field.

2.4 Speed Measurement

To measure the speed we use a chopper (see figure 5). This consists of a motor attached to a pair of blades that chop the beam at the exit of the first skimmer. As indicated in figure 10 the chopper allows a narrow pulse of clusters to be transmitted. When the clusters are detected we observe this narrow pulse and determine the time interval from

the chopping of the beam to the arrival at the ionization chamber. Since we know the distance between the chopper and the ionization point (2.45 m), the speed is determined.

Because the motor works in vacuum its brushes cannot be made out of carbon, because they will only last for a couple of hours. The motor we use (Portescap, 22S) has precious metal brushes that should last several years.

When one of the blades is obstructing the beam, the other one is obstructing the light in a sensor placed at exactly the opposite side. This way the signal from the sensor coincides with the chopping of the beam and is used for timing and to synchronize the triggering of the experiment. Care was taken to assure that the two events happen simultaneously.

An actual example of how the intensity is lost as time is changed is shown in figure 11. The particular example shown corresponds to a cobalt cluster beam, but it applies to any cluster beam. The sharp central intensity peak is clearly distinguished. The typical accuracy of the speed measurement is 1.5% (accuracy of the average speed measured). Notice also that the beam disappears uniformly, which shows that different cluster species have the same speed regardless of their masses.

The speed is measured under the same conditions used in the experiment. In particular we keep the time between the YAG laser and the excimer constant. Figure 12 shows the timing of the apparatus when measuring the speed. One of the blades of the chopper triggers the experiment (the signal is divided by ten, so only one out of ten pulses is really a triggering signal). We can adjust the delay between that signal and the following steps by using three delay-pulse generators (Stanford Research Systems, DG535). About 1 ms before the YAG laser the second pulsed valve opens letting the cold helium enter the cavity. Then the YAG laser pulses and ablates the target rod. Clusters are formed and they exit the cavity. The beam starts traveling the 2.51 m towards the detector, passing through the collimators and in between the electric deflection plates. The same blade of the chopper crosses now the path of the beam, chopping it if the timing is right. At about 10

ms later the beam gets to the mass spectrometer. The excimer laser (Lambda Physik, Optex) pulses for about 8 ns ionizing the clusters. 10 μs after the excimer laser the voltage switch closes creating an electric field that accelerates the ions. At the same point the TOF analyzer starts timing the flight and will record the arrival of the signal from this instant.

Once we observe the depletion of the beam it will mean that the blade of the chopper is cutting the beam. We know the delay between that blade and the YAG. We also know the time between the YAG and the excimer laser because it is a fixed time (the same used in the normal experiment). All we need to know is the time between two blades to know how long it takes for the beam to get from the chopper to the mass spectrometer.

Notice that the TOF analyzer starts at the same time as the closing of the high voltage switch. If the switch closed before the excimer laser or at the same time there would be an uncertainty of 8 ns in the starting of the flight which would spoil the resolution, that is why there is a delay between these two events. Also, we should mention that the time between the excimer and the YAG laser is chosen to get maximum intensity of the beam and it depends on the temperature.

In order to measure the speed of the beam we need to know the period of the chopper. To do this we treat the signal from the chopper to produce a single square wave that has a width equal to the time between two blades. Then, this signal is timed.

When the chopper is running the motor turns at 6000 RPM (100 Hz). The blades interrupt the beam (and the light in the sensor) twice per revolution; these events are synchronized so when the light is obscured the other blade is in the way of the beam. This produces the signal shown in figure 13a at the sensor output. The signal is inverted in a TTL chip as shown in figure 13b and sent to a one-shot circuit. This produces a single square wave of 1.1 ms duration and period equal to the time between two blades of the chopper as shown in figure 13c. Then the signal is sent to a counter in a PC card (National Instruments, PCI-

1200) which is programmed to divide the signal by two. The output of the counter is a single square wave with a width equal to the time between the two blades of the chopper (figure 13d). Finally this square wave is sent to the gate of another counter (which has an internal clock running at 2Mhz, figure 13e) and is programmed to start at 50000 and count down when the gate is high. The final value is read and subtracted from 50000 which gives us the time between the blades in halves of microseconds (figure 13f). One other timer in the PCI-1200 card is used to divide the signal of the chopper by ten and trigger the experiment.

2.5 Time of Flight Mass Spectrometer

The neutral clusters are ionized in the last chamber of the machine. Typically we use an ArF excimer laser (Lambda Physik, Optex) as shown in figure 14. The energy per photon is 6.4 eV which is enough to ionize all the niobium clusters except the monomer [M.B. Knickelbein, 1990]. After the clusters are ionized a high voltage switch (Behlke, HTS31) is closed applying 1200 volts to a plate and generating an electric field perpendicular to the beam velocity, which accelerates the ions. They pass through a metallic grid into a region of zero field and after passing a second grid they are further accelerated towards a third grid, which is at –7.71 kV, into a flight tube. The time of flight is proportional to the square root of the mass.

To detect the arrival of the ions a microchannel plate (MCP, Galileo) is placed at the end of the flight chamber. When a MCP is correctly polarized it generates an avalanche of electrons when it is hit by an ion. These electrons leaving the plate are at –5.5 kV and are accelerated towards a grounded grid. Beyond the grid an anode plate collects the electrons and generates a current pulse, which is amplified (Amplifier Ortec, 9327), discriminated and sent to a multi channel analyzer (Fast Comtec, 7886) where it is recorded. This analyzer also records the closing of the voltage switch and so measures the time of flight. It works at 2 GHz, so the bins where the pulses are counted are 0.5 ns in width, which defines the ultimate time resolution of the TOF.

There are two voltages to control in the mass spectrometer. We can set those voltages in such a way that the time-of-flight is almost independent of the initial position. This mode yields very high mass-resolution as shown in figure 15. In this mode, a typical mass resolution is 5000, which means that we can distinguish a single proton in a fifty-atom niobium cluster or an oxygen atom in an 800-atom cluster.

In normal operation we use the position-sensitive mode. In this case one of the acceleration voltages is changed so the TOF is a function of the initial position as shown in figure 16. The mass resolution is reduced, but it is still in the order on 1000. Enough to distinguish an oxygen atom in a 160-atom cluster. One advantage of this kind of mass spectrometer is the high volume (several cm^3) that it can handle. It is also an advantage that there is only one voltage to be tuned to get high resolution or position sensitivity. All clusters (typically 100 sizes) are recorded at the same time so experiments are time-efficient.

Better mass resolution means better spatial resolution when working in the position-sensitive mode, which means less counts to get meaningful statistics in experiments. So it is important to have as high resolution as possible. Among the factors that limit the resolution are:

- The bin-width of the multi-channel analyzer. In our case it is 0.5 ns and that would be the ultimate limit in time resolution.

- Variations in the acceleration voltages. The first voltage is switched on and off and it is typically 1200 volt. An oscillation of 1 volt would mean an error of $5x10^{-5}$ in time of flight (TOF). The second voltage is constant throughout the experiment (it is not switched) and typically 7.71 kV, which means an error of $3x10^{-5}$ in the TOF for a change of 1 volt.

- The fact that the grids are made of wires makes the electric field distorted close to the boundaries between one acceleration region and the next [T. Bergman, 1989]. This can account for an error of the order of $1x10^{-5}$ for a 10 000 amu-cluster in the third grid where the worst distortion happens. This error is mass dependent, the larger the mass the larger the error.

- When the machine works in the high-resolution mode the TOF is almost independent of the initial position, however after considering second order effects this can account for an error of $3x10^{-5}$ if the beam is 1 cm wide. This error will decrease if a narrower beam is used.
- The timing and shape of the V_1 pulse are important. A change of 2 ns in the leading edge of the voltage will reduce the resolution by adding an error of $3x10^{-5}$ in the TOF for a cluster of 100 amu. In this case, the larger the cluster the less affected the TOF.

- Precise alignment of the plates and grids is also important. They have to be parallel if we want to avoid distortions in the TOF. A misalignment of $1x10^{-3}$ radians would reduce the resolution by adding an error of $1x10^{-6}$ in the TOF for a 1000 amu cluster.

These sources of error are minimized to get the maximum resolution possible. Furthermore, voltage sources are chosen so the do not drift. We wait for the electronics to warm up before starting the experiments. The grids are electroformed and carefully aligned before installing and the electric switch for the first voltage (Behlke, HTS31) was chosen to have sharp transitions. Figure 17 shows an example of a high-resolution spectrum of niobium. Notice the clear separation of different species.

2.6 Calibration

To calibrate the machine we measure the polarizability of the aluminum atom, whose value is well known [P.Milani, 1990]. Given this value and the geometry of the electric deflection plates we can find the product of the electric field and its gradient. For

calculations of polarizabilities that is all that is required and for dipole moments we can also find the electric field gradient alone.

2.7 Data Analysis Methods

The time of flight data is collected in a PC-card (Fast Comtec, 7886). This card has memory bins where the counts are stored. Each shot of the experiment is added to the previous spectrum. Every minute the acquisition is stopped and the data saved in the hard disk of the PC (Dell, GXa) while at the same time changing the conditions of the experiment (changing the magnetic field, for example) and then the acquisition resumes. A program written in LabView (National Instruments, V5.0) controls these events. At the end of the experiment there are two data files, one taken with the field applied and the other without the field for comparison. These files are transferred to another computer (Apple, G4) where they are analyzed using programs written in Matlab (The Math Works, V5.2.0).

The analysis of the data starts with the identification of the peaks. The time-of-flight is used to calculate the mass and with the atomic weight we can determine the size of the clusters. Other peaks are also identified, like oxides or clusters with impurities. Then, the acceleration voltages used in the mass spectrometer determine a scale between time of flight and initial position. For example, if V_1=1700 V and V_2=12000 V (Refer to figure 14) for a Nb_{10} cluster, 1mm is equivalent to 9.3 ns. This way, deflections measured in time of flight are translated to distance.

A typical peak in a mass spectrum has a full width at half the maximum of 0.5 mm and the shape of the peak can be approximated by a gaussian. So to get an error of less than 5 microns in the position we need about 3000 counts in the peak. This normally takes a few hours to obtain.

In measurements of the zero-moment of the peaks (i.e. the total intensity as defined in equation 17, where I(x) is the intensity as a function of position) counting statistical errors give an uncertainty of $\sqrt{N}$, where N is the number of counts. In experiments where we measure ratios, the errors of both peaks are compounded to estimate the uncertainties.

$$I_o = \int I(x)\,dx \tag{17}$$

The usual way to measure deflections by calculating the first-moment of the distribution (as defined in equation 18) is susceptible of errors due to noise. That is because counts which are far from the peak (and are certainly due to noise) receive the same weight as counts that are truly due to clusters. To avoid this problem there are two approaches that we use, one is to estimate the noise level and subtract the background, or fit the data with a gaussian function. The background subtraction works well when the noise is uniform, but the gaussian fitting is the most robust method in all cases. Of course, the ideal is to have low noise levels and then all the methods converge.

$$I_1 = \frac{\int xI(x)\,dx}{I_o} \tag{18}$$