A new time-of-flight mass spectrometer.

Richard M. Lum
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A NEW TIME-OF-FLIGHT MASS SPECTROMETER

by

Richard M. Lum

A Thesis
Submitted to the Faculty of Graduate Studies through the Department of Physics in Partial Fulfillment of the Requirements for the Degree of Master of Science at the University of Windsor.

Windsor, Ontario
1964
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96365
ABSTRACT

A new, high resolution, non-magnetic time of flight mass spectrometer has been constructed, which has already attained a mass resolution of one part in $2^{400}$ at the base of the mass peaks. An improvement by another factor of 70 in resolution seem to be quite easily within reach of the new instrument. This represents an enormous gain in resolution over previous non-magnetic time of flight instruments and signals the entrance into the field of high resolution mass spectrometry by this type of instrument.

The operating principles of the new instrument are based on the application of r.f. electric fields directed perpendicularly to the ion beam at two points along its path. Velocity filtering is effected and the atomic masses are separated according to their time of flight down an evacuated drift tube. Mass differences are then observed either in terms of frequency differences of the r.f. field or voltage differences in the high voltage accelerating potential.

Preliminary experimental values for the mass doublet CH$_4$-O are presented. The formulae for the theoretical mass resolution, and the deflection and displacement of the ion beam are worked out in detail. The theoretical mass resolution is in good agreement with the observed resolution.
ACKNOWLEDGEMENTS

I would like to express my appreciation to Dr. Arie van Wijngaarden for his supervision of my work and for his assistance in the preparation of this thesis. I would also like to thank Mr. W. Grewe for the construction of the apparatus.
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CHAPTER I

INTRODUCTION

A. General Description of Mass Spectrometers

Mass spectrometry is based on the production, separation, and recording of ionic masses. The separation is achieved according to the mass to charge ratios of the ions. Thus, there are three basic components to every mass spectrometer; the ion source, a mass analyser, and an ion detector. Each of these components can be based upon a variety of principles. For example, the mass analysis may be effected by the use of electrostatic, magnetic, or radio-frequency electric fields, or any combination and arrangement of these. Detection of the ions may be achieved by photographic methods or electrically. Various combinations of the different principles used in the three basic components will result in unique types of mass spectrometers, each being especially well adapted to some particular analysis.

Mass spectrometers can be used for the measurement of ionic masses, for the determination of their relative abundances, and for the study of the ionization process that takes place in the source. Usually only singly charged positive ions are measured, but no difficulty is encountered using negative ions. In order to minimize the probability of an ion suffering a collision with another ion or molecule before reaching the detector, pressures of approximately $10^{-6}$ mm. of Hg. are used. This provides the
ion with a mean free path that is long compared to its trajectory.

The most important application of mass spectrometry is in the precise determination of atomic masses. The resolution of an instrument is a measure of the accuracy to which it can determine atomic masses. If two ions of mass $M$ and $M + \Delta M$ can just be separated, the resolution is given by the ratio $\frac{\Delta M}{M}$. However, what constitutes this separation of two mass peaks is rather arbitrary. The height of the valley between two adjacent peaks is an indication of their separation. In our work the resolution was referred to the base of the mass peaks, i.e. $\Delta M$ is the width of the peaks at their base. Other workers have chosen $\Delta M$ at half height and half width of the peaks.

B. **Magnetic Deflection Mass Spectrometers**

In precision mass determinations the most widely used mass spectrometers are the magnetic deflection type instruments in which a diverging ion beam entering the magnetic field is brought to a focus at its exit. A typical mass spectrometer of this type will now be discussed.

Figure 1 is a schematic diagram of a Dempster type mass spectrometer which consists of a $90^\circ$ radial electrostatic analyser followed by a $180^\circ$ magnetic analyser. Ions produced in the source are accelerated by a potential $V$ between slits $S_1$ and $S_2$. During acceleration the ions acquire a kinetic energy given by

$$\frac{1}{2}mv^2 = eV$$

(I-1)
Figure 1. Dempster Type Mass Spectrometer
where \( v \) is the velocity after full acceleration. There is, however, a spread in the final energy due to the energy spread among the ions leaving the source (III,A,5). This spread in energy is greatly reduced by projecting the ions into a radial electrostatic field. Upon entering the electrostatic analyser the ions experience a force \( eE \) normal to their direction of motion. The ions thus describe a circular orbit of radius \( r_e \) given by

\[
\frac{m v^2}{r_e} = eE
\]

(\( I-2 \))

It will be noted that only those ions that possess the kinetic energy

\[
\frac{1}{2}mv^2 = \frac{1}{2}eE r_e
\]

(\( I-3 \))

will pass through the instrument. The electrostatic analyser is, therefore, an energy filter.

The electrostatic analyser can be so constructed (Duckworth, 1958) that a diverging beam of ions entering it is brought to a focus at the exit slit \( S_2 \). This has been shown in Figure 1 by the cross hatched ion beam.

The energy resolution of this instrument is given by

\[
\frac{\Delta E}{E} = \frac{S_2 + S_3}{r_e}
\]

(\( I-4 \))

where \( S_2 \) and \( S_3 \) represent the widths of these slits, respectively and \( r_e \) is the radius of the central ion beam. It will be noted that the energy spread, \( \Delta E \), of the ions emerging from slit \( S_3 \) can be reduced by either decreasing the slit widths of
and or by increasing the radius, \( r_e \), of the electrostatic analyser.

The ion beam entering the magnetic analyser is thus nearly mono-energetic. This magnetic analyser can also be constructed in such a manner as to display direction focusing similar to that achieved in the electrostatic analyser. In the magnetic field, which is normal to the direction of the ion beam, the ions describe a circular orbit of radius \( r_m \) given by

\[
 r_m = \frac{Mv}{eB} \tag{I-5}
\]

Thus, the ions are deflected in the magnetic analyser according to their momentum.

Eliminating \( v \) from Equation (I-2) and the above equation results in

\[
 \frac{M}{e} = \frac{(Br_m)^2}{E_e} \tag{I-6}
\]

From the preceding equation it is seen that the heavier ions will describe larger orbits than the lighter ones. This is depicted in Figure 1 where \( M_2 > M_1 \). Mass resolutions of one part in \( 10^5 \) have been achieved using this type of instrument.

C. Time of Flight Mass Spectrometers

A linear time of flight instrument, whose chief advantage was in the dispensing of the magnet and all its attendant problems, was first constructed by Smythe and Mattauch (1932). In this instrument r.f. electric fields, normal to the direction...
of the ion beam, were applied to two pairs of deflecting plates so that velocity filtering was effected. The ion beam traverses the first set of plates and travels a relatively short distance before entering a second set. In traversing the first set of plates only those ions whose time of flight in the plates is an integral number of periods of the applied r.f. field will receive as much acceleration in one direction as in the other. Consequently, upon leaving this set of plates the ions are traveling parallel to their original direction of motion but are displaced. They then enter the second set of plates where the r.f. field is opposite in phase relative to the first set. The beam is thus displaced in the opposite direction with the result that the ions emerge from the r.f. analyser suffering no net deviation or displacement. Ions traveling with any velocity other than that allowed are deflected. Thus, the r.f. analyser is sensitive to the velocity of an ion rather than to its mass. To achieve mass analysis the beam is then sent through a radial electrostatic analyser and detected electrically. In practice, fringing fields from the deflecting plates allowed ions with certain other velocities to get through. These gave rise to "ghost" peaks which complicated the analysis of the mass spectrum. The mass resolution of this instrument was about one part in 50.

The most straightforward type of time of flight instrument is one in which the source is located at one end of
an evacuated tube and the detector at the other. If there is no energy spread in the source, the time of flight of ions down a drift tube of length \( L \) is given by

\[
t = \frac{L}{v}
\]

(I-7)

where \( v \) is the velocity of the ions. The ions from the source are accelerated by a potential \( V \). During acceleration the ion acquires a kinetic energy given by

\[
y_0 \mathbf{v}^2 = eV
\]

(I-1)

Using this, the expression for the time of flight becomes

\[
t = \left( \frac{L^2 M v^2}{2eV} \right)^{\frac{1}{2}}
\]

(I-8)

An instrument based on these principles was first constructed by Cameron and Eggers (1948). The ion source is pulsed and a short burst of ions travel down the drift tube to the detector. Since, in this instrument, all ions possess the same kinetic energy, the velocity of an ion is characteristic of its mass and the resulting velocity analysis is thus equivalent to a mass analysis. All ions created in a single pulse are detected by an electron multiplier and recorded on an oscilloscope.

This time of flight mass spectrometer has the additional advantage that the entire mass spectrum can be obtained every few \( \mu \)-sec.

Since 1955 rapid improvement has been made in time of flight instruments. Wilely and McLaren (1955) describe an instrument similar in principle to the one just discussed, but with a greatly increased resolution of approximately one part in 200 at the base of the mass peaks. This was obtained.
mainly by the use of an improved source. Although such a resolution is many times better than was first achieved in the field, it is still several orders of magnitude lower than that obtained with conventional magnetic deflection instruments. A wealth of other time of flight instruments (Duckworth, 1958) have been developed which make use of retarding potentials, r.f. voltages applied to grids and various arrangements of these grids. These all employ the same general principles described above and differ merely in detail. However, the one common feature they all do possess, and one which has kept them in the background in precision mass determinations, is poor resolution. Consequently, these instruments are used mainly as analytical tools.

More recently, a non-magnetic high resolution instrument has been developed by Paul et al (1958). This instrument is an electric quadrupole mass spectrometer. Mass separation is obtained when an ion beam is projected along the axis of a four component, hyperbolic cross section, electrode system. Opposite pairs of electrodes are connected and a r.f. voltage is superimposed on a small D.C. voltage. The time of flight of ions is long compared to the period of the r.f. field. Whether an ion travels through the system undeflected or not depends on its mass and the frequency and amplitude of the electrode voltages. Theoretically, in traversing the electrode system the ions perform oscillations in a plane normal to their direction of motion. If the oscillations are stable, i.e. when their amplitude is constant, the ion will emerge undeflected.
However, if the oscillations are unstable, their amplitude increases exponentially to infinity and the ions are deflected. In practice, however, mass separation does not depend on whether the oscillations are stable or unstable, but on whether an ion is able to travel through an analyser of finite length without striking an electrode. A resolution of better than one part in 15000 at half height of the mass peaks has been achieved for masses greater than 130 a.m.u. This instrument, therefore, can be used for precision mass determinations (Von Zahn, 1962).

D. New Time of Flight Mass Spectrometer

The new time of flight mass spectrometer, described in this work, incorporates several features of both the r.f. and drift tube time of flight methods. Like the Smythe-Mattauch model, r.f. deflecting plates are employed. However, in the new instrument the traversal time of the ions through the deflecting plates is much smaller than the period of the applied r.f. field. Also, the velocity filtering does not depend on whether the r.f. field is in phase on all sets of deflecting plates or not. An attractive feature of the previous time of flight instruments was the absence of narrow slits, thus dispensing with alignment and beam intensity problems. The new instrument sacrifices these points, but thereby gains in the area of higher resolution. Collimating slits are placed just before and after each set of deflecting plates.
E. Mass Doublets

In principle, masses could be determined with the Dempster type instrument by substitution of the appropriate values into Equation (1-6). However, the accuracy to which the electronic charge, the electric field, the magnetic field and the radius of both the electrostatic and magnetic analysers can be determined is too low for precision mass determinations. The maximum precision with which masses can be compared to one another is presently as high as one part in $10^7$. Thus, in the accurate determination of ionic masses a standard of mass has to be employed. The earliest physical standard chosen was the $^0\text{O}^{16}$ isotope to which a value of precisely 16 a.m.u. was assigned. Recently $^0\text{C}^{12}$ has been adopted as the standard because of the large mass region occupied by hydrocarbons.

The mass dispersion of precision mass spectrometers is so large that atomic masses differing by only one a.m.u. cannot pass through the instrument simultaneously. Thus, precision mass determinations are performed using mass doublets. A mass doublet consists of two different ions whose masses differ by only a small fraction of an a.m.u. Consequently, both masses of the doublet can pass through the instrument at the same time.

The components of a particular doublet are detected as two separate mass peaks. If the mass of one of the ions of the doublet is known, then the mass of the other can be
determined by the measurement of the separation between the two peaks. Most of the tabulated precision mass values have been determined in this manner.

F. Peak Matching and Precision

The precision in mass measurements of a doublet depends on the accuracy to which the peak separation of the components of the doublet can be determined. This separation can be observed accurately by so called "peak matching".

Since this technique has been employed in a variety of manners, it will now be discussed only in general terms. A square wave sweep is applied to whatever parameter is to be varied enabling a mass peak to be displayed on an oscilloscope. That parameter is changed by such an amount that, on alternate sweeps, a second mass peak can also be displayed on the oscilloscope in apparent coincidence with the first. If the peaks are of the same shape, then the amount by which they are displaced relative to one another can be determined in terms of a voltage difference $\frac{\Delta V}{V_0}$. See Equation (I-6).

In this manner the accuracy in the measurement of the peak separation can be increased by at least a factor of one hundred. Thus, for example, a mass spectrometer with a resolution of one part in $10^5$ is then able to measure masses to a precision of one part in $10^7$.

G. The Need For a New Type of Instrument

The precise determination of atomic masses has previously come from two sources; high resolution, magnetic deflection mass spectrometers and Q value determinations from
nuclear physics. The latter method involves nuclear transmutations and depends on the equivalence of mass and energy. Values from the two sources were not in agreement within experimental error. This suggested the presence of systematic errors in the mass spectrometer values. Accurate mass determinations were then attempted using mass spectrometers based on different principles in an effort to emphasize these errors. Such instruments were based on the magnetic time of flight principle. Yet, these instruments still rely on a magnetic field for their operation. Thus, the entrance into the field of high resolution mass spectroscopy by non-magnetic, time of flight instruments should be a further aid in the determination of the possible systematic errors encountered by the magnetic deflection type instruments.
CHAPTER II

OPERATING PRINCIPLES OF THE NEW INSTRUMENT

A. Conditions For Detecting Ions

Figure 2 is a schematic diagram of the present instrument. Positive ions, produced in the source, are accelerated in the region between slits $S_1$ and $S_2$. Next they pass through a collimating stage, a parallel plate condenser, a drift tube, another identical parallel plate condenser, a second collimating stage and then enter a detection system. At the parallel plates, called r.f. stages, the ions are subjected to a radio frequency varying electric field which acts perpendicular to the path of the ion beam.

Upon emerging from the first collimating stage, the ions will be able to enter slit $S_5$ only if they pass the first set of deflecting plates at a time when the applied r.f. field is approximately zero. Ions passing through the r.f. stage when the electric field is appreciably larger than zero will be deflected out of the central path of the ion beam. Similarly, only the ions that emerge from the second r.f. stage will be able to pass slit $S_7$ if the electric field here, also, is nearly zero. Hence, the condition for detection of the ions is that their time of flight in the drift tube, $\frac{L}{v}$, is an integral multiple, $n$, of half periods, $\frac{T}{2}$, of the applied r.f. field. Thus,

$$\frac{L}{v} = \frac{nT}{2} \quad \text{(II-1)}$$
Figure 2. The New Time of Flight Mass Spectrometer
Velocity filtering is thus effected. Since all the ions were accelerated to the same energy, it can be seen from Equation (I-1) that a velocity analysis is then equivalent to a mass analysis. The frequency, \( f \), of the r.f. field at which the ions are detected is found, from Equations (I-1) and (II-1), to be

\[
f = \frac{n}{2L} \left( \frac{2eV}{M} \right)^{1/2}
\]

(II-2)

or

\[
f = nf_0
\]

(II-3)

where \( f_0 \), the fundamental frequency, is the lowest frequency at which the ions of mass \( M \) can be detected.

In our initial investigations the electron multiplier was mounted directly behind slit \( S_1 \). In this case the instrument is well suited for analytical investigations. The mass spectrum is scanned when, at a constant accelerating potential, the frequency is varied. At relatively low frequencies the analysis of the mass spectrum is very simple: the heavier masses are detected at the lower frequencies and the lighter masses appear at the higher frequencies. However, at relatively high frequencies the heavier masses appear again in the spectrum at multiples of their fundamental frequencies. This complicates the analysis of the mass spectrum. Because of this and because high frequencies \((IV,E)\) are required for precision mass measurements, a low resolution magnetic analyser was inserted into the detection system.

Our mass measurements were performed by using mass doublets \((I,E)\). A given mass doublet was selected by varying
the magnetic field at a fixed accelerating potential. Because of the low resolution of the magnetic analyser, about one part in 50, the two components of the doublet were able to pass through the analyser simultaneously. All masses other than those which constituted the doublet under investigation were deflected from the ion beam. The ion beam was detected by an electron multiplier whose output was connected to an electrometer which fed a recorder.

B. Mass Analysis

1. Introduction. In measuring masses by the doublet method the r.f. field applied to the deflecting plates was first set at zero. The accelerating potential was then varied until a mass peak, which is comprised of both components of the particular doublet under study (II,A), was detected. The r.f. field was then applied to the deflecting plates. In this case the components of the mass doublet will be detected at two different frequencies when the accelerating potential is kept constant or at two different accelerating potentials when the frequency is kept constant [see Equation (II-2)]. The mass difference can then be related to either the frequency difference or to the accelerating potential difference respectively, as will be explained in the next section.

2. Frequency Scanning. When, at a constant accelerating potential, the frequency is scanned, the mass difference of the two components of the mass doublet is measured in terms of the difference between the frequency at which the masses
are detected. To see this, consider two ions of mass $M_1$ and $M_2$, where $M_2$ is given by

$$M_2 = M_1 + \Delta M \quad (\text{II-4})$$

and let these masses be detected at frequencies $f_1$ and $f_2$, respectively. Then from Equation (II-2) it follows that

$$M_1 = \frac{K}{f_1^2} \quad (\text{II-5})$$

and

$$M_2 = \frac{K}{f_2^2} \quad (\text{II-6})$$

where $K = \frac{n^2 eV}{2L^2}$ is a constant. By using Equations (II-4), (II-5) and II-6) it is found that

$$\frac{\Delta M}{M_2} = \frac{f_1^2 - f_2^2}{f_1^2} \quad (\text{II-7})$$

which for small $\Delta M$ values reduces to approximately

$$\frac{\Delta M}{M} \approx \frac{2 \Delta f}{f} \quad (\text{II-8})$$

where $M_1 \simeq M_2 = M$, $f_1 \simeq f_2 = f$ and the frequency separation, $\Delta f$, is given by

$$\Delta f = f_1 - f_2 \quad (\text{II-9})$$

On substitution of Equation (II-3) into the preceding equation it is seen that

$$\Delta f = n(f_{o1} - f_{o2}) \quad (\text{II-10})$$

It will be noted that the frequency separation, $\Delta f$, varies linearly with $n$, i.e. linearly with the applied frequency.

Because of the finite resolution of the instrument, the
mass M will be detected over a small frequency range $\delta f$ $(IV,C)$. Two masses in a doublet can just be separated when $\Delta f$ equals $\delta f$. In this case [see Equation (II-8)]

$$\frac{\Delta M}{M} \approx \frac{2 \delta f}{f}$$ (II-11)

Thus, the observed mass resolution can be obtained by measuring the peak width, at its base, in a plot of the ion current versus the frequency.

3. **Voltage Scanning.** When the frequency is kept at a fixed value and the accelerating potential is varied, the masses in the doublet are detected at two different accelerating potentials. The mass difference is then measured in terms of the difference in accelerating potential. By using Equation (II-2) it can easily be shown that the mass difference is given by

$$\frac{\Delta M}{M} = \frac{\Delta V}{V}$$ (II-12)

where $\Delta V$ is the difference in accelerating potential and $M$ is the mass detected at the accelerating potential $V$.

Because of the finite widths of the collimating slits the ions will be detected over a small accelerating potential range $\delta V$, where $\delta V$ is the width of the mass peak at its base in a plot of the ion current versus the accelerating potential. Two masses can just be resolved when $\Delta V$ equals $\delta V$. In this case [see Equation (II-12)] the observed mass resolution is given by

$$\frac{\Delta M}{M} = \frac{\delta V}{V}$$ (II-13)
4. **Comparison Between Light and Heavy Masses.** The new instrument possesses the unique ability to directly measure precise mass differences between certain atoms differing in mass by several atomic mass units. To see this suppose that at a fixed frequency mass $M_1$ and mass $M_2$ are detected at the accelerating potentials $V_1$ and $V_2$, respectively. If the difference in accelerating potential, $\Delta V$, is given by

$$\Delta V = V_2 - V_1$$

(II-14)

then, using Equation (II-2) and the preceding equation, it is found that

$$f = C n_1 \left( \frac{V_2 - \Delta V}{M_1} \right) = C n_2 \left( \frac{V_2}{M_2} \right)^\frac{1}{2}$$

(II-15)

where $C = \left( \frac{e}{2M} \right)^\frac{1}{2}$ is a constant and $n_1$ and $n_2$ are positive integers. Then, squaring Equation (II-15) results in

$$n_1^2 \frac{V_2 - \Delta V}{M_1} = n_2^2 \frac{V_2}{M_2}$$

(II-16)

From which it can easily be shown that

$$\frac{M_2 - (n_2^2)^2 M_1}{M_2} = \frac{\Delta V}{V_2}$$

(II-17)

Because of practical considerations (I,F) the accelerating potential is scanned only over a small voltage region. Thus, in practice $\Delta V$ is small and from Equation (II-17) it is seen that

$$M_2 \sim (n_2^2)^2 M_1$$

(II-18)

Therefore, for example, if at a set frequency $O^{16}$ is detected at the accelerating potential $V_2$ and $^4\text{He}$ is detected.
at the accelerating potential \( V_1 \), then

\[
\frac{M(\text{O}^{16}) - 4M(\text{He}^4)}{M(\text{O}^{16})} = \frac{\Delta V}{V_2}
\]

In order to record such a doublet the detection system must be modified so that the magnetic analyser will allow both masses to be detected simultaneously. This can be accomplished by the addition of a second electron multiplier (not shown in Figure 2).
CHAPTER III
APPARATUS

A. Source

1. General Operating Principles. A schematic diagram of the electron bombardment source used in our apparatus is shown in Figure 3. The sample gas enters the ionization chamber through a small nickel tube inserted into a quartz plate, Q, where the gas is subjected to electron bombardment. The electrons are emitted from a tungsten filament, F, which is heated by the 12 volt lead storage battery. There electrons are accelerated by the 45 volt "B" batteries and pass through slit S₀ into the ionization chamber. Here the electrons suffer inelastic collisions with the gas molecules, thus producing positive ions.

A positive potential can be applied to the repeller plate R by means of the 22½ volt "B" battery which is connected across the 100k ohm resistor. This potential repels the positive ions through the exit slit S₁ of the source.

2. The Electron Beam. The number of ions produced increases with the electron current and depends on the electron energy. No measurement of the electron current was attempted in the experiments. However, Nier (1940) using a tungsten ribbon filament 0.025 mm. thick, 1 mm. wide and 1 cm. long obtained a total electron emission of about 450 µamp. The filament current was 5 amp. This is comparable to the arrangement which was used here. The electron beam must be highly
Figure 3. The Electron Bombardment Ion Source
collimated by narrow slits to minimize the energy spread in the ion beam leaving the source (III,A,5).

3. The Ionization Chamber. The introduction of the gas sample into the ionization chamber was regulated by "Speedivac" vacuum leaks. The ionization chamber was designed so that it was roughly vacuum tight except for the exit slit. Thus, the amount of un-ionized gas flowing into the accelerating region was very small. This allows relatively large quantities of gas to be leaked into the ionization chamber without raising the pressure appreciably in the accelerating region. The source region is usually well above room temperature due to radiation from the heated filament and was therefore constructed of stainless steel.

4. The Ionization Process. Electrons with sufficient energies can ionize molecules upon bombardment by a number of processes. The formation of singly charged ions is the most important process because it occurs much more frequently than any other reaction. An electron will be removed from a molecule upon impact if the bombarding electron has an energy equal to, or higher than, the ionization potential of the particular molecule. Such a process is represented by

\[ XY + e^- \rightarrow (XY)^+ + 2e^- \]  (III-1)

Suppose the energy of the electron beam equals the ionization potential of the molecule. In this case an electron can only ionize the molecule if it transfers practically all of its kinetic energy to the molecule, i.e. if the electron
suffers a head-on collision. The probability for such a process to occur is relatively small. On the other hand, if the incident kinetic energy of an electron is larger than the ionization potential of the gas molecules, there will be several values of impact parameters at which an inelastic collision between an electron and a molecule can take place. Thus, the cross section for ionization increases with the kinetic energy of an electron for energies just above the threshold energy for ionization.

At these higher kinetic energies, the amount of energy transferred by an electron to the molecule may exceed the ionization potential. In this case fragmentation, or dissociation, of the molecular bond occurs. Thus, atomic and/or molecular ions are obtained from larger parent molecules. This reaction is represented by

\[ XY + e^- \rightarrow X^+ + Y + 2e^- + W \]  (III-2)

where \( W \) is the excess energy with which the particles are formed over the dissociation energy. The term \( W \), which includes the kinetic energy of the fragments after their formation, contributes to the energy spread of the ions leaving the source (III,A,5).

For energies much larger than the ionization potential, the cross section for ionization decreases with increasing kinetic energy of an electron. The reason for this effect might be that the de Broglie wavelength of an electron decreases as its momentum increases.
The maximum ionization efficiency for gases lies approximately in the energy range 90 to 150 eV. Thus, the maximum ion current is obtained when the electrons are accelerated to these energies. In the present instrument ion currents of the order of $10^{-9}$ amp. were detected behind slit $S_2$.

5. The Energy Spread of the Ions Leaving the Source.

Ideally, after acceleration the ions should be completely mono-energetic. This will not be so in practice because the energy spread of the ions leaving the source is superimposed on the ion beam after the acceleration. The causes for this energy spread will now be briefly discussed.

When a positive potential is applied to the repeller plate $R$, a potential gradient is formed in the ionization chamber from $R$ to $S_1$, the exit slit of the source. There is, in addition, a penetration of the main accelerating field into the ionization chamber. Thus, ions formed in different parts of the chamber will fall through different potentials in arriving at $S_1$. This introduces an energy spread in the ions, which is superimposed upon the thermal energy they had before ionization and any kinetic energy (III,A,4) with which they may be formed. Thus, the ions emerge from $S_1$ in a somewhat divergent beam and with a small spread in energy.

That portion of the energy spread which is caused by the ions being formed in different regions of the ionization chamber can be overcome by insuring that the ions will be created along an approximately equipotential surface. Thus,
Ideally, the electron beam should be infinitely narrow. All slits, however, are of finite width. To collimate the electron beam other workers have applied a magnetic field parallel to the direction of the beam. This constrains those electrons which tend to diverge from the beam to spiral, in helical paths of small radius, about the central path of the electron beam.

B. Vacuum System

To prevent collision of the ions with the gas molecules in the instrument the pressure was kept at about $10^{-6}$ mm. of Hg. This was achieved by the use of one Model EO2 and two Model F203 Edwards oil diffusion pumps. These pumps were placed at the middle of the first collimating stage, at the first r.f. stage and at the end of the second collimating stage, respectively. In this manner differential pumping was employed with the source and the first collimating stage; the drift tube; and the second collimating stage and detection system being pumped separately. This allowed relatively large amounts of gas to be leaked into the source region without appreciably raising the pressure in the remainder of the apparatus. The pressure was measured with a Veeco Model RG-75P ionization gauge.

Except for a glass pipe, which electrically insulated the source from the rest of the equipment, the drift tube and the collimating stages were constructed of brass pipes which had an outer diameter of 1.5 inches. The source assembly was
mounted to a bellows so that the plane of the exit slit, \( S_1 \), of the source could be adjusted parallel to the plane of the entrance slit, \( S_2 \), of the first collimating stage. The ion current could be measured by lowering a Faraday cup, which was connected to a bellows assembly, into the path of the ion beam. Three such cups, which were mounted, respectively, at the middle of the first collimating stage, just behind the first r.f. stage and just behind slit \( S_7 \) of the second collimating stage, were employed. These cups were used to initially detect the ion beam and to align the slits \((V, A)\).

C. The High Voltage

The high voltage, H.V, was obtained from a Fluke Model 430A High Voltage Power Supply. The input of the power supply was regulated by a Sorensen Model 2000S A.C. Voltage Regulator which was accurate to \( \pm 0.1\% \) against line changes. To accurately measure the high voltage, the output of the power supply was connected to a Fluke Model 80D-30 High Voltage Divider whose resistance ratios were known to a precision of \( \pm 0.01\% \). A Fluke Model 821A Differential Voltmeter was then used to measure the output potential of the voltage divider to an accuracy of \( \pm 0.01\% \). Thus, the output of the high voltage power supply was determined with an accuracy of \( \pm 0.02\% \).

When doublet mass measurements were carried out using the voltage scanning method (II,B,3), the apparatus for the accelerating potential, \( V \), shown schematically in Figure 4,
Figure 4. The Voltage Scanning Circuit

\[ V = H.V + \Delta V \]
was employed. A ten turn, 100 kilohm precision potentiometer, R, was connected across the battery, B. The slider of the potentiometer was driven by a reversible 25 r.p.m. synchronous motor. The accelerating potential, V, was then equal to the sum of the output of the high voltage power supply, H.V, and the potential across the potentiometer which was indicated by the voltmeter, \( \Delta V \). Thus, V can be varied linearly in time by driving the potentiometer. The scale readings on the voltmeter were accurate to about \( \pm 0.8\% \).

D. The R.F. Stage

Figure 5 is a detailed diagram of one of the r.f. stages. The deflecting plates, \( P_1 \) and \( P_2 \), are sandwiched between two teflon sheets, \( T_1 \) and \( T_2 \), which serve as electrical insulators. In the present instrument the length, \( l \), of the plates was 0.125 inches and the distance, \( d \), between the plates was 0.020 inches. The whole assembly accurately fits into the brass pipe by means of the relatively long collar on flange \( F_1 \). The r.f. field was applied to the deflecting plates by means of a General Radio Type 1330A Bridge Oscillator. This oscillator had an output of only 10 volts. However, when it was connected with long leads to the deflecting plates it was found that a resonance effect was set up, which increased the voltage applied to the plates to nearly 50 volts, in the frequency range of about 13 to 16 Mc/sec. When mass measurements were carried out using the frequency scanning method (II,B,2), the frequency was varied by employing a \( 7\% \) r.p.m. synchronous motor to drive the tuning capacitor of
Figure 5. The R.F. Stage Assembly
the oscillator.

Due to the fact that the output impedance was not matched to the input impedance of the oscillator, the dial readings on the tuning capacitor were accurate only to about ± 0.5%. Presently, while investigating the operating principles of the instrument, no improvements have been made in the frequency measurements.

E. The Electron Multiplier

Figure 6 is a schematic diagram of the ion detector, a Bendix Model 306 Electron Multiplier. Here the multi-element dynode structure of the conventional multiplier has been replaced by two quartz plates, called the dynode and field strip, respectively, each of which has been coated with a thin, and therefore highly resistive, metal layer. The multiplier uses crossed electric and magnetic fields for its operation. The potential differences were applied across the strip ends by a Fluke High Voltage Supply, Model 412A. These potentials were adjusted to produce the equipotential surfaces as shown, by the dotted lines, in the diagram. The magnetic field, whose direction is perpendicular to the plane of the paper, is produced by small permanent Alnico magnets.

The positive ions pass through the entrance grid onto the cathode, which consists of a tungsten plate. On impact secondary electrons are emitted. These electrons are accelerated by the electric field and will describe a simple cycloidal motion normal to the magnetic field. The electrons
Figure 6. The Magnetic Electron Multiplier
strike the dynode strip, before they can complete a full cycle, with a sufficiently large enough kinetic energy so that, on impact, further secondary electrons are emitted with a gain greater than one. These electrons, in turn, perform the same type of motion and a cascading action results. A current gain of $10^7$ is achieved. The output of the electron multiplier was measured by a Keithley Electrometer, Model 621.

The tungsten cathode has a relatively high work function ($\sim 4.5\text{eV}$). Because of this, the electron multiplier does not respond to visible light and the number of accidental electrons emitted from the cathode, at room temperatures, will be very small. The dark current was less than 0.1 electron per second referred to the cathode.
CHAPTER IV

THEORY

A. The Deflection of Ions by the R.F. Stage

The operation of the new instrument depends on the fact that ions which arrive at the r.f. stage about a time interval when the r.f. field is zero emerge undeflected, while ions entering the r.f. stage at any other time suffer a large angular deflection. The formulae for the change in momentum and angular deflection of the ions passing through the deflecting plates at the time when the electric field is nearly zero, and the formula for the mass resolution will now be derived.

For a sinusoidally varying r.f. signal, of amplitude $V_y$, the electric field between the deflecting plates is given by

$$ E_y = E_0 \sin \omega t $$

(IV-1)

where $E_0$ is equal to $V_y$ divided by the distance, $d$, between the deflecting plates.

i.e.

$$ E_0 = \frac{V_y}{d} $$

(IV-2)

The ions will pass through slits $S_j$ and $S_g$ in Figure 2 only when $E_y$ is approximately zero, i.e. when $\omega t$ is approximately equal to $n\pi$. Then Equation (IV-1) becomes, after substitution of Equation (IV-2)

$$ E_y \sim \frac{V_y}{d} \omega t $$

(IV-3)

The rate of change in momentum when the ions are acted upon
by the electric field in the r.f. stage is

\[
\frac{d(Mv_y)}{dt} = \frac{eV_y \omega}{d}
\]  

(IV-4)

or

\[
Mv_y = \frac{eV_y \omega}{d} \int t \, dt
\]

(IV-4a)

Here \( \Delta t \) is the time that the ions take to traverse the deflecting plates. Thus,

\[
\Delta t = \frac{l}{v}
\]

(IV-5)

where \( l \) is the length of the deflecting plates.

Figure 7 is a schematic representation of the r.f. signal.

The inset in the figure shows that the time interval, \( \Delta t \), consists of two parts, \( \Delta t^- \) and \( \Delta t^+ \), which denote the time interval for which the ions are acted upon when the electric field is negative and positive, respectively. Thus,

\[
\Delta t = \Delta t^+ + \Delta t^-
\]

(IV-6)

The integral in Equation (IV-4a) can therefore be written as

\[
M \Delta v_y = \frac{eV_y}{d} \omega \int_{-\Delta t^-}^{+\Delta t^+} t \, dt
\]

(IV-7)

Upon integration this becomes

\[
M \Delta v_y = \frac{\omega}{2} \frac{eV_y}{d} \left[ (\Delta t^+)^2 - (\Delta t^-)^2 \right]
\]

(IV-8)

or

\[
M \Delta v_y = \frac{\omega}{2} \frac{eV_y}{d} (\Delta t^+ + \Delta t^-) (\Delta t^+ - \Delta t^-)
\]

(IV-9)

Substituting Equations (IV-5) and (IV-6) into the above equation results in

\[
M \Delta v_y = \frac{\omega}{2} \frac{eV_y}{d} \frac{l}{v} (\Delta t^+ - \Delta t^-)
\]

(IV-10)
The small angular deflection, $\Delta \theta$, of the ion beam in passing through the r.f. stage is approximately given by

$$\Delta \theta \sim \frac{M \Delta v}{v} = \frac{\lambda}{4} \frac{eV}{MV} \frac{L}{d} (\Delta t^+ - \Delta t^-) \tag{IV-11}$$

In this equation the kinetic energy, $\frac{1}{2} M v^2$, can be replaced by $eV$, the product of the electronic charge and the accelerating potential [See Equation (I-1)]. Thus,

$$\Delta \theta = \frac{\lambda}{4} \frac{V}{V_y} \frac{L}{d} \Delta t^+ - \Delta t^- \tag{IV-12}$$

Consequently, the time difference, $(\Delta t^+ - \Delta t^-)$, required to deflect the ion beam through an angle $\Delta \theta$ is given by

$$\Delta t^+ - \Delta t^- = \frac{4}{\lambda} \frac{V}{V_y} \frac{d}{l} \Delta \theta \tag{IV-13}$$

B. Transmission Time Interval

An expression for the time interval during which ions are transmitted through the instrument will now be derived. This will be done with reference to Figure 8, which is a schematic diagram of the drift tube, the first r.f. stage and the first collimating stage.

The angular divergence of the ion beam entering the r.f. stage, described by ray 1 and ray 2 of the ion beam, is denoted by the angle $2 \alpha$ where $\alpha$ is given by

$$\alpha = \frac{w}{L} \tag{IV-14}$$

Ray 1 and ray 2 will be transmitted through slit $S_5$ when they both suffer an angular deflection equal to $2 \alpha$, i.e. when

$$\Delta \theta = 2 \alpha \tag{IV-15}$$
Figure 8. The Angular Divergence of the Ion Beam
or [See Equation (IV-14)] when

\[ \Delta \theta = \frac{2w}{L} \quad \text{(IV-16)} \]

The required time difference, \((\Delta t^+ - \Delta t^-)\), needed to deflect ray 1 through an angle of 2\(\alpha\) is found by substituting Equation (IV-16) in Equation (IV-13). Thus,

\[ (\Delta t^+ - \Delta t^-)^+ = \frac{9}{w} \frac{V}{V_y} \frac{d}{L} \frac{w}{L} \quad \text{(IV-17)} \]

where \((\Delta t^+ - \Delta t^-)^+\) means that \(|\Delta t^+| > |\Delta t^-|\). Similarly, the time difference required to deflect ray 2 through an angle 2\(\alpha\) is given by

\[ (\Delta t^+ - \Delta t^-)^- = -\frac{8}{w} \frac{V}{V_y} \frac{d}{L} \frac{w}{L} \quad \text{(IV-18)} \]

where \((\Delta t^+ - \Delta t^-)^-\) means that \(|\Delta t^+| < |\Delta t^-|\).

Thus, the transmission time interval that ions pass through slit \(S_5\) is given by

\[ \delta t = (\Delta t^+ - \Delta t^-)^+ - (\Delta t^+ - \Delta t^-)^- \quad \text{(IV-19)} \]

Substituting Equations (IV-17) and (IV-18) into the above equation results in

\[ \delta t = \frac{16}{w} \frac{V}{V_y} \frac{d}{L} \frac{w}{L} \quad \text{(IV-20)} \]

C. Resolution

Consider two ions of mass \(M_1 = M\) and \(M_2 = M + \Delta M\), where \(\Delta M\) is small, which are accelerated by the same potential, \(V\). After the acceleration both ions possess the same kinetic energy.

i.e. \[ \frac{1}{2} M v^2 = \frac{1}{2} (M + \Delta M) v'^2 \quad \text{(IV-21)} \]

where \(v > v'\). Let the difference in velocities be denoted by \(\Delta v\), i.e.

\[ \Delta v = v - v' \quad \text{(IV-22)} \]
Thus, Equation (IV-21) can be written as

\[
\frac{1}{2} M v^2 = \frac{1}{2} (M + \Delta M) (v - \Delta v)^2 \quad (IV-23)
\]

On neglecting terms which are doubly small, it follows that

\[
\frac{\Delta M}{M} \sim \frac{2 \Delta v}{v} \quad (IV-24)
\]

From Equation (II-1), the velocity can be related to the period of the fundamental frequency \(f_0\) of the r.f. field by

\[
v = \frac{2L}{T_0} \quad (IV-25)
\]

Thus,

\[
v - \Delta v = \frac{2L}{T_0 + \Delta T_0} \quad (IV-26)
\]

From which it can easily be shown that

\[
\frac{\Delta v}{v} = \frac{\Delta T_0}{T_0} \quad (IV-27)
\]

Now, two masses can just be resolved when

\[
\Delta T_0 \sim \delta t \quad (IV-28)
\]

Thus, the mass resolution is found by combining Equations (IV-24), (IV-28) and (IV-20). Hence

\[
\frac{\Delta M}{M} \sim \frac{32}{\omega T_0} \frac{V}{V_y} \frac{d}{L} \frac{w}{l} \quad (IV-29)
\]

Substituting \(\omega = \frac{2\pi}{T} (\frac{\omega T}{2\pi})\) in the above equation gives the following expression for the mass resolution.

\[
\frac{\Delta M}{M} = \frac{16}{\pi} \frac{V}{V_y} \frac{d}{L} \frac{w}{l} \frac{1}{n} \quad (IV-30)
\]

where it will be remembered that;

- \(V\) is the accelerating potential
- \(V_y\) is the amplitude of the applied r.f. voltage
\( n \left( \frac{f}{f_0} \right) \) is the integral multiple of the fundamental frequency.

\( d \) is the distance between the deflecting plates.

\( l \) is the length of the deflecting plates.

\( w \) is the width of the slits.

\( L \) is the length of both collimating stages and the drift tube.

Equation (IV-30), the mass resolution formula, was derived for an instrument in which the lengths of the first collimating stage, the drift tube and the second collimating stage are all equal. However, in the present instrument the length of both collimating stages was 50 inches, and the length of the drift tube was 100 inches. In future computations for the resolution, the value taken for \( L \) will be 70 inches, the average of the above values.

Practical considerations of the quantities in Equation (IV-30) limits the actual resolution that may be achieved. For instance, \( w \) cannot be made infinitely small and \( L \) infinitely large at the same time. If the slits are made very narrow, then \( L \) must be such a length that the intensity of the beam is still strong enough to be detected. Likewise, if \( d \) is made small, then \( l \) must also be small, as will be explained later (IV,D). Also, the larger \( n \) is, the larger \( V \) must be, in order to satisfy the condition that the time of flight of the ions through the deflecting plates be appreciably smaller than the period of the applied frequency. Thus, the values of the parameters in Equation (IV-30) cannot be chosen arbitrarily.
Typical operating values of these parameters were;

\[ V = 20,000 \text{ volts} \]
\[ V_y = 50 \text{ volts} \]
\[ d = 0.020 \text{ inches} \]
\[ L = 0.125 \text{ inches} \]
\[ w = 0.015 \text{ inches} \]
\[ L = 70 \text{ inches} \]
\[ n = 200 \]

which results in a theoretical resolution of

\[ \frac{\Delta M}{M} \sim \frac{1}{2800} \]

D. Displacement of the Ion Beam

From Equation (IV-30) it is seen that the resolution is proportional to the ratio \( \frac{d}{L} \), where \( d \) is the distance between the deflecting plates and \( L \) is their length. To find the values of these two parameters which will maximize the resolution it is necessary to calculate the total vertical displacement, \( y_{\text{max}} \), of the ion beam after traversing the deflecting plates. If this displacement of the ion beam were larger than the slit widths, the ion beam would not be able to pass through the next slit. The displacement, therefore, must be small. This condition, which will now be determined, limits the values for \( d \) and \( L \).

Only those ions will be detected which have passed through the r.f. stage during a time interval about which the electric field is zero. Thus, only the time regions in which
the sinusoidally varying electric field is given by

$$E_y = \frac{V_x}{d} \omega t.$$  \hspace{1cm} (IV-3)

will be considered. Those ions which suffer an appreciable angular deflection do not pass through the instrument. Therefore, the computation of the displacement will be limited to those particles which do not suffer an angular deflection.

The force on the ion beam while traversing the deflecting plates is given by

$$M \frac{dv_y}{dt} = \frac{eV_y \omega}{M} t.$$  \hspace{1cm} (IV-4)

The \(y\)-component of velocity is found from

$$\int dv_y = \frac{eV_y \omega}{Md} \int t \, dt.$$  \hspace{1cm} (IV-31)

which, on integration, yields

$$v_y = \frac{eV_y \omega}{Md} \frac{t^2}{2} + C_1$$  \hspace{1cm} (IV-32)

where \(C_1\) is a constant. The ion beam under consideration enters and emerges from the deflecting plates with a zero \(y\)-component of velocity at the times \(t = -\frac{L}{2v}\) and \(t = +\frac{L}{2v}\) \[See Equations (IV-5) and (IV-6),\] respectively. Thus,

$$v_y = 0 \text{ when } t = \pm \frac{L}{2v}$$

Applying this condition to Equation (IV-32) results in

$$C_1 = -\frac{eV_y \omega}{2Md} \frac{L^2}{4v^2}.$$  \hspace{1cm} (IV-33)
which on substitution into Equation (IV-32) gives

\[ v_y = \frac{eV_y \omega}{2Md} (t^2 - \frac{p^2}{4v^2}) \]  

(IV-34)

The displacement, \( y \), can now be easily calculated from

\[ dy = v_y dt \]  

(IV-35)

or

\[ \int dy = \frac{eV_y \omega}{2Md} \int (t^2 - \frac{p^2}{4v^2}) dt \]  

(IV-36)

which, upon integration, becomes

\[ y = \frac{eV_y \omega}{2Md} \left( \frac{t^3}{3} - \frac{p^2}{4v^2} t \right) + C_2 \]  

(IV-37)

where \( C_2 \) is a constant of integration. Let \( y \) be zero for the central ion beam entering the r.f. stage. Thus,

\[ y = 0 \quad \text{when} \quad t = -\frac{p}{2v} \]

Applying this condition to Equation (IV-37) results in

\[ C_2 = -\frac{eV_y \omega}{2Md} \frac{p^3}{12v^3} \]  

(IV-38)

which on substitution into Equation (IV-37) yields

\[ y = \frac{eV_y \omega}{2Md} \left( \frac{t^3}{3} - \frac{p^2}{4v^2} t - \frac{p^3}{12v^3} \right) \]  

(IV-39)

The maximum displacement, \( y_{\text{max}} \), occurs at the time \( t = \frac{p}{2v} \).

Substituting this, together with \( \frac{\omega M v^2}{2} = eV \), into the previous equation gives

\[ y_{\text{max}} = -\frac{\omega}{24} \frac{V_y}{v^{3/2}} \frac{p^3}{d} \left( \frac{M}{2e} \right)^{3/2} \]  

(IV-40)

Figure 9 (a) and 9 (b) is a sketch of the velocity versus time and of the displacement versus time, respectively.
Figure 9:  (a) A Sketch of the \(y\)-component of Velocity versus Time

(b) A Sketch of the Vertical Displacement versus Time
To prevent an appreciable loss in intensity of the ion beam, \( |y_{\text{max}}| \) must be smaller than the slit width, \( w \). Say,
\[
|y_{\text{max}}| \leq 0.1w \quad \text{(IV-41)}
\]
This requirement still allows 90% of the ion beam to pass through the collimating slits after traversing the deflecting plates.

The displacement, \( y_{\text{max}} \), for \( M \approx 20 \) a.m.u. in the present instrument, using the parameters which were listed in the preceding section, is found from Equation (IV-40) to be
\[
|y_{\text{max}}| \approx 4 \times 10^{-5} \text{ inches}
\]
This is negligible compared to one tenth of the slit widths (\( W = 0.015 \) inches). \( y_{\text{max}} \) will be equal to about \( 0.1w \) when the present value of \( l \) is increased by approximately a factor of 3.

E. The Upper Limit of the Frequency

For the proper operation of the velocity filter the time required for the ions to travel through the r.f. stage should be less than half a period of the applied r.f. field. Thus,
\[
\frac{k}{v} \leq \frac{T}{2} \quad \text{(IV-41)}
\]
or
\[
f \leq \frac{v}{2l} \quad \text{(IV-42)}
\]
The expression for the velocity, obtained from Equation (I-1), is
\[
v = \left( \frac{2eV}{M} \right)^{\frac{1}{2}} \quad \text{(IV-43)}
\]
Therefore,

\[ f \leq \frac{1}{2\ell} \left( \frac{2eV}{M} \right)^{1/2} \]  

(IV-44)

For the purpose of a crude estimate of the maximum allowable frequency suppose that \( M \sim 20 \text{ a.m.u.} \). Then on substitution of this value, along with \( \ell = 0.125 \text{ inches} \) and \( V \sim 20,000 \text{ volts (IV,C)} \) into the preceding equation, the upper limit for the frequency in the present apparatus is roughly

\[ f \sim 70 \text{ Mc/sec.} \]
TECHNIQUE AND EXPERIMENTAL RESULTS

A. Alignment of the Instrument

A misalignment of the collimating slits of the instrument results in a loss of ion current intensity and/or broadening of the ion beam. Thus, the instrument must be aligned to the ion beam. This was accomplished in the following manner. First, with the aid of an accurate level, all the slits were aligned horizontally. Then by means of several adjustments, which will be described below, the slits were adjusted vertically until a maximum ion current was obtained.

The exit slit, $S_1$, of the source was first adjusted, by means of a bellows arrangement (III,B), until a maximum ion current was registered by the Faraday cup situated behind slit $S_2$. Then by means of an adjustment assembly mounted just before the first r.f. stage, the relatively thin brass pipe was flexible enough so that it could be forced vertically until the ion current, registered this time by the second Faraday cup situated just behind the first r.f. stage, was again maximized. A similar vertical adjustment placed just before slit $S_7$ allowed the ion current, as registered by the third Faraday cup located just behind slit $S_7$, to be brought to a maximum. Finally, the output of the electron multiplier was maximized by means of another vertical adjustment just before the detection system. In this manner, the collimating slits were accurately aligned to the ion beam.
B. Frequency Scanning Analysis

CH$_4$ and O$_2$ were leaked into the source. The accelerating potential was kept constant at about 26.4 kV. Figure 10 is a typical recorder plot of the ion current versus the frequency for the mass doublet CH$_4$-O. The frequency was plotted, at regular intervals of the dial readings on the tuning capacitor, by placing markers on the recorder chart.

It will be noted that the CH$_4$ ions, being the heavier component of the doublet, appear at the lower frequency. From the figure, it is seen that the frequency separation, $\Delta f$, between the CH$_4$ and O$^{16}$ peaks is

$$\Delta f = 17 \text{ kc/sec.}$$

Substituting the above value for $\Delta f$, together with $f = 14.8 \text{ Mc/sec.}$ and $M = 16$ a.m.u., in Equation (II-8)

$$\frac{\Delta M}{M} \sim \frac{2 \Delta f}{f} \quad (\text{II-8})$$

results in

$$\Delta M(\text{CH}_4-\text{O}) \sim 3.68 \times 10^{-2} \text{ a.m.u.}$$

More accurately determined values for this doublet are:

$\Delta M(\text{CH}_4-\text{O}) = 3.63933 \pm 0.00005 \times 10^{-2}$ a.m.u. (Quisenberry, Scolman and Nier, 1956).

$\Delta M(\text{CH}_4-\text{O}) = 3.639733 \pm 0.000011 \times 10^{-2}$ a.m.u. (Smith, 1958)

The average width of the peaks, at the base, is

$$\delta f = 4 \text{ kc/sec.}$$

Thus the observed mass resolution is [See Equation (II-11)]

$$\frac{\Delta M}{M} \left( = \frac{2 \delta f}{f} \right) = \frac{2 \times 4}{14.8 \times 10^3} \sim \frac{1}{1800}$$
Figure 10. A Recorder Plot of the Ion Current versus Frequency for the Mass Doublet CH₄-0
C. Voltage Scanning Analysis

The mass peaks displayed in Figure 11 are a typical recorder trace of the ion current versus the accelerating potential for the CH\(_4\)-O mass doublet. The radio frequency was kept constant at 16.121 Mc/sec. With the reversible motor (IV,3) being used to vary the accelerating potential \( V \), it is seen from Equation (II-2) that, if \( M_2 > M_1 \), the chart recorder will trace first, say, the mass peaks \( M_1 \) and \( M_2 \) in succession as \( V \) increases, and then the peaks \( M_2 \) and \( M_1 \) in succession as \( V \) decreases. The values of the accelerating potential were plotted on the recorder chart at regular intervals of the scale reading of the voltmeter, \( \Delta V \).

A series of 30 measurements were taken which gave an average value for the difference in accelerating potential, \( \Delta V \), between the CH\(_4\) and \( O^{16} \) mass peaks as

\[
\Delta V = 64.25 \text{ volts}
\]

Substituting this value for \( \Delta V \), together with \( V = 28,267 \) volts and \( M = 16 \text{ a.m.u.} \), in Equation (II-12)

\[
\frac{\Delta M}{M} = \frac{\Delta V}{V}
\]

results in

\[
\Delta M(\text{CH}_4-O) = 3.645 \times 10^{-2} \text{a.m.u.}
\]

The difference in accelerating potential was determined with the voltmeter which is only accurate to 0.8%. The error in \( V \) is much less (0.02%). Thus, the error in \( \Delta M \) is also approximately \( \pm 0.8\% \). The value for the CH\(_4\)-O doublet given
above agrees, within experimental error, with the more accurately determined values presented in the previous section.

The average width of the peaks, at the base, is

$$\delta V = 11.75 \text{ volts}$$

Thus, the observed mass resolution is [See Equation (II-13)]

$$\frac{\Delta M}{M} \approx \frac{\delta V}{V} = \frac{11.75}{28,267} \approx \frac{1}{2400}$$

This is in good agreement with the theoretical mass resolution (IV,C).
CHAPTER VI
CONCLUSION

A. The Expected Improvements in Resolution

The new instrument has attained a mass resolution of one part in $2^{400}$ (V,C) at the base of the mass peaks, which is the best ever achieved by linear time of flight methods. It is still about two orders of magnitude lower than the highest resolution achieved by the large magnetic deflection mass spectrometers. However, the limits of the new instrument have not yet been attained and an improvement by an appreciable factor in the resolution seems to be quite easily within reach, as we shall now discuss.

The present values of the parameters of Equations (IV-30) are by no means optimum values. For example, the applied frequency can be raised from the present 15 Mc/sec to about 70 Mc/sec (IV,E). This will increase $n \propto f$, See Equation (II-3) by a factor of about 4. Furthermore, with an oscillator of improved design it is expected that the amplitude of the r.f. signal can be increased by at least a factor of 2. A further factor of 3 in resolution can be gained by decreasing the slit widths to 0.005 inches. This has already been done (Van Wijngaarden et al, 1964) without adversely affecting the ion beam intensity. The resulting resolution was one part in 8000, which is comparable to that obtained in the quadrupole mass spectrometer (I,C). As mentioned previously (IV,D), $\lambda$ can be increased by a factor of approximately 3
over its present value.

The total effect of the above changes would be to improve the theoretical resolution by a factor of approximately 70. Thus, a resolution of about one part in $2 \times 10^5$ is believed possible for the new velocity filter, provided that mono-energetic ion beams are employed. The mass resolution of the instrument, of course, is limited because of the energy spread of the ions leaving the source. To overcome this hindrance, an electrostatic analyser will be required.

B. Evaluation of the New Instrument

The performance of the new instrument must be judged not only against the background of other time of flight instruments, but also against the array of high resolution magnetic deflection mass spectrometers. The new instrument lends itself to both analytical and high precision work with equal facility. The instrument shows much promise in both areas.

The earliest time of flight instruments were built mainly because of their application of a new principle to mass spectrometry. However, even as these kinds of instruments became more sophisticated it was apparent that they could not compete with the more complex magnetic instruments in precision mass measurements. Thus, most of the time of flight instruments were designed with the idea in mind that they be employed chiefly as analytical tools. Their most important applications were in the fields of chemical and industrial research dealing with such topics as fast chemical reactions and solids analysis.
It was here that the complexity and bulkiness of the magnetic instruments were a great disadvantage. Operated in this mode, the new time of flight instrument offers all the advantages of the others, with the exception that it employs several collimating slits which present alignment problems. However, its improved resolution more than offsets this disadvantage. Moreover, in the new instrument the mass range is unlimited. Using the electron bombardment source, old samples are quickly removed and new ones introduced. This type of instrument is ideally suited for applied research since it is sturdy, comparatively simple to operate, has a high resolution and allows rapid analysis.

It is in the field of high resolution mass spectrometry that the new instrument will probably make its most significant contributions. The preliminary results presented in Chapter IV, and more recent work (van Wijngaarden et al, 1964), indicate that the instrument is capable of accurate mass measurements approaching the precision of the magnetic mass spectrometers. If, as seems possible, a resolution of one part in $2 \times 10^5$ is achieved with the new instrument, then the mass of an atom may be determined with a precision of at least a factor of 100 times the resolution with the use of peak matching $(I,F)$. This would allow us to determine masses to a precision of one part in about $2 \times 10^7$, which is of higher precision than the most precise results obtained with the magnetic deflection type instruments. The information obtained by the two methods would be a check against any possible systematic errors in precision mass measurements.
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