A MOLECULAR BEAM SPECTROMETER

USING DIELECTROPHORESIS

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CHAPTER I

INTRODUCTION

The use of a molecular beam as a research tool has been fruitful in
the studies of the properties of molecules. It is the purpose of this
paper to extend the usefulness of this technique by presenting the de-
sign of a new molecular beam apparatus. The apparatus will select un-
charged molecules on the basis of mass and polarizability or dipole
moment and is based on the use of dielectrophoresis.

Dielectrophoresis is defined as the motion of an <u>uncharged</u> particle
in an electric field due to the inhomogeneity of the field. It occurrs
as the result of either induced or permanent dipoles. Dielectrophoresis
should be distinguished from electrophoresis which is the motion of a
<u>charged</u> particle in an electric field.

The use of dielectrophoresis on a molecular beam to investigate the
properties of molecules is not new. The first attempts were made by
Wrede (1) who passed a beam of KI molecules parallel to a charged wire
and a short distance from it. He showed that there was a detectable
deviation of the beam towards the wire. A few years later, Scheffers (2)
used electric-deflection methods to measure the polarizability of several
different atoms. By using an improved electrode design and an electric
resonance technique, Hughes (3) was able to select various rotational
states in CsF molecules on the basis of their effective permanent dipole
moment. Trischka (4) refined Hughes' apparatus and observed the various

vibrational states of the CsF molecule. A slightly different use of essentially the same apparatus was made by Herm (5) to analyze rotational excitation in reactive scattering. Good reviews of molecular beam techniques in general and electric deflection techniques in particular are given by Fraser (6) and Ramsey (7).

It should be pointed out however, that in all of the above mentioned work, the results were complicated by the use of a broad spectrum of molecular velocities. This was necessary to obtain adequate intensities. We believe that modern detection methods coupled with the apparatus to be described here will permit the use of only a selected velocity range which should then increase the resolution and usefulness of the results.

The present suggested form of a molecular beam spectrometer using dielectrophoresis would include the following essential components: an "oven" as a source of molecules, a collimator to define the beam size, a velocity selector (of the rotating disc type), an electrode system in a circular track configuration to provide the proper nonuniform field, a detection system, and a vacuum system enclosing the entire appartus. It would differ from previous kinds in that it could be used to separate molecules according to their mass. This would be especially useful for large molecules which break up into fragments upon ionization in conventional mass spectrometers. Another important difference is that the spectrometer is designed to provide a force which is constant along the dimensions of the beam. As a result the beam can be in the shape of a ribbon rather than a pencil as in earlier work. This permits a very considerable increase in beam size and thus easier detection.

In the subsequent sections we shall discuss the various assumptions upon which the feasibility of the proposed instrument will be assessed.

Key problems to be examined will be the applicability of the spectrometer to both polar and nonpolar molecules, the high electric fields required, the dimensions of the electrode system, the resolution of the apparatus, and the intensity of the detected beam.

CHAPTER II

MATERIALS IN NONUNIFORM FIELDS

A nonuniform electric field exerts a force on matter. Just exactly how this occurrs will now be considered. The effect of an electric field on a particle free to move depends on certain basic properties of the material considered. It is determined by the charge, dipole moment, and polarizability of the particle. If it possesses a net charge, then there is an electrostatic interaction between the charge and the field, producing a resultant motion. This is known as electrophoresis. If the material contains permanent dipoles, the dipoles tend to become aligned with the field and if the field is not uniform, the dipoles will experience a force in the direction of strongest field. The material will also contain induced dipoles as a result of the separations of the atomic centers of positive and negative charge. These dipoles will also be urged in the direction of increasing field strength. The translational motion of dipoles, either permanent or induced, resulting from the effects of a nonuniform electric field is termed dielectrophoresis.

All materials experience induced-dipole dielectrophoresis, but the other two electric field forces may or may not be present, depending on the material in question. For a given electric field, the electrophoretic effect is normally many orders of magnitude larger than the dielectrophoretic effects. The permanent dipole effect, in turn, is considerably larger than the induced-dipole effect.

Induced Dipoles

To obtain a qualitative picture of how the dielectrophoretic force arises, let us consider an uncharged, isotropic molecule having no permanent dipole moment. When the molecule is put into a nonuniform electric field, such as the one shown in Fig. 1 created by two concentric cylinders, the positive charge is attracted towards the outer electrode and the negative charge is attracted towards the inner electrode. There is thus a separation of charge or polarization and a dipole is created. For the polarized molecule the negative charge lies in a stronger field than does the positive charge, so that the inward force is greater than the outward force. The result is a net force on the molecule in the direction of the central electrode. The result will be the same if the polarity of the field is reversed.

Quantitatively, the force on a dipole is given by the vector equation

$$\vec{F} = (\vec{\mu} \cdot \vec{\nabla}) \vec{E}, \qquad (II.1)$$

where $\vec{\mu}$ is the dipole moment and $\vec{E}$ is the electric field strength (8). For isotropic molecules the induced dipole moment is proportional to and in the direction of the applied electric field. This is shown by the equation

$$\vec{\mu} = \alpha \vec{E}, \qquad (II.2)$$

where the proportionality constant α is called the polarizability and is dependent on the type of molecule being considered. For induced dipoles then the force equation becomes

$$\vec{F} = (\alpha \vec{E} \cdot \vec{\nabla}) \vec{E} = \frac{\alpha}{2} \vec{\nabla} E^2. \qquad (II.3)$$
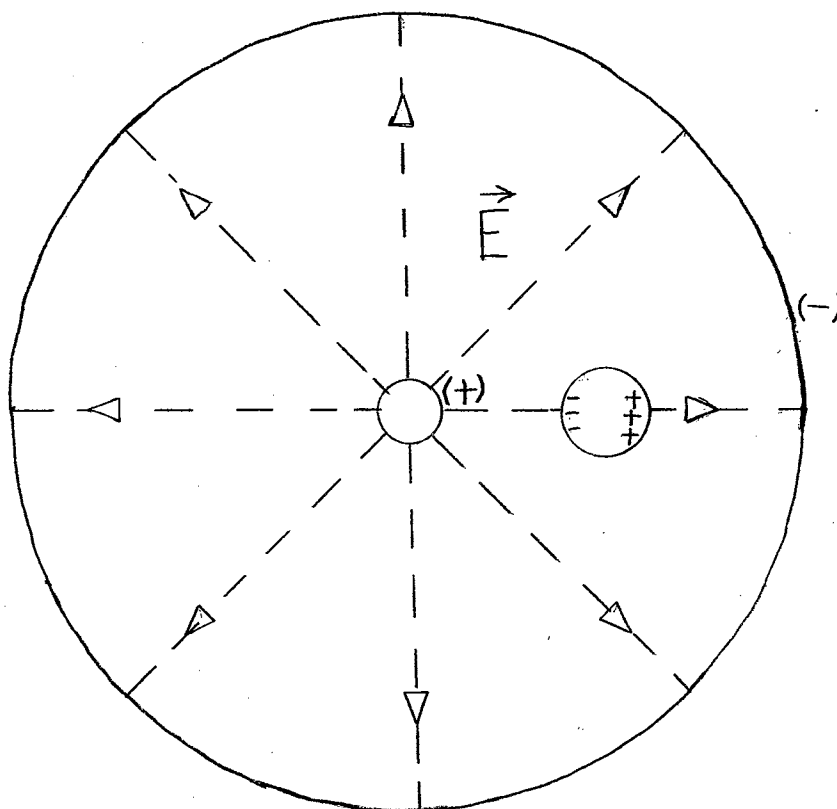
Figure 1. Particle Polarized by Nonuniform Electirc
Field

Thus if the electric field strength is known as a function of position, then the force can also be found as a function of position.

If the molecule is not isotropic then the induced dipole moment is no longer necessarily in the direction of the field, but will have a component in the field direction depending on the orientation of the molecule. This means that the polarizability α is no longer a scalar but is now a tensor quantity (9). For molecules which are rotating about an axis of symmetry, the effective dipole moment and consequently the force will be quantized, according to the rotational state of the molecule (9a). Thus a selection between molecules of different

rotational states should be possible.

Permanent Dipoles

The situation for molecules possessing permanent dipole moments is quite similar to the induced dipole case. If the dipole is not already aligned with the field, then it will experience a torque which will tend to align it. If there are sufficient frictional effects to dissipate the rotational energy gained by the turning dipole then the dipole and field will become well aligned and the results are exactly the same as for the isotropic induced dipole.

When the necessary frictional effects are not present, which is the case in a molecular beam experiment, then a permanent dipole will possess rotational energy and will not become completely aligned with the field. The situation is then similar to the anisotropic nonpolar case in that the effective dipole moment is dependent on the rotational state of the molecule. This dependence can be calculated quantum mechanically by pertubation methods.

When a rotating molecule of energy $\mathcal{E}_o$ with a permanent moment is placed into an electric field, it's energy according to pertubation theory becomes approximately

$$\mathcal{E}_r = \mathcal{E}_o - \vec{\mu} \cdot \vec{E} \qquad (II.4)$$

where $\vec{\mu}$ is the average dipole moment and $\vec{E}$ is the field strength. It can be shown that for linear molecules and symmetric top molecules that the average dipole moment is given by (9)

$$\vec{\mu} = -\frac{4\pi^2 A \mu_o^2}{h^2} \left[\frac{J(J+1) - 3M^2}{J(J+1)(2J-1)(2J+3)} \right] \vec{E}, \qquad (II.5)$$

where A is the moment of inertia of the molecule, μ_o is the dipole
moment, h is Planck's constant, J is the angular momentum quantum num-
ber, and M is the electric quantum number. Thus for a given rotational
state, the effective dipole moment is proportional to the field strength
or

$$\vec{\mu} = \Omega \vec{E}. \qquad (II.6)$$

This equation is completely analogous to the nonpolar case where Ω is
an effective polarizability. For these simple molecules then, Eq.
(II.3) becomes

$$\vec{F} = \frac{\Omega}{2} \nabla E^2. \qquad (II.7)$$

For various combinations of J and M in Eq. (II.5), Ω can be made
either positive or negative. This gives rise to attractive and repul-
sive forces, both of which have been observed experimentally (1). The
repulsive forces can be attributed to the dipole spending more time
pointing in a direction opposite the field than aligned with it. The
attractive forces are often quite strong and are as much as 100 times
as strong as the nonpolar forces. The repulsive forces, which could not
be utilized in the spectrometer as proposed, could however be used in
one with a track of opposite curvature. The probability that a partic-
ular rotational energy state $\mathcal{E}_r$ with quantum numbers J and M is occupied
is given by

$$f_Q = Ce^{-(\mathcal{E}_r/kT)} \qquad (II.8)$$

where C is a normalizing constant (6). So that if a particular state is
to be selected, only the fraction f_Q of the molecules in the beam can
be used.

CHAPTER III

THE SPECTROMETER

Isomotive Field

As the first consideration in the design of a dielectrophoresis
spectrometer we shall look at the manner in which the deflecting force
depends on position. A desirable force is one that is constant through-
out the region of interest and thus independent of position. Such a
force field, termed the isomotive field, has been designed which is
applicable to both nonpolar and simple polar molecules. The following
derivation is for nonpolar molecules, but is equally valid for the polar
case when Ω from Eq. (II.6) is used instead of α.

For a bounded region containing no volume charge, the potential V
must satisfy Laplace's equation. That is

$$\nabla^2 V = 0$$

throughout the region. A solution of this equation in polar coordinates
is

$$V = A\, r^n \sin n\theta \qquad\qquad (III.1)$$

where A and n are constants to be determined by boundary conditions.
Using the fact that

$$\vec{E} = -\nabla V$$

along with Eq. (III.1) we get

$$\vec{E} = -nAr^{n-1} (\sin n\theta\, \vec{r}_1 + \cos n\theta\, \vec{\theta}_1).$$

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Then

$$E^2 = \vec{E} \cdot \vec{E} = n^2 A^2 r^{2n-2} \tag{III.2}$$

and

$$\nabla E^2 = (2n-2)(n^2 A^2 r^{2n-3})\vec{r}_1.$$

It then follows from Eq. (II.3) that the force is

$$\vec{F} = (\alpha/2)(2n-2)(n^2 A^2 r^{2n-3})\vec{r}_1. \tag{III.3}$$

If the force is to be a constant, say K_1, then the exponent of r must be zero, which requires that

$$n = 3/2.$$

Eq. (III.3) can then be solved for A to get

$$A = (2/3)(\frac{2K_1}{\alpha})^{1/2}.$$

Substitution of A and n into Eq. (III.1) gives the equation of the potential as

$$V = (2/3)(\frac{2K_1}{\alpha})^{1/2} r^{3/2} \sin 3\theta/2. \tag{III.4}$$

This equation is plotted for constant potential in Fig. 2. Since n is not an integer, not all values of θ are allowed. So that a wedge electrode positioned as shown in Fig. 3 must be used to produce the proper field.

If a molecule is placed in the field such that θ is equal to zero, the force, being entirely radial, will be along the x-axis. By curving the z-axis such that the center of curvature is at a large distance to the right of the origin, the dielectrophoretic force can be used as a centripetal force. The fact that the z-axis is curved rather than a straight line should not affect the validity of the derivation significantly, if the radius of curvature is large compared to the dimensions
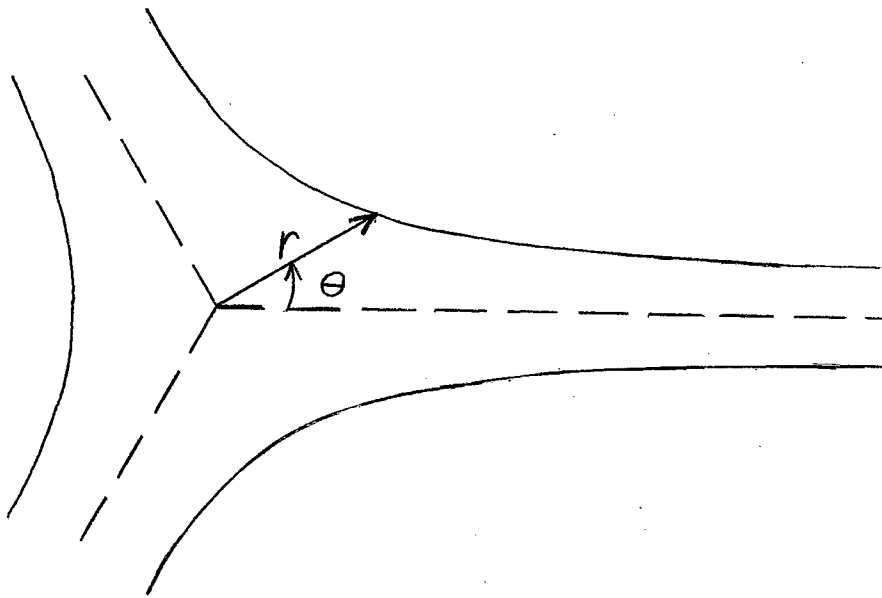
Figure 2. Lines of Constant Potential for Isomotive Field
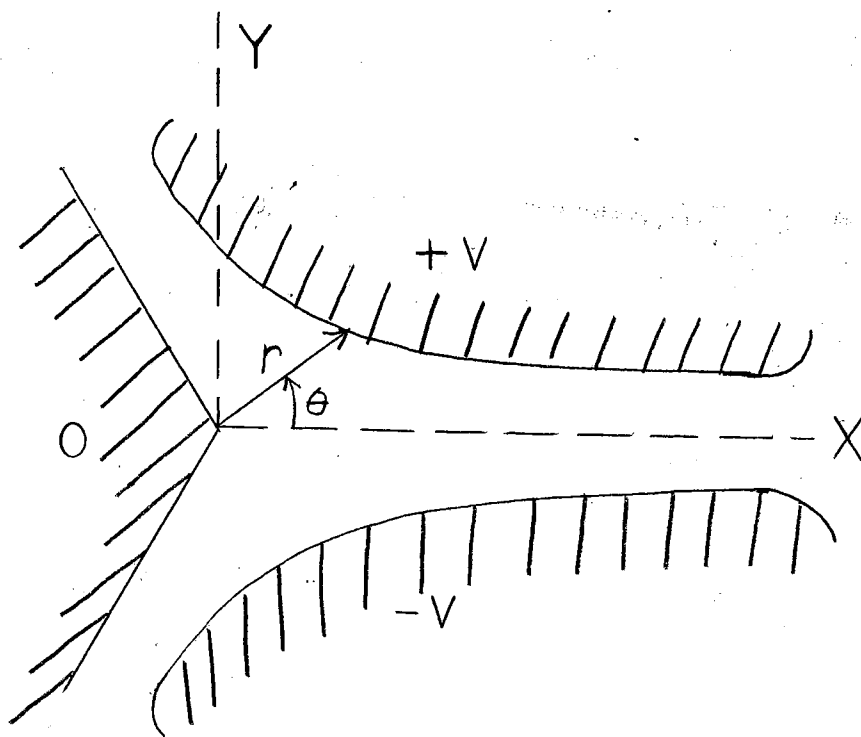
Figure 3. Electrode Positions for Isomotive Field

of the electrodes.

A physical picture of origin of the force can be gained with the help of Fig. 4. For a molecule positioned on the x-axis, the polarized charges will lie off the axis. Here the charges will experience forces which are not perpendicular to the axis, but have a component in the x-direction. Since the molecule is symmetric, the y-values of the forces will cancel, giving a resultant force in the positive x-direction.

Returning now to Equation (III.2) and substituting the values of A and n, we get

$$E^2 = \frac{2K_1 r}{\alpha}.$$

Since E^2 is proportional to r, the maximum field required is determined by the maximum dimension r_m of the electrodes, and

$$E_m = \left[\frac{2K_1 r_m}{\alpha} \right]^{1/2}. \qquad (III.5)$$

Rearrangement of this equation gives the force as

$$K_1 = \frac{\alpha E_m^2}{2r_m}. \qquad (III.6)$$

Substitution of this expression into Eq. (III.4) gives

$$V = \frac{2}{3} E_m r_m \sin \left(\frac{3\theta_m}{2} \right), \qquad (III.7)$$

where θ_m is the angle associated with r_m.

The centripetal force necessary to keep a molecule of mass m, with a tangential velocity v, in a circle of radius R, is

$$F = \frac{mv^2}{R}.$$

Using the dielectrophoretic force as the centripetal force, Eq. (III.6) becomes
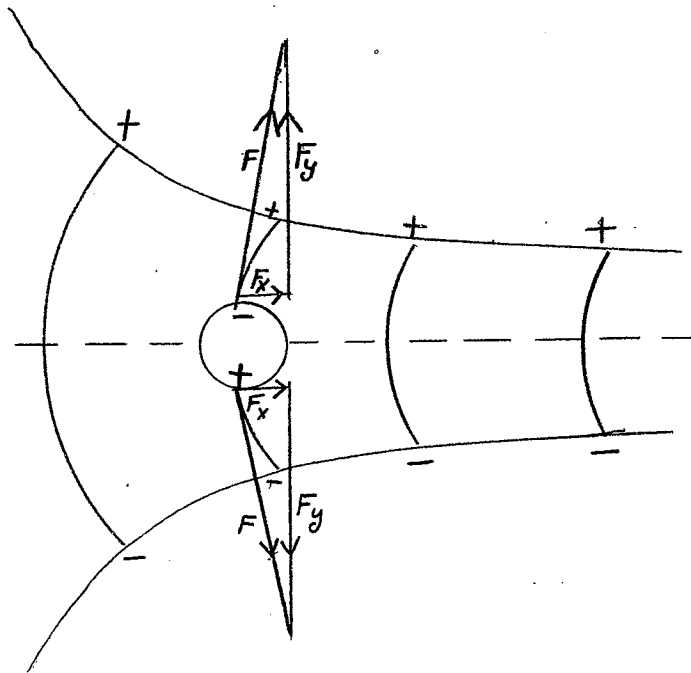
Figure 4. Physical Origin of Axial Force

$$K_1 = \frac{\alpha E_m^2}{2r_m} = \frac{mv^2}{R} \, ,$$

which upon rearrangement gives

$$R = \frac{2mv^2 r_m}{\alpha E_m^2} \, . \tag{III.8}$$

For a gas at temperature T the most probable molecular velocity is

$$j = \sqrt{\frac{2kT}{m}} \, . \tag{III.9}$$

If the velocity at which a molecule is traveling is some fraction B of the most probable velocity, it will be given by

$$v = Bj = B\sqrt{\frac{2kT}{m}} \, .$$

Substitution of this expression into Eq. (III.8) gives

$$R = \frac{4B^2 kTr_m}{\alpha E_m^2} \qquad\qquad (III.10)$$

In order to obtain the voltage as a function of molecular weight, E_m is determined from the above equation and substituted into Eq.(III.7). This gives the voltage as proportional to the square root of the molecular weight. The fractional change in voltage is then expressed by

$$\frac{V_2 - V_1}{V_1} = \frac{\Delta V}{V_1} = \frac{\sqrt{M_2} - \sqrt{M_1}}{\sqrt{M_1}} \quad .$$

If the spectrometer is set at a voltage of V_1 to select a molecular weight of M_1, then the change in voltage necessary to cause the selection of a different molecular weight M_2 is

$$\Delta V = V_1 \left(\frac{\sqrt{M_2} - \sqrt{M_1}}{\sqrt{M_1}} \right). \qquad\qquad (III.11)$$

Eq. (III.10) gives the relation between the molecular properties of velocity and polarization, and the macroscopic parameters of radius of curvature, electrode size, electric field strength, and temperature. For a particular sample, α is already determined, but the remaining quantities are variable parameters in the design of the apparatus. We shall now suggest particular values for some of these parameters, and briefly discuss each of the components making up the spectrometer. A diagram of the apparatus is shown in Fig. 5.

Equipment

The first parameter to be assigned a particular value will be the radius of curvature R. Since it determines the centripetal force, R should be made as large as intensities will permit and still be of laboratory size. Preliminary calculations led us to select R to be 2

O. Source Oven
S. Velocity Selector
C. Collimator
E. Electrodes
I. Ionizer
D. Detector
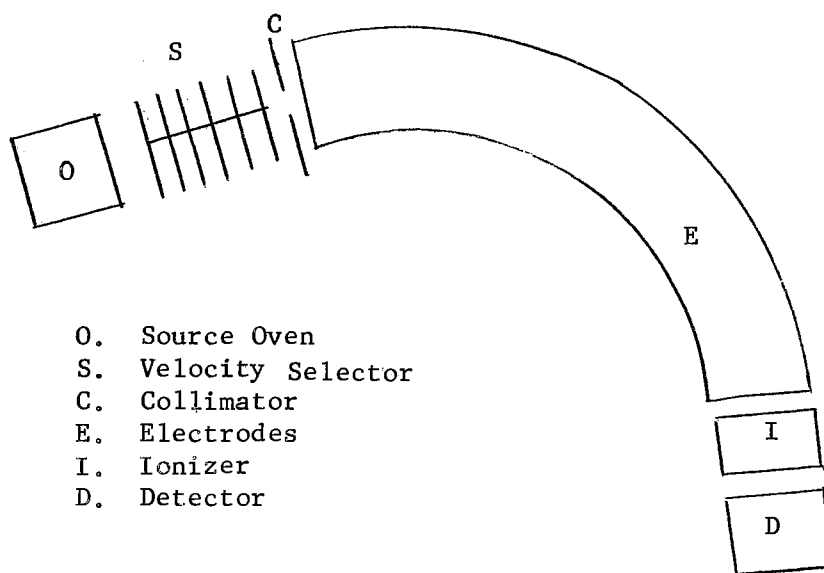
Figure 5   Block Diagram of Spectrometer

meters. The electrode dimension r_m should be much smaller then R but

large enough to allow a sizable molecular beam. These requirements are

satisfied if r_m is 2.5 cm. The parameters R and r_m, after once being

selected, are built into the spectrometer and can not be varied from

sample to sample. This means that these selected values must be within

the range of applicability for all of the samples to be considered. It

will be shown later that with these values of R and r_m the proper condi-

tions for some typical molecules are obtainable.

One other dimension which has not been previosly mentioned is the

minimum separation of the electrodes. This dimension determines the

voltage necessary to achieve a particular field strength, and it has

arbitrarily been set at 2 mm.

The material from which the electrodes are made must have several

important properties. The most important of these, aside from being a

good conductor, is to have the ability to withstand high electric fields with little or no current emission. Two possible choices are nickel and tungsten. Nickel has been shown to withstand field strengths on the order of 5×10^7 v/m without excessive current emission (11). However from preliminary reports, it appears that with the proper conditioning tungsten can withstand fields of up to 10^8 v/m (11a). At the lower field strengths which will be used, tungsten electrodes should have less emission current than nickel, therefore the electrode material chosen will be tungsten and the maximum field strength will be 10^8 v/m.

Any molecular beam apparatus must have some provision for a source of molecules. It usually consists of an enclosure or oven with a small exit slit. The source material must often be maintained at a particular temperature and pressure, so that the oven must be equipped with both temperature and pressure controls. For instance in order to obtain molecular effusion rather than a gas jet, the source pressure should usually be less than .10 mm of Hg. There must also be some method for introducing and removing the sample without contamination. A good review of source requirements and design is given by Ramsey (7).

The velocity selector will consist of a set of 6 discs mounted on a rotating shaft. Each disc will have a given number of slots spaced uniformly around it. The distance L between the first and last discs will determine the speed of rotation necessary to select a particular molecular velocity. It is also used in conjunction with the collimator width to determine the angular dispersion and intensity of the beam. To allow for the intermediate rotational speed, L has been selected to be 1 meter. If very high speeds are available, L can be shortened to

increase the beam intensity. Other quantities such as slot size and slot separation will be left unspecified, to be determined by the intensity requirements of the particular sample under consideration.

Once the molecules have been deflected by the field, they must be detected. It is usually quite difficult to detect neutral particles, so the first step in the detection process is to ionize the molecules. Probably the easiest and most widely applicable method is to allow the molecular beam to pass through a crossed beam of electrons. The ensuing collisions then ionize the molecules. This type of ionizer is described in detail by Wessel (12), and its ionization efficiency has been estimated as 1/3000 for gold, silver, and potassium. For large hydrocarbons, the fraction of molecules ionized would probably be about this value, but the resulting current should be greater because there should be more ions per molecule.

After the molecules have been ionized, they can be detected by various methods. For very small currents a multiplier tube must be used. Of the many types of multiplier tubes, a particularly simple and highly sensitive one is described by Goodrich (13). This multiplier uses resistance strips in a magnetic field to produce a gain of up to 10^7. Coupling this with a very sensitive electrometer will give a detecting device which can measure currents as low as 10^{-19} amp, or about 1 electron/sec.

The detector must not only be able to detect small beam intensities, but must also be able to discriminate between the beam and the background. This is often done by the use of a pulsed beam and an appropriate electronic circuit designed to detect only the pulses. Coupling

this with a conventional mass spectrometer to isolate the beam ions from the background ions, Fricke (14) has been able to detect a beam when the ratio of beam density to background density was 3.33×10^{-6}.

In order for a molecular beam to travel several meters without encountering considerable scattering, it must be traveling in a high vacuum. The vacuum necessary will be determined by the resolution required of the spectrometer, since the beam will be broadened by collisions with residual molecules and since the beam must be detectable against the background. It will be assumed that a pressure of 10^{-8} mm of Hg will meet the necessary conditions.

To achieve pressures below 10^{-4} mm of Hg diffusion pumps must be used. These pumps require a forevacuum of 10^{-2} to 10^{-1} mm of Hg and it is usually supplied by a rotary mechanical pump. The gauges necessary to measure down to the desired pressure consist of a manometer and a McLeod gauge for the higher pressures and a hot cathode ionization gauge for the lower pressures.

The system will have to be constructed of materials which can be heated to fairly high temperatures. This bake out procedure removes adsorbed gas molecules and is necessary to achieve high vacuums. A very good discussion of general vacuum techniques as related to spectrometers is given by Tasman (15), and a step by step description of bake out procedures to obtain pressures as low as 5×10^{-11} mm of Hg for a particular ultra-high vacuum spectrometer is given by Reynolds (16).

CHAPTER IV

RESOLUTION

The resolving power of a spectrometer, which is selecting on the basis of a particular quantity, is defined as the reciprocal of the smallest fractional change in that quantity which can still be detected. For a particular spectrometer the resolving power depends on several things. Among these are the original size of the molecular beam, the spread of the beam due to different molecular velocities, the spread of the beam due to the different original directions, and the separation of the molecules by the force field. The resolving power will be the greatest when the ratio of the separation to spread is the largest. The separation can not be changed for a particular sample but the spreading effects can be decreased. However this does reduce the intensity, so that the ultimate resolution available is dependent on the minimum intensity that can be detected. In the subsequent sections a particular resolving power will not be calculated. Instead the restrictions will be found which will give the necessary resolution for any sample. It must then be determined for each sample whether or not these restrictions permit adequate intensities.

For the spectrometer under consideration using nonpolar molecules, selection can be made on the basis of either mass or polarizability. For polar molecules the effective dipole moment determines an effective polarizability which can also become the basis for selection. The nonpolar

case will be considered with the understanding that the results are applicable to simple polar molecules when the effective polarizability Ω is substituted for the polarizability α.

Velocity Spread

For circular motion and constant field conditions Eq. (III.8) gives the radius as a function of mass, velocity and polarizability. It can be rewritten as

$$R = K_2 \frac{mv^2}{\alpha} \qquad\qquad (IV.1)$$

where

$$K_2 = \frac{2r_m}{E_m 2} = \frac{\alpha}{K_1} .$$

Differentiating Eq. (IV.1) and dividing by R gives

$$\frac{dR}{R} = \frac{dm}{m} - \frac{d\alpha}{\alpha} + \frac{2dv}{v} .$$

For finite changes and average values this becomes

$$\frac{\Delta R}{R} = \frac{\Delta m}{m} - \frac{\Delta \alpha}{\alpha} + \frac{2\Delta v}{v} \qquad\qquad (IV.2)$$

which expresses the fractional change in the radius in terms of the fractional changes in the mass, polarizability, and velocity. If selection is to be made on the basis of polarizability then Δm should be made zero. Conversely, if the apparatus is to be a mass spectrometer, it would be desirable to have $\Delta \alpha$ equal to zero. In either case the fractional change in the radius should be due primarily to a change in the selecting quantity. This will be true in the first case if

$$\frac{\Delta \alpha}{\alpha} \geq 5 \left(\frac{2\Delta v}{v} \right)$$

and in the second if

$$\frac{\Delta m}{m} \geq 5(2\frac{\Delta v}{v}) = 10 \frac{\Delta v}{v} \qquad\qquad (IV.3)$$

Since these two conditions are similar, a particular resolution for mass changes will provide the same resolution for equal polarizability changes. Therefore the resolution will be considered in terms of mass changes only, with the assumption that $\Delta\alpha$ is negligible.

The restriction on the velocity spread as taken from Eq. (IV.2) was based on the assumption that all of the molecules entered the deflecting field at the same point traveling in the same direction, and as a result of their different masses, polarizabilities, and velocities, were forced to describe different paths. We shall now investigate the situation in which we have identical molecules with identical speeds, but which enter the field at different points along the x-axis, traveling in different directions. Following that, we shall consider the difficulties intro-duced by those molecules which do not enter along the x-axis of Fig. 3.

Angular Dispersion

Fig. 6 is a diagram of the entrance to the force field through collimation slits. The second slits are centered a distance R, equal to the radius of curvature of the field, from the center of curvature C. We assume that the velocity selector is adjusted to select molecules of velocity v_o and that the field strength is adjusted so that the deflect-ing force is equal to mv_o^2/R. Then any molecule entering the field at point H and headed normal to the slit opening will travel in a circle of radius R. Those molecules which do not enter the field at H or which do not head in a normal direction, are the ones to be considered.

There are two methods of attack which are applicable. One method
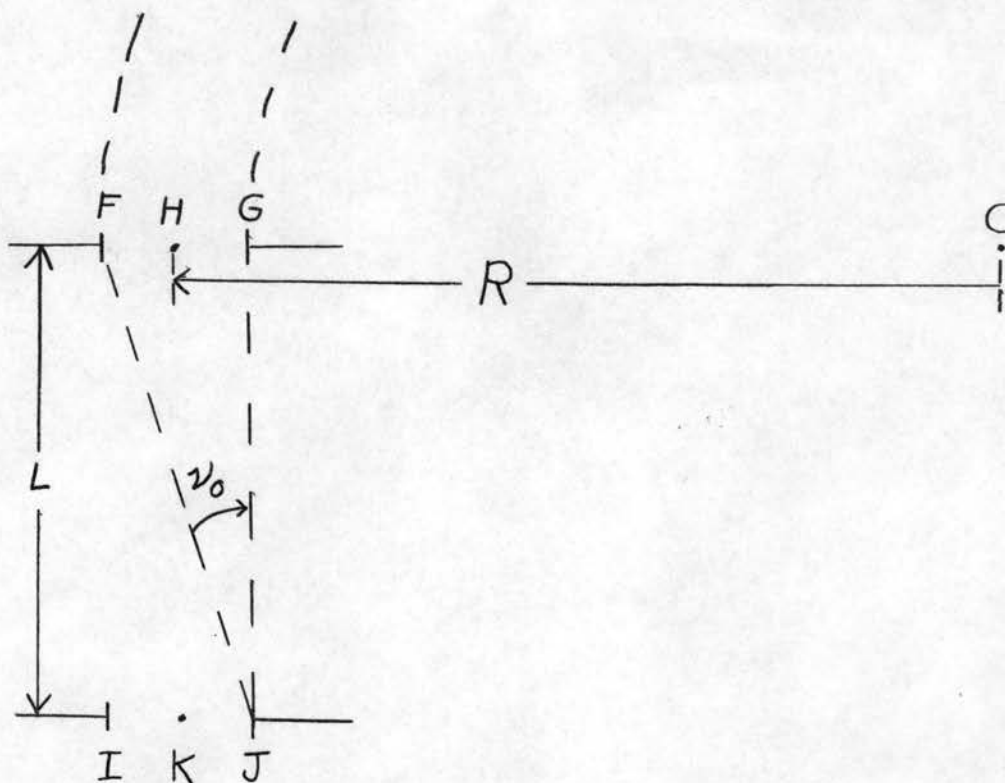
Figure 6 Entrance to Force Field Through Collimating Slits

is to try to determine the orbital equation by integration (17).
For some force fields the integration is not too difficult. But for a
constant force, the integral is an elliptic integral which must be bro-
ken up into three simpler integrals. When these other integrals are
evaluated, the result is so complicated that it cannot be solved explic-
itly.

The other method is to consider the noncircular paths as simple
slight deviations from a circular orbit. If the circular orbit is
stable, then a molecule which is displaced slightly from this orbit will
oscillate about the circular orbit, rather than spiral in or fly out.

To determine whether or not a circular orbit is stable, the one-
dimensional effective potential energy of the system must be considered.

If it is a minimum at the circular radius, then for small deviations the molecules will approximate simple harmonic motion in the radial coordinate. The effective potential will be a minimum if its second derivative is greater than zero.

For a constant force of K_1, the effective potential energy of a molecule is

$$U(r) = -K_1 r + h^2/2mr^2, \qquad (IV.4)$$

where h is the angular momentum of the molecule at a radius r from the center of curvature. The second derivative evaluated at the circular radius R is then

$$U''(R) = 3h^2/2mR^4 = K \qquad (IV.5)$$

which is of course greater than zero. Thus a constant central force does give rise to a stable circular orbit. $U''(R)$ is also the force constant K for the simple harmonic motion.

It can be shown that for any central force field of the form r^{-g}, the angle through which a molecule travels while making one complete oscillation about the circular orbit is given by (17)

$$\Psi_o = 2\pi/\sqrt{3-g} . \qquad (IV.6)$$

For a constant force field this gives

$$\Psi_o = 2\pi/\sqrt{3} = 208^o.$$

Now since the motion is approximately simple harmonic, the position of a molecule at any angle Ψ can be determined in terms of Ψ_o, if the initial position and direction are known. This means that the size of the beam can be calculated at any point. Since the separation of two different masses can also be calculated at any point, the path length

which gives the best beam resolution can be found.

Again consider the apparatus as shown in Fig. 6. Any molecule which passes through IJ and FG will enter the field, all others being blocked. The stable circular orbit occuurs, as previously noted, when the molecule enters along the normal path KH. The maximum angle of deviation v_o is that made by a molecule entering along IG or JF.

A molecule passing through FG at a distance x_o from H, the center of the slit, will have a radial velocity v_r and an angular velocity v_o depending on the angle v.

The total one dimensional effective energy is

$$\mathcal{E} = K\, x_o^2/2 + mv_r^2/2. \tag{IV.7}$$

When the displacement x from the circular orbit is a maximum, the energy is entirely potential and

$$\mathcal{E} = K\, x_m^2/2. \tag{IV.8}$$

Combination of Eq. (IV.5), (IV.7), and (IV.8) gives

$$x_m = (x_o^2 + R^2 v_r^2/3v_\theta^2)^{1/2}.$$

But v_r/v_θ is just the tangent of the angle v, so that

$$x_m = (x_o^2 + R^2 \tan^2 v/3)^{1/2}. \tag{IV.9}$$

From the figure it is seen that $\tan v_o = 2w/L$, where 2w is the width of the slits so that Eq. (IV.9) becomes

$$x_m = w(x_o^2/w^2 + 4R^2\tan^2 v/3L^2\tan^2 v_o)^{1/2}. \tag{IV.10}$$

This equation gives the maximum deviation for any initial position and direction in terms of the slit half-width w. For a particular value of x_o, $\tan v/\tan v_o$ can vary from zero to $(w + x_o)/2w$.

For simple harmonic motion the deviation x can be expressed as a function of time by

$$x = x_m \sin\left(\frac{2\pi t}{\tau} + \theta_o\right), \qquad (IV.11)$$

where τ is the period of oscillation and the phase angle θ_o is a constant. If $t = 0$ when the molecule crosses the second slit, then Eq. (IV.11) gives

$$x_o = x_m \sin \theta_o,$$

so that

$$\theta_o = \sin^{-1}(x_o/x_m). \qquad (IV.12)$$

Since

$$t/\tau = \Psi/\Psi_o$$

Eq. (IV.11) can be rewritten as

$$\frac{x}{w} = \frac{x_m}{w} \sin\left(2\pi\frac{\Psi}{\Psi_o} + \theta_o\right). \qquad (IV.13)$$

Here Ψ is the angle through which the molecule has traveled during the time t.

For any given initial conditions, x_m/w and θ_o can be calculated from Eqs. (IV.10) and (IV.12). Eq. (IV.13) can then be used to calculate x/w for any value of the path angle Ψ. When this is done for various combinations of initial conditions the maximum value obtained for x/w at a particular Ψ is a measure of the beam spread at that point. Then the ratio of the beam spread to the mass separation gives an estimate of the resolution. It is shown in appendix A that the separation S of two molecules with different masses traveling in circular orbits with differ-ent radii is given by

$$S = \Delta R \ (1 - \cos \Psi), \qquad\qquad (IV.14)$$

where ΔR is the difference in radii. The optimum angle of travel then

is that angle which gives the maximum ratio of separation to beam spread.

This will occur when the ratio

$$(1 - \cos \Psi)/(x/w)max$$

is a maximum. Table I shows calculated values of $(1 - \cos \Psi)$, $(x/w)max$,

and their ratio for different values of Ψ when $R = 2m$ and $L = 1m$. It is

seen from this data that the best resolution occurs at $\Psi = 104^{\circ}$. This is

just one half an angular period so that at this point the initial condi-

tions are duplicated and the beam width is equal to the entrance slit

width.

For adequate resolution it will be assumed that the separation must

be five times the maximum deviation. For $\Psi = 104^{\circ}$, this gives

$$S = 5w.$$

Eq. (IV.14) then becomes

$$w = (0.248)\Delta R. \qquad\qquad (IV.15)$$

Assuming no variation in velocity or polarizability, Eq. (IV.2) reduces

to

$$\Delta R = \frac{\Delta m}{m} R,$$

which gives

$$w = (0.248)\frac{\Delta m}{m} R. \qquad\qquad (IV.16)$$

For R equal to 2 meters, w becomes

$$w = (0.496)\frac{\Delta m}{m} \text{ meters}. \qquad\qquad (IV.17)$$

It is seen from this expression that the restriction on the slit half-

width w depends on the average mass and the change in mass of the sample

TABLE I

RATIO OF SEPARATION TO SPREAD AT DIFFERENT ANGLES FOR R = 2 METERS

Path Angle Ψ	Spread $(x/w)_{max}$	Separation $(1 - \cos \Psi)$	"Resolution Ratio" $(1 - \cos \Psi)/(x/w)_{max}$
20°	2.14	.060	.028
30°	2.42	.134	.055
40°	2.52	.234	.093
50°	2.38	.357	.150
60°	2.00	.500	.250
70°	1.45	.658	.454
80°	0.78	.826	1.060
90°	0.91	1.000	1.100
100°	0.98	1.174	1.198
104°	1.00	1.242	1.242
110°	1.40	1.342	.959
120°	1.97	1.500	.763
130°	2.34	1.643	.703
140°	2.51	1.766	.703

under consideration, so that the slit width must be made adjustable to give the spectrometer maximum flexibility.

Another restriction must also be placed on w. The maximum deviation must not be so great that the particles leave the field. This requires that $x_m \leq \dfrac{r_m}{2}$ at all positions along the path. From Table I, the largest value of $(\frac{x}{w})_m$ for R = 2m is 2.52. Thus the requirement on w is

$$w \leq \frac{r_m}{5.04} . \qquad\qquad (IV.18)$$

For a given substance, the calculations of w from Eq. (IV.16) and Eq. (IV.18) should be made and the smaller value chosen as the one to be used.

As will be discussed later, the beam cross section must have one dimension which is no greater than the mean free path of the molecules. This small dimension will be the height of the beam, rather than the width, and will normally be less than 1mm. By making this dimension variable, maximum intensity can be obtained for different oven pressures without affecting w and the resolution of the beam.

Off-Axis Deviation

Since the slit height must be of finite size, not all of the molecules will enter the field along the line $\theta = 0$, of Fig. 3. Those which enter off axis will experience a radial force in terms of the electrode coordinate system but the force will not be radial in terms of the radius of the spectrometer. The x-component of the force will serve as the centripetal force while the y-component will tend to draw the molecules from the x-axis. The farther they get off axis the stronger the y-component becomes. As a molecule moves farther off the axis, the centripetal

force decreases causing the molecule to move in the negative x direction. The pattern of the molecules should thus be similar to that shown in Fig. 7. The detector can then be set to pick up molecules along this pattern so that most of the intensity of the beam is received. However it may be that some or perhaps even many of the molecules will be pulled completely out of the force field and lost from the beam, while making the trip down the entire path of the spectrometer. If this were the case then it would be necessary to insert refocussing segments at selected intervals along the path. These segments would draw the molecules back toward the x-axis and might have a cross-section like either of those shown in Fig. 8. Although these do refocus in the y-direction, they necessarily cause dispersion in the x-direction. Several different shapes could be tested to see which gave the best refocussing to dispersion ratio.

It should be pointed out that this problem could be the most significant one concerning the spectrometer. It is the only one which could not be estimated and so must be left to experiment. Before a full-scale spectrometer is assembled, the y-dispersion of a circular segment of the isomotive field should definitely be measured.

For polar molecules in the proper rotational state this problem can be eliminated. When the effective polarizability Ω is negative, then the force on the molecule is radially inward in the electrode coordinate system. By constructing a spectrometer with an opposite curvature, this force can also be used as the centripetal force. Only now all of the off-axis molecules are forced towards the x-axis. This produces a focussing effect and increases the intensity of the beam.
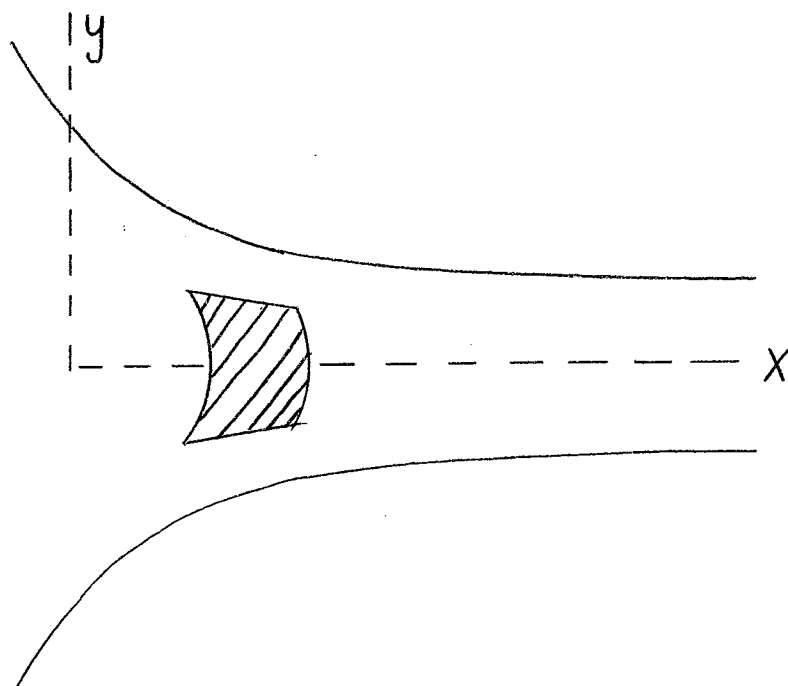
Figure 7 Beam Pattern Due to Off-Axis Defocussing
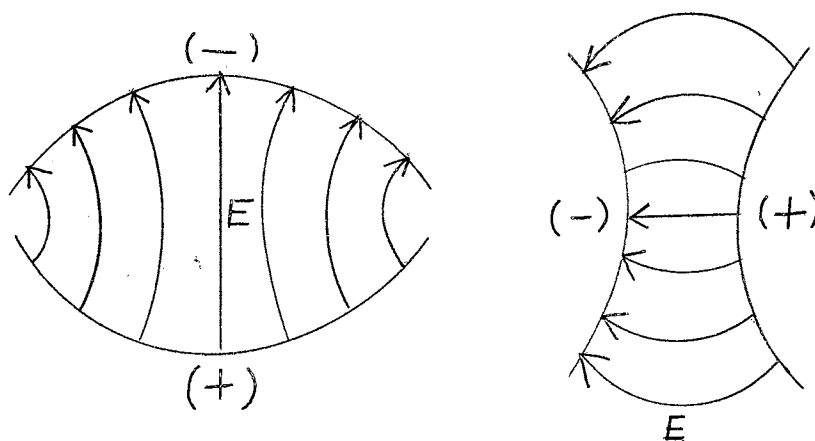
Figure 8 Possible Refocussing Segments

CHAPTER V

BEAM INTENSITY

One of the most critical points concerning any molecular beam appa-
ratus is that of intensity. This chapter will deal with the intensity
of the molecular beam and how it is affected by the velocity selector,
the scattering action of the residual gas, and the scattering action of
the cold cathode current between the electrodes.

Angular Distribution

Consider a chamber containing a gas or vapor with a small exit slit
of area, a. Molecules will emerge from the slit in all directions, but
the density will be the greatest in the direction normal to the slit
area. For this direction, elementary kinetic theory gives the rate at
which molecules pass through a collimator opening at a distance L and
also of area a , as

$$\eta = \frac{(1.18 \times 10^{22}) p a^2}{L^2 \sqrt{MT}} \text{ molec/sec,} \qquad (V.1)$$

where the pressure p is in mm of Hg and all other terms are in cgs units
(7). The intensity at this point is then just

$$I_o = \eta/a = \frac{(1.18 \times 10^{22}) p a}{L^2 \sqrt{MT}}. \qquad (V.2)$$

It should be noted that in the derivation of these equations it is
assumed that the source slit is small enough to allow molecular effusion

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rather than hydrodynamic flow. The strict requirement for this condition

is that the smallest slit dimension h be much less than λ, the mean free

path of the molecules. However in practice it is found that the source

is still effective if (7)

$$h \le \lambda. \qquad\qquad (V.3)$$

Velocity Distribution

The molecules which travel in the direction appropriate to pass

through the collimator will have a wide range of velocities. If it is

desired to use only molecules having velocities within a particular

range, some kind of velocity selector must be used to reject the unwanted

molecules. This selection reduces the intensity of the beam by an amount

which will now be considered.

The velocity distribution inside the source is given by the Maxwell

distribution law. If N is the total number of molecules per unit volume

in the source and dN is the number in the velocity interval v to v+dv,

then the Maxwell law gives

$$\frac{dN}{dv} = \frac{4Nv^2}{\sqrt{\pi}\,j^3} e^{-(v^2/j^2)} \qquad\qquad (V.4)$$

where j is defined in Eq. (III.9).

Since the probability of a particle being in the beam is proportion-

al to its velocity, Eq. (V.4) must be multiplied by v to obtain the ve-

locity distribution in the beam. The intensity dI of molecules in the

range v to v+dv is then

$$dI = v\ dN = \frac{4Nv^3}{\sqrt{\pi}\,j^3} e^{-(v^2/j^2)} dv.$$

Normalizing this equation to the total intensity I_o gives

$$dI = \frac{2I_o}{j^4} v^3 e^{-(v^2/j^2)} dv. \qquad (V.5)$$

Thus the intensity due to molecules with velocities between v_1 and v_2 can be obtained by integrating Eq. (V.5) between these limits. The fraction of molecules within this range is,

$$f_v = I/I_o = \left[(1 + v^2/j^2) \ e^{-(v^2/j^2)} \right]_{v_1}^{v_2} \qquad (V.6)$$

and the intensity of the beam is reduced by this amount.

It should be pointed out that the most probable velocity in the beam is not j, but is $\sqrt{3/2} \ j$. This can be seen by setting d^2I/dv^2 equal to zero from Eq. (V.5) and solving for v.

The fractional intensity for a particular velocity range of $v-\Delta v$ to $v+\Delta v$ may be easily found by expanding Eq. (V.6) into a simpler form. With $v_1 = v-\Delta v$, $v_2 = v+\Delta v$, $B = v/j$, and $X = \Delta v/j$, Eq. (V.6) becomes

$$f_v = \left[(1 + v^2/j^2) e^{-v^2/j^2} \right]_{j(B-x)}^{j(B+x)} \qquad (V.7)$$

Evaluation of this expression at the two limits when $x^2 \ll 1$, gives

$$f_v \approx 4B^3 x e^{-B^2}. \qquad (V.8)$$

Since x can be expressed by

$$x = B\frac{\Delta v}{v},$$

Eq. (V.8) becomes

$$I/I_o = f_v \approx 4B^4 e^{-B^2} \frac{\Delta v}{v} \qquad (V.9)$$

So that for a particular resolution determined by $\Delta v/v$, the intensity reduction depends on the velocity ratio B.

Intensity Reduction by Selector

A velocity selector not only reduces the intensity of a molecular beam by rejecting the molecules of the wrong velocity, but it also necessarily rejects some of the molecules with the correct velocity. This may be understood by considering an example velocity selector consisting of two rotating discs as shown in Fig. 9.

The selector operates on the principle that of all the molecules which go through the opening in the first disc, only those with the appropriate velocity will reach the second disc at the proper time to pass through the second opening. But the only molecules that are passed by the first disc are those which happen to reach it coincident with the slot. Thus even some of the molecules with the proper velocity will be excluded if they happen to strike the disc instead of the slot.

The fraction of the beam intensity which is allowed to pass the first disc is just the ratio of the area of the slot to the total area of the disc. If the slot is cut as a sector of angle θ, the fraction becomes simply

$$f_s = \theta / 2\pi$$

If there are n slots in the disc, f_s becomes

$$f_s = n\theta / 2\pi. \tag{V.10}$$

In the construction of a velocity selector, one needs to consider the number of slots, the width of the slots, and the separation between them. The number of slots should be the maximum possible for the required width and separation.

Referring to the figure, a molecule with velocity v_o and grazing
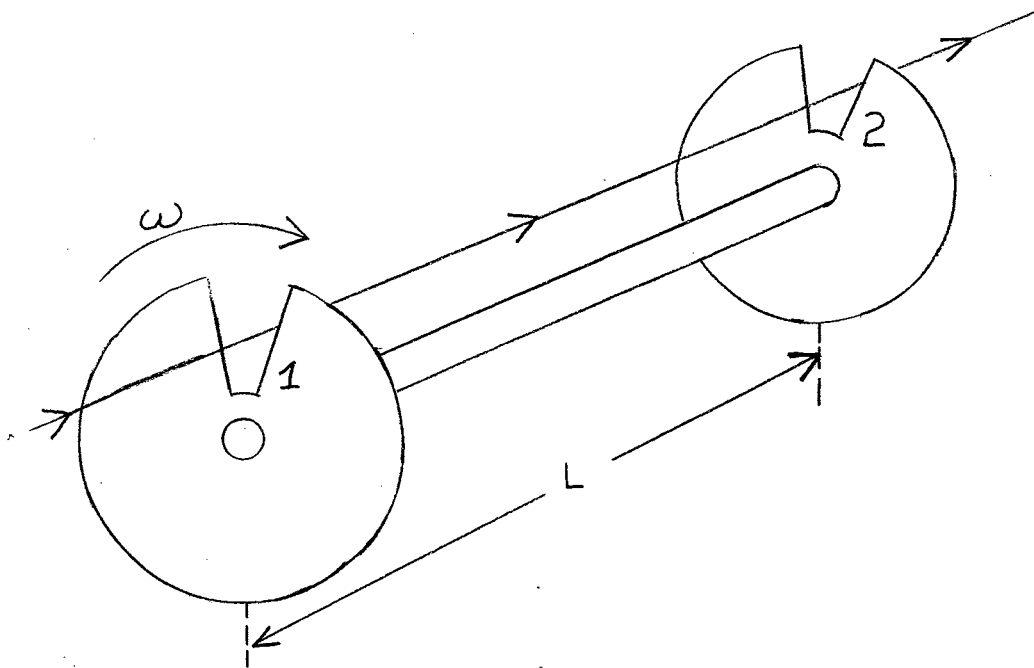
Figure 9   Two-Plate Velocity Selector - Side View

the left edge of slot 1 will reach the second disc after a time

$$t_o = L/v_o \ .$$

It will just graze the left edge of slot 2 if the speed of rotation of the discs is

$$\omega = \varphi/t_o = \varphi v_o/L \ , \qquad\qquad (V.11)$$

where φ is the phase angle between slot 1 and slot 2.

If the molecule is traveling at a faster velocity v_+, such that it just grazes the right edge of slot 2, then its time of travel is

$$t_+ = L/v_+$$

and the phase angle turned by disc 2 during this time is

$$\varphi - \theta = \omega t_+ = \omega L / v_+ \quad . \tag{V.12}$$

This is the minimum angle through which disc 2 can turn and still allow a molecule to pass through the correct slot. The velocity deviation is then given by

$$\Delta v = v_+ - v_o = \frac{\omega L}{\varphi - \theta} - \frac{\omega L}{\varphi} = \frac{v_o \theta}{\varphi - \theta} \quad . \tag{V.13}$$

If θ is much less than φ, the fractional deviation is

$$d = \frac{\Delta v}{v_o} \approx \frac{\theta}{\varphi} \quad . \tag{V.14}$$

The path difference due to this deviation must be small enough to be negligble when compared to the deviation due to mass difference.

It is desirable to have the spacing between the disc slots as small as possible, since for a given slot size, the closer the slots, the greater the intensity of the beam. However if the slots are too close together, molecules with velocities not too different from the one being selected will be passed by going through a slot in the second disc adjacent to the correct one, thus producing velocity side bands. Let δ be the angle between slots as shown in Fig. 10. Then for a molecule to go through a slot in disc 2 adjacent to the correct slot, it must have a velocity such that φ is either increased or decreased by an amount equal to δ, during the molecules time of flight. For the first case,

$$\varphi + \delta = \frac{\omega L}{v'_-} \tag{V.15}$$

where v'_- is the velocity of the molecule and is less than the desired velocity v_o. Here it is assumed that $\theta \ll \delta$. Using Eqs. (V.11) and (V.15) the deviation becomes
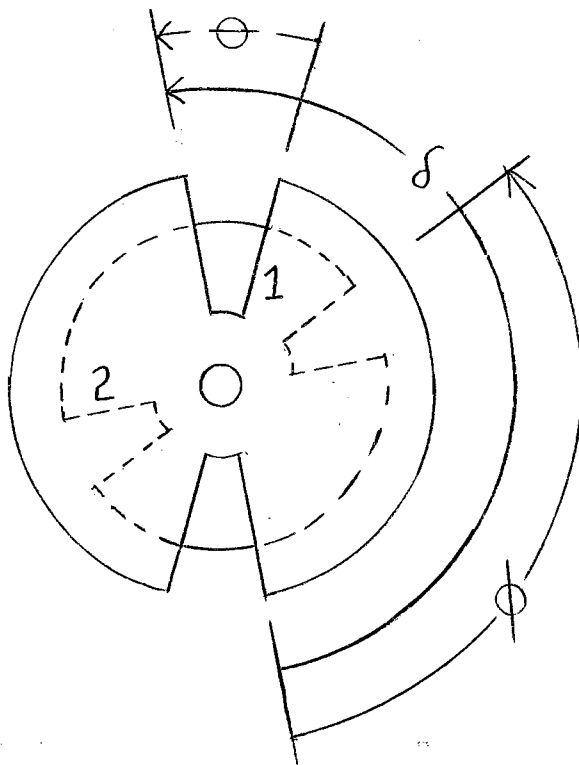
Figure 10 End View of Velocity Se-
lector Showing Sector
Angle θ, Phase Angle φ,
and Angle Between Slots
δ.

$$\Delta v' = v_o - v'_- = \frac{\omega L}{\varphi} - \frac{\omega L}{\varphi + \delta} = \frac{v_o \delta}{\varphi + \delta} \qquad (V.16)$$

and the fractional deviation is

$$d' = \frac{\Delta v'}{v_o} = \frac{\delta}{\varphi + \delta} \qquad (V.17)$$

Combining Eqs. (V.14) and (V.17) gives the ratio of slot size to slot

separation as

$$\frac{\theta}{\delta} = \frac{d(1-d')}{d'} \qquad (V.18)$$

It should be stressed that Eqs. (V.17) and (V.14) are not consider-

ing the same deviation. Eq. (V.14) considers molecules with different

velocities passing through the same slots, while Eq. (V.17) is concerned
with molecules whose velocities are so different that they pass through
adjacent slots in the second disc after entering through the same slot
in the first disc. The fractional deviation d must be made so small
that it is negligible and d' must be so large that its effects would not
be confused with those due to mass differences. Any velocity between v_-
and v'_- could not pass through the slot system and so these do not have
to be considered.

The relative values of θ, δ, d, and d' must now be estimated. Re-
calling Eqs. (IV.3) and (V.14), we see that for good resolution we must
have

$$\frac{\Delta m}{m} \geq 10d = 10\frac{\theta}{\varphi} \, . \tag{V.19}$$

The requirement that the effect of d' be unimportant will be satisfied
if the mass separation is no greater than one-fifth the velocity separa-
tion. That is if

$$5\frac{\Delta m}{m} \leq 2d'$$

or

$$d' \geq 2.5\frac{\Delta m}{m} \, . \tag{V.20}$$

When the equality signs hold in Eqs. (V.19) and (V.20), Eq. (V.18) be-
comes

$$\frac{\theta}{\delta} = \frac{(1 - 2.5\Delta m/m)}{25} \, . \tag{V.21}$$

For molecules with molecular weight of over 50, and for small changes in
mass number, this is approximately

$$\frac{\theta}{\delta} \approx \frac{1}{25} \, . \tag{V.22}$$

And since δ is equal to $2\pi/n$, Eq. (V.10) gives the fractional intensity passed by the selector as just

$$f_s = \theta/\delta \approx 1/25 \ . \tag{V.23}$$

The preceding derivation for d', beginning with Eq. (IV.16), has been for molecules with velocities slower than the desired velocity by an amount necessary to allow them to pass through an adjacent slot. If we consider those molecules which have velocities greater than v_o which pass through an adjacent slot, then Eq. (V.21) takes the form

$$\frac{\theta}{\delta} = \frac{(1 + 2.5\Delta m/m)}{25} \ ,$$

which also reduces to Eq. (IV.22) for large molecules. For small molecules or large mass changes, this simplification is not correct. The result is that the resolution is not as good as predicted, in that the mass difference effect is of the same order as the effect of the velocity side bands. Eq. (V.21) must then be used to determine the ratio of θ to δ.

By using selectors with more than just two plates, the ratio can be increased without decreasing the resolution. In fact if N_p is the number of plates, evenly spaced, then Eq. (V.21) must be multiplied by (N_p-1); that is

$$f_s = \theta/\delta = \frac{(N_p-1)(1 - 2.5\Delta m/m)}{25} \ . \tag{V.24}$$

So that for a six-plate selector,

$$f_s = \theta/\delta = \frac{(1 - 2.5\Delta m/m)}{5} \approx 0.2 \ . \tag{V.25}$$

Scattering

Two final problems to be considered concerning intensity reduction

are the scattering of the molecules out of the beam by the residual mole-
cules in the system and the scattering by the current between the elec-
trodes. The residual molecules will be considered first.

The probability that a molecule will pass through a distance 1
without experiencing a collision is given by

$$P = e^{-1/\lambda} \qquad\qquad (V.26)$$

where λ is the mean free path of the molecule. At a pressure of 10^{-6} mm
of Hg the mean free path of the air at room temperature is 300 m (7).
For laboratory distances, P is very nearly unity. For example with 1 =
3m, P is .990. Therefore it is concluded that the intensity is not
appreciably affected by the residual gas, and so will not be considered
further.

When two separated electrodes are subjected to very high electric
fields, a current flows across the gap between them. This cold cathode
emission, which has been treated extensively in the literature, could
cause considerable scattering of the molecular beam (11, 18-21). The
amount of current is given theoretically by the Fowler-Nordheim theory
and it is dependent on the electric field strength (22). But it has
been found experimentally that the current for large electrodes is con-
siderably larger than that predicted by theory. A good review article
on cold cathode emission has been presented by Alpert (18).

The current across extended nickel surfaces has been measured by
Brodie (11) for various field strengths and the result was an exponent-
ially varying current which was affected only slightly by the method of
surface polishing. The current density varied from about 10^{-8} to $2x10^{-6}$
amp/cm^2 as the field was varied from 2.6x10^7 to 4.0x10^7 v/m. Thus at

the higher field of 4.0×10^7 v/m, the current across electrodes with sur-faces of area 10^3 cm^2, which is slightly larger than the proposed spec-trometer electrode area, is about 2.0 milliamp. To see what effect this current will have on the molecular beam, consider the ionizer discussed by Wessel (12), which uses a crossed electron beam to ionize a molecular beam. It is estimated that the apparatus ionizes about 1 out of every 3000 molecules when the electron current is from 3 to 15 milliamp. If it is assumed that for every ten molecule-electron collisions there is only one molecule ionized, then the collision ratio is one out of every 300 molecules.

Applying these results to the spectrometer electrodes, the colli-sion ratio should be less than 1/300 because the current is smaller and the electrons are faster than for the ionizer. Therefore it is assumed that the cold cathode current is too small to interfere significantly with the intensity of the molecular beam.

CHAPTER VI

APPLICATION TO EXAMPLES

Having described the spectrometer and presented the various re-
strictions in general terms, we now proceed to calculate the intensi-
ties of several example molecules when these restrictions are met. We
shall consider the nonpolar molecules methane and napthalene and the
polar molecule hydrogen chloride in its two lowest attractive rotational
states, with the results summarized in Table II.

Methane

Methane is a simple molecule with tetrahedral symmetry. It will
therefore have a practically isotropic polarizability of $3.10 \times 10^{-40} \text{Coul}^2$-
m/Nt-Molecule.

For good molecular effusion, the source pressure should not be
greater than 0.1 mm. of Hg. The vapor pressure of methane is 0.1 mm. of
Hg at a temperature of 59° K, so it is at this temperature that the
calculations will be made.

The mean free path of methane at a pressure of 0.1 mm. of Hg and
a temperature of 59° K is about 0.1 mm. This restricts the source slit
height to be 0.02 cm. For methane, Eq. (IV.18) places the restriction
on the slit width 2w to be 0.9 cm. This gives an area of $1.8 \times 10^{-2} \text{ cm}^2$.
The intensity I_o of the beam as it enters the field is then given by Eq.
(V.2) to be 6.53×10^{13} molec $/\text{cm}^2$- sec.

The most probable source velocity at $59°$ is 2.46×10^4 cm/sec. Solving Eq. (III.10) for B with a maximum field strength of 4×10^7 v/m gives $B = 0.11$. This corresponds to selecting a velocity of 2.71×10^3 cm/sec. From Eqs. (IV.3) and (V.9) we see that this leads to a value for the fractional reduction of intensity f_v of 3.68×10^{-6}. For a six plate velocity selector, the intensity reduction f_θ in Eq. (V.25) is about 0.2. Thus the intensity I' of the beam as it enters the field is just the product $I_o f_v f_\theta$ which is 2.4×10^7 molec/cm^2-sec.

Assuming that there is little scattering of loss of molecules in the field, this same intensity will occur at the detector. To determine if this intensity is detectable, it must be compared to the density of the residual gas. The density of the beam is the intensity divided by the velocity and is equal to 8.90×10^3 molec/cm^3. The density of the residual gas at 10^{-8} mm of Hg is 3.21×10^8 molec/cm^3, which gives a signal-noise ratio of 2.78×10^{-5}. A measurable ratio is given by Fricke (14) as 3.3×10^{-6}.

The inefficiency of the ionizer will further reduce the intensity by a factor of 10^{-3} to 2.4×10^4 ions/cm^2-sec. This corresponds to a current of 6.9×10^{-17} amp, which can be easily detected with the aid of a multiplier tube.

Using Eqs. (V.19), (V.23), and (V.11), we get a set of selector parameters which will select a velocity of 2.7×10^3 cm/sec. These include a slot size of $\pi/10$, with 4 slots per disc, a selector length of 100 cm, a phase angle of 8 rev., and an angular velocity of 1.30×10^4 rpm.

The voltage requirement, taken from Eq. (III.7) turns out to be 4.0×10^4 v for $M = 16$. For a mass number of 17, the change in voltage is given by Eq. (III.11) as 1.23×10^3 v.

Napthalene

We now extend the range of consideration to a more complicated substance. Napthalene is a two ring organic compound with some planar symmetry but without the spherical symmetry of methane. This leads to an anisotropic polarizability, but for the sake of calculations, it is assumed that a napthalene molecule will exhibit an average polarizability approximately equal to that obtained from dielectric constant measurements. This value is 1.67×10^{-39} $Coul^2$-m/Nt. Since this is considerably higher than the polarizability of methane, it might seem that the effects in the spectrometer would be more pronounced. This however is not the case. Napthalene requires a much higher temperature to achieve comparable vapor pressures and so requires a larger polarizability to offset the higher molecular velocities. The higher velocities also require greater intensities to give measurable signal to noise ratios.

When the vapor pressure of napthalene is 0.10 mm, the temperature is 300° K. Since $\frac{\Delta m}{m}$ is quite small, Eq. (IV.17) is used to calculate a slit width of 0.778 cm. With these conditions the intensity at the field entrance without velocity selection is 1.11×10^{13} $molec/cm^2$-sec. Using an applied field of 7.05×10^7 v/m, a velocity fraction B of 0.20 can be obtained. This corresponds to an intensity reduction of 4.84×10^{-6}. Again assuming the intensity reduction due to the selector to be 0.20, we get the intensity at the field entrance with velocity selection to be 1.07×10^7 $molec/cm^2$-sec. At a background pressure of 10^{-8} mm, the resulting signal to noise ratio is 8.44×10^{-6}. After ionization the intensity is 1.07×10^4 $molec/cm^2$-sec, which gives a detector current of 1.67x

10^{-17} amp. If there is more than one ion produced per molecule, then the current will be correspondingly increased.

A possible set of velocity selector parameters is to have 40 slots per disc, a slot size of $\pi/100$, an angular velocity of 1.55×10^5 rpm, and a phase angle of 6.5 rev.

The voltage required to produce the necessary field is 7.05×10^4 v and the difference in voltage between the selection of mass numbers 128 and 129 is 274 v.

Other Nonpolar Molecules

From the above calculations, it is seen that the electric field spectrometer is applicable to methane and napthalene. By comparing the properties of these materials to those of other materials, it seems likely that the spectrometer could be applied to a wide range of compounds. For example, there are several common organic molecules which have a polarizability nearly equal to that of napthalene and have smaller molecular weights and higher vapor pressures. Among these are cyclopentane, hexane, cyclohexane, n-heptane, and benzene. N-octane has a polarizability even larger than napthalene and should be a very satisfactory sample. There are also many inorganic compounds with high polarizabilities, but their molecular weights are too large and their vapor pressures too low to produce adequate intensities.

Hydrogen Chloride

Hydrogen chloride is a linear molecule with a permanent dipole moment. It has a small moment of inertia so that at reasonably low

temperatures only the first few rotational states are significantly occu-
pied. It has a sizable dipole moment of 3.50×10^{-30} Coul-m, so that it
is a good sample molecule. The first calculations will be for the lowest
rotational state of $J = 0$.

When the vapor pressure of HCl is 0.10 mm of Hg, the temperature is
110° K. With a source slit area of 0.90 cm^2, the intensity of the beam
without velocity selection is 3.19×10^{13} molec/cm^2-sec. The moment of iner-
tia of HCl is 2.72×10^{-47} kg-m^2, so that the effective polarizability Ω
of the state as given from Eqs. (II.5) and (II.6) is 1.00×10^{-38} $Coul^2$-m/
Nt.

With a field strength of 4.0×10^7 v/m, the velocity fraction B can
be 0.459. This corresponds to an intensity reduction of 3.72×10^{-4}. The
reduction by the selector and the ionizer is again assumed to be 0.20
and 10^{-3} respectively. For polar molecules there is a further reduction
since, according to Eq. (II.8), only a fraction of the molecules occupy
the correct state. For the $J = 0$ state, at a temperature of 110° K,
this fraction f_Q is 0.130. Including all of these intensity reductions,
the detector current turns out to be 8.90×10^{-16} amp and the signal to
noise ratio is 9.53×10^{-5}. The voltage required is 4.0×10^4 v and to
change mass numbers from 36 to 37 takes a voltage change of 552 v. A
suggested set of velocity parameters is included in Table II.

The next rotational state which exhibits a positive effective polar-
izability is the degenerate state determined by $J = 1$, $M = \pm 1$. The cal-
culations for this state and the lowest state are largely identical.
Using the same values for slit size, source pressure and source tempera-
ture, we get the same initial intensity I_o. But since the effective

polarizability is now smaller, the same field strength can be used only for slower molecules. This is evident from the smaller velocity ratio of 0.251, which reduces the final beam intensity. The detector current is 1.47×10^{-16} amp with a signal to noise ratio of 2.82×10^{-5}. The voltage requirements and velocity selector parameters are the same as for the lowest rotational state.

TABLE II

SAMPLE CALCULATIONS

Symbol	Meaning	Units	Methane	Napthalene	HCl $J=0$	HCl $J=1, M=\pm 1$
R	Radius of beam path	m	2	2	2	2
r_m	Maximum electrode radius	cm	2.5	2.5	2.5	2.5
Ψ	Angle of curvature	degrees	104	104	104	104
P_o	System pressure	mm of Hg	10^{-8}	10^{-8}	10^{-8}	10^{-8}
ρ_o	Density of background	$\dfrac{molec}{cm^3}$	3.21×10^8	3.21×10^8	3.21×10^8	3.21×10^8
M	Molecular weight	amu	16.04	128	36	36
$\dfrac{M}{\Delta M}$	Resolving power for unit ΔM	---	16	128	36	36
α or Ω	Polarizability	$\dfrac{Coul^2 - m}{Nt}$	3.10×10^{-40}	1.67×10^{-39}	1.00×10^{-38}	3.00×10^{-39}
P	Source pressure	mm of Hg	0.10	0.10	0.10	0.10
T	Source temperature	$^{\circ}K$	59	300	110	110
2h	Source slit height	cm	0.020	0.025	0.020	0.020
2w	Source slit width	cm	0.90	0.778	0.90	0.90
a	Source and collimator slit area	cm^2	1.80×10^{-2}	1.95×10^{-2}	1.80×10^{-2}	1.80×10^{-2}
L	Source to field distance	cm	100	100	100	100
I_o	Intensity at field without veiocity selection	$\dfrac{molec}{cm^2 - sec}$	6.53×10^{13}	1.11×10^{13}	3.19×10^{13}	3.19×10^{13}

TABLE II (CONTINUED)

Symbol	Meaning	Units	Methane	Napthalene	HCl J=0	HCl J=1, M=±1
j	Most probable source velocity	$\frac{cm}{sec}$	2.46×10^{4}	1.98×10^{4}	2.25×10^{4}	2.25×10^{4}
E_m	Maximum field strength	$\frac{volt}{m}$	4.0×10^{7}	7.05×10^{7}	4.0×10^{7}	4.0×10^{7}
B	Selected velocity ratio	---	0.11	0.20	0.459	0.251
v	Selected veolcity	$\frac{cm}{sec}$	2.71×10^{3}	3.96×10^{3}	1.03×10^{4}	5.65×10^{3}
$\frac{\Delta v}{v}$	Fractional velocity spread	---	6.25×10^{-3}	7.82×10^{-4}	2.78×10^{-3}	2.78×10^{-3}
f_v	Fraction with correct velocity	---	3.68×10^{-6}	4.84×10^{-6}	3.72×10^{-4}	4.07×10^{-5}
f_θ	Fraction passed by selector	---	0.20	0.20	0.20	0.20
f_Q	Fraction with correct J, M	---	---	---	0.130	0.197
I'	Intensity at field with velocity selection	$\frac{molec}{cm^{2}-sec}$	2.40×10^{7}	1.07×10^{7}	3.09×10^{8}	5.11×10^{7}
ρ	Beam density	$\frac{molec}{cm^{3}}$	8.90×10^{3}	2.70×10^{3}	3.06×10^{4}	9.06×10^{3}
$\frac{\rho}{\rho_o}$	Beam to background ratio	---	2.78×10^{-5}	8.44×10^{-6}	9.53×10^{-5}	2.82×10^{-5}
f_i	Fraction of molecules ionized	---	10^{-3}	10^{-3}	10^{-3}	10^{-3}
I	Ion intensity at detector	$\frac{ions}{cm^{2}-sec}$	2.40×10^{4}	1.07×10^{4}	3.09×10^{5}	1.47×10^{-16}
i	Detector current	amp	6.90×10^{-17}	1.67×10^{-17}	8.90×10^{-16}	1.47×10^{-16}

TABLE II (CONTINUED)

Symbol	Meaning	Units	Methane	Napthalene	HCl J=0	HCl J=1, M=±1
V	Voltage	Volts	4.00×10^4	7.05×10^4	4.00×10^4	4.00×10^4
ΔV	Change in voltage for mass change of 1 amu	Volts	1.23×10^3	274	552	552
n	Slots per disc in velocity selector	---	4	40	24	24
θ	Slot angle	Radians	$\frac{\pi}{10}$	$\frac{\pi}{100}$	$\frac{\pi}{60}$	$\frac{\pi}{60}$
ω	Selector velocity	rpm	1.30×10^4	1.54×10^4	1.86×10^4	1.02×10^4
φ	Phase angle	Radians	16π	13π	6π	6π

CHAPTER VII

CHARACTERISTICS OF A STRAIGHT TRACK

Up to this point, the spectrometer has been assumed to be circular in shape. We would now like to diverge and consider briefly the possibility of using a straight beam path or track.

For a constant sideways force K_1, the deflection S of a molecule after traveling a distance D is given by

$$S = \frac{K_1 D^2}{2mv^2} \qquad (VII.1)$$

where m is the mass and v is the original velocity. For the isomotive field, the force is

$$K_1 = \frac{\alpha E m^2}{2r_m} ,$$

so that the deflection becomes

$$S = \frac{\alpha E m^2 D^2}{4mr_m v^2} . \qquad (VII.2)$$

The fractional change in deflection is then approximately

$$\frac{\Delta S}{S} = \frac{\Delta \alpha}{\alpha} - \frac{\Delta m}{m} - \frac{2\Delta v}{v} . \qquad (VII.3)$$

This result is just the negative of the result for the circular case given in Eq. (IV.2) so that the same restrictions on $\frac{\Delta v}{v}$ apply.

An advantage of a straight track over the circular arrangement is that the off-axis behavior of the molecules is known. Since the force

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radial, all of the molecules will be displaced radially and the y co-ordinate of a molecule after a radial displacement S is given by

$$y = \frac{y_o (S + r_o)}{r_o},$$
(VII.4)

where r_o and y_o determine the initial position of the molecule. Since the molecules which lie off-axis are not deflected in the x direction as much as those lying on the axis, an entering beam of curved cross-section can be made to emerge with the curvature removed. An illustration of this is given in Fig. 11.

One disadvantage of the straight track arrangement is that there is no oscillation about a stable path so that the beam continues to spread as it travels. Another disadvantage is that the deflection of the mole-cules is limited to the width of the electrode system. Then in order to obtain a large deflection so that a moderate change in deflection can be observed, a large apparatus must be constructed.

Since the apparatus selects molecules on the basis of their mass, polarizability and velocity, it is suggested that it be considered as a velocity selector for nonpolar molecules. It would be more efficient than the usual velocity selectors because it would pass every molecule with the proper velocity. This is in contrast to the rotating disc type which, for the restrictions discussed in Chapter V, passes only 20% of the proper molecules.

If the mass and polarizability of the molecule is known, then the electric field required to select a particular velocity at a deflection S is given in Eq. (VII.2). If the mass or polarizability is not known then the selector may be "calibrated" by combining it with a conventional

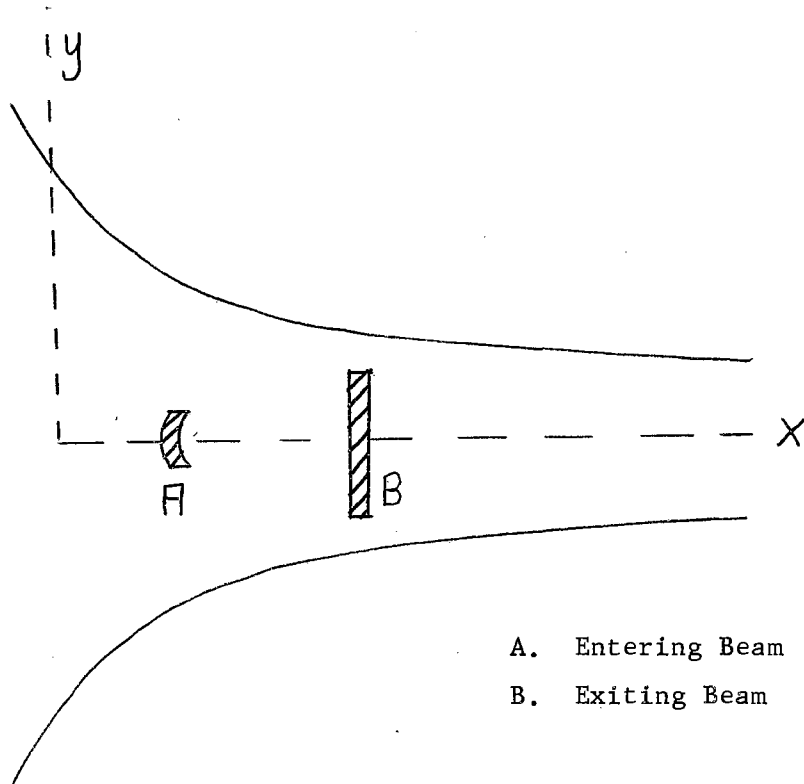Figure 11   End View of Entering Beam With Curved
            Cross-Section and Exiting Beam With
            Curvature Removed.

velocity selector set at the desired velocity and then adjusting the

voltage until the molecules pass through the exit slit. Of course, the

spectrometer could only be used as a velocity selector for molecular

beam experiments which were not concerned with the polarizability.

CHAPTER VIII

SUMMARY AND DISCUSSION

It has been suggested that a new molecular beam spectrometer might
be possible which uses a constant force field to produce dielectrophore-
sis. This isomotive force field has been derived and a general descrip-
tion of the auxillary equipment has been given. Some of the problems
concerning the feasibility of the spectrometer were considered, and then
calculations were made for selected samples.

From the results of the calculations in Chapter VI, it appears that
a spectrometer operating with an isomotive field is feasible for some
molecules and could be of significant value. It would select on the
basis of mass, polarizability, dipole moment, velocity, or rotational
state of the sample molecules.

It may seem that the instrument is just barely feasible since the
electric fields are very high and the intensities are quite low. But
it must be remembered that the restrictions placed on the beam to insure
good resolution for mass separation were somewhat stringent. In practice
these could probably be relaxed, especially if only approximate measure-
ments are to be made instead of separations. By relaxing these condi-
tions, the intensities could be increased and the field strengths de-
creased.

Another point to be noted is that even though the beam-to-background
density ratios are only slightly above the minimum as given by Fricke

(14), they can be increased by lowering the background pressure of the system. About the lowest pressure which can be conveniently obtained is the 5×10^{-11} mm of Hg used by Reynolds (16) in his mass spectrometer. At this pressure the ratios are increased by a factor of 200 which would then be easily detectable. Since the detector currents are several orders of magnitude above the minimum detectable current, the beam intensities as already calculated should be more than sufficient at the lower pressures.

A final point concerning the feasibility of the circular track spectrometer should be mentioned again. That is the problem of the possible loss of molecules which do not enter the field along the electrode axis. If this loss, which is discussed in Chapter IV, is appreciable, despite the use of refoccussing segments, then the intensity of the beam might be too small to be detected. If this were the case, then the circular track arrangement would be unworkable and the straight track geometry would have to be used.

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APPENDIX A

Separation Between Two Circular Paths

Assume that two molecules traveling in circles of different radii R_1 and R_2 enter the field at the same point. From the R_2 triangle of Fig. 12, we see that

$$S + L + 2d \cos \Psi = [R_2^2 - d^2 \sin^2 \Psi]^{1/2}.$$

From the R_1 triangle we get

$$L = [R_1^2 - d^2 \sin^2 \Psi]^{1/2}.$$

Combining these two equations gives the separation as

$$S = [R_2^2 - d^2 \sin^2 \Psi]^{1/2} - [R_1^2 - d^2 \sin^2 \Psi]^{1/2} - 2d \cos \Psi.$$

If

$$d^2 \ll R_1^2,$$

then S is approximately given by

$$S \cong R_2 - R_1 - 2d \cos \Psi.$$

But since

$$2d = R_2 - R_1 = \Delta R,$$

this equation becomes
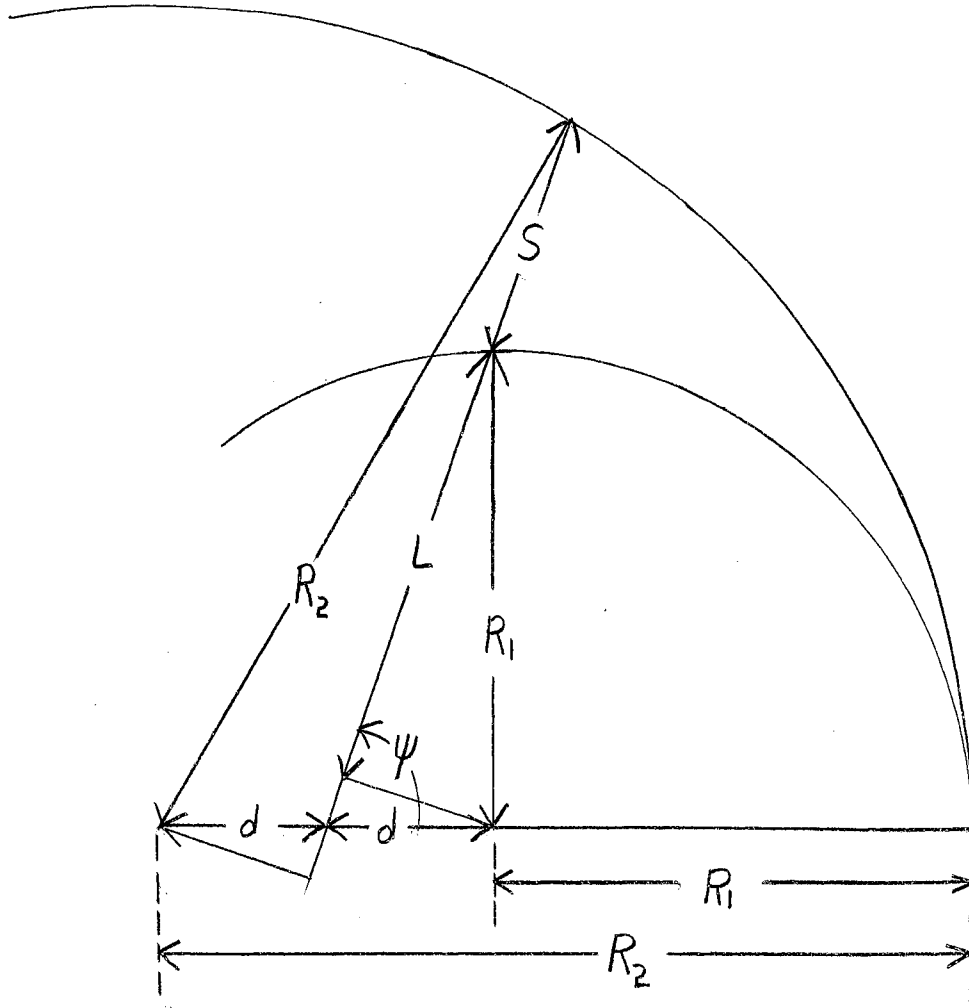
$$S \cong \Delta R (1 - \cos \Psi).$$

Figure 12   Separation Between Two Circular Paths Having the
Same Initial Point.

APPENDIX B

Definition of Symbols

A   Moment of inertia; Constant of integration

a   Area of source, collimator, and detector slits

B   Velocity fraction, v/j

D   Length of straight track spectrometer

d   Fractional velocity deviation

d'   Nearness to first velocity side band

$\vec{E}$ Electric field strength

$\vec{E}_m$ Maximum field strength in region

$\mathcal{E}_o$ Energy of a rotating molecule

$\mathcal{E}_r$ Energy of rotating molecule in electric field

$\vec{F}$ Force

f_i Fraction of molecules ionized

f_Q Fraction of molecules in selected rotational state

f_s Fraction of molecules passed by first disc of selector

f_v Fraction of molecules in selected velocity range

h   Angular momentum; Planck's constant; slit height

I   Beam intensity

I_o Beam intensity without velocity selection

I'   Beam intensity with velocity selection

i   Detector current

J   Angular momentum quantum number

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j   Most probable molecular velocity in source

K   Force constant for simple harmonic motion

K_1 Constant force in isomotive field

k   Boltzmann's constant

L   Source-to-collimator distance

M   Molecular weight; electric quantum number

m   Mass

N   Molecular density of source in molecules/volume

N_p Number of plates in velocity selector

n   Integration constant; number of slots per selector disc

η Rate of molecules passing a given area

P   Pressure

R   Radius of curvature of spectrometer

r_m Maximum electrode dimension

S   Separation between molecules; molecular deflection

T   Temperature

t   Time

U   One-dimensional effective potential energy

V   Electric potential

ΔV Change in V needed to select a different M

v   Molecular velocity

v_r Radial velocity

v_θ Angular velocity

w   Slit half-width

x   Displacement from the circular orbit; cartisian coordinate

x_o Initial displacement from circular orbit

x_m Maximum displacement from circular orbit

α Polarizability

δ Angle between disc slots

θ Angular size of disc slots

θ_m Angle corresponding to r_m

θ_o Phase angle

λ Mean free path

μ Effective dipole moment

μ_o Permanent dipole moment

υ Angle of entrance into field

ρ Beam density

ρ_o Background density

τ Period of oscillation

φ Phase angle between first and last selector discs

Ψ Path angle

Ψ_o Angular period of oscillation

Ω Effective polarizability of a permanent dipole

ω Angular velocity of selector

∇ Del operator

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