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MOLECULAR RAYS

WORTH H. RODEBUSH
CHEMISTRY DEPARTMENT, UNIVERSITY OF ILLINOIS

INTRODUCTION

IT HAS been recognized for a long time that peculiar effects are to be expected in gases at very low pressure where the mean free path is large compared to the dimensions of the containing vessel. These effects had been observed in the evaporation of metallic atoms from hot filaments, where for example, if an object is placed between the filament and the wall, no metallic deposit is produced on the part of the wall that is in the "shadow" of the object.

Apparently the first experiments with a unidirectional beam of molecules were made by Dunnoyer.[1] The first serious experiments with molecular beams were made in 1919 by Professor Otto Stern at the Institute of Theoretical Physics at Frankfurt.[3,4,5] Stern formed this molecular beam by evaporating silver atoms through slits. He demonstrated the distribution of velocities by producing a smeared out image of the beam when the apparatus was rotated rapidly. In 1922 Stern and Gerlach[6,7] began their brilliant work upon the deflection of atoms in an inhomogeneous magnetic field.

In 1924 Dr. John B. Taylor began work upon the mean free path in gases, as a problem for a doctors thesis under the author's direction. The method proposed involved the measurement of the decrease in intensity of a molecular beam at different pressures. Taylor made some progress with the method and it has since been used successfully by others. About this time the first work of Stern and Gerlach came to our attention. Professor Jakob Kunz of the Department of Physics offered to cooperate in the research and in particular offered the loan of a large electromagnet. Accordingly Taylor[12,13] completed his thesis under joint direction upon the magnetic moment of sodium and potassium. At this time the newer developments in the quantum theory had made the magnetic moment of hydrogen atom of especial interest. At the author's suggestion Dr. Taylor took up this problem and with the assistance of Dr. T. E. Phipps of this laboratory, this problem was solved.[14,15]

Recently Ellett and others at the University of Iowa, and Johnson at the Franklin Institute have studied the reflection of molecular beams from crystals.

THEORY OF MOLECULAR RAYS

A beam of molecular rays is usually formed by the escape of gas molecules at low pressure through a sequence of slits. (Fig. 1). Beams may be formed by direct evaporation from solid or liquid surfaces but since the intensities obtained in this way are usually low, in ordinary practice the beams originate in the gas phase. The term *molecular* ray is justified since any particle which has independent existence in the gas phase may be properly termed a molecule. Molecular beams are formed at low pressure, where the mean free path is large compared to the dimensions of the apparatus and the number of collisions occurring in the beam after it leaves the first slit is negligible. It should be noted here that in a number of experiments that have been reported in the literature on chemical reactions in molecular beams, a true molecular beam was not obtained, because conditions were not such as to insure absence of collisions in the beam.

In order that a beam be formed it is necessary that the pressure be low enough so that the mean free path is of the same order of magnitude as the width of the slit. If the pressure is high collisions will occur beyond the first slit, and the molecules will not travel in straight lines away from the slit. This situation has been described by Stern as "cloud" formation. The source of the beam under favorable conditions is in front of the first slit at a distance which depends upon the free path but since the free path is different for each molecule the source is an indefinite element of volume. We may speak of the mid-point of this volume as the location of the "effective" source of the beam. If the pressure is so high that cloud formation occurs, then the source is a wide area on the surface of the cloud between slits and a diffuse image will be obtained on the target. Since the length of the beam in most experiments is 10 cm or more, satisfactory results are not likely to be obtained if the pressure is greater than 10^{-4} mm of mercury at any point beyond the first slit.

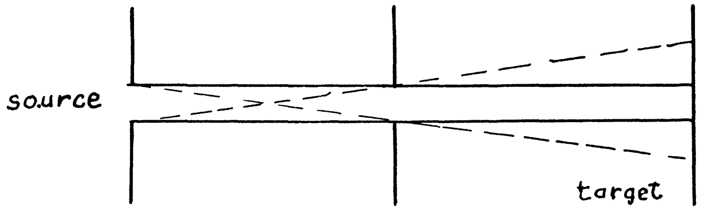

Fig. 1. The formation of a beam by two slits showing umbra and penumbra.

Effective Pressure in the Beam

The number of molecules striking on an area σ on the wall of the containing vessel per second in a gas at low pressure is given the expression,

$$n = \frac{\sigma p}{(2\pi m k T)^{1/2}} \tag{1}$$

and this expression may be used to calculate the effective pressure in a beam, when the number of molecules impinging on the unit area of the target per second is known. The effective pressure in a beam in terms of initial pressure, area of slit and length of beam may be easily derived by reference to Fig. 2. The molecules move in straight lines in all directions away from the first slit. The number of molecules passing through the first slit in any direction and impinging on an area on the surface of the hemisphere per second is proportional to the area of the first slit projected in this direction and to the area of the surface. This may be written:

$$dn = K\sigma_1 \cos\alpha\, d\sigma. \tag{2}$$

Where σ_1 is the area of the first slit, α is the angle the chosen direction makes with the normal and $d\sigma$ is the area on the hemisphere. If we integrate over the surface of the hemisphere then we obtain for the total number of molecules escaping from the slit per second

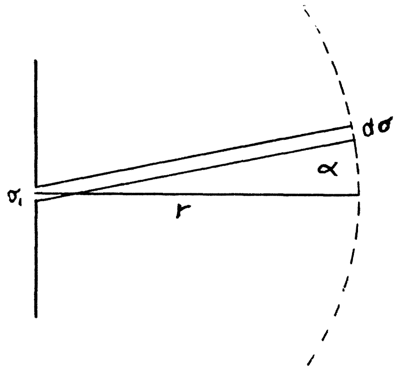

Fig. 2.

$$n = K\sigma_1\pi r^2. \tag{3}$$

But by Eq. (1)

$$n = \frac{\sigma_1 p}{(2\pi mkT)^{1/2}}$$

so that

$$K = \frac{p}{\pi r^2(2\pi mkT)^{1/2}}\cdot \tag{4}$$

Hence the number of molecules striking the area σ_2 on the target directly opposite the first slit ($\cos\alpha = 1$) is

$$n' = \frac{\sigma_1\sigma_2 p}{\pi r^2(2\pi mkT)^{1/2}}\cdot \tag{5}$$

The effective pressure in the beam as it hits the target is given (Eq. (1)) by

$$p' = \frac{n'}{\sigma_2}(2\pi mkT)^{1/2} \tag{6}$$

Hence

$$p' = \frac{\sigma_1}{\pi r^2}\,p \tag{7}$$

where p is the pressure in front of the first slit.

The effective pressure in the beam is thus directly proportional to the area of the first slit and inversely proportional to the square of the distance. The effective pressure in a beam 10 cm from the slit, with a pressure of 0.2 mm and slit area of 0.1 mm^2 is thus only 10^{-6} mm. This very low effective pressure makes the detection of beams difficult, since the pressure in the target chamber may be easily greater than the effective pressure in the beam itself.

In the foregoing discussion no reference was made to second slit. The effect of the second slit is to define the area of the target upon which the beam impinges. By reference to Fig. 1 it will be seen that unless the target is very close to the second slit, the image produced on the target by condensing the molecules will consist of a denser portion surrounded by a lighter portion. This phenomenon is analogous to the umbra and penumbra of a shadow. This phenomenon affects the sharpness of the image and no account was taken of this effect in the calculation of the effective pressure in the beam that was made above. The calculation is exact for the denser portion of the image, however.

No *diffraction* effects are to be anticipated in molecular rays so long as the slit width is greater than 10^{-3} mm.

Effect of Tube Slits and Multiple Slits

It is often difficult to maintain satisfactory vacuum conditions between slits. No matter how effective the vacuum pumps may be if a liquid air trap is used a long connecting passage intervenes between pumps and apparatus which offers a great deal of resistance to the flow of gases. This difficulty can be removed by decreasing the amount of gas that must be removed by the pumps. The number of gas molecules escaping per second through a thin edged orifice is given by Eq. (1). If the orifice is replaced by a tube of circular cross section the number escaping per second is now given approximately by the equation

$$n = \frac{\sigma_1 d}{l} \frac{p}{(2\pi m k T)^{1/2}} \tag{8}$$

where d is the diameter of the tube and l its length. It is clear that the amount of gas escaping through a long tube is only a small fraction of the amount escaping through the thin edged orifice. Since the tube offers resistance only to the molecules colliding with its walls, if it is properly aligned with the second slit, the intensity of the beam will not be affected and it is only the stray molecules which are stopped. This relieves the burden upon the pumps. With such a tube slit it is often possible to increase the initial pressure and hence the beam intensity. The pressure in the tube must be low enough to allow a free path in the tube and if the pressure is increased too much the source of the beam will be displaced so that it lies at the end of the tube slit and all advantage is lost.

The same conclusions in general will hold for a tube slit which is not circular in cross section. Multiple slits will serve practically the same purpose as a tube slit, since stray molecules instead of being retarded, are removed by separate pumps between slits. In addition multiple slits make it possible to increase the initial pressure of the beam. The maximum effective pressure in a beam is to be anticipated when the source of beam is located in a region of maximum pressure gradient. Such a maximum gradient can be obtained in the surface of cloud formed by a tube slit. Such a slit arrangement is shown in Fig. 3. No one seems to know what the upper limit is, to the attainable pressure in a beam or what the optimum conditions are for beam formation. If a beam is formed from condensable vapor it is much easier to maintain proper vacuum conditions, since it is not necessary to remove the stray molecules by the pump, but they may be condensed when they strike the walls between slits. It is probable that a greater intensity of beam can be obtained with a condensable vapor, than with a noncondensable gas.

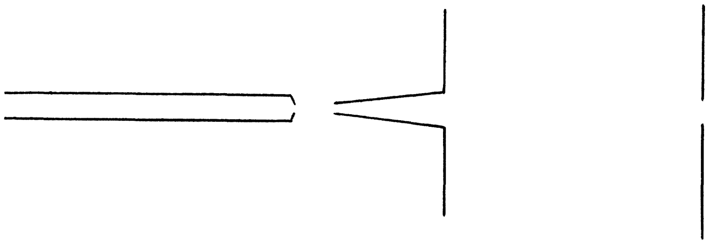

Fig. 3. Design of slits for high intensity.

Distribution of Velocities in a Beam

Under ordinary conditions there is no reason to assume that any departure exists from the Maxwellian distributions of velocities. The average velocity of the molecules striking a wall is of course greater than the average velocity of all the molecules in the gas. In a molecular beam there is a further selection of high velocity molecules. This comes about from the fact that only those molecules can travel in the beam whose velocities lie within the solid angle of the narrow cone defined by the slits (Fig. 4). Since there is the ordinary Maxwell distribution of lateral components of velocity, it follows that there will be a selection favoring the molecules of higher velocities. The distribution law is easily set up. Maxwell's law for the distribution of actual velocities in the gas is:

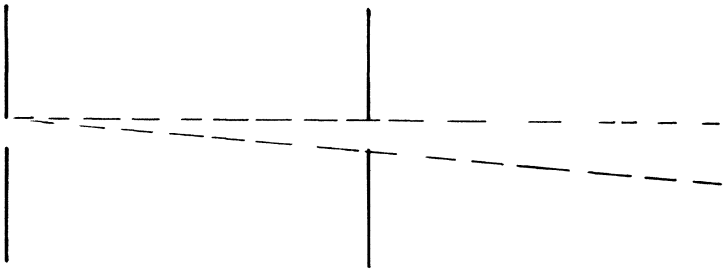

Fig. 4. Cone of velocities in a beam.

$$dn = \alpha e^{-\beta v^2} v^2 dv. \tag{9}$$

There are dn molecules which have a velocity between v_1 and v_1+dv per cubic centimeter of gas. Of these only the fraction ϵ are so located and directed that they can escape through the slits. The number of these escaping per second is $\epsilon v dn = \epsilon\alpha e^{-\beta v^2} v^3 dv$. The number of molecules with a velocity lying in any other interval is given by a similar expression and the general expression for the distribution of velocities in a beam is:

$$d\bar{n} = \alpha e^{-\beta v^2} v^3 dv. \tag{10}$$

There is no reason to suppose that this distribution is departed from appreciably under ordinary conditions.

Details of Slit Construction

In Stern's laboratory the slit systems have usually been made of metal. Metal slit systems have many advantages from the standpoint of exact construction and alignment. Dr. T. E. Phipps of this laboratory has perfected the technique of the construction and alignment of all-glass slit systems. An all-glass slit system requires much less pumping to establish and maintain a good vacuum. This is especially true because it is unnecessary to use any sealing wax or cementing material.

Detection of Beams

The simplest method of detecting a molecular beam is to condense it on the target. Most substances have a "critical" temperature as was shown by Knudsen,[2] above which they will not condense, or if they do condense reevaporation takes place. This temperature is really surprisingly high for many substances. For the condensation of most substances it is desirable to cool the target with liquid air. Gases such as hydrogen chloride, oxygen, nitrogen, etc., would require liquid hydrogen temperatures for condensation.

Stern showed that images produced by the condensation of metallic atoms, which are too faint to be visible, can be developed by the deposition of metallic silver from a reducing solution. If the development is carried out carefully the image will be faithfully reproduced. In this laboratory an image has been obtained from a beam of palladium atoms in a few seconds, that could be developed to a sharp, visible image by the deposition of silver. The method of development seems to offer great possibilities in the rapid detection of beams.

For molecules which are active chemically a simple method is to coat the target with a solid substance with which the molecules of the beam will react. This method works very well for atomic hydrogen. Molybdenum trioxide is readily reduced with a marked color change. Atomic oxygen also reduces molybdenum trioxide and oxydizes litharge. The author has investigated the chemical reactivity of beams of a number of more or less active gases and finds that a visible amount of reaction takes place in a disappointingly small number of cases. The lack of chemical activity is perhaps due to the small effective pressure in the beam.

In the detection of beams by an image by condensation or reaction on a target, it is usually desirable to observe and photograph the image without removing the target from the vacuum. This is easily done by placing an optical window in the apparatus and using a telescopic camera.

In theory the most satisfactory detector for a molecular beam of non-condensable gas is some sort of a manometer. No success was had in the use of manometers until Stern introduced the ingenious device of the tube slit on the vessel in which the beam is received. If the beam impinges on a thin edged orifice, the pressure builds up in the receiving vessel until the number of molecules entering is equal to the number of molecules escaping. The number of molecules entering per unit area of orifice per unit time is given by Eq. (5). The number escaping is given by the expression:

$$n' = \frac{\sigma_r p'}{(2\pi m k T)^{1/2}} \cdot \qquad (11)$$

Where p' is the pressure in the receiving vessel. Equating the two expressions we have

$$p' = \frac{\sigma_1}{\pi r^2} p. \qquad (12)$$

Suppose now that the thin edged orifice in the receiving vessel is replaced by a tube slit properly aligned. The molecules enter at the same rate as before but the rate of escape of gas is greatly reduced so that the equilibrium pressure builds up to several times what it was before. The most satisfactory means of measuring the pressure in the receiver is the hot wire manometer although the ionization gauge may be used.

In this laboratory a considerable amount of time has been spent in studying the vane manometer and the thermocouple as a means of detection. The vane manometer was mounted as a torsion instrument on a quartz fiber. This manometer has a high sensitivity but is very unstable. The thermocouple is in theory a very promising detector since it responds to the higher velocity molecules and acts as a velocity selector. It has all the defects that are associated with any instrument that is sensitive to radiation.

An ingenious method of detecting beams of alkali metal atoms had been developed by Dr. J. B. Taylor.[36] Langmuir has observed that alkali metal atoms colliding with a hot, positively charged tungsten filament, are re-evaporated as positive ions. By interposing such a filament in the path of the beam, the intensity of the beam is readily determined by measuring the positive ion current from the filament. This is the most accurate and reliable detector known but its use is limited to beams of atoms of low ionizing potential.

THE STERN-GERLACH EXPERIMENT

The now classical experiment of Stern and Gerlach on the deflection of a beam of silver atoms in an inhomogeneous magnetic field, was perforned in order to demonstrate the existence of space quantization. Let us consider the case of an atom which has a magnetic moment μ which is oriented parallel to the field (Fig. 5). Let the inhomogeneity of the field $\delta H/\delta s$ be assumed constant throughout the path of the atom. Then the atom is exposed to an attraction $\mu(\delta H/\delta s)$ and the path of the atom will be a parabola with a deflection

$$S = \frac{1}{2}\frac{\mu}{m}\left(\frac{\partial H}{\partial s}\right)t^2. \tag{13}$$

Where t is the time required by the atom in passing through the field. Since

$$t = \frac{l}{v}\cdot \tag{14}$$

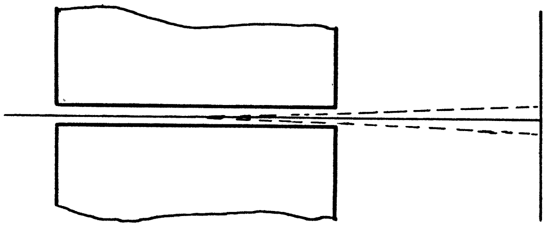

Fig. 5. Deflection of a beam in an inhomogeneous magnetic field.

Where l is the distance through the field and V is the velocity of the atom, we have for the deflection

$$S = \frac{1}{2}\frac{\mu l^2}{mv^2}\left(\frac{\partial H}{\partial s}\right). \tag{15}$$

An atom with anti-parallel orientation would be deflected in the opposite direction.

Eq. (15) gives the deflection the atom has suffered by the time it has passed through the field. If now the distance which the atom traversed after leaving the field, before it strikes the target be l_1, a further deflection will take place which is given by the following considerations. By the time the atom leaves the field it has acquired a velocity in the direction of deflection, at right angles to its original path

$$\frac{\partial s}{\partial t} = \frac{\mu}{m}\left(\frac{\partial H}{\partial s}\right)t \tag{16}$$

where as above

$$t = \frac{l}{v}\cdot \tag{17}$$

The time required to reach the target, t_1 is given by the relation

$$t_1 = \frac{l_1}{v}\cdot \tag{18}$$

Hence a further deflection S_1 occurs as the atom travels to the target where

$$S_1 = \frac{1}{2}\frac{\mu}{m}\left(\frac{\partial H}{\partial s}\right)\frac{ll_1}{v^2}\cdot \tag{19}$$

The total deflection is therefore

$$S + S_1 = \frac{1}{2}\frac{\mu}{m}\left(\frac{\partial H}{\partial s}\right)[l^2 + 2ll_1]. \tag{20}$$

In the Stern-Gerlach experiment it is necessary to employ a magnetic field of great strength in order to obtain a large value for the inhomogeneity. This is obtained by providing a powerful electromagnet with a wedge shaped piece for one pole and opposed to this a flat pole piece which is slotted parallel to the knife edge. In their original design the value of $\delta H/\delta s$ was not constant so that the image was split into a loop when the field was on. By proper design of the pole pieces, a cross section of which is shown in Fig. 6, a constant value of $\delta H/\delta s$ is obtained in the region traversed by the beam. A beam consisting of para-magnetic atoms with parallel and anti-parallel orientations will be split into two beams which will give an image of two parallel lines as shown in Fig. 7. The trace of the beam is indicated Fig. 6.

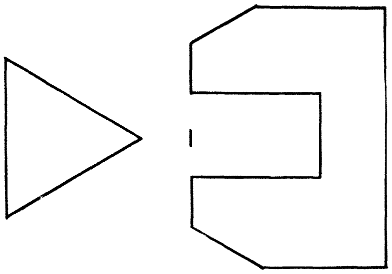

Fig. 6. Design of pole pieces for uniform inhomogeneity.

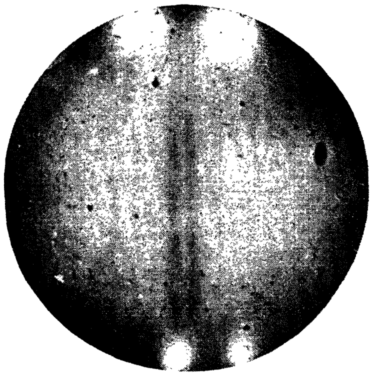

Fig. 7. Image produced by atomic hydrogen in the Stern-Gerlach experiment.

The field inhomogeneity may be mapped by the standard method of measuring the force exerted on a bismuth wire. As a matter of fact the simplest method of calibration is to perform the Stern-Gerlach experiment on atomic hydrogen. An ingenious modification of the pole piece arrangement described above was suggested and demonstrated by Rabi. Rabi used flat rectangular pole pieces, 2×5.4 cm^2 with a 2.2 mm gap between the faces (Fig. 8). If a beam is brought into the gap between the pole pieces at a low angle with the edge of the pole pieces, the atoms in the parallel orientation are pulled into the field and this part of the beam suffers a deflection exactly analogous to refraction of a beam of light by a prism. The atoms in the anti-parallel orientation are repelled and this part of the beam is refracted in the opposite direction. A further separation between beams takes place if the beams leave the field at the proper angle. This design of pole piece has certain advantages particularly in the measurement of electrostatic deflections.

From inspection of Eq (5) it is evident that the deflection experienced by an atom is inversely proportional to the square of the velocity and on account of the distribution of velocities a beam which produces a sharp image in the absence of a field will produce a smeared out image when split in a field. In Fig. 9 are curves showing the intensity of the image. The inner edge of the deflected image is relatively sharp while the outer edge is diffuse. The average deflection is of course inversely proportional to the absolute temperature and independent of the mass of the atom. Some difficulty exists in defining the average deflection however.

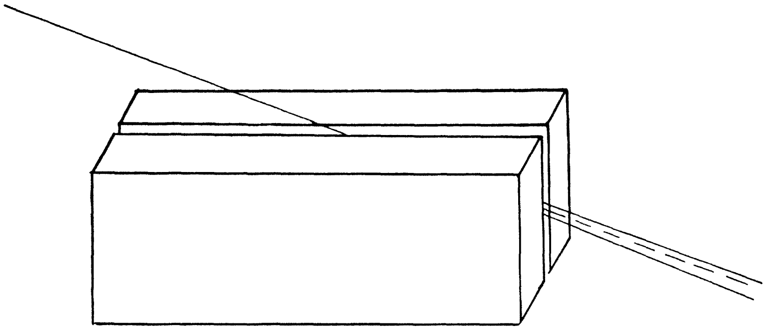

Fig. 8. Pole piece design used by Rabi.

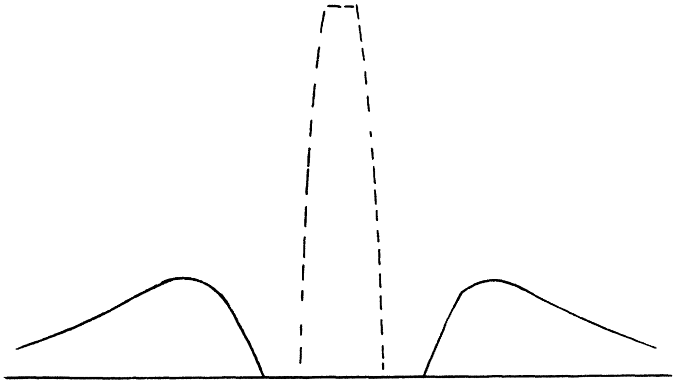

Fig. 9. Intensities of undeflected beam (dotted lines) and deflected beam (solid lines) in the Stern-Gerlach experiment.

Much of this difficulty would be avoided by using a beam of atoms of nearly uniform velocity and the only way such a beam can be produced is by the elimination of all molecules except those with velocities lying in a narrow range. The author[19] suggested a simple type of velocity selector consisting of two coxaial rotating sectors. Experiments have been made with this type of velocity selector by a number of investigators, including Eldrige,[23] Costa, Smythe and Compton[25] and Laumert [35] and Zartman.[46] The results have not been very gratifying, on the whole.

The average kinetic energy of the atoms in a beam is $2kT$. The most probable kinetic energy for the atoms is $3/2kT$. Since the deflection is inversely proportional to the kinetic energy, the beam will be spread out as has been stated above. It might be expected, that the densest part of the image would be found where the atoms of most probable kinetic energy strike, but theory shows that the densest part of the image is that produced by atoms of kinetic energy $= 6KT$. This is true for a beam of infinitesimal width and if the field inhomogeneity is uniform. For slits of finite width however an overlapping effect occurs which displaces the point of maximum density toward the part of the target which is hit by atoms of lower kinetic energy.

Semenoff[9] was the first to derive an equation for the distribution of intensities but the question has been discussed by others.[19,20] The general form of the equation which applies is

$$I = \tfrac{1}{2} I_0 \left[e^{-y}(y + 1) \right]_{s_{\alpha}{}^{s-\alpha}}^{s_{\alpha}{}^{/s+a}} \tag{21}$$

where I^0 is the intensity of the undeflected image, I the intensity at a distance s from the center of the undeflected image, α is 1/2 the width of the beam and s_α the deflection suffered by the atoms with the most probable kinetic energy.

Since the maximum is not sharp it cannot be located with exactness anyway. If the image is produced by condensation or chemical reaction there remains the further question, whether the density of the image is proportional to the intensity in the beam. Densitometer readings cannot be relied upon too heavily.

If the field inhomogeneity is not uniform in the region traversed by the beam, as is usually the case, then the distribution of intensity in the deflected beam varies in a still more complicated manner. It will be seen that the Stern-Gerlach experiment is not adapted to the exact determination of magneton values unless a beam of nearly uniform velocities can be produced.

Kunz and Tykociner[24] have suggested a modification of a velocity selector which involves oscillating shutters. The difficulty with any velocity selector is the greatly reduced intensity of beam that must result. Perhaps the simplest method of selecting velocities is by means of reflection from a crystal surface. This method will be discussed later in that connection.

THE RELATIONS BETWEEN THE STERN-GERLACH EFFECT AND THE SPECTROSCOPIC TERM OF THE ATOM

A paper published in 1922 by Einstein and Ehrenfest[8] on the orientation of atoms in a magnetic field, unfortunately gave the impression that there was something mysterious about the sudden orientation of atoms in the Stern-Gerlach effect. There is nothing mysterious about the process. If we consider the old model of the atom with the electron moving in a definite orbit then the orientation comes about as a result of the Larmor precession.

The atom spends a period of time of about 10^{-4} seconds in the field in the Stern-Gerlach experiment.

The period of the electron in its orbit is about 10^{-8} seconds so that a great many revolutions are made by the time the atom has fairly entered the field. At each revolution the motion of the electron approaches nearer to a simple precession about the field. The quantum theory limits the angles which the electron precesses about the field to certain discrete values. If j is the angular momentum of the electron and m the component of in the direction of the field, then m takes on only the values

$$-j, \ -(j-1)-(j-2)\cdots(j-1), j$$

In the vector model of the atom with Russell-Saunders coupling the theory is complicated by the introduction of the electron spin. The resultant angular momentum of the atom J is compounded of electron spin and orbital angular momentum and the orientations correspond to values of m differing by unity from $-J$ to $+J$ as before. The effective magnetic moment of the atom however is mg where g is the Landé factor. By the new quantum mechanics

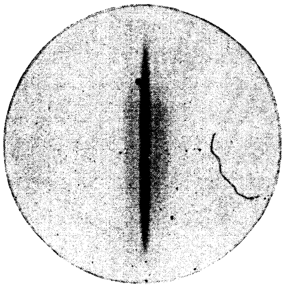

Fig. 10. Image produced by atomic oxygen in the Stern-Gerlach experiment.

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \tag{22}$$

Where S is the resultant spin of the atom and L the resultant angular momentum as calculated from the vector model. J is, of course, the vector sum of L and S.

A beam passing through an inhomogeneous magnetic field will therefore be split into as many beams as there are values of m between $-J$ and $+J$. The deflection of each beam will be that given by Eq. (15) for a magnetic moment of mg.

The application of the theory can be illustrated by reference to the work of Phipps and Kurt on the oxygen atom. At ordinary temperatures the oxygen atom is distributed between spectroscopic states: $^3P_2$, $^3P_1$, and $^3P_0$. The $^3P_2$ state is the lowest and the percentages in the three states as calculated by the Boltzmann distribution law are 65.3, 27, and 7.7 respectively. The $^3P_0$ state gives an undeflected beam. The $^3P_1$ state has values of $m=-1$, 0, $+1$ and $g=3/2$ respectively. The $^3P_2$ state gives values of ± 2, ± 1 and 0 respectively, with corresponding values for mg of ± 3, $\pm 3/2$, 0. The result of the superposition of these nine different beams is shown in Fig. 10. The beams with values of $mg=3$ and $mg=3/2$ are superposed to such an extent that they give a single maximum in the densitometer curve. The oxygen image was obtained by the action of atomic oxygen on a target covered with freshly sublimed litharge.

Some of the data for the experiment are given as by way of illustration

Length of pole pieces—6.0 cm
Distance from pole piece to target—2.3 cm
Width of undeflected line—0.012 cm
$(\delta H/\delta s)$ estimated—20,000
Deflection of densest part of combined image—0.02 cm

The Stern-Gerlach experiment has been of great aid in determining the correct spectroscopic terms for the atoms. The experiment of Phipps and Taylor[18] on the hydrogen atom helped to confirm the hypothesis of electron spin of Uhlenbeck and Goudsmit. Results of the Stern-Gerlach experiment can of course be predicted for atoms whose spectroscopic states are known. The value of the experiment in the future is therefore limited to those cases where there is uncertainty as to the spectroscopic term. For example, Dr. M. J. Copley in this laboratory has demonstrated that the ground term of the palladium atom is ^1S. This point had previously been in doubt. The case of iron has not been settled satisfactorily since Stern and Gerlach found no deflection but there seems to be little doubt that this result is wrong since the spectroscopic evidence is quite certain that the lowest term of the iron atom is $^5D_4$.

The Stern-Gerlach experiment has not been performed on any atoms which have $j-j$ coupling. The expression for the Lande factor g would be different in this case.

A question which has often been raised is, "What would happen if one of the deflected beams, for example, the one containing the hydrogen atoms in the parallel orientation were to be allowed to pass into a second mganetic field. The answer seems to be that, barring some disturbance which might bring about a random orientation, the atoms would all remain quantized in the same way as originally.

THE MAGNETIC MOMENT OF THE FREE ELECTRON

Numerous experiments have been devised for measuring the magnetic moment of the free electron. Bohr and others have shown that the conventional form of the experiment involves an uncertainty of the order of magnitude of the quantity that is to be measured. It is possible that some form of experiment may be devised which evades this difficulty.

THE STERN-GERLACH EXPERIMENTS FOR MOLECULES

Molecules in the $^1\Sigma$ state behave like atoms in the ^1S state and pass undeflected through an inhomogeneous magnetic field. It is predicted that molecules in the $^3\Sigma$ state will at low temperatures, where the rotational energy is small, be split into three beams with values for m, the effective moment, of -2, 0, and 2. This would come about because in a strong field the electron spins should be quantized with respect to the magnetic field. At higher temperatures where the rotational energy increases the electron spins will be quantized with respect to the rotational axis. Under these conditions no definite splitting into beams is to be anticipated but only a broadening of the central image. The experiment has not yet been made on molecular oxygen because of the difficulty of detecting beams of molecular oxygen, although there is little doubt as to the result. The only experiment of this kind that has been reported in the literature was tried in this laboratory on the S_2 molecule. The result was a general broadening of the image indicating that the lowest state of S_2 molecule is a $^3\Sigma$ state, as might be expected. In one of the experiments however in which the sulfur vapor which was the source of the S_2 molecules, was at a particularly low temperature, a side line was obtained on the side of the central image where the field was strongest. It is entirely possible that in this case the magnetic field was strong enough to uncouple the spin axis from the rotational axis of the molecules with a resulting deflection corresponding to two magnetons.

For molecules in π states only a broadening of the central images is to be expected, since the rotation of the molecule will prevent the quantization of the magnetic moment with respect to field.

Stern[16] has performed an interesting experiment on the water molecule. Because of molecular rotation the water molecule should possess a very small magnetic moment since it has a considerable dipole moment. In addition it might show a very small magnetic moment because of the proton spin of the hydrogens.

In order to obtain the maximum inhomogeneity in the magnetic field he used flat pole pieces placed very close together. Grooves were cut in one of the pole pieces and the beam passed through the grooves. Since the grooves were very small, in order to obtain a sufficient intensity a large number of grooves were cut converging on the target. This device Stern has called a "multiplikator."

In the experiment with a beam of water molecules the water was condensed on the target by the use of liquid air. Evidence was obtained for a slight deflection which may have been due to either of the causes suggested above.

NUCLEAR MOMENTS

The spin of the proton gives rise to a magnetic moment 1/1840 that of the electron. Iodine, for example, has a nuclear spin of several half units. Dr. W. A. Nichols,[39] Jr. working with the author in this laboratory, made an attempt to determine the nuclear noments by the Stern-Gerlach experiment. Hydrogen iodide was the substance chosen for the experiment since its vapor can be cooled to a low temperature. This cooling gives two advantages. In the first place a large deflection is to be anticipated. In the second place some of the molecules will be in the zero rotational state and a favorable orientation of the nuclear spin should be obtained. It was estimated that the image obtained with the field off should be broadened by as much as 0.01 mm with the field on. This broadening should be easily observable if the edges of the image were sharp, but unfortunately the edges of the image obtained were too diffuse to enable a decision to be made. The image was formed by condensing the hydrogen iodide on a target, cooled with liquid air under reduced pressure.

Polar Molecules in an Inhomogeneous Electrostatic Field

An experiment analogous to that of Stern and Gerlach at once suggests itself for the electrostatic case. The new quantum theory shows that the dielectric constant of polar gases depends only upon the molecules in the zero rotational states. The molecules in the higher rotational states are oriented in the field but the resultant moments cancel so that no resultant polarization results for the gas. If however a beam of polar molecules is passed through an inhomogeneous electrostatic field, the different rotational states will be quantized in various positions in the electrostatic field, with the result that some of the molecules will be repelled and others attracted. Because of the velocity distribution it is not likely that these various rotational states would be separated in the field, but we should rather expect a widening of the central beam.

The first experiments along this line were made in Stern's laboratory by Wrede.[21] Wrede obtained an inhomogeneous electrostatic field by applying a high potential to a wire stretched in the center of a cylinder. Wrede used beams from the vapors of alkali halides. Because of the high temperature the deflection obtained was small and the results not very definite. The most promising polar molecule upon which to experiment is hydrogen chloride. This molecule has a large dipole moment and can be cooled to a low temperature where most of the molecules are in the lower rotational states and a large deflection is to be anticipated. The difficulty with the hydrogen chloride molecule is that there appears to be no satisfactory method of detecting a beam of hydrogen chloride. It cannot be condensed on a liquid air cooled target. Dr. Copley[30] of this laboratory has spent a great deal of time upon this problem with only partially satisfactory results. The method which he used in condensing hydrogen chloride, consists in first freezing a layer of ammonia on a target and then condensing the hydrogen chloride on the ammonia. It is not certain what the initial process is, but the final result is the formation of ammonium chloride, which is easily visible. The difficulty with this method is to get the proper thickness of the ammonia layer. Recently Dr. Copley has been experimenting with hydrogen iodide which can be condensed with liquid air. He has obtained for both of the hydrogen halides images which are considerable broadened.

The design of pole pieces suggested by Rabi is of great advantage in electrostatic deviation experiments because it is as easy to maintain a difference of potential between large plates as small plates. The difference of potential which is ordinarily maintained varies from 10,000 to 20,000 volts. This difference of potential is easily maintained by a transformer and kenotron.

Estermann[33] has performed electrostatic deflection experiments upon a number of polar organic molecules. The difficulty here is that the polarizability of the molecule, which always causes deflection in one direction, is of the same order of magnitude as the dipole moment. Molecular-ray experiments do not appear to offer a very satisfactory method for the determination of dipole moments of molecules.

THE DIFFRACTION OF MOLECULAR RAYS BY CRYSTALS, DEBROGLIE WAVES

Stern[15] suggested in 1926 that the existence of deBroglie waves could be verified by study of a molecular beam impinging on the surface of a crystal. It was not until recently however that he actually turned his attention to the problem. In the meantime the problem was taken up by others; in particular by Ellett, Olson, and Zahl;[38] T. H. Johnson,[27,28] and Kirschbaum.[37] It may be pointed out that there are four possible types of reflection of a beam of atoms from the plane surface of crystal. If the surface is rough we should expect diffuse reflection and this is often obtained. If the surface is very smooth it might be anticipated that a specularly reflected beam would result. On the other hand, if the atom behaves as though guided by a deBroglie wave of wave length, $\lambda = h/mv$, and the crystal acts as a grating, there are two possible types of behavior. If the crystal acts as a plane grating we should expect specular reflection for all velocities and in addition diffracted beams at certain angles depending upon the velocity of the atoms. On the other hand, if the crystal acts as a layer grating then we should expect the Bragg type of reflection. A specularly reflected beam will be obtained but only for atoms of a certain velocity at a given angle.

All of the authors mentioned above studied the reflection of molecular beams from the fresh cleavage surfaces of sodium chloride crystals. All of these reported specular reflection of the beams by the crystal. Johnson worked with hydrogen atoms. Ellett, Olson and Zahl reported specular reflection of cadmium, mercury, arsenic, and antimony beams from sodium chloride crystals. In all cases the percentage reflected depends upon the angle of incidence. Ellett, Olson, and Zahl reported in addition that a selection of velocities took place in the reflection, indicating that the reflection was of the Bragg type, since the deBroglie wave-length associated with the atom is given by the formula

$$\lambda = \frac{h}{mv} \tag{24}$$

and hence depends upon the velocity. They demonstrated this velocity selection in two ways. In the first method they analyzed the velocities in the reflected beam by the velocity selector, developed by Eldridge. In the second method they showed that a beam which had been reflected at a given angle from one crystal, could only be reflected from a second crystal if the angle of incidence is the same as for the first crystal. In their calculations however they found it necessary to assume that the wave-length was that of the hydrogen atom instead of the wave-length corresponding to the element from which the beam was formed. Recently Zahl[43] has made further experiments upon the reflection of beams of cadmium and zinc atoms from sodium chloride crystals. His results do not appear to confirm the earlier work and further experimentation seems to be required.

The demonstration of the actual diffraction of molecular rays by a crystal was first accomplished by Stern[34,42] in 1929 and constitutes an experimental achievement equal to the demonstration of the Stern-Gerlach effect. Stern began this work by studying the reflection of molecular beams of helium atoms and hydrogen molecules from sodium chloride crystals. His first results were not very conclusive due in part to diffuse reflection and in part to the fact that the crystal and detector were not oriented in such a manner as to insure the detection of the diffracted beam. Stern found that by using lithium fluoride the difficulties with diffuse reflection disappeared entirely. When he modified his apparatus so that the plane of the crystal could be tipped, he was able to verify the deBroglie wave theory in a very striking manner.

Stern has summarized his results in the following statement: When a beam of molecules strikes the surface of a crystal, the reflected and diffracted beams show a distribution of intensity that agrees with that to be expected for waves diffracted by a cross grating. When the distance between ions is taken as the grating constant, then the maximum of the diffracted beam corresponds to the wave-length, $\lambda = h/mv$ where v is the velocity of the molecules calculated from the Maxwell distribution for which the greatest intensity in the diffracted beam is to be expected.

It will be noted that the angle of the diffracted beam depends upon the velocity of the molecules and hence a selection of velocities takes place. On the other hand, the specularly reflected beam from a cross grating will show no selection of velocities. This result is in disagreement with the results of Ellett, Olson and Zahl who found a selection of velocities in the specularly reflected beam indicating the Bragg type of reflection.

No explanation has as yet been offered as to why lithium fluoride crystals give so much less diffuse reflection than any other crystal that has as yet been tried. One possible explanation is that the lithium ion is constitutionally similar to the helium atom and hydrogen molecule. On the other hand Langmuir has suggested that the surface of the lithium fluoride crystal is covered by a layer of adsorbed water molecules. If this is the case the adsorbed layer must preserve the lattice structure. Some evidence bearing on this point has been obtained by Davisson and Germer[47] in their work on the diffraction of electrons from the surface of crystals of metallic nickel.

Stern obtained the diffracted beams corresponding to four different orders of diffraction from a cross grating. After his results were obtained Johnson[44] was able to obtain diffracted beams with hydrogen atoms from the surface of a lithium fluoride crystal. Recently Johnson has reported evidence of a diffraction pattern which may be due to the mosaic structure postulated by Zwicky.

Taylor[45] has studied the reflection of beams of alkali metal atoms from sodium chloride and lithium fluoride crystals. In no case did he obtain anything but diffuse reflection although his method of detection was very sensitive and he varied the temperature of the crystal over a wide range. It seems probable that in Taylor's experiments the atoms were adsorbed and re-evaporated in which case the intensity of the scattered beams would vary according to the cosine law as he found.

An exhaustive series of experiments were made by Dr. Phipps of this laboratory on the diffraction of hydrogen atoms by thin metal films. The experiments were analogous to those of Rupp on the diffraction of electrons by these films. Dr. Phipps produced metallic films which were from ten to one hundred atoms thick but he was not able to obtained evidence that a beam of hydrogen atoms would pass through these films.

POSSIBLE USES FOR MOLECULAR RAYS

One of the most interesting recent applications of molecular rays is in the study of molecular association. Stern has recently repeated the Stern-Gerlach experiment upon sodium vapor in his laboratory in order to obtain the percentage of association. The Na_2 molecules are of course undeflected by the field and, by means of the thermionic detector developed by Taylor, it is possible to make very accurate measurements of the relative intensity. The results are in agreement with those obtained from vapor density by Rodebush and Walters.[41] A similar experiment has recently been performed by Zartman[46] upon bismuth vapor. In this experiment a velocity selector was used to determine the distribution curves for bismuth atoms and molecules. This method is not capable of as high accuracy as the method first described. The molecular-ray technique appears to offer a possible method for the study of a number of problems which could not be approached by any other method. Whenever the molecular or atomic species is uncharged, the Stern-Gerlach experiment offers a means of identifying the particle, determining its velocity and its spectroscopic state. It must of course be recongized that the mean life of excited states of atoms or molecules is often too short to permit the Stern-Gerlach experiment to be performed.

One such experiment is being attempted by Mr. L. A. Murray at the present time in this laboratory. According to the wave mechanics the collision of an 11 volt electron with a hydrogen molecule produces a $^3\Sigma$ state. The molecule in this state dissociates into atoms which carry about 3.5 volts of kinetic energy. These extremely high speed atoms should be practically undeflected in a magnetic field. In their work upon the magnetic moment of the hydrogen atom Phipps and Taylor obtained a very faint undeflected line. It is entirely possible that this line was due to high velocity hydrogen atoms. Mr. Murray has not yet succeeded in producing a beam of sufficient intensity for the Stern-Gerlach experiment.

Perhaps the most promising use for molecular rays is in the study of the mechanism of gaseous chemical reactions. In spite of all the study that has been made upon gaseous reactions, it can scarcely be affirmed that we know the exact mechanism of a single reaction. This is particularly true for the so-called "chain" reactions. The molecular ray technique offers a method of removing from the reaction the fugitive molecular species which actually take part in the reaction. The Stern-Gerlach experiment or other experiments may make possible the identification of these experiments. Of course, as has been pointed out, the life of excited states of atoms or molecules may be too short for identification even by these methods. On the other hand, there is reason to believe that chemical reactivity does not usually depend upon excited states of short life, although Rollefson has postulated the $^2P_{\frac{1}{2}}$ state as the active form of the chlorine atom in the hydrogen chlorine reaction.

TABLE I. *Results obtained by the Stern-Gerlach experiment.*

Element	References	Magnetic moment (mg)
Ag	(6, 7, 10)	1
Cu	(10, 11)	1
Au	(10, 11)	1
Tl	(10, 11)	1/3
Sn	(10, 11)	0
Pb	(10, 11)	0
Sb	(10, 11)	?
Bi	(10, 11, 49)	0.85 ± .015
Ni	(10)	2?
Fe	(10)	?
H	(14, 18, 21)	1
K	(12, 13, 22)	1
Na	(12, 13, 22)	1
Cd	(22)	0
Li	(26)	1
O	(31)	0, 3/2, 3
Pd		0
S_2	(40)	2?

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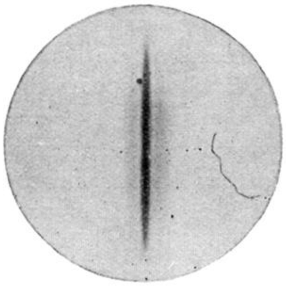

Fig. 10. Image produced by atomic oxygen in the Stern-Gerlach experiment.

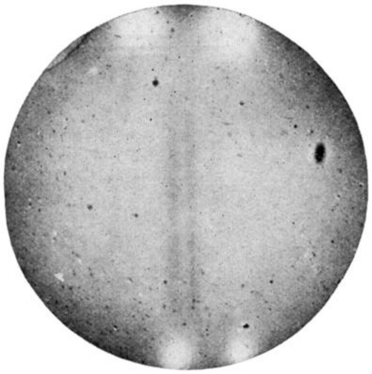

Fig. 7. Image produced by atomic hydrogen in the Stern-Gerlach experiment.