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The Deflection of Molecular Rays in an Electric Field: The Electric Moment of Hydrogen Chloride

IMMANUEL ESTERMANN AND RONALD G. J. FRASER*

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A comparison of the method for determining electric moments of molecules by deflection of molecular beams by inhomogeneous electric fields with the dielectric constant method shows that the molecular beam method has certain advantages. This method determines the electric moment of gases directly and is able to detect the effect of higher rotational states of non-gyroscopic molecules. Moreover, a deviation of the axis of the dipole moment from that of the axis of rotation by other than 90° should be detected. The additional energy due to an electric field is proportional to

the square of the field intensity and is a function of the quantum numbers m and j , if the electric moment is perpendicular to the axis of rotation. Otherwise there will be a linear dependence on the intensity of the electric field. An experimental method of the Rabi type for studying the HCl molecule is described. The patterns produced by the undeflected and deflected molecules are given and from these patterns the electric moment of the HCl molecule is found to be approximately 1.95×10^{-18} e.s.u. *Editor.*

I. INTRODUCTION. SCOPE OF METHOD

DURING the last decade, the method of molecular rays has been notably developed as a tool in research, especially in the Institute of Physical Chemistry at Hamburg. The method aims at the production of directed, collision-free beams of neutral molecules, moving with thermal velocities in vacuo; and the study of, for example, their scattering in gases, reflection and diffraction at solid surfaces, or deflection in magnetic and electric fields. The essential feature of the method is its extreme directness; for, on the one hand, the unidirectional nature of the beams usually makes the effect of given external conditions proximately interpretable, while on the other hand their collision-free character eliminates the disturbing factor of molecular interactions. It is these features in particular which often make the method of peculiar value in the study of problems of molecular structure.

The application of the method which concerns us here is to the behavior of molecules in an electric field. An electric dipole in an inhomogeneous electric field is acted on by a ponderomotive force; hence if a ray of dipole molecules SID , selected by the image aperture I from the bundle of rays emerging from the source aperture S , is directed through an inhomogeneous electric field F , it suffers a deflection, the extent and character of which, as determined by the detector D , allow a determination of the molecular dipole moment, and in certain cases the deduction of details of molecular structure. (Fig. 1.)

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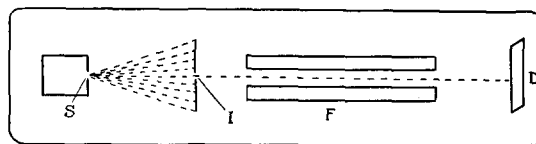


FIG. 1.

The standard method of determining molecular electric dipole moments, due to Debye,¹ depends on measurements of the dielectric constant of the substance, either as a gas, or dissolved in a non-polar solvent. The accuracy of the dielectric constant method is in most cases far in excess of that of the method of molecular rays at the present stage of its technical development. On the other hand, the deduction of the value of the dipole moment of the individual molecules from measurements of the dielectric constant of the

* The experiments described in this paper were begun by one of us (R. F.) while an 1851 Exhibitioner, in the Institute of Physical Chemistry at Hamburg (1928-29); and continued by the other (I. E.) in the Department of Chemistry of the University of California at Berkeley (1931-32), while holding a Fellowship of the Rockefeller Foundation.

¹ cf. P. Debye, *Polar Molecules*, New York, 1929.

gas or solution in bulk involves the use of often complicated statistical reasoning; which must take account, not only of the macroscopic interaction of the electric medium with the field; but also of molecular interactions, about which assumptions must be made which are often of doubtful validity, especially at high densities of the fluid. It is just in the characteristic absence of statistics from the interpretation of the results of an electric deflection experiment that the molecular rays method again shows its special heuristic advantages.

We enumerate the following more practical advantages.

(1) The dielectric constant method is subject to the limitations imposed, on the one hand by the considerable pressures required for reasonably accurate dielectric constant measurements in the gas phase, on the other by the solubility of the substance it is desired to examine in a suitable nonpolar solvent. It may therefore happen, for a given substance, not only that the temperature required to obtain the necessary gaseous pressure is inconveniently high *per se* or else leads to decomposition of the substance, but also that the substance is insoluble in nonpolar solvents. On the other hand, the pressures required in the source of a molecular beam are at the most of the order of a millimeter; and again, the applicability of the method is clearly independent of the solubility of the substance in a particular solvent. Thus the molecular rays method may prove applicable to the measurement of dipole moments in cases where the dielectric constant method fails completely; a notable example is that of pentaerythritol and its derivatives.²

(2) Nevertheless the discovery that symmetrically built molecules may often possess large permanent dipole moments has led one to recognize that the relative motions, of vibration or rotation, of the component parts of a complicated molecule may exert a decisive influence on its dipole moment. In certain cases, moreover, a dependence of the dipole moment on the temperature may be expected.³ Now Debye's theory

of the variation of the dielectric constant with temperature, which is the basis of the measurement of dipole moments by the standard method, presupposes a temperature-independent dipole moment. Thus a possible temperature variation of the dipole moment could reveal itself only as a departure of the temperature variation of the dielectric constant from that to be expected on Debye's theory. Apart from the fact that in general only a small range of temperature is available, other complications (e.g., association) impose a severe restriction on the range of the dielectric constant method, and reliable measurements of the temperature variation of the dipole moment by this method have been reported so far for isolated cases only.⁴ On the other hand, since the molecular rays method measures the dipole moment *directly*, it should be immediately applicable to the study of this question, and moreover in particular to just the type of molecule which would in any case prove difficult of attack by the dielectric constant method on the grounds of (1) above. So far, no experiments of this kind have been reported.

(3) It will appear in the next section (p. 393) that if the angle between the axis of the dipole moment of a molecule and the axis of rotation is only a few degrees other than a right angle, the deflection of a beam of such molecules in an inhomogeneous electric field is very markedly greater than is the case when the axes are strictly perpendicular to one another. Thus a merely qualitative inspection of the scale of the deflection pattern might suffice to give a decision in cases where an intramolecular configuration is in doubt.

(4) It has been shown by the application of wave mechanics that in the case of non-gyroscopic diatomic molecules the contribution of the permanent dipole moment to the dielectric constant arises entirely from molecules in the lowest energy state $j=0$.⁵ In such case, higher rotation states escape detection by the dielectric constant method. On the other hand, the method of molecular rays is capable of detecting, and has already detected in a qualitative way, the exist-

² I. Estermann, *Zeits. f. physik. Chemie* **B2**, 287 (1929); Estermann and Wohlwill, *ibid.* **20**, 195 (1933).

³ cf. Sack, *Naturwiss.* **8**, 337 (1929); also Wolf and Fuchs' article *Sterischer Bau und elektrische Eigenschaften*, in Freudenberg's *Stereochemie*, Leipzig, 1932.

⁴ Zahn, *Phys. Rev.* **40**, 291 (1932); Greene and Williams, *ibid.* **42**, 119 (1932).

⁵ Van Vleck, *Phys. Rev.* **29**, 727; **30**, 31 (1927); also Debye, reference 1, p. 153.

ence of these states.⁶ Further, we shall show (p. 391) that at low temperatures direct evidence of the splitting of the rotational energy levels in an electric field (quadratic Stark effect) may be expected to follow the application of the molecular rays method under the appropriate conditions. The experiments on hydrogen chloride described in the third section of this paper are a first step in this direction.

Thus the method of molecular rays offers several advantages in the study of the behavior of molecules in an electric field. Technical difficulties have hitherto made progress in this direction relatively slow; but the work which has been done, and the results which have been obtained, are sufficient to justify further development which shall make it possible to follow up some of the promising lines of advance we have indicated. We propose therefore in the remainder of this paper to outline the principles which must govern such a development and to illustrate their application to a number of problems which have already successfully been attacked, with special reference to the behavior of the HCl molecule in an electric field.

II. THEORETICAL

We shall restrict our discussion in the main to a simple model of a polar diatomic molecule, considered as a rigid dumb-bell; the conclusions arrived at need not therefore be immediately applicable to polyatomic molecules.

1. The time-averaged moment

If a polar molecule, moment μ , is shot into an electric field E , the *instantaneous* change of energy is of amount

$$\Delta W = \mu_E \cdot E, \quad (1)$$

where μ_E is the component of μ in the direction of E ; but the molecule executes a uniform temperature rotation whose period is short compared with the time the molecule takes to traverse the field in a deflection experiment; hence μ_E changes sign every half period, the time-averaged energy change $\overline{\Delta W}$ vanishes to the first order, and the

molecule is unaffected by its passage through the field.

The presence of the field, however, distorts the motion of uniform rotation of the dipole, and there results a time-averaged moment $\bar{\mu} = \beta \cdot E$, proportional to the field strength, in the direction of the field. Thus to the second order

$$\overline{\Delta W} = \frac{1}{2} \beta E^2. \quad (2)$$

If the center of gravity of the dipole be taken as the origin of an arbitrary system of coordinates xyz , then the components of the force acting on the dipole are clearly

$$F_x = \bar{\mu} \cdot \partial E / \partial x; \quad F_y = \bar{\mu} \cdot \partial E / \partial y; \quad F_z = \bar{\mu} \cdot \partial E / \partial z \quad (3)$$

since $\bar{\mu} = \beta \cdot E$.

According to quantum theory, $\overline{\Delta W}$ in (2) can take only certain discrete values determined by the rotational quantum number $j=0, 1, 2, \dots$, and the equatorial quantum number m , an integer defined by the relation $-j \leq m \leq j$. That is β is a function $\beta(j, m)$ of the quantum numbers j and m . The values of $\bar{\mu} = \beta(j, m) \cdot E$ for the rigid dumb-bell molecule were obtained independently by Mensing and Pauli⁷ and by Kronig.⁸ They are

$$\bar{\mu} = \left. \begin{aligned} & \frac{8\pi^2 I \mu^2 E}{h^2} \frac{1}{(2j-1)(2j+3)} \left(\frac{3m^2}{j(j+1)} - 1 \right) \\ & \qquad \qquad \qquad \text{if } j \neq 0, \\ & = \frac{1}{3} 8\pi^2 I \mu^2 E / h^2 \qquad \qquad \qquad \text{if } j = 0, \end{aligned} \right\} \quad (4)$$

where I is the moment of inertia of the molecule and h is Planck's constant.

For large values of j (high temperature), (4) takes the classical form

$$\bar{\mu} = \frac{\mu^2 E}{2I\omega_0^2} (3 \cos^2 \phi - 1) = \frac{\mu^2 E}{4\epsilon_r} (3 \cos^2 \phi - 1), \quad (5)$$

where ω_0 is the (unperturbed) angular velocity of rotation, ϕ is the angle between the axis of rotation and the field, and ϵ_r is the rotational energy. This expression was first obtained by Kallmann and Reiche⁹; it can be derived very simply by considerations due to Stern.¹⁰

⁷ Mensing and Pauli, *Phys. Zeits.* **27**, 509 (1926).

⁸ Kronig, *Proc. Nat. Acad. Sci.* **12**, 488 (1926).

⁹ Kallmann and Reiche, *Zeits. f. Physik* **6**, 352 (1921).

¹⁰ See Fraser, *Molecular Rays*, Cambridge, 1931, p. 156 ff.

⁶ Wrede, *Zeits. f. Physik* **44**, 261 (1927); Estermann, *The Dipole Moment and Chemical Structure*, ed. P. Debye, London 1931, p. 15 ff. (Leipziger Vorträge, 1929).

The result (5) still holds for more complicated molecular types, provided that their structural symmetry is sufficient to allow their temperature motion to be referred to a single axis of rotation; and provided also that the direction of the dipole moment is normal to this axis. In a complicated molecule, however, the latter proviso may not hold; in which case it is easy to show that if the angle between the axes of dipole moment and rotation deviates by only a few degrees from normality, then in spite of temperature rotation there will remain *to the first order* a dipole moment, independent of the field strength. Hence the deflection of a beam of such molecules in an inhomogeneous electric field will be a comparatively large first order effect, not a second order effect as in the case of the dumb-bell model (cf. I(3), p. 391 above).

2. Theory of a deflection experiment

Two successful forms of the deflecting field have been devised: (a) the beam is sent parallel to a charged wire^{6,11}; the directions of E and $\partial E/\partial s$ are the same (say z); $F_x = F_y = 0$ in (3); (b) the beam is sent at an angle between the plates of a parallel plate condenser; E and $\partial E/\partial s$ are at right angles.¹² (See Fig. 2.)

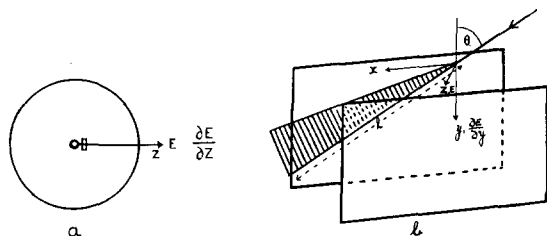


FIG. 2. Experimental arrangements for securing inhomogeneous electric fields.

In the first case, the deflection s of a single molecule at the exit of the field is given by

$$s = \frac{1}{4} \bar{\mu} (\partial E / \partial s) (l^2 / \epsilon_v), \quad (6)$$

where l is the length of path in the field, and ϵ_v is the energy of translation corresponding to the velocity v .

In the second case,

$$s = \frac{1}{4} \bar{\beta} \cdot \bar{E}^2 \cdot l \tan \theta / \epsilon_v \quad (7)$$

¹¹ Estermann, *Zeits. f. physik. Chemie* **B1**, 161 (1928).

¹² Rabi, *Zeits. f. Physik* **54**, 190 (1929).

to a first approximation; where θ is the angle of incidence of the beam, and \bar{E}^2 is averaged in the y direction over the distance $y' = l \cos \theta$. (See Fig. 2b.)

Eqs. (6) and (7) refer to the deflection of a single molecule, having a given velocity and value of $\bar{\mu}$ (or $\bar{\beta}$). In order therefore to examine more closely the character of the deflection suffered by a beam of molecules, we must consider how the value of v and $\bar{\mu}$ permitted under the temperature conditions of the experiment by Eqs. (4) or (5) are distributed amongst the molecules of the beam. We begin with the case of high temperature.

High temperatures. Substituting the value of $\bar{\mu}$ (or $\bar{\beta}$) from (5) in (6) and (7), we get

$$s = C \cdot \frac{3 \cos^2 \phi - 1}{\epsilon_v \epsilon_r}, \quad (6a), \quad s = C' \cdot \frac{3 \cos^2 \phi - 1}{\epsilon_v \epsilon_r}, \quad (7a),$$

where

$$C = (\mu^2/16) \cdot E \cdot (\partial E / \partial s) \cdot l^2, \quad C' = (\mu^2/16) \cdot \bar{E}^2 \cdot l \tan \theta$$

are constants of the experiment. Thus the deflection s suffered by a given molecule is decided by particular values of ϵ_v , ϵ_r , the probabilities of whose occurrence at high temperature are governed by a Maxwell distribution law; and of ϕ , all values of which are equally probable, since the beam is collision-free.

If $\epsilon_v = \epsilon_r = kT$ and $\phi = 0$, the corresponding deflection is

$$s_0 = 2C/(kT)^2 = 2C'/(kT)^2, \quad (8)$$

for the field dispositions (a) and (b) respectively; and the deflection s of any molecule referred to s_0 as norm is thus $s = \sigma \cdot s_0$.

It is convenient to calculate the intensity distribution in the deflected beam in terms of the quantity $\sigma = s/s_0$ rather than s . Fig. 3 shows the

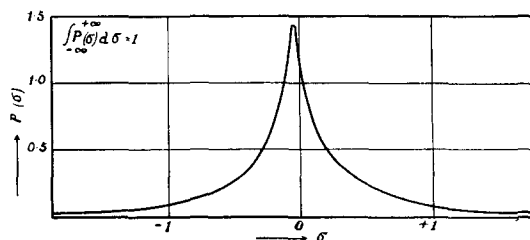


FIG. 3. Calculated intensity distribution in a deflected beam.

result of such a calculation, assuming a parent beam of negligible width; in the figure the probability $P(\sigma)d\sigma$ for the occurrence of deflections lying between σ and $\sigma+d\sigma$, obtained by numerical and graphical integration over the individual probabilities $P(\epsilon_v)d\epsilon_v$, $P(\epsilon_r)d\epsilon_r$, $P(\phi)d\phi$, is plotted against σ .¹³

It should be noted that the molecules are still assumed to be rigid in calculating the curve of Fig. 3; actually the electron configuration is distorted by the field, resulting in a polarization $\alpha \cdot E$ of the molecule in the field direction, the deflection due to which is superimposed on the deflection arising from the time-averaged moment.

The intensity distribution in the component of the deflection pattern arising from the electron polarizability is easily shown to depend on the equations

$$\left. \begin{aligned} P_p(\sigma)d\sigma &= e^{-1/\sigma} \cdot 1/\sigma^3 \cdot d\sigma, \\ \sigma &= s/s_0, \end{aligned} \right\} \quad (9)$$

where $P_p(\sigma)d\sigma$ is the probability for the occurrence of deflections between σ and $\sigma+d\sigma$, and s_0 is obtained from (6) or (7) with α substituted for β and kT for ϵ_v . Thus an actual deflection pattern is the summation of the curve of Fig. 3 and that expressed by (9). It frequently happens, however, particularly if the field conditions are properly chosen, that the contribution of (9) to the summation curve is negligible.

The feature of the intensity distribution revealed in Fig. 3 which is of chief importance from the experimental standpoint is the fact that the maximum of the curve lies very close to the position of the undeflected beam; thus the effect observed in a deflection experiment is a diminution of intensity at the position of the undeflected trace, coupled with a broadening of the beam, rather than a lateral deviation of the beam as a whole. The way in which this diminution of intensity can be made the basis of a quantitative evaluation of the dipole moment is exemplified for HCl in Part III.

Low temperature. The deflection suffered by a molecule in a given state j, m is obtained by substituting the appropriate value of $\bar{\mu}$ (or β)

from (4) in (6) or (7). In this case there is only one continuously variable quantity, namely ϵ_v ; and we define $s_0(j, m)$ for each state j, m as the deflection of a molecule in that state having an energy of translation $\epsilon_v = kT$. Then for each state in turn we can calculate the probability $P_{j, m}(\sigma)d\sigma$ for the occurrence of deflections $\sigma_{j, m} = s(j, m)/s_0(j, m)$ lying between $\sigma_{j, m}$ and $\sigma_{j, m} + d\sigma$. Now the probability that a molecule is in the state j, m is

$$P_{j, m} = e^{-E_j/kT} / \sum_{j, m} e^{-E_j/kT}, \quad (10)$$

where E_j is the energy of rotation in the state j ; the summation extends over all states, the energy differences of the states having the same j but different m being neglected. Thus the intensity distribution in a deflected beam at low temperature, containing molecules in a number of energy states, is obtained by plotting the $P_{j, m}(\sigma)d\sigma$ vs. σ curves for the individual states, properly weighted in accordance with (10), and constructing the summation curve. An example of such a curve, for the case of HCl at 120°K, is given in Fig. 4; for the sake of clearness, the individual $P_{j, m}(\sigma)d\sigma$ curves are shown for the three lowest rotation states only. As in the corresponding high temperature curve (Fig. 3) a parent beam of negligible width has been assumed, and the ordinates chosen to make the area under the summation curve unity. It will be seen that the lowest energy state $j=0$, which alone contributes to the observed dielectric constant, gives rise to *attracted* molecules ($\sigma+ve$) only in a deflection experiment. Thus the repelled molecules which have in fact been observed (at high temperature) are direct qualitative evidence of the presence of the higher rotation states (cf. I(4) above). In order to identify the individual j, m states, however, it will be necessary to carry out the deflection experiment with a velocity selector; otherwise as seen in Fig. 4, only a single maximum can be expected.

III. EXPERIMENTAL

1. Intensity measurements

It will have been evident, from consideration of the character of the deflection patterns of Figs. 3 and 4, that in order to evaluate the dipole moment, or in fact to make any quantitative

¹³ Feyerabend, Hamburger Staatsexamensarbeit; see Fraser, reference 10, p. 162 ff.

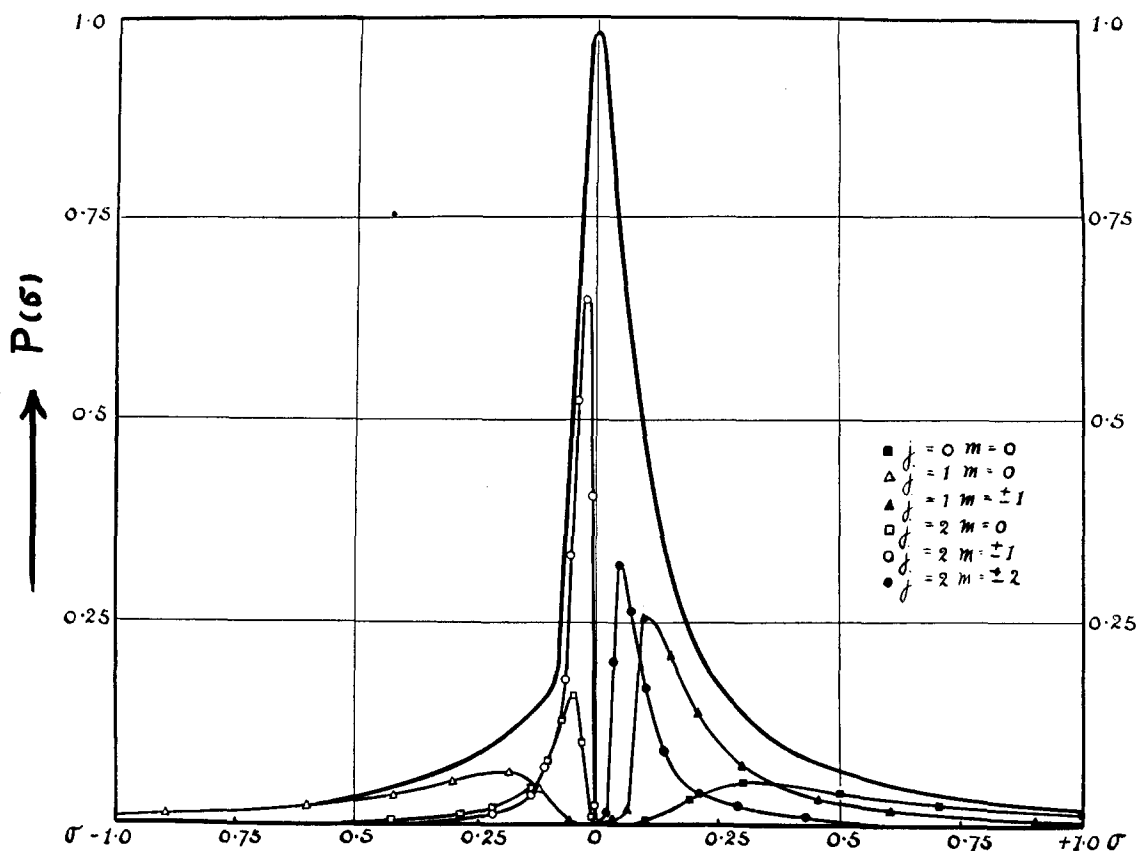


Fig. 4. Calculated intensity distribution in a beam at low temperatures taking account of the distribution of molecules in different rotational states.

deductions therefrom, a quantitative method of measuring the intensity distribution in the deflected beam was absolutely essential. The earlier work in this field had all been done using the condensation target as detector; hence the results could only be regarded at best as semi-quantitative. It was necessary to find suitable quantitative methods of detection for two chief classes of substances: on the one hand, easily condensable organic substances, where examples of the problems enumerated under I(1) and I(2) more particularly arise; on the other, gases and volatile substances which it is possible to examine at low temperature. For the first class of substances, a special form of detector making use of the heat of condensation was worked out and applied to *p*-nitranaline¹⁴; for the second class exemplified here by HCl, it was only necessary suitably to adapt an already existing method for

the detection of gases, namely to allow the beam to enter by a slit an otherwise closed vessel containing a hot wire gauge, and to measure the resulting equilibrium pressure.¹⁵

2. The deflecting field

It is much easier to obtain comparatively large deflections with the charged wire field arrangement than with the parallel plate condenser. Nevertheless, the Rabi field is to be preferred for quantitative measurements on the following grounds:

(1) It is impossible except by recourse to beams of very small cross section to obtain a high inhomogeneity near a charged wire which shall at the same time be constant over the cross section of the beam.

(2) It is difficult to estimate the values of E and $\partial E/\partial s$ (Eq. (6)) near the wire on account of

¹⁴ Wohlwill, *Zeits. f. Physik* 80, 67 (1933).

¹⁵ Knauer and Stern, *Zeits. f. Physik* 53, 766 (1929).

the departure of practical arrangements from the form of the ideal cylindrical condenser; on the other hand, \bar{E}^2 (Eq. (7)) is readily obtained, if the plates are properly designed, from the theory of the parallel plate condenser.

(3) The field near a charged wire varies as the inverse cube of the distance from its center; hence the contribution of the electron polarization $\alpha \cdot E$ to the deflection pattern can easily become unduly prominent.

(4) The convenience of the method of estimating the dipole moment from the diminution of intensity at the position of the undeflected beam can actually make a small deviation of the maximum of the deflection pattern from that position an advantage.

For these reasons, the parallel plate condenser field was chosen for use in measuring the dipole moment of hydrogen chloride.

3. Apparatus

The apparatus in its final form is shown in Fig. 5. The beam system, consisting of the source slit S_s ; the fore slit F_s ; the image slit I_s ; the parallel plate condenser C ; and the detecting system, a pair of Pirani gauges P_g , is mounted on a rail R . The upper surface of the rail is ground true, and the slits are adjusted parallel to this surface, by means of a rider carrying a knife edge, before inserting the beam system into the apparatus.

The image and fore slits are carried each on a

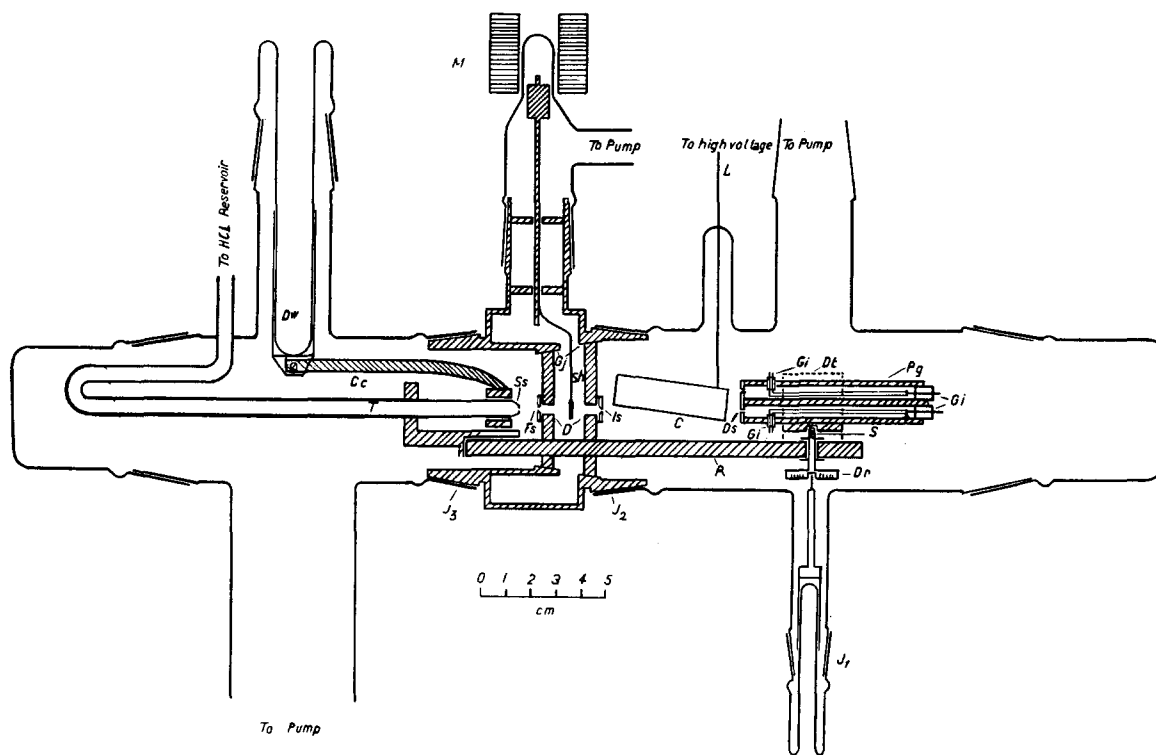


FIG. 5. Experimental arrangement of the apparatus.

very short male cone, fitting the corresponding female seating G_j in the central housing of the apparatus. In this way, the apparatus is divided into three chambers: the source chamber, the collimator chamber, and the observation chamber. Each chamber is separately evacuated by means of a butyl phthalate diffusion pump

specially designed for high pumping speed.¹⁶ The vacuum envelopes for source chamber and observation chamber are of Pyrex, and are connected to the central housing by the ground joints J_3 and J_2 , respectively. The central hous-

¹⁶ Estermann and Byck, Rev. Sci. Inst. 3, 482 (1932).

ing is of Monel metal, as are all metal parts, this material having been found to resist the corrosive action of HCl rather well.

The beam is defined by the slits S_s and I_s , which are 0.016 mm and 0.04 mm wide, respectively. The function of the fore slit F_s is not to define the beam, but to step down the vacuum from about 5.10^{-4} mm in the source chamber to about 10^{-6} mm in the observation chamber, the pressure in the central chamber being about 10^{-5} mm; its width is therefore comparatively large, about a tenth millimeter. The source slit is given a wedge-shaped form in order to reduce the Knudsen resistance between it and the fore slit, the distance between them being only 7.3 mm.

The detecting system diverges markedly in design from that used in previous work on gas beams.¹⁵ There the detector slit was connected via a narrow tube to a glass-walled gauge outside the apparatus, the gauge being immersed in liquid air to give increased sensitivity. Now HCl is strongly adsorbed on glass walls, and moreover it is too readily condensible to make cooling profitable; therefore the gauge was made of Monel metal, and was placed inside the apparatus. In this way it was possible to make the volume of the gauge very small, thus reducing the incidence of adsorption.

The detector slit D_s , in the form of a canal 3 mm high, 0.04 mm wide, and 1.5 mm deep, communicates directly with the gauge; immediately above it, but outside the range of the beam, an exactly similar canal communicates with a second gauge, the function of which is the compensation of pressure and temperature variations.¹⁵ The two gauges are made from the solid: two parallel holes are drilled in a block of Monel metal; these holes are closed at each end, at the front by plugs carrying the canals, at the rear by glass insulators G_i carrying each a platinum hook. Near the front end of each gauge a second glass insulator enters from the side, carrying the platinum leads for the gauge filament F . The latter, of platinum strip 0.05 mm wide, and 0.003 mm thick, is looped double over the platinum hook as seen in Fig. 5.

The block housing the gauges is mounted on a dovetailed slide Dt , and can be traversed across the beam by means of the screw S operated by a screwdriver carried on the ground

joint J_1 . The position of the detector slit D_s can be read off on the graduated drum Dr , each scale division corresponding to a movement of the detector slit of 0.01 mm.

The gauges form two adjacent arms of a Wheatstone bridge; thus stray pressure changes occurring in both gauges simultaneously are not registered by the galvanometer. A pressure change of 10^{-6} mm in the measuring gauge gave a galvanometer deflection of 3 cm at a scale distance of 130 cm; the galvanometer sensitivity was 10^{-7} volt/mm at one meter. To eliminate zero creep, timed readings were taken at intervals of 15 sec. with the beam alternately allowed to enter the detector slit and cut off therefrom by the electromagnetically operated shutter Sh , working in the central chamber.

The deflecting field is produced at the entrance of the parallel plate condenser C . One plate is mounted, with provision for adjustment, directly on the rail R , which is earthed via the central housing; the other plate is carried on the first by a glass U , and is connected by the lead L to a high-voltage source consisting of a transformer and one wave rectifying set (Kenotron and Leyden jar). The plates are 40 mm by 10 mm, with a gap of 2.3 mm. The angle between the edges of the plates and the beam was 7° . The edges are carefully rounded to follow in outline as far as possible the equipotentials at the entrance of an ideal parallel plate condenser; in this way it was possible to calculate the average field E^2 with confidence from the theory of the parallel plate condenser.

The gas was fed to the source slit, which can be cooled if necessary by the Dewar Dw through a heavy flexible lead of copper Cc , from a reservoir in which the pressure of HCl was held constant at about 2 mm, this reservoir being fed in turn from a high-pressure reservoir through an adjustable leak. Before starting a run, however, it was found necessary to fill the apparatus with HCl at some centimeters pressure for several hours, in order first to saturate the walls of the gauges with the gas.

The intensity distribution in the beam was measured first without field, then with field, and finally again without field. Since the intensity in the parent beam is not absolutely constant, the intensity at a given point in the deflected beam

was compared with the average value of the intensity at that point observed in the bracketing runs without field; but only those complete runs in which the parent intensity remained constant to within 10 percent were accepted.

4. Results

An example of the results obtained is given in Fig. 6, which shows the intensity distribution in an undeflected beam, and that in the same beam after passage through the electric field.

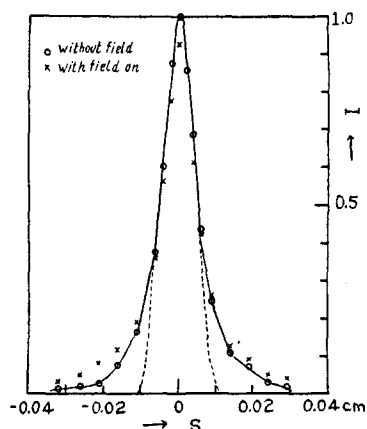


FIG. 6. Experimental distribution of molecules in a deflected and an undeflected beam.

The dipole moment of the HCl molecule is evaluated from the intensity diminution at the position of the maximum of the undeflected trace. The argument is as follows: The width of

the undeflected beam is not negligible in comparison with that of the deflected beam, as was assumed in calculating the ideal curve of Figs. 3 and 4, but has the form shown in Fig. 7. Let $f(\sigma_0)$ be the equation of the curve representing it; then the equation of the deflected beam is clearly

$$F(\sigma_0) = \int f(\sigma_0 + \sigma) P(\sigma) d\sigma, \quad (11)$$

where $P(\sigma)$ is the shape of the deflected beam arising from a parent beam of negligible width, $\int P(\sigma) d\sigma$ being normalized to unity. In particular the ordinate at the center of the deflected beam, assuming it coincident with the center $\sigma_0 = 0$ of the undeflected beam, is

$$F(0) = \int f(\sigma) P(\sigma) d\sigma \quad (12)$$

and is obtained by multiplying each ordinate of the undeflected beam by the appropriate $P(\sigma)$ and then integrating.

In order to evaluate μ , therefore, the abscissae of the experimental curve for the undeflected beam are reduced to the same abscissae σ as the curve of Fig. 3 for a certain assumed value of s_0 (see Fig. 7): the ordinates being reduced so that I_{\max} is unity. Multiplication of each ordinate of this reduced curve by the appropriate $P(\sigma)$ gives the dotted curve of Fig. 7, the area under which (cf. Eq. (12)) represents I'_{\max} , the intensity at the maximum of the deflected curve for

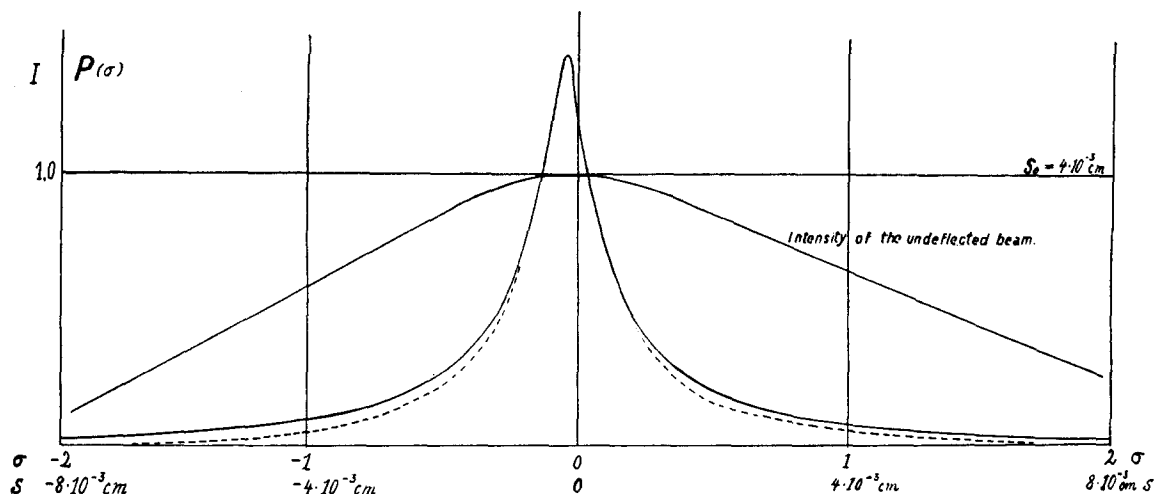


FIG. 7.

the particular value of s_0 assumed. In this way I'_{\max} could be plotted as a function of $s_0 = (\mu^2/8(kT)^2) \cdot \overline{E}^2 \cdot l \tan \theta$ for a given set of experimental conditions.

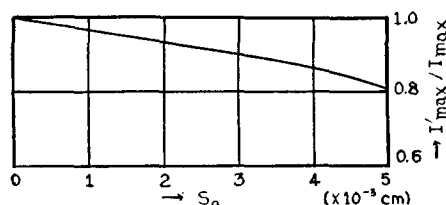


FIG. 8.

Such a plot under the conditions of the present experiments is given in Fig. 8. The value of s_0 corresponding to a given value of I'_{\max}/I_{\max} is read off from the curve, and μ evaluated. Table I gives a summary of the results.

TABLE I.

$$\mu^2 = s_0 \cdot 8(kT)^2 / \overline{E}^2 \cdot l \tan \theta$$

$l = 4.72$ cm; $\theta = 83^\circ$; $T = 290^\circ$; $\overline{E}^2 = 0.6E^2$ e.s.u.; Condenser gap $d = 2.3$ mm; $V = 0.23E$ e.s.u.

Run No.	V kilovolt	I'_{\max}/I_{\max}	$10^4 \cdot s_0$	$\mu \cdot 10^{18}$
I	35	0.95	14	1.69
II	32	0.97	10	1.56
III	35	0.92	24	2.21
IV	35	0.93	21	2.07
V	40	0.90	31	2.20
Mean value: $\mu = 1.95 \times 10^{-18} \pm 0.1_3$ e.s.u.*				

* The limit of error given above does not of course account for systematic errors which may arise, e.g., in determining the form of the curve for the undeflected beam.

Two assumptions have been made in the calculations, which must be justified. (1) The maxima of the deflected and undeflected beams have been assumed coincident. Now the mean value

s_0 from Table I is 2.10^{-3} cm; the value of σ at the maximum of the probability curve of Fig. 3 is 0.04; hence the displacement $\sigma \cdot s_0$ of the maximum of the deflected curve from that of the undeflected curve is $s \sim 1\mu$, and can be neglected. (2) No account has been taken of the electron polarizability. The polarizability α of HCl as measured by Zahn¹⁷ is 1.70×10^{-24} e.s.u.; with the field strengths used $\alpha \cdot E \sim 2 \cdot 10^{-22}$; insertion of this value in Eqs. (9) shows that the effect of the polarizability on the height of the deflected maximum is less than 3 percent, and it can therefore be neglected.

Great accuracy is not claimed for the present experiments. They should rather be regarded, together with the parallel investigation on easily condensable substances referred to on p. 395, as a first attempt to obtain quantitative data on dipole moments from molecular ray experiments. It should be readily possible, for example by using narrower beams and stronger fields, greatly to improve the accuracy of the method.¹⁸

It is intended to repeat the experiments under improved conditions, and moreover with a cooled source slit, in order to realize the case of low temperature dealt with in Section II of this paper, where the influence of the quantum distribution of the rotational states becomes noticeable.

We are glad of this opportunity to express our several thanks to Professor O. Stern and Professor G. N. Lewis, who successively gave the above work the ready hospitality of their respective laboratories.

¹⁷ Zahn, Phys. Rev. **24**, 400 (1924).

¹⁸ Owing to the expiration of the Fellowship held by one of us (I. E.), the experiments had again to be interrupted; but we considered the results so far obtained to be sufficiently interesting methodically to justify publication.