The Dipole Moments of the Alkali Halides

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Citation: The Journal of Chemical Physics **4**, 372 (1936); doi: 10.1063/1.1749861
View online: http://dx.doi.org/10.1063/1.1749861
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/4/6?ver=pdfcov
Published by the AIP Publishing

believes, on the basis of his own experiments and those of his co-workers, that the reaction is simple—at least, he seems to feel that complications of the type envisaged by Baker and Hasche do not occur. More recently Bodenstein[14] has stated his belief that $(NO)_2$ is an intermediate and has cited the work of Eucken and d'Or[1] and Johnston and Weimer[3] as indicating its existence. He has also mentioned experiments which indicate that the change of temperature coefficient at low temperatures found by Briner, Pfeiffer and Malet[15] and discussed in my article does not actually exist.

It should, perhaps, be remarked that this correction is completely consistent with our previous assumptions about the liquid only if it is independent of the amount of association in the liquid.

[14] Bodenstein, Helv. Chim. Acta **18**, 745 (1935).

[15] Briner, Pfeiffer and Malet, J. Chim. Phys. **21**, 25 (1924).

JUNE, 1936 JOURNAL OF CHEMICAL PHYSICS VOLUME 4

The Dipole Moments of the Alkali Halides

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(Received April 3, 1936)

THE dielectric constants of highly polar substances may not be determined in solution because of the polarity of the solvent necessary, nor in the vapor state at high temperatures because of the conductivity of the vapors, especially when in contact with metal surfaces. The only method available is the molecular ray method, and this method has been applied by Stern[1] and his collaborators to a number of substances under conditions which were not favorable to precise determinations of the moment. Because of the complicated situation produced by the superposition of the translational and rotational distributions on the space quantization of rotating dipoles in an electrostatic field, a very exact quantitative measurement of beam intensity is required for a calculation of the moment. Some years ago, one of the authors[2] found that the Taylor[3] hot filament detector worked as well for alkali halides as for alkali metals, and it was at once apparent that it would be possible to determine the moments of the alkali halides by the beam method. This research has been continued in various forms of apparatus for several years. The moments obtained were always of the same order of magnitude, but there were so many sources of uncertainty that publication has been delayed until these were eliminated so far as possible. A preliminary report of this work was given at the Oxford meeting of the Faraday Society in 1934. Since then, Scheffers[4] has published results for three salts obtained by using a method similar to ours. Our results are not in agreement with those of Scheffers. Possible reasons for the discrepancy will be discussed later in this article.

THE POLAR CHARACTER OF SALT MOLECULES

It may be predicted from general considerations of a chemical character and perhaps more definitely from wave mechanics considerations that the alkali halides should have a higher dipole moment than is ordinarily observed in diatomic molecules. If one assumes, as has usually been done, that this moment is of the order of magnitude of 10 Debye units, then a very simple consideration shows that a considerable tendency to association should exist. The situation in the saturated salt vapor at temperatures below the melting point of the salt is analogous to the situation in dilute solutions in a solvent of low dielectric constant, where Kraus[5] has found evidence of association. From familiar analogies one would expect this association to be limited to double molecules which would have zero moment, and one is thus led to the paradox that a high dipole moment should not be observed at all. This conclusion is evidently contrary to fact, and it is not possible to make any predictions as to association or how it should vary with the temperature of the

[1] I. Estermann and R. G. J. Fraser, J. Chem. Phys. **1**, 391 (1933).

[2] W. H. Rodebush and W. F. Henry, Phys. Rev. **39**, 386 (1932).

[3] J. B. Taylor, Zeits. f. physik. Chemie **57**, 242 (1929).

[4] H. Scheffers, Physik. Zeits. **35**, 425 (1934).

[5] R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc. **57**, 1 (1935).

saturated vapor. It is possible that the associated molecules may have a greater moment than the single molecules. The moments reported here are the apparent moments as measured, and the question of association will be discussed elsewhere.

Method and Apparatus

The experiment consists in passing a beam of salt vapor through a Rabi type of electrostatic field and mapping the beam, with the field on and off by means of the positive ionization detector. An elaborate description of the apparatus is not necessary, since the various constituent parts of the apparatus have been described elsewhere.[6] A schematic drawing of the furnace slit system field plates and detector is shown in Fig. 1. In order to simplify the problem of alignment, the furnace, slit system, and field plates were mounted upon a metal base which was removable as a unit from the vacuum chamber. The vacuum chamber consisted of a brass tube of $4\frac{3}{4}$ in. internal diameter and 30 in. length. The ends of this tube were closed by glass plates which were ground to give a vacuum-tight joint when lubricated with a suitable stopcock grease. The vacuum was produced by glass pumps, using dibutyl phthalate as a vapor. These pumps were provided with the high speed turbine type of nozzles designed by Drs. Copley and Phipps[7] in this laboratory. With these pumps it was possible to maintain at all times a pressure of about 10^{-6} mm of mercury.

The furnace of tungsten steel was similar to the one designed by Lewis.[8] Tungsten coils were suspended in holes drilled in the walls of the furnace, the heat from the coils being transmitted by radiation. Some difficulty was experienced in early work with electrolysis of the salt. In order to avoid this, a special removable crucible was placed inside the furnace. This crucible was in contact with the furnace only at its base. The temperature of the furnace was controlled by a thermocouple, photoelectric cell, thyratron tube, set-up which proved to be highly satisfactory. In measuring intensities with the field, off and on, it is of the utmost importance to avoid temperature fluctuations. The temperature variations were ordinarily less than 0.2 degree. The accuracy with which the absolute temperature is known is of less importance for the measurement of the moments.

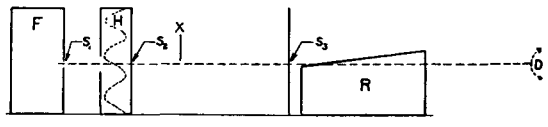

Fig. 1.

The plates for the Rabi type field were mounted 1.65 mm apart on quartz rods of sufficient rigidity, to maintain the separation against the mechanical forces due to the electrostatic field. The electrostatic field was produced by the customary arrangement of transformer, kenotron and condenser. Elaborate tests were made to demonstrate the constancy of the field.

The detector consisted of a tungsten filament, cylindrical plate, and high sensitivity galvanometer. The detector filament was mounted eccentrically on a ground-glass joint, and the position of the filament was indicated by a protractor arm of $8\frac{1}{2}$ in. length. The filament was 0.05 mm in diameter. So far as the conditions of this experiment are concerned, two slits are sufficient to define the beam, but it was found simpler to use three slits in actual practice. In the simple design of furnace used, the outside of the slit was somewhat cooler than the inside, so that difficulty was experienced in keeping the slit free from deposited salt when the slit was small enough to define the beam. Accordingly, an intermediate slit, designated as a "heated slit," was introduced. This slit was cut in a nickel cylinder on the inside of which a tungsten filament was suspended so that the slit could be heated at frequent intervals to drive off salt deposits. It proved very satisfactory in operation.

The distance between the second and third slit was 5.7 cm. The distance from the third slit to the point of incidence of the field was 1.5 cm and the distance from the point of incidence to the detector filament was 7.6 cm. A magnetically controlled shutter was provided, so that the beam could be turned off and on at will.

[6] R. G. J. Fraser, *Molecular Rays* (Cambridge University Press, 1931).
[7] M. J. Copley and T. E. Phipps, Rev. Sci. Inst. **6**, 265 (1935).
[8] L. C. Lewis, Zeits. f. physik. Chemie **69**, 786 (1931).

The detection of beam intensity by the positive ion current is enormously complicated by the presence in the apparatus of a somewhat unsteady high potential on the field plates, which inevitably must affect the sensitive galvanometer required for detection. This difficulty was avoided by using the method introduced by Rabi[9] in which the salt molecules are deposited on a cold filament for a measured period of time. At the end of this period, the shutter is closed, the field on the plate switched off, and the filament is flashed, the resulting positive ion current being then measured by the ballistic throw of the galvanometer. Experiment shows that, when more than about five percent of the filament surface is covered, not all the alkali atoms come off as ions, so that the deflection is no longer proportional to the time of exposure. The limiting time of exposure, for which the deflections were proportional to the time, varied, as might be expected, with the size of the salt molecule for a given beam intensity. Most of the readings were made with an exposure period of three minutes. The galvanometer had a ballistic sensitivity of 4×10^{-11}.

Theoretical Considerations

The theory of the deflection of diatomic molecules in an inhomogeneous electrostatic field has been discussed by Fraser[6] and by Fraser and Estermann.[10] One is dealing here with a superposition of three distributions of the molecules in the field. These distributions are with respect to linear velocity, rotation and space quantization in the field. The moment that is effective in the deflection is the moment averaged over a complete rotation. Feierabend has made the very laborious calculation of the form of the distribution curve for a beam of zero width. In the actual experiment, however, we find that there are two further complications; the finite slit width and the finite width of the detector filament.

The latter quantity has an important bearing upon the design of the slit system, and will be considered first. When the beam is defined by two slits identical in size and shape, the intensity

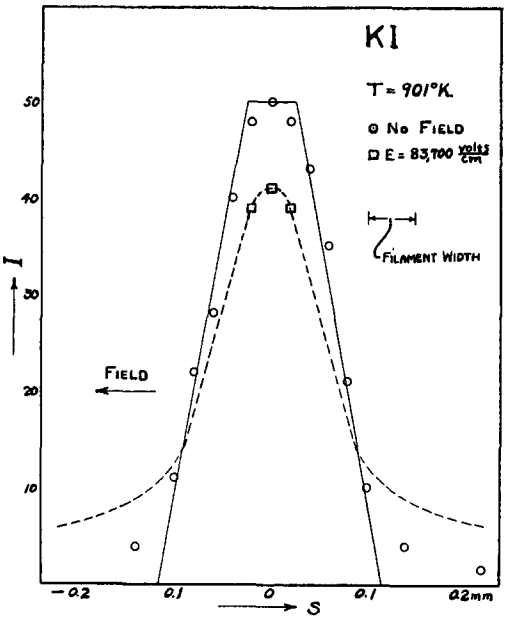

Fig. 2.

in the beam plotted against a space coordinate taken perpendicularly to both beam and slits forms a trapezoid (Fig. 2). The flat part of the trapezoid corresponds to the umbra, and the sides to the penumbra. This is for the undeflected beam. With the field on, the intensity curve is altered in a way that may be approximately described as a trapezoid of lower altitude and broader base. It turns out that the most important measurements are the altitudes of the trapezoids in the two cases. In order that the altitude be measured with certainty, the flat part of the beam should be at least as wide as the detector filament. In order to obtain the maximum sensitivity, which means the maximum decrease in the altitude of the trapezoid when the field is on, the beam should not be wider than this. The best conditions, therefore, appear to be obtained when slits and detector filament are of the same width. In our experiments the slits were approximately 0.05×0.5–0.8 mm.

As the detector filament is moved through the beam, the "corners" of the trapezoid are rounded off and "tails" are produced by the overlapping, so that the actual curve of galvanometer deflections obtained is that corresponding to the circles (Fig. 2). If the geometry of the slit system is known with sufficient exactness, the trape-

[9] I. I. Rabi and V. W. Cohen, Phys. Rev. **46**, 707 (1934).
[10] I. Estermann and R. G. J. Fraser, J. Chem. Phys. **1**, 390 (1933).

zoidal curve may be inferred from the actual curve obtained, but the only points on the two curves that correspond are the maximum and the mid-portions of the sides. If a sufficient number of readings are taken, a satisfactory correspondence may be established between the curve of galvanometer deflections and the true trapezoidal intensity curve, but experience has shown that the true intensity curve may be calculated from the geometry of the slits, provided they are carefully constructed, with an accuracy quite equal to that obtained by careful mapping of the actual beam by galvanometer deflections. The measurement on the undeflected beam is, therefore, in practice limited to the measurement of the maximum intensity.

Similarly, for the deflected beam, it turns out that the only measurement of significance is the maximum intensity. Since, in deflection experiments of this character, the two maxima apparently coincide in space, when once the position of the maximum has been located a series of readings may be taken with the field alternately on and off without moving the filament.

The intensity curve of the deflected beam may be considered as a distorted trapezoid lowered and broadened with sides which are no longer straight lines.

The upper corners of the trapezoid will also be rounded off so that the top of the trapezoid is no longer flat, and the maximum reading obtained with the detector filament is not the actual maximum intensity of the beam, but something less. It is not possible to reconstruct the intensity curve, therefore, from galvanometer deflections with any certainty, except in the edges of the beam where the intensity is too low to permit accurate determinations. It is possible, however, to assume an approximate value of the moment and calculate the exact shape of the curve in the neighborhood of maximum intensity from theoretical considerations. The exact shape of the curve being known, it is, therefore, possible to calculate the exact maximum intensity from the galvanometer reading, and hence the true value of the moment as a second approximation. In our experiments, the actual galvanometer readings of maximum intensity were shown to be about one percent too low.

The general shape of the intensity curve with the field on is given by the dotted line in Fig. 2. This shows the general characteristics of similar curves obtained in beam experiments in that the upper part of the curve does not appear changed in shape, but only decreased in height.

The dipole moment is, therefore, calculated from the percentage decrease in maximum intensity of the beam when the field is applied and the accuracy depends upon the accuracy with which this percentage decrease is measured. The percentage decrease may be made greater in magnitude by decreasing slit width and increasing the distance between the field and detector filament, but this change is accompanied by a decrease in the magnitude of the deflection so that there is no advantage in changing dimensions of the apparatus beyond a certain point. Similarly, increasing the sensitivity of the galvanometer does not increase the reliability of the measurements. A possible way of increasing the precision of the measurements would be to increase the strength of the field on the Rabi plates, but there are practical limitations here too.

We have finally to consider the effect of finite slit width on the calculation of the moment. The curve calculated by Feierabend, previously referred to, gives the distribution of the intensity in a beam from slits of infinitesimal width. We may represent the Feierabend curve as a function of the deflection in mm $P_{(s)}$. The intensity curve of the undeflected beam may be represented in a similar way as $f_{(s)}$, where s is now the displacement of the detector filament in mm. It has been shown by Estermann[10] that the intensity at the maximum of the deflected beam is given by the integral

$$I=\int_{-\infty}^{+\infty} f_{(s)}P_{(s)}ds.$$

The integral must be obtained by quadrature, since the function $P_{(s)}$ is not known. The values for $P_{(s)}$, as given by Feierabend, are not given for actual deflection, but for an argument,

$$\sigma=s/s_0,$$

where s is the actual deflection, and s_0 is the deflection that a molecule would experience when in certain quantum states that are taken as an

TABLE I.

DATA FOR SAMPLE RUN KI	
Temperature	901°K
Field intensity	83,700 volts/cm
Average maximum intensity undeflected beam	64.8
Average maximum intensity deflected beam	55.3
Distance field plates to detector	76 mm
θ	7° 48′
s_0	0.00263 mm
μ	11.1×10^{-18} l.s.

TABLE OF RESULTS

SALT	TEMPERATURE	$\mu\times10^{18}$	RESULTS OF SCHEFFERS
KCl	949°K	9.74	6.3 (1023°K)
	"	9.74	
	"	9.25	
	"	9.40	
	"	9.54	
KBr	916	10.8	
	925	10.9	
KI	894	11.0	6.8 (950°K)
	901	11.1	
CsI	873	12.1	

average or standard state. s_0 is actually given by the equation

$$s_0=\mu^2E^2l/8(kT)^2\tan\theta,$$

where kT is the Boltzmann factor, E the field intensity, l the distance from the point of incidence to the detector filament and θ is the angle between the incident beam and the field plates.

μ is, of course, the dipole moment, and the calculation of the maximum intensity of the deflected beam is made by assuming different values of μ until one is obtained which gives a value in agreement with the experimental results.

By reference to Table I, it is seen that the values as calculated from our experiments are much greater than those obtained by Scheffers. The order of arrangement of the salts according to moment appears to be the same in the two experiments. A rough prediction of this order could be made from a consideration of the ionic radii.

Scheffers' results are at higher temperatures and pressures than ours. The discrepancy between the two sets of experiments could be accounted for by association. Until the question of association is settled, one may not draw conclusions as to the actual moment of the molecules.

Scheffers used an inhomogeneous electrostatic field produced by a wire and concentric cylinder. This type field gives a greater deflection, but it is necessary to locate the beam with exactness with respect to the wire. The Rabi type of field does not introduce any serious uncertainty so long as the angle of incidence is not made too small, but it does not give as large a deflection. We have tested the Rabi field for "end effects" by changing the point of incidence of the beam. No change in the apparent moment was observed. We have not checked the calculation of Fraser that the effective square of the electric moment is 0.6 times the field between the plates. If this conclusion is in error, then our results would be in error by a corresponding amount.

It is difficult to estimate errors in a measurement which involves so many variables in such a complicated way, but with a great many measurements made under different conditions we have never obtained more than a ten percent variation in the effective moment.

In every case we tested the beams for ions by applying a low field to the Rabi plates, but only in the case of cesium fluoride did we observe an appreciable diminution of intensity.

The purity of the salts used was tested. They were shown to be free from appreciable amounts of impurities.

The fact the dipole moments obtained are of the order of magnitude expected and increase with the ionic radii may be considered as evidence favoring the conclusion that the salt vapors contain single molecules only. The density of salt vapors has been investigated at some length in this laboratory by Dr. V. Deitz, and the results of his investigations will be published elsewhere.

The dipole moment obtained indicates that a mixture of the ionic and homopolar types of bonding prevails in salt molecules. If the bonding were purely ionic in character, a still larger dipole moment would be anticipated than has been observed.

The authors wish to acknowledge their indebtedness to Drs. M. J. Copley and T. E. Phipps of this laboratory for many helpful suggestions.