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Author
Story Jr., T.L.

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T. L. Story, Jr. and A. J. Hebert

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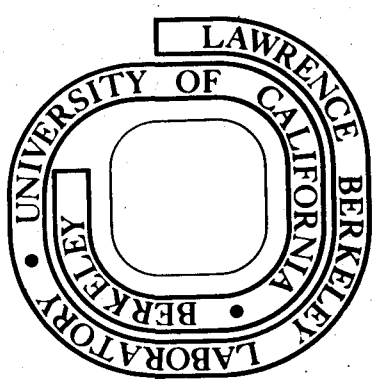

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DIPOLE MOMENTS OF KI, RbBr, RbI, CsBr, AND CsI BY THE ELECTRIC DEFLECTION METHOD*

T. L. Story, Jr.† and A. J. Hebert

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

September 1975

ABSTRACT

Electric deflection experiments using a velocity selected molecular beam apparatus have given the following electric dipole moments:

Molecule	μ_e (Debye)
KI	10.82 (10)
RbBr	10.86 (10)
RbI	11.48 (10)
CsBr	10.82 (10)
CsI	11.69 (10)

†Present address: Howard University, Department of Chemistry, Washington, D. C. 20001

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I. INTRODUCTION

The electric dipole moments of most of the alkali halides have been accurately determined from their Stark spectra using the molecular-beam electric-resonance (MBER) method. Due to the complexity of the spectra and beam intensity considerations, five of the heavier alkali halides, KI, RbBr, RbI, CsBr, and CsI, have eluded MBER practice to date. Most MBER spectrometers (including our own) sacrifice some intensity in order to obtain high resolution, and while it may be possible to design a spectrometer to measure the dipole moments of these molecules, this would be a rather expensive undertaking. To obtain some moderately accurate electric dipole moment values (about 1%), we have run deflection experiments using a velocity selected molecular beam apparatus.

Early experiments[1,2] indicated the feasibility of determining dipole moments by analysis of the deflection characteristics of molecular beams in an inhomogeneous electric field. The accuracy of these experiments was limited by the thermal distribution of molecular velocities, uncertainties as to the polymer content of the beam, and the necessity of an accurately known field gradient along the molecular trajectory. In the present experiments the first two of these difficulties were largely eliminated by the use of velocity selection and the third by making measurements relative to alkali halides with accurately known dipole moments.

II. THEORY OF THE DEFLECTION EXPERIMENTS

The electric deflection method as used in our experiments involves first measuring the intensity of a velocity selected molecular beam; then, the beam is deflected by an inhomogeneous electric field perpendicular to the beam axis and the intensity measured again. The theoretical expressions necessary for interpreting the experiments have been given by Fraser[1,3] for the case of a thermal

distribution of velocities. For the case of a velocity selected beam the derivations follow in a straightforward way and only the necessary minor changes in notation and the final results will be given here.

Fraser's analysis assumes a rigid rotor of dipole moment μ, thermal equilibrium of the rotational states, and a temperature sufficiently high so that the rotations can be treated classically. The distance of deflection s of a molecule in the direction x, perpendicular to the beam axis is given by

$$s = \frac{1}{8} \frac{\mu^2 E}{m} \left(\frac{\partial E}{\partial x}\right) \frac{\ell^2}{v^2} \frac{3\cos^2\phi - 1}{W_r} ,$$

where E is the electric field intensity, m the mass of the molecule, ℓ the length of the trajectory in the field, v the molecular velocity, ϕ the angle between the axis of rotation and the field, and W_r the rotational energy. If s_0 is taken to be the deflection of a molecule with

$\phi = 0$, $W_r = kT$, and velocity v, then

$$s_0 = \frac{1}{4} \frac{\mu^2 E}{m} \left(\frac{\partial E}{\partial x}\right) \frac{\ell^2}{v^2} \frac{1}{kT} ,$$

and deflections can be conveniently expressed in terms of the dimensionless quantity σ where

$$\sigma = s/s_0 = \frac{1}{2} (3\cos^2\phi - 1) \frac{kT}{W_r} .$$

The probability $P(\sigma)d\sigma$ that a molecule will be deflected through a distance between σ and $\sigma + d\sigma$ is given by

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$$P(\sigma)d\sigma = \int_{P_1}^{P_2} \left(\frac{3p^2-1}{2\sigma^2}\right) \exp\left(-\frac{3p^2-1}{2\sigma}\right) dp d\sigma,$$

where $p = \cos\phi$. This is just the result given by Fraser without the integration over the velocity distribution. Taking s and σ to be positive in the direction of increasing field gradient, then

$$s > 0 \quad \text{when} \quad \frac{1}{3} < p^2 \leq 1$$

$$s < 0 \quad \text{when} \quad 0 \leq p^2 < \frac{1}{3}.$$

Whereas for a thermal distribution of velocities the integration of $P(\sigma)d\sigma$ must be done numerically (this was done by Feyerabend and reported by Fraser[3]), in the present case the results of the integration can be expressed in terms of tabulated error functions and Dawson functions;

$$P(\sigma_+) = \frac{1}{\sqrt{12}} \frac{1}{\sigma_+} \left[\sqrt{\frac{2}{\sigma_+}} (\sigma_+ - 1) \frac{\sqrt{\pi}}{2} \left\{\exp\left(\frac{1}{2\sigma_+}\right)\right\}\right.$$

$$\left. \times\left(\operatorname{erf}\sqrt{\frac{3}{2\sigma_+}} - \operatorname{erf}\sqrt{\frac{1}{2\sigma_+}}\right) - \sqrt{3}\left\{\exp\left(-\frac{1}{\sigma_+}\right)\right\} + 1\right]$$

$$P(\sigma_-) = \frac{1}{\sqrt{12}} \frac{1}{\sigma_-} \left[\sqrt{\frac{2}{\sigma_-}} (\sigma_- + 1) \left(\mathrm{DAW}\sqrt{\frac{1}{2\sigma_-}}\right) - 1\right].$$

Here we defined σ_+ as the distance deflected in the direction of increasing field gradient and σ_- as the distance deflected in the opposite direction. Figure 1 compares a plot of $P(\sigma)$ vs. σ for the velocity selected case with the results of Feyerabend. The effect observed in a deflection experiment is a

decrease in the intensity of the undeflected beam maximum and a broadening of the beam.

The method for including the effects of beam width and detector width has been given by Estermann and Fraser.[1] If $f(\sigma_0)$ is the equation of the curve representing the intensity distribution in the undeflected beam, then the equation of the deflected beam is

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

σ_0 is the position of a hypothetical detector of negligible width and the center of the undeflected beam is assumed to be coincident with the center position of the detector at $\sigma_0 = 0$. After numerical integration of the above equation $F(\sigma_0)$ vs. σ_0 is plotted for each value of s_0 used. The area under each curve cut off by the width of the detector slit corresponds to the total detected intensity I after deflection in the electric field region. The area under the undeflected intensity distribution curve $f(\sigma_0)$, cut off by the width of the detector, corresponds to the total detected intensity I_0 with the field off.

The solid line in Fig. 2 is the theoretical I/I_0 vs. s_0 curve calculated assuming a trapezoidal beam shape. Trapezoid dimensions are taken from the measured slit geometry (see Fig. 3). This plot indicates the manner in which the dipole moment could be determined. It would only be necessary to measure the undeflected and the deflected beam intensity and calculate the dipole moment from the corresponding value of s_0, if the beam shape, field, field gradient, velocity, and temperature are well known.

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In practice, accurate determination of the beam shape, field, and field gradient is rather difficult. To avoid the necessity of knowing these quantities accurately, in the experiments reported here measurements were made relative to molecules with well known dipole moments.

III. EXPERIMENTAL

A detailed description of the molecular beam apparatus which was used for the present experiments is given in Ref. 4. Figure 3 is a schematic diagram of the important elements. As shown by the dotted line in Fig. 3, molecules effuse from the oven, move through the apparatus, and strike the detector. In the middle of the apparatus molecules may be velocity selected by the mechanical rotor and deflected in the inhomogeneous electric field region.

The same stainless steel oven was used for all alkali halide experiments. These ovens were of the single chamber Kusch-type design, with a 1.588 cm diameter sample chamber and a 1 mil thick slit. Temperature measurements were made with 10 mil diameter Pt-10% Rh thermocouple which was encased in a ceramic tube for insulation and mounted near the front of the oven. In order to insure good thermal contact with the oven walls, the hot junction was embedded in a copper rod. Temperature measurements are believed to be accurate to better than ±1%.

The beam geometry is defined by three slits - a 0.0127 cm wide × 0.3969 cm high × 0.00254 cm thick buffer chamber slit, a 0.0127 cm wide razor edge collimator slit, and a detector slit of the same dimensions as the buffer slit. The detector slit is located 3.1 cm in front of the detector.

Molecules are detected by surface ionization on a tungsten filament. The positive ion pulses produced are mass analyzed and then detected by an electron multiplier. The signal is further processed by a system which includes a

fast count linear amplifier and single channel analyzer, and is then recorded by an electronic counter.

The design and construction of the velocity selector used in the deflection experiments is described in detail elsewhere, and only a brief description will be given here.[4] The selector is the slotted disk type and consists of six disks. It is characterized by a transmission of 30.5%, a maximum rotational speed of 40,000 rpm, and a resolution of 3.5%. Rotation and transmission are allowed in the forward and reverse directions, thus allowing the angle of orientation of the rotor axis with respect to the beam axis to be determined. Velocities can then be corrected for any error due to misalignment.

A 0 to 10 kV D.C. power supply, with a 20 position switch, was used to supply the potential across conventional dipole type deflecting field electrodes.[4] Voltages at the different switch positions are calibrated to better than 1% and are reproducible to better than 0.1%.

In order to assure that any polymer present in the beam under our experimental conditions could be taken into account, velocity distributions were taken of CsCl and RbCl. The CsCl results indicated that the molecular beam source and velocity selector give results which are in agreement with the predictions of kinetic theory. This sets an upper limit of 2% on the polymer content of CsCl. For RbCl, it was necessary to assume the presence of about 5% dimer in order to fit the experimental velocity distributions. The present CsCl and RbCl results are in agreement with the previous results of Miller and Kusch who used a similar experimental arrangement.[7]

Data for the deflection experiments were taken in the following manner. A 60 second count is taken of the undeflected intensity I_0 at a velocity of 6.06×10^4 cm/sec (this velocity was selected to give low polymer content and reasonable intensities). The deflecting field is then applied and a 60 second

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count is taken of the deflected intensity I; the field is turned off and another 60 second count is taken of the undeflected intensity. Hot wire background counts are measured and subtracted from the measured values of I and I_0. Several measurements are taken in this manner, and averaged. The procedure is repeated at different deflecting field voltages. The dipole moments determined here correspond to I/I_0 ratios in the range 0.921 to 0.799.

IV. RESULTS AND DISCUSSION

Previous electric deflection studies have indicated that all the lithium halide dimers are non-polar.[5] It is assumed here that the rubidium halide dimers and potassium halide dimers are non-polar, and will not be deflected. This assumption seems to be justified by the present dipole moment determinations of KCl which are in good agreement with MBER results,[6] and by the good internal consistency in the RbCl deflection experiments at different concentrations of $(RbCl)_2$. At the beam velocity and oven temperature which were used for all of the deflection experiments, polymer corrections to the observed I/I_0 values were necessary for only RbCl and KCl. At an oven temperature of about 860°K and at a beam velocity of 6.06×10^4 cm/sec, less than 0.2% dimers are expected to be present in the velocity selected CsCl beam.[7,8] Under these conditions there is no dimer correction for CsCl in the I/I_0 range 1 to 0.8. Beams of the heavier Cs halides, CsBr and CsI, are expected to contain even less dimer, and dimer corrections were not made for these molecules. The ratio of dimer to monomer, $a_2 = 0.052$, which was determined in this work was used for the RbCl dimer corrections. A value of $a_2 = 0.079$ at 872°K for KCl was taken from the work of Miller and Kusch[7] in order to make dimer corrections for KCl. Corrections amounted to about 1/2% at $I/I_0 = 0.806$ for RbCl, and about 2.75% at $I/I_0 = 0.811$ for KCl. For KI, the results of Miller and Kusch[7] indicate that dimer corrections are

unnecessary at the beam temperatures and velocity used here. Beams of the heavier Rb halides are expected to contain less dimer than RbCl under the present experimental conditions and no dimer corrections were made for RbBr and RbI.

The points in Fig. 2 show the results of a series of runs using RbCl and CsCl, whose dipole moments are accurately known from MBER measurements. The s_0 values were calculated from the expression for s_0 given earlier using the values of the deflecting field length, field strength and field gradient derived from the apparatus geometry. The small squares show the results of a series of experiments using CsCl which were made over a period of several months. The circles and triangles show the results of a second series of experiments, using both CsCl and RbCl, which also extended over a period of several months but were made at a later date. These results indicate that although the short term stability of the apparatus is good and at times the beam parameters approach quite closely those calculated from the apparatus geometry, the beam shape and position can change sufficiently over long periods of time to introduce uncertainties in the dipole moment measurements of the order of 3%. To avoid this difficulty (and to make unnecessary an exact knowledge of the beam shape and field gradients) only relative measurements were used in determining the unknown dipole moments. A standard molecule of known dipole moment was run before and after each unknown molecule to assure that the beam geometry had remained constant. The experimental intensity vs. s_0 curve for the standard molecule was used in determining the unknown dipole. The dipole moments were calculated directly from the ratio

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$$\frac{(s_0)_u}{(s_0)_s} = \frac{\frac{\mu_u^2 E}{m_u}\left(\frac{\partial E}{\partial x}\right)\frac{\ell^2}{\nu^2}\frac{1}{kT_u}}{\frac{\mu_s^2 E}{m_s}\left(\frac{\partial E}{\partial x}\right)\frac{\ell^2}{\nu^2}\frac{1}{kT_s}} = \frac{\frac{\mu_u^2}{m_u}\frac{1}{T_u}}{\frac{\mu_s^2}{m_s}\frac{1}{T_s}},$$

where subscripts s and u refer to the standard and unknown molecules. Thus, the uncertainties in beam shape and trajectory do not effect the results as long as they do not change between the standard run and the unknown run.

CsCl was used as the standard for CsBr and CsI; and RbCl was used as the standard for RbBr, RbI, and KI. The advantage of using a standard molecule not too different from the unknown arises in two ways. First, the already small effect of molecular polarizability is partially cancelled and can be ignored at the fields used. Second, the experiments actually compare the dipole moments averaged over the vibrational states present in the beam, and using similar molecules reduces the uncertainties due to the vibrational population to a few tenths of a percent.

The dipole moments of KI, RbBr, RbI, CsBr, and CsI are given in Table I, and correspond to the equilibrium values μ_e. The relative measurements should give dipole moments with an accuracy of about 1%. As an overall check on the method, KCl was treated as an unknown molecule and its dipole moment determined using RbCl as a standard. As shown in Table I, agreement with the more accurate MBER result is within the expected accuracy.

FOOTNOTES AND REFERENCES

* Work performed under the auspices of the U. S. Atomic Energy Commission.

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Table I. Experimental Dipole Moments, μ_e (Debye units).

	CsCl Standard
CsI	11.69±0.1
CsBr	10.82±0.1
	RbCl Standard
RbI	11.48±0.1
RbBr	10.86±0.1
KI	10.82±0.1
KCl	10.18±0.1
	Previous MBER results[6]
KCl	10.238±0.001
RbCl	10.483±0.006
CsCl	10.358±0.005

FIGURE CAPTIONS

Fig. 1. Probability of deflection $P(\sigma)$ vs σ. Case 1: For a thermal distribution of molecular velocities. Case 2: For a single molecular velocity.

Fig. 2. Theoretical (solid line) and experimental (dotted line) deflection curves. (a) Solid line coincides with best fit to first series of CsCl data (squares). (b) Dotted line is best fit to a later series of CsCl data (triangles) and RbCl data (circles).

Fig. 3. Schematic diagram of the molecular beam apparatus.

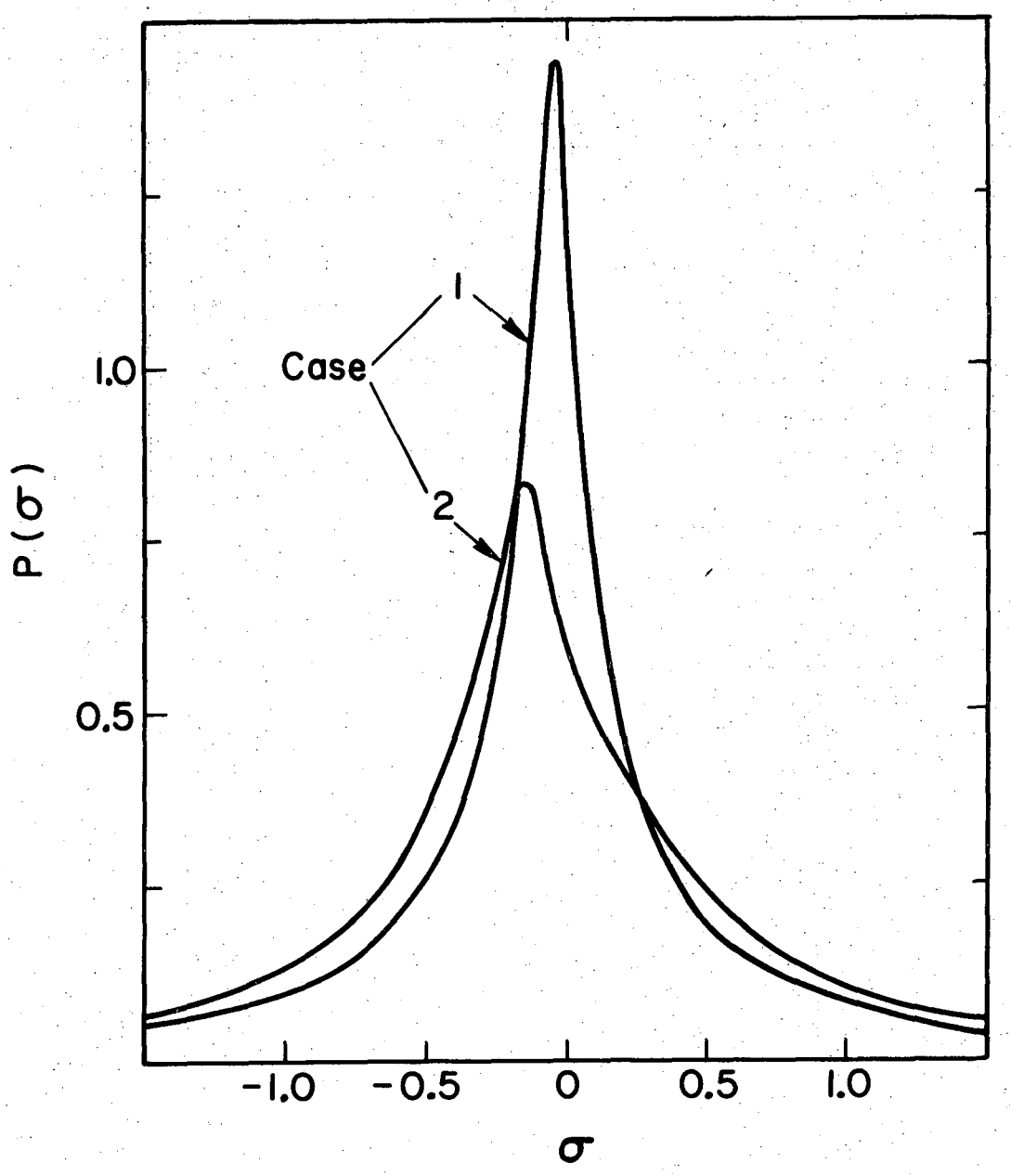

Fig. 1

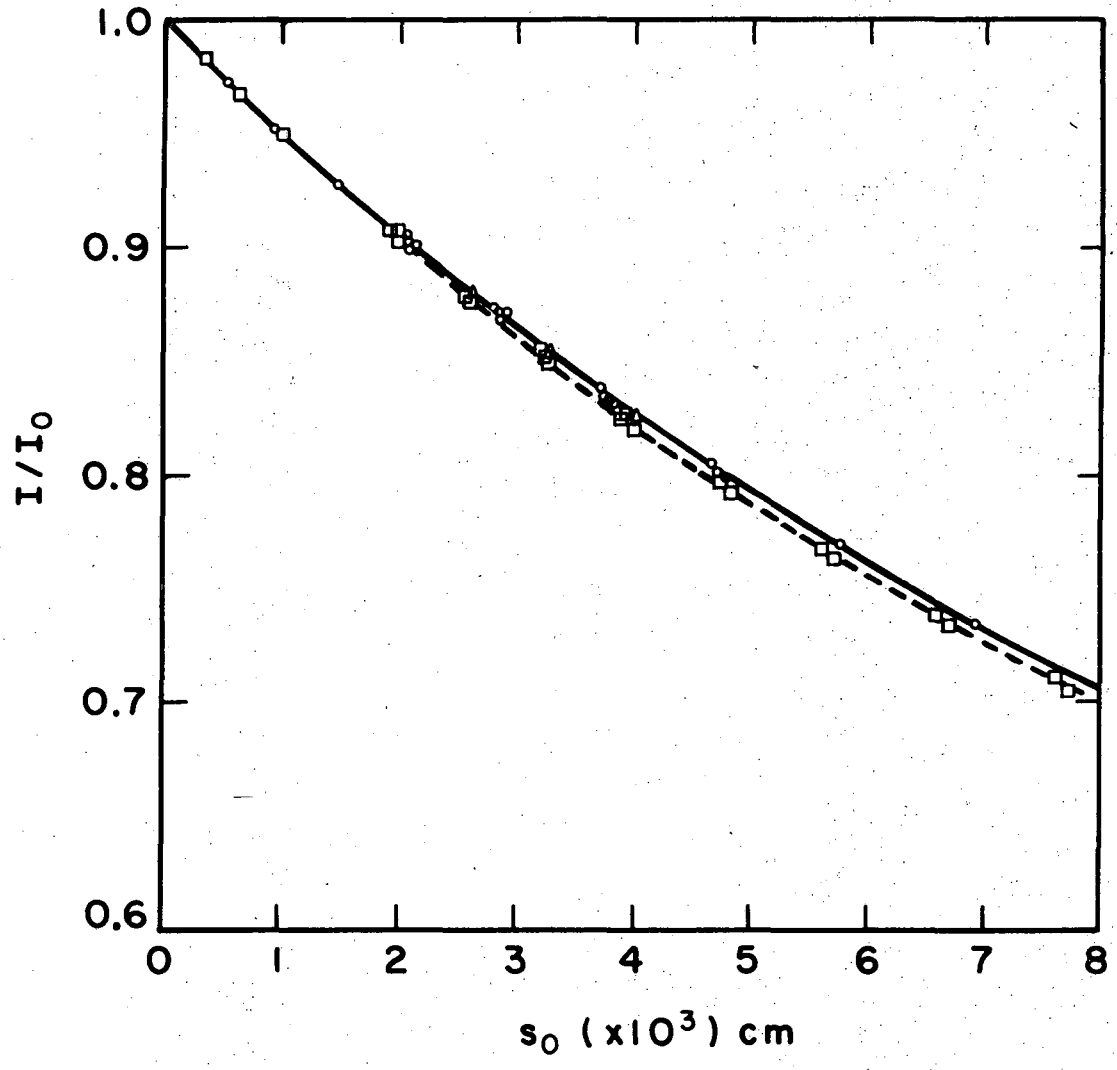

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Fig. 2

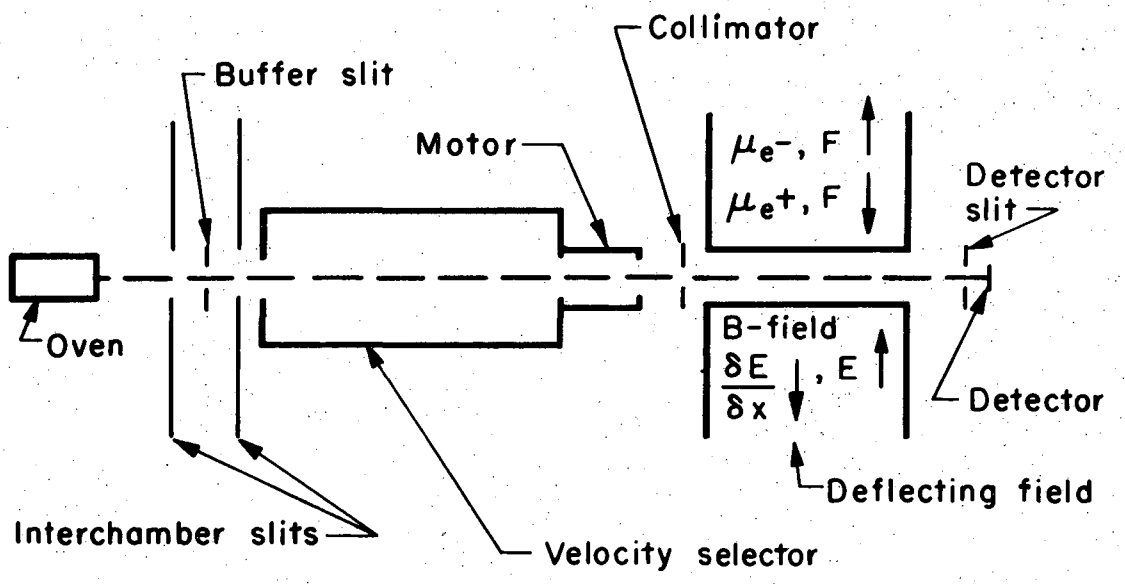

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Fig. 3

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