

TABLE XXII.  $y(f^8, v^4U, v^4U')$ .

	$v^4(00)$	$v^4(10)$	$v^4(20)$	$v^4(30)$	$v^4(40)$
$v^4(20)^\dagger$	0	0	$6/(55)^\dagger$	$2(42/5)^\dagger$	$6(2/55)^\dagger$
$v^4(20)$	0	0	$-61/(770)^\dagger$	$8(3/5)^\dagger$	$-6/(385)^\dagger$
$v^4(21)$	0	$3(22)^\dagger$	$(2/7)^\dagger$	$-\sqrt{3}$	$1/(7)^\dagger$
$v^4(22)$	$-4(33/5)^\dagger$	0	$-1/(22)^\dagger$	0	$2/(11)^\dagger$

TABLE XXIII.  $y(f^7, v^4U, v^4U')$ .

	$v^4(20)$	$v^4(21)$	$v^4(22)$
$v^4(00)$	0	0	$-12(11)^\dagger$
$v^4(10)$	0	$6(33)^\dagger$	0
$v^4(20)$	$-(5/7)^\dagger$	$2(11/7)^\dagger$	-1

TABLE XXIV.  $y(f^7, v^2U, v^2U')$ .

	$v^2(00)$	$v^2(10)$	$v^2(20)$	$v^2(30)$	$v^2(40)$
$v^2(11)$	0	0	0	$2(10)^\dagger$	0
$v^2(20)$	0	0	$-16/(77)^\dagger$	$-2(6)^\dagger$	$6(2/77)^\dagger$
$v^2(21)$	0	$-(66)^\dagger$	$(6/7)^\dagger$	1	$(3/7)^\dagger$

From (71) and from the orthogonality between the functions  $\psi((00)S)$ ,  $\psi((40)S)$ , and  $\psi((22)S)$  follow the relations

$$\sum_L (2L+1) (U | \chi(L) | U) = \sum_L (2L+1) (U | \varphi(L) | U) = 0 \quad (88)$$

and

$$\sum_L (2L+1) (U | \chi(L) | U') (U' | \varphi(L) | U) = 0, \quad (89)$$

which were useful for checking Tables VI and XIV.

## The Moment of Inertia and Electric Dipole Moment of CsF from Radiofrequency Spectra\*

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The electric resonance method of molecular beam spectroscopy was used to obtain spectra resulting from induced changes in the space-quantization of the rotational state  $J=1$  of CsF in a homogeneous electric field. An analysis of the spectra for several values of the field intensity and for two different vibrational states gave the following molecular constants,  $I_e = (151 \pm 6) 10^{-40}$  g cm<sup>2</sup>,  $\mu_e = (7.88 \pm 0.17) 10^{-18}$  e.s.u.,  $B_e = (185 \pm 7) 10^{-3}$  cm<sup>-1</sup>,  $\alpha_e = (1.85 \pm 0.19) 10^{-3}$  cm<sup>-1</sup>,  $r_e = (2.34 \pm 0.05) 10^{-8}$  cm,  $\omega_e = 270 \pm 30$  cm<sup>-1</sup>.  $I_e$  is the moment of inertia,  $\mu_e$  is the electric dipole moment,  $B_e$  and  $\alpha_e$  are rotational constants,  $r_e$  is the internuclear distance and  $\omega_e$  is the vibrational constant.

THE molecular beam electric resonance method<sup>1</sup> yields spectra in the radiofrequency region resulting from changes in the space-quantization of a single rotational state of the molecule when the molecule passes through a homogeneous electric field, upon which is superposed a weak, transverse, oscillating field. In previous experiments with CsF determinations were made of the moment of inertia and electric dipole moment,<sup>1</sup> and of several nuclear-molecular interaction constants.<sup>2</sup> In this paper the results of further experiments with CsF under the high resolution conditions described in reference 2 are presented. The moment of inertia and electric dipole moment are redetermined with considerably greater accuracy and additional constants are obtained from a study of the vibrational effects.

The apparatus has been described in detail elsewhere.<sup>1,2</sup> The spectra were observed by fixing the frequency of the oscillating electric field and varying the

magnitude of the steady, homogeneous field, a valid method of observation if the electric field intensity is sufficiently strong,<sup>2</sup> as was the case in the present experiments. Frequency was measured to 1 part in 10,000 with a General Radio Type 624A heterodyne frequency meter, which had been checked against standard frequencies broadcast by WWV. The electric field intensity in the homogeneous field was calculated from the potential drop across the field and the distance between the parallel plates forming the field boundaries.<sup>3</sup> "B" batteries were used as a voltage supply. A Type K potentiometer, connected to a calibrated volt box, was used to measure voltage to 1 part in 5000. The standard cell of the potentiometer was checked with another cell recently calibrated at the Bureau of Standards. No effects due to thermal e.m.f.'s were observed.

All voltage readings were corrected for the contact potential difference between the plates of the homogeneous field. This quantity was measured by making a run with the applied field intensity in one direction,

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<sup>1</sup> H. K. Hughes, Phys. Rev. **72**, 614 (1947).

<sup>2</sup> J. W. Trischka, Phys. Rev. **74**, 718 (1948).

<sup>3</sup> There is a typographical error in the value of the field gap reported in reference 2. The distance between the plates was  $0.4931 \pm 0.0004$  cm.

TABLE I. Quantities required for the calculation of  $\mu$  and  $I$  for the first two vibrational states.

$\nu$ (mc/sec.)	$E$ (volts/cm)	$E^2 \times 10^{-4}$	$\nu/E^2$
		$\nu=0$	
18.180	206.15	4.2498	427.78 $\pm$ 0.39
44.460	322.67	10.412	427.01 $\pm$ 0.35
94.520	471.57	22.238	425.04 $\pm$ 0.41
189.53	670.49	44.956	421.59 $\pm$ 0.32
297.37	843.80	71.200	417.65 $\pm$ 0.31
		$\nu=1$	
18.021	202.78	4.1121	438.24 $\pm$ 0.34
94.520	465.81	21.698	435.62 $\pm$ 0.38
297.37	833.68	69.502	427.86 $\pm$ 0.30

then a second run with the field in the opposite direction. The contact potential difference found as a result of several such runs at several different applied field intensities was  $0.07 \pm 0.01$  volt.

#### LINE POSITIONS

The transitions observed for CsF with the electric resonance apparatus at strong field intensities were between the states  $m_J=0$  and  $m_J=\pm 1$  for the rotational state  $J=1$ . The nature and theory of the spectra have been discussed in detail in references 1 and 2. For the purposes of the present paper the positions of the spectral lines may be represented by

$$\nu' = \nu + \nu_n,$$

where  $\nu$  is the frequency corresponding to the transitions between states given by the  $\mu \cdot E$  term in the Hamiltonian, and  $\nu_n$  is the shift from  $\nu$  produced by the nuclear-molecular interactions.  $\mu$  is the electric dipole moment and  $E$  is the electric field intensity. If the electric field intensity is such that

$$e^2 q' Q \ll \lambda^2 \hbar^2 / 2I \ll J(J+1)(\hbar^2 / 2I), \quad (1)$$

$\nu_n$  is, within present experimental error, independent of the field intensity.  $e^2 q' Q$  is a measure of the nuclear quadrupole interaction,  $I$  is the moment of inertia, and  $\lambda = \mu E / (\hbar^2 / 2I)$ .

In order to calculate  $\mu$  and  $I$  it is necessary first to determine  $\nu$ . Since  $\nu_n$  is known for the CsF spectra,<sup>2</sup> this calculation is hindered only by the fact that the fine-structure produced by  $\nu_n$  is unresolved at the values of  $E$  required for an accurate determination. Thus, for the transition  $(1, 0) \rightarrow (1, \pm 1)$ , a single line is observed for molecules in a given vibrational state. In the absence of an exact knowledge of the shape of the spectral window the shape of this line could not be accurately predicted from the known fine-structure. Fortunately, an accurate prediction was not necessary because of the relatively small extent, 500 kc/sec., of the fine-structure. Therefore, two extreme estimates of the line shape were made, one estimate based on a rectangular spectral window, the other on a triangular window. With these estimates as a guide the following scheme was decided on as the best one for finding the position of  $\nu$ : the outermost lines of the fine structure

were assumed to be equidistant from the sides of the experimental line at one-third its maximum intensity.

Since the experimental lines were actually a result of the variation of beam intensity with changes in  $E'$ , while the frequency was held constant, the quantity actually found by the above procedure was  $E$ . This required no essential change in the scheme described above because the extent of the fine-structure was always small compared with the frequencies at which observations were made.

Table I shows the calculated values of  $E$  and the corresponding frequencies. The determination of the value of  $E$  at 18 mc/sec. was made by a method different from that described above. At this frequency there was sufficient resolution to use one of the fine-structure lines as a basis for finding  $\nu$ . Calculations were made to insure that the observations met the conditions specified by Eq. (1).<sup>4</sup>

#### CALCULATION OF $\mu$ AND $I$

The best representation of the data in Table I is in a plot of  $\nu/E^2$  versus  $E^2$ . Such a plot of the data results in the straight line

$$\nu/E^2 = a - bE^2. \quad (2)$$

This corresponds in form to Brouwer's theoretical formula,<sup>1,5</sup> but closer study reveals that for the values of  $\lambda$  covered in these experiments Lamb's exact formula<sup>1</sup> must be employed. Since the experimental results are best summarized by Eq. (2), the following, linear, least-squares approximation to Lamb's curve was made for the range  $\lambda=0.1$  to  $\lambda=0.6$ .

$$\Delta\epsilon/\lambda^2 = 0.14998 - 0.01031\lambda^2, \quad (3)$$

where  $\epsilon = h\nu / (\hbar^2 / 2I)$  and  $\Delta\epsilon = \epsilon_{1,0} - \epsilon_{1,\pm 1}$ .<sup>6</sup>

The values of the constants in Eq. (2) and of the molecular constants obtained by use of Eqs. (2) and (3) are given in Table II.<sup>7</sup> The values of  $a$  and  $b$  were determined from the least-squares line fitting the data in Table I.

TABLE II. Molecular constants for the first two vibrational states.

$\nu$	0	1
$I, 10^{-40}$ g cm <sup>2</sup>	152 $\pm$ 6	152 $\pm$ 7
$\mu, 10^{-18}$ e.s.u.	7.89 $\pm$ 0.17	7.98 $\pm$ 0.18
$\mu^2 I, 10^{-76}$	9443 $\pm$ 28	9674 $\pm$ 30
$a$	428.48 $\pm$ 0.26	438.98 $\pm$ 0.30
$b, 10^{-5}$	1.52 $\pm$ 0.06	1.60 $\pm$ 0.07

<sup>4</sup> The author wishes to thank Dr. M. Slotnick for making these calculations.

<sup>5</sup> F. Brouwer, dissertation (Amsterdam, 1930).

<sup>6</sup> Hughes has recently made a detailed comparison of the Lamb and Brouwer formulas for the transition  $(1, 0) \rightarrow (1, \pm 1)$ . See H. K. Hughes, to be submitted for publication in Phys. Rev.

<sup>7</sup> The field intensity in Table I is in international volts/cm. It was necessary, therefore, to convert to absolute volts, using the relation: 1 international volt = 1.00034 absolute volts (Circular C459 of the National Bureau of Standards, 1947). The conversion formula 1 statvolt = 299.796 absolute volts was also used.

## EFFECT OF VIBRATION

The values of  $I$ ,  $\mu$  and  $\mu^2 I$  in Table II must be interpreted as the result of averaging over the vibration.<sup>2</sup> This means that for a given vibrational state  $I$  and  $\mu$  should be denoted by  $I_v$  and  $\mu_v$ , where<sup>3</sup>

$$I_v = m / \langle 1/r^2 \rangle_{Av}, \quad (4)$$

and, to a first approximation

$$\mu_v = e_{\text{eff}}(r)_{Av}. \quad (5)$$

$r$  is the internuclear distance at any instant during the vibration, and  $e_{\text{eff}}$  is, by definition, the effective charge.

Knowing  $I_v$  and  $\mu_v$  for two vibrational states it should be possible to calculate  $I_e$  and  $\mu_e$ , the values of  $I$  and  $\mu$  for the hypothetical state of no vibration. In addition, the small constant,  $\alpha_e$ , could then be computed from the equation<sup>9</sup>

$$B_v = B_e - \alpha_e(v + \frac{1}{2}), \quad (6)$$

where  $B$  is the rotational constant. Finally, it should then be possible to calculate the coefficient,  $g$ , of the cubic term in the potential function from<sup>10</sup>

$$\alpha_e = 24B_e^3 r_e^3 g / \omega_e^3 - 6B_e^2 / \omega_e. \quad (7)$$

At present  $g$  can be found with an accuracy of about  $\pm 40$  percent because of the poor accuracy of  $\omega_e$ , the vibrational constant.<sup>2</sup>

An examination of Table II shows that the errors in  $\mu_v$  and  $I_v$  are too large to allow their use in a direct calculation of  $I_e$ ,  $\mu_e$ ,  $\alpha_e$  or  $g$ . Therefore, the calculation of these quantities must proceed in a more roundabout way from the values of  $I_v$  and  $\mu_v$ , and from the difference between  $\mu_0^2 I_0$  and  $\mu_1^2 I_1$ .

Because  $\mu_v^2 I_v$  involves the averaging over a vibration of both  $\mu$  and  $I$  it is not at once clear what will be the individual contributions of  $\mu$  and  $I$  in the process. To clarify this question we can state to a first approximation that

$$\Delta \mu_v^2 I_v / \mu_0^2 I_0 = 2\Delta \mu_v / \mu_e + \Delta I_v / I_e, \quad (8)$$

where the  $\Delta$  symbolizes the difference between the values of a quantity for  $v=1$  and  $v=0$ . From Eqs. (4) and (5) we deduce

$$\Delta \mu_v / \mu_e = \Delta \langle r - r_e \rangle_{Av} / r_e, \quad (9)$$

and, approximately,

$$\Delta I_v / I_e = \Delta \langle 1/r^2 \rangle_{Av} / \langle 1/r_e^2 \rangle. \quad (10)$$

From Eqs. (6) and (10) we can then conclude that, approximately,

$$\Delta I_v / I_e = \alpha_e / B_e = 2\Delta \langle r - r_e \rangle_{Av} / r_e - 3\Delta \langle (r - r_e)^2 \rangle_{Av} / r_e^2. \quad (11)$$

But this is the basis for the calculations leading to

<sup>8</sup> Gerhard Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939), p. 113.

<sup>9</sup> G. Herzberg, reference 8, p. 114.

<sup>10</sup> E. Teller, *Hand-u. Jahrb. d. chem. Phys.* 9, II, 43 (1934). The formula is reprinted in Herzberg, reference 8, p. 116.

TABLE III. Molecular constants of CsF.

Quantity	Value
$I_e$ , $10^{-40}$ g cm <sup>2</sup>	151 $\pm$ 6
$\mu_e$ , $10^{-18}$ e.s.u.	7.88 $\pm$ 0.17
$B_e$ , $10^{-3}$ cm <sup>-1</sup>	185 $\pm$ 7
$\alpha_e$ , $10^{-3}$ cm <sup>-1</sup>	1.85 $\pm$ 0.19
$r_e$ , $10^{-8}$ cm	2.34 $\pm$ 0.05
$\omega_e$ , cm <sup>-1</sup>	270 $\pm$ 30

Eq. 7. Hence, from Eqs. (7), (8), (9) and (11), we obtain

$$\alpha_e / B_e = \Delta \mu_v^2 I_v / 2\mu_0^2 I_0 - 3B_e / \omega_e. \quad (12)$$

Substituting  $B_0$  for  $B_e$  in Eq. (12), a first approximation to  $\alpha_e$  results. Using this value the errors introduced by the various approximations can be corrected and a final value of  $\alpha_e$  achieved. From this point on the calculation of the other constants for the "state" of no vibration is simple.

Table III shows the constants deduced from the CsF spectra. The value of  $\omega_e$ , already reported in reference 2, is included for completeness. Results computed from the two vibrational states were averaged to give the values in the table.

## EXPERIMENTAL ERRORS

The experimental errors in the quantities reported in Tables I, II, and III arise from two kinds of errors, systematic errors and random errors. The separation of errors into these two categories was made on the following basis. Errors which were common to all the values of  $\nu/E^2$  in Table I were called systematic errors, since they could be taken into account after  $a$  and  $b$  were determined. Errors which did not have this property were called random errors.

The most important systematic error was that in the magnitude of the field gap. This error was conservatively considered as the sum of the error in the length of the spacers separating the plates of the field,  $\pm 0.04$  percent, and the deviation from planeness of the plates,  $\pm 0.05$  percent. The error in the contact potential difference between the plates of the homogeneous field was considered to be a systematic error for the vibrational state  $v=1$  and a random error for  $v=0$ . This situation occurred because the applied field intensities were in the same direction for all of the measurements for  $v=1$ , whereas, this was not the case for  $v=0$ .

The random errors were the error in the voltage measurement,  $\pm 0.02$  percent, the error in frequency measurement,  $\pm 0.01$  percent, and the error in the estimation of line position,  $\pm 0.01$  percent on the average.

The errors given for  $\nu/E^2$  in Table I are the sum of the propagated random errors. No errors in  $E^2$  are shown since the errors in this quantity have a negligible effect on the values of  $a$  and  $b$ . The errors in  $a$  and  $b$  in Table II were computed by applying the least-squares law of propagation of errors to the least-squares

formulas for the slope and intercept of a straight line. The error in  $I$  in Table II came entirely from the errors in  $a$  and  $b$ , since the absolute value of the field intensity is not required to find  $I$ . The error in  $\mu$  in this table includes errors in  $a$  and  $b$  and the error in the field gap. The error in  $\mu^2 I$  is a result of the propagation of the errors in  $a$ , in the field gap, and in Planck's constant,  $h$ .<sup>11</sup>

In Table III,  $r_e$  and  $B_e$  are derived from  $I_e$  and their errors result only from the error in this quantity. The errors in  $I_e$  and  $\mu_e$  are the same as the errors in  $I_v$  and  $\mu_v$ , since negligible error is introduced by the error in  $\alpha_e$ . The error in  $\alpha_e$  is a result of the propagation of the errors in  $B_e$ ,  $\omega_e$ , and  $\Delta\mu^2 I/\mu_0^2 I_0$ . In computing the error in the last mentioned quantity only random errors need be taken into account. Furthermore, the error in the volt box, which produces part of the random error in  $\mu^2 I$ , will not appear here since the data for both vibrational states was taken with the same setting of the volt-box. Hence,  $\Delta\mu^2 I/\mu_0^2 I_0 = 231 \pm 6$ . An error comparable to this is introduced in  $\alpha_e/B_e$  by the term  $3B_e/\omega_e$ , so that  $\alpha_e/B_e = (10.0 \pm 0.6)10^{-3}$ . Multiplication of this quantity by  $B_e$  gives  $\alpha_e$ .

#### DISCUSSION

The constant  $r_e$  in Table III is of considerable interest because it is at such wide variance with the value 2.67Å computed from the empirical formula of Schomaker and Stevenson.<sup>1,12</sup> Since their formula gives agreement within a few percent with the experimental values for other alkali halides, including some Caesium halides,<sup>13</sup>

<sup>11</sup> The value of  $h$  used in all calculations was  $(6.6234 \pm 0.0011) \times 10^{-27}$  erg sec. [see J. W. M. DuMond and E. R. Cohen, *Rev. Mod. Phys.* **20**, 82 (1948)].

<sup>12</sup> Schomaker and Stevenson, *J. Am. Chem. Soc.* **63**, 37 (1941).

<sup>13</sup> Maxwell, Hendricks, and Mosley, *Phys. Rev.* **52**, 968 (1937).

CsF appears to be a striking exception. The peculiar nature of CsF is made more emphatic by the fact that its interatomic distance is less than that for CsH,<sup>14</sup> for which  $r_e = 2.49\text{Å}$ .

A rough check on the present experiments can be obtained by a comparison with the results of Hughes,<sup>1,6</sup> who found  $r = 2.55 \pm 0.16\text{Å}$ . Because of his low resolution his value corresponds to a distance somewhere between the interatomic distances for the first and second vibrational states, for which  $r_0 = 2.35\text{Å}$  and  $r_1 = 2.36\text{Å}$ , according to the present experiments. There is, then, agreement within experimental error.

In view of the seemingly anomalous value of  $r_e$  and the small overlapping with Hughes' value the work reported here was very carefully reviewed for errors, and several additional runs were made to check the data. The evidence for the correct identification of the rotational state has already been presented.<sup>2</sup> The value of  $I_e$ , from which  $r_e$  is computed, depends only on relative values of the electric field intensity. Hence, any systematic errors in  $E$  drop out.

As a check on the assumptions made in the theory of the experiment, order of magnitude calculations were made for the effect of distortion of the molecular electrons by the electric field and for the effect of the field on the vibrational states. Both effects were found to be entirely negligible.

The amount of ionic character, defined by  $\mu/r_e$ ,  $e$  being the electronic charge, is 70 percent.

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<sup>14</sup> G. M. Almy and M. P. Rassweiler, *Phys. Rev.* **53**, 890 (1938).