

## Electric Dipole Moments of the Lower Vibrational States of Molecular CsF and CsCl

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where  $k$ ,  $N$ , and  $e$  are the usual fundamental constants and  $T$  is the absolute temperature. This relation is readily extended for the general electrolyte.

Carrying the dielectric correction through a standard D-H treatment,<sup>3</sup> we satisfy the requirements for self-consistency. Then application of the Debye charging process yields the part of the free energy due to the mutual electrical interaction of the various ions in the form

$$F^{\text{el}} = - \sum_i \frac{N_i Z_i^2 |e|^2}{D_0 b^3 \kappa_0^2} \left[ \frac{b^3}{a(b^2 + a^2)} \ln \left( 1 + \frac{a \kappa_0}{(1 - b^2 \kappa_0^2)^{1/2}} \right) - \frac{ab}{2(b^2 + a^2)} \ln(1 - b^2 \kappa_0^2) - \frac{b^2}{(b^2 + a^2)} \sin^{-1} b \kappa_0 \right]. \quad (4)$$

Here  $N_i$  and  $z_i |e|$  are the number and charge of the  $i$ th ion and  $a$  is the usual mean radius of the hydrated ion. The corresponding value for the mean stoichiometric activity coefficient, neglecting volume changes in the charging process, is

$$\log \gamma_{\pm} = - \frac{Z_+ |Z_-| |e|^2}{2 D_0 K T} \frac{\kappa_0}{(1 - b^2 \kappa_0^2)^{1/2} + a \kappa_0 (1 - b^2 \kappa_0^2)} \quad (5)$$

which reduces to the D-H expression as  $b^2$  goes to zero.

We interpret  $b^2$  as the mean surface area of the unhydrated ion at any given instant which is effective in ion-solvent interaction, including the breaking down of the quasi-crystalline structure of water. This interaction accounts for the observed change in dielectric constant.<sup>1</sup> A few typical values of  $b^2$  obtained by using Eq. (3) and the experimental values of  $\delta$  given by Haggis, Hasted, and Buchanan, are

$$\text{NaCl: } b^2 = 1.89 \times 10^{-16} \text{ cm}^2; \quad \text{LiCl: } b^2 = 1.77 \times 10^{-16} \text{ cm}^2;$$

$$\text{KCl: } b^2 = 1.65 \times 10^{-16} \text{ cm}^2;$$

all of which are consistent with the above interpretation of  $b^2$ . Other corrections to the D-H expression for  $\log \gamma_{\pm}$  could still be taken care of by the usual empirical expansion in powers of concentration.

<sup>1</sup> Haggis, Hasted, and Buchanan, *J. Chem. Phys.* **20**, 1452 (1952).

<sup>2</sup> Smyth, *Dielectric Behavior and Structure* (McGraw-Hill Book Company, Inc., New York, 1955).

<sup>3</sup> Fowler and Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, New York, 1949), Chap. IX.

### Tin-Hydrogen Bond Distance\*

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(Received August 13, 1956)

AS part of an investigation of the molecular spectra and molecular structures of the fourth-group hydrides<sup>1-4</sup> the infrared spectra of  $\text{SnH}_4$  and  $\text{SnD}_4$  have been obtained.<sup>5</sup> In common with other tetrahedral molecules the analysis of these spectra is complicated by strong Coriolis perturbations. An easier approach to the determination of the Sn-H distance is to analyze a parallel band of  $\text{SnH}_3\text{D}$  or  $\text{SnHD}_3$ . In this communication we wish to report the results of such an analysis of the Sn-H stretching vibration ( $\nu_3$ ) of  $\text{SnHD}_3$ .

A sample of  $\text{SnD}_4$  containing a small percentage of  $\text{SnHD}_3$  was prepared by the reduction of  $\text{SnCl}_4$  with  $\text{LiAlD}_4$  in *n*-dibutyl ether solution.<sup>6</sup> The spectrum of the Sn-H stretching vibration was recorded with a grating spectrometer<sup>7</sup> using a 2400-line per inch NPL 6X6-in. grating in the second order and a PbTe detector. Lines separated by  $0.1 \text{ cm}^{-1}$  were resolved. Absorption lines of  $\text{DBr}^8$  were used for calibration in this region of the spectrum.

Because of the many (10) isotopes of tin, it was quite impossible to observe the  $K$  structure for each  $J$  value in the  $P$  and  $R$  branches and, hence, no extrapolation to  $K=0$  was possible. Thus, it was necessary to measure the position of maximum absorption of the

many components making up each "line." The usual combination plots<sup>9</sup> lead to the following molecular constants:

$$\begin{aligned} \nu_0 &= 1905.91 \text{ cm}^{-1} & B_0 - B_1 &= 0.00425 \text{ cm}^{-1} \\ B_0 &= 1.3373 \text{ cm}^{-1} & D^J &\approx 10^{-6} \text{ cm}^{-1} \\ B_1 &= 1.3327 \text{ cm}^{-1} \end{aligned}$$

Under the assumption of tetrahedral angles, equality of the Sn-H and Sn-D bond distances, and a mean atomic weight for tin of 119, the tin-hydrogen bond length is calculated to be  $1.701 \pm 0.001 \text{ \AA}$ . This value is in excellent agreement with that of  $1.700 \pm 0.015 \text{ \AA}$  reported by Lide from an analysis of the microwave spectra of  $\text{CH}_3\text{SnH}_3$ .<sup>10</sup>

We wish to thank Professor W. C. Price for use of the spectrograph and laboratory facilities and Dr. T. S. Piper for preparing a sample of  $\text{SnD}_4$ . One of us (GRW) is indebted to the Institute of Petroleum for a grant.

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<sup>1</sup> S. R. Polo and M. K. Wilson, *J. Chem. Phys.* **22**, 1559 (1954).

<sup>2</sup> L. P. Lindeman and M. K. Wilson, *J. Chem. Phys.* **22**, 1723 (1954).

<sup>3</sup> J. H. Meal and M. K. Wilson, *J. Chem. Phys.* **24**, 385 (1956).

<sup>4</sup> L. P. Lindeman and M. K. Wilson, *Z. physik. Chem.* (to be published).

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<sup>6</sup> G. W. Schaffer and M. Emilias, *J. Am. Chem. Soc.* **76**, 1203 (1954).

<sup>7</sup> Ford, Price, and Wilkinson, *J. Sci. Instr.* (to be published).

<sup>8</sup> F. L. Keller and A. H. Nielsen, *J. Chem. Phys.* **22**, 294 (1954); J. Overynd and H. W. Thompson, *Proc. Roy. Soc. (London)* **234**, 306 (1956).

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<sup>10</sup> D. R. Lide, Jr., *J. Chem. Phys.* **19**, 1605 (1951).

### Electric Dipole Moments of the Lower Vibrational States of Molecular CsF and CsCl†

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THIS note gives the experimentally determined dipole moments of CsF and CsCl for a number of their lower vibrational states. These values are more accurate and include a much larger number of vibrational states than values from any previous measurements of this type.<sup>1</sup> The measured dipole moments for various vibrational states are of interest (1) because of their possible use for testing the validity of molecular models and (2) because they may be useful in empirical deductions of the manner in which the dipole moment varies with internuclear distance.

The dipole moments of CsF and CsCl have been calculated from hitherto unpublished electric resonance measurements of the Stark effect in these molecules. At the time the measurements were made it was not possible to obtain accurate values of the dipole moments from them because only the product of the square of the dipole moment,  $\mu_v^2$ , and the moment of inertia,  $A_v$ , could be obtained with high accuracy, whereas  $\mu_v$  and  $A_v$  could be determined separately with an accuracy of only about one percent. The recent accurate determinations of the rotational constants of CsF and CsCl by the authors of reference 1 has made possible the accurate calculations of values of  $\mu_v$  from the Stark effect data.

The Stark effect data for CsF were taken by the author and were used in making Fig. 3 in reference 2.<sup>2</sup> In the experiment the frequency was fixed and the electric field varied to find the

TABLE I. Field strengths,  $E$ , at which CsF resonance occurs for different vibrational states,  $v$ , at  $\nu = 94,520 \text{ mc/sec.}^a$

$v$	$E$
0	471.73
1	465.97
2	460.41
3	454.76
4	449.61

<sup>a</sup> The error in  $\nu$  is  $\pm 0.004 \text{ mc/sec}$ . The random error in  $E$  is  $\pm 0.02\%$  and the systematic error in  $E$  is  $\pm 0.08\%$ .  $E$  is in absolute  $\text{v/cm}$ .

resonance lines. In Table I are presented the fields which produce the molecular Stark splitting of the given frequency for a number of vibrational states. The  $J, m_J \rightarrow J, m_J'$  transition was  $1, 0 \rightarrow 1, 1$ . The numerical field values differ from those given in reference 3 for the  $v=0$  and  $v=1$  states because the values in Table I are in absolute v/cm whereas those in reference 3 are in international v/cm.<sup>3</sup>

The data for CsCl are presented in the Doctoral thesis of R. G. Luce,<sup>4</sup> and curves based on this data are shown in Fig. 4 of reference 5.<sup>5</sup> The data in this case are extensive, including the  $4, 1 \rightarrow 4, 2$  transitions for  $0 \leq v \leq 6$ , the  $3, 0 \rightarrow 3, 1$  transitions  $0 \leq v \leq 4$  and the  $2, 0 \rightarrow 2, 1$  transitions for  $0 \leq v \leq 5$ . There are three sets of data for the  $2, 0 \rightarrow 2, 1$  transitions.

The results of the calculations of  $\mu_v$  can be presented in the form of an equation which is, within experimental error, linear in  $v$  for both CsF and CsCl. If Debye units are used, then for CsF

$$\mu_v = (7.875 \pm 0.006) + (0.0722 \pm 0.0003)v$$

and for CsCl

$$\mu_v = (10.42 \pm 0.02) + (0.056 \pm 0.002)v.$$

The errors in (1) and (2) require special comment. The measurements of the rotational constant produce negligible errors in the results. Two kinds of errors in the original Stark effect measurements produce errors in the final results. First there are random errors in the measurements of the field intensities and in the estimates of the resonance line centers. Second, there are systematic errors common to all the vibrational states of a given  $J, m_J \rightarrow J, m_J'$  transition.

Consequently, the measured change in dipole moment from one vibrational state to the next is affected only by the random error, while the absolute value of the dipole moment for any state is affected by the systematic error as well. This means that if each of the Eqs. (1) and (2) is visualized as the equation of a straight line, then the slope and intercept of the line were separately calculated; and hence, their errors must be considered separately.

† Supported in part by the Office of Naval Research.

<sup>1</sup> Previous results are summarized in Table II of Honig, Mandel, Stitch, and Townes, *Phys. Rev.* **96**, 629 (1954).

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

<sup>3</sup> J. W. Trischka, *Phys. Rev.* **76**, 1365 (1949).

<sup>4</sup> R. G. Luce, doctoral dissertation, Syracuse University (1951).

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## Collisional Processes and Similarity under the Low-Frequency Silent Electric Discharge in Air

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IN cases where all the processes of ionization are functions of  $X/p$  alone and space charges and cumulative processes have no influence on the breakdown, the breakdown potential,  $V_m$ , for arbitrary electrode arrangements of a geometrically similar shape, is known to be a function of  $ap$ , where  $a$  is a linear dimension of the arrangement and  $p$  is the gas pressure. For discharges between coaxial cylinders,  $V_m = rX \log(R/r) = f(rp)$ , where  $r$  and  $R$  are the radii of the inner and the outer cylinders, respectively,  $X$  is the field strength, and  $f$  denotes a function. For geometrically similar systems,  $\log(R/r)$  is a constant and the  $rX-rp$  curves for such tubes should coincide if the similarity principle were obeyed. For plane parallel electrodes this condition reduces to the Paschen's law, which is merely a special case of the similarity principle.

Observations of the threshold potential in these laboratories have revealed that for the low-frequency silent electric discharge in air under external sleeve excitation,<sup>1</sup> and also using plane parallel glass electrodes,<sup>2</sup> the Paschen's law holds well indicating that, at least for potentials near  $V_m$ , space charges do not play an important role and all the significant processes of ionization are functions of  $X/p$  alone. Moreover, the predominant mechanism for the liberation of secondary electrons under this type of

discharge appeared to be<sup>3</sup> photoelectric emission from the cathode. These studies have now been extended to the coaxial cylinder corona in air.

The general experimental arrangement and procedure were similar to those employed earlier.<sup>2</sup> The discharge tubes were essentially all glass ozonizers of the Siemen's type. Typical results obtained for two geometrically similar tubes, with outer diameters of the outer glass cylinders,  $2R=2.6$  and  $1.3$  cm, and the inner diameters of the inner glass cylinders,  $2r=0.6$  and  $0.3$  cm, respectively, are shown in Fig. 1. It is seen that the similarity

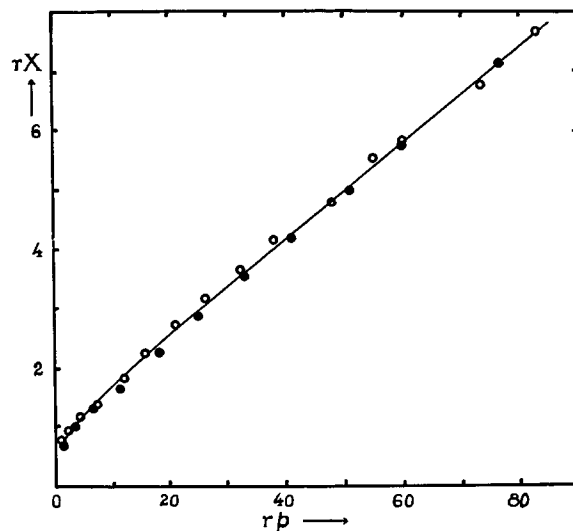


FIG. 1. The  $rX-rp$  curves showing similarity relationship for two geometrically similar tubes.  $rX$  is measured in kv (peak), and  $rp$  in mm Hg cm. Circles denote data for tube 1 ( $2R=1.3$  cm and  $2r=0.3$  cm). Dots denote data for tube 2 ( $2R=2.6$  cm and  $2r=0.6$  cm).

theorem holds good for this type of discharge also, indicating that all the processes here are functions of  $X/p$  alone. However, in order to explain the production of high-frequency pulses observed on the current wave form in this type of discharge, a mechanism essentially similar to field emission of electrons from the surface charge has been proposed by some authors.<sup>4,5</sup> The present results indicate that such an emission process which depends on  $X$ , and not  $X/p$ , is not probable. Details will be published elsewhere.

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## Critical Point and the Born-Green Equation

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WHEN the set of equations relating the hierarchy of particle distribution functions is closed by the superposition approximation a nonlinear integrodifferential equation is obtained. Kirkwood<sup>1</sup> and Born and Green<sup>2</sup> formulated this equation in essentially similar ways. Green<sup>3</sup> obtained an approximate solution in terms of Fourier transforms by linearizing the equation and replacing the unknown function by its average value in certain places. The solution possesses a branch point which was interpreted as marking the division between the liquid and gas; i.e., the