EVALUATION OF A STARK VOLTMETER

BY

Y. BEERS AND T. W. RUSSELL

Reprinted from IEEE TRANSACTIONS
ON *INSTRUMENTATION AND MEASUREMENT*
Volume IM-15, Number 4, December, 1966
pp. 380-388

Evaluation of a Stark Voltmeter

Y. BEERS, MEMBER, IEEE, AND T. W. RUSSELL

Abstract—**An absorption Stark voltmeter, using a Fabry-Perot absorption cell with a rotational transition of CH_3CN at 36 GHz, has been built and evaluated. The rotational constant and dipole moment of this molecule have been redetermined and found to have the values 9198.56 ± 0.10 GHz and 3.9185 ± 0.0020 Debye, respectively. The short term precision of the device when used as a standard cell was better than that of the equipment which was used to test it, and was probably better than one part in 10^5, but there were unexplained drifts of 2 parts in 10^4 per day. The accuracy of the device, as a means of measuring voltage in terms of atomic and molecular constants, is 5 parts in 10^4. The principal errors are due to the measurement of the plate spacing (which could be reduced by using an optical interferometer to measure spacing), pulling the interferometer resonance by the external circuit, and the effects of field non-uniformities due to the coupling holes.**

A GENERAL discussion of the use of the Stark effect to measure voltage and a description of the method used in the present experiment is contained in an earlier publication [1]. There it was pointed out that the Stark effect, which concerns the splitting of a spectral line into components when an electric field is applied to the substance giving rise to the line, may be used to measure the voltage in terms of a parameter of the substance, the dipole moment. Strictly speaking, the Stark effect depends explicitly upon the field strength rather than upon the voltage, and therefore, if voltage is to be determined, the spacing of the electrodes and corrections for non-uniformities of field must be determined. At the present time there is no independent method of measuring the dipole moment with accuracy comparable to the precision of the Stark method. Therefore, only relative voltage can be obtained unless the Stark method is used with a known voltage to deter-

---

Manuscript received June 23, 1966. This paper was presented at the 1966 Conference on Precision Electromagnetic Measurements, Boulder, Colo. The work was supported in part by the Advanced Research Projects Agency under Project DEFENDER and was monitored by M. I. Witow under ARPA order no. 515.

The authors are with the National Bureau of Standards, Boulder, Colo.

mine the dipole moment. One of the objectives of the present experiment has been to measure the dipole moment of the substance used, CH_3CN, known as either acetonitrile or methyl cyanide, under a variety of experimental conditions. Its degree of constancy can be used to evaluate some of the errors of the method.

In the region of 37 GHz, this molecule is capable of absorbing energy only at a single frequency, about 36.794 GHz, if no static electric field is applied and if some small hyperfine effects are ignored. This absorption is due to the $(J=2,\ K=1)\leftarrow(J=1,\ K=1)$ rotational transition. If, as in the present experiment, a static field is applied in a direction perpendicular to the RF electric field as a result of the Stark effect, absorptions are observable at six distinctly separated frequencies as illustrated in Fig. 1 (the so-called $\Delta m=\pm 1$ transition).

The spacing of these six components or Stark lines increases approximately linearly with field strength and is about one MHz per one volt per cm for the outermost ones and about one-third as great for the others. Standard textbooks [2] describe various methods for calculating the frequency shifts of the lines in terms of the dipole moment and field strength. However, for the reduction of the data of the present experiment a numerical table prepared by Shirley specially for us was used. In this table, which is an extension of one published by him [3], a relevant portion has been carried out to two more significant figures, and the interpolation intervals have been reduced by the inclusion of more values.

In the present experiment, however, observations were not made over a range of frequencies, as suggested by Fig. 1. Instead, the apparatus was operated at a single frequency, offset from the zero field absorption frequency, and then, as the voltage is increased, the Stark lines are observed one by one. If it is desired to observe the complete Stark pattern, it is necessary to observe at two frequencies, one above and one below the zero field resonance. Conventionally, these lines are labeled by the *m* quantum numbers of the levels involved in the respective transition, as given by the numbers in parentheses on the diagram. However, for convenience in the present discussion, they will be labeled by a number corresponding to their order of appearance in this experiment. It should be noted, however, that the present labeling is not unique; on the high-frequency side a different pair of quantum numbers are involved than for the line of the same number on the low-frequency side.

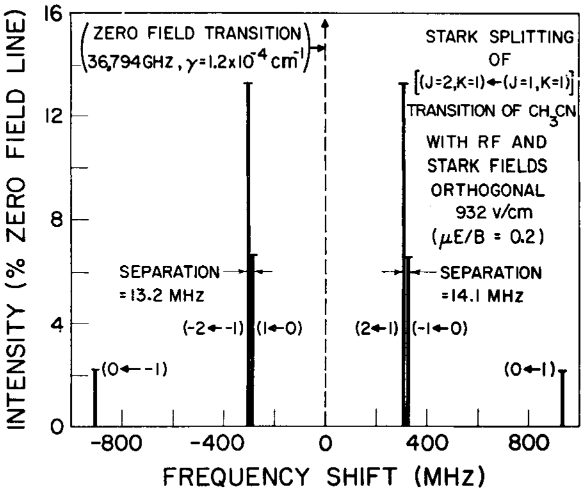

Fig. 1. Stark splitting of the $(J=2,\ K=1)\leftarrow(J=1,\ K=1)$ transition of CH_3CN at 36.8 GHz.

The substance which has been used, CH_3CN, appears to be a favorable choice. It has a Stark effect which conveniently is approximately linear with voltage. Its dipole moment is about the largest of any molecule which is easy to obtain in form of a vapor at room temperature and which has an approximately linear effect. Because of the large dipole moment, the Stark splitting is very large, and also the absorption is very strong, the computed coefficient, $\gamma=1.2\times10^{-4}$ cm^{-1} being one of the largest known to occur in this frequency region. On the other hand, the large dipole moment causes this molecule to have a large linewidth parameter (estimated to be between 100 to 200 MHz for a pressure of 1 mm Hg), but the previously mentioned advantages outweigh this disadvantage. In spite of the fact that it is a cyanogen compound, it is not corrosive or dangerous to handle because only a small quantity is required and because the vapor pressure is not very high. In the present experiment commercial samples were used. Material of commercial grade is cheap and easy to obtain. However, it contains the isotopic species N^{14}, which produces a small broadening of the line due to a hyperfine structure extending over about 3 MHz. In a refined experiment, it would be desirable to use an isotopically refined sample using N^{15}, which has a very much smaller hyperfine structure.

I. The Apparatus

A slightly simplified block diagram of the apparatus is shown in Fig. 2. The absorption cell consists of a parallel plate Fabry-Perot resonator contained within a vacuum chamber. The Stark voltage is applied between the plates of the interferometer. The plates are 8 inches in diameter. One of them, a thin copper foil, contains an array of holes in a pattern 2 inches square. By means of these and a transparent dielectric window in the chamber, RF energy from a horn is coupled into the interferometer. The horn is fed from a klystron through a directional coupler (or at higher frequencies, where the power is lower, by a "magic T"). The main waveguide connected to the horn is impedance matched (by the use of tuners not shown) to a crystal detector which receives power reflected by the interferometer. The presence of absorption by the gas is manifest by a change in the crystal current. Applied to the interferometer through a decoupling network is a small 10 kHz modulating voltage, which makes it possible to use a phase sensitive detector. The diagram shows an RC decoupling network, but, before important measurements were made, the resistor was replaced by a low resistance reactor so that voltage drops due to leakage currents were made negligible. The dc voltage ranged from 350 to

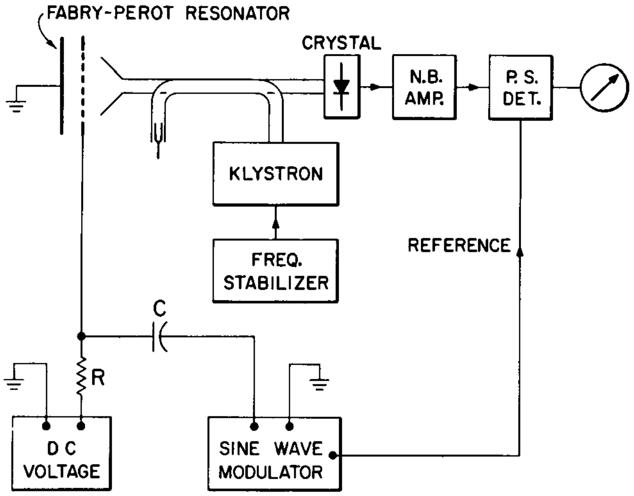

Fig. 2. Block diagram of apparatus.

3 500 volts, while the modulation voltage never exceeded 0.5 volt rms and was held to 0.25 volts for some of the lower voltage measurements. With such low modulation voltages errors due to non-linear contributions to the Stark coefficients were supposed to be negligible. This assumption was verified by control experiments which showed that the modulation amplitude can be increased above these values without apparent shift in the dc voltage at resonance. With this type of detection scheme, the response ideally is such that the output meter of the phase sensitive detector gives zero exactly at resonances with deflections of opposite signs on either side: that is, it is a so-called "dispersion" response. This presentation was particularly convenient for setting upon resonance. Actually, the line shape can be distorted by mistuning of the RF system, and great pains were taken each time the system was retuned to adjust it so that the response was symmetrical, and the off resonance negative and positive maxima were made equal within a few percent.

Figure 2 shows a double-directional coupler with a movable plunger connected with the other high level waveguide. By adjustment of this plunger, extra power can be reflected directly from the klystron to the detector, increasing the sensitivity by homodyne action. However, it was found that the apparent response curve of the resonator could be "pulled" by adjustment of this plunger. Therefore, a variable attenuator was inserted in front of this plunger. In preliminary adjustments, the attenuation was set to a minimum to improve the sensitivity, but in later measurements, the attenuation was set to a maximum so that the arm became a dummy load. It was found that the precision of the measurements was noticeably improved with maximum attenuation although the signal-to-noise ratio was poorer.

What the diagram denotes as the "klystron" is actually an X-13 klystron driving a varactor frequency tripler. The frequency of the klystron is stabilized by means of a commercial phase-locked stabilizing circuit, which, however, permits operation at only a discrete set of frequencies. A transfer oscillator and counter are available, and occasional checks indicate that the stabilization is so good that for all practical purposes the frequency can be assumed to be known exactly.

The vacuum system employs an oil diffusion pump. In the final measurements, the pressure was from 2 to 3 microns, as indicated on an uncalibrated thermocouple gauge.

The spacing between the interferometer plates is determined by means of the resonance condition given by the elementary formula that the spacing be equal to M half wavelengths, where M is an integer. The limitations upon the validity of this formula will be discussed later. Since the spacing is limited to a maximum of one inch, at 36 GHz, M is restricted to values between 1 and 6, inclusive, and the Q is of the order of a few thousand. Therefore, the precision in the measurement of the spacing is serious limitation upon the precision of the entire experiment. Obviously, the precision can be improved if some other method of measurement, such as coupling with an optical Michelson interferometer, is incorporated in the apparatus, but no provision for this has been made.

The pattern of coupling holes was selected by a method described earlier [4] to give a fairly good impedance match at resonance; that is, at resonance there was little power reflected by the interferometer. At 36 GHz, the pattern consists of 0.089 inch diameter holes in a square array with spacings of 0.156 inch, while at 55 GHz (the frequency of the $(J=3)\leftarrow(J=2)$ transitions of CH_3CN) the pattern consists of 0.041 inch diameter holes with spacings of 0.099 inch. The foil thicknesses are both 0.007 inch.

A closer examination of the resonator system reveals that it is actually a system comprised of two coupled resonators, the other one being an interferometer using the horn and the first Fabry-Perot plate as reflectors. Therefore, the apparent resonance of the Fabry-Perot resonator depends to some extent upon the position of the horn. The setting of the Fabry-Perot spacing for resonance has a periodic dependence upon the horn spacing, with a space period of one half wavelength. The amplitude of this variation changes gradually with spacing. The horn spacing was selected so as to make the amplitude of the periodic variation a minimum. Nevertheless, this causes a contribution of about 2×10^{-4} to the error of the entire experiment. This optimum spacing occurred at a moderate value of the horn spacing. The fine adjustment of the horn spacing was made by throwing the Fabry-Perot off resonance and adjusting the horn spacing for maximum detector current. Then Fabry-Perot resonance was indicated by a dip in the crystal current. The adjustments were then trimmed to give a symmetrical response on the phase sensitive detector, as mentioned earlier. In a few control experiments, the horn spacing was set to give a minimum crystal current with the Fabry-Perot off resonance, and then resonance in the latter was indicated by a maximum. The adjustments were then trimmed as before. No significant change in the voltage required for a Stark resonance was observed. However, if a random value of the horn spacing was used and if the adjustments were trimmed to give the best possible approach to symmetry of response, some shift in the Stark voltage at Stark resonance was observed. Therefore, it is necessary to assign an error of 2×10^{-4} to this cause.

In the final experiments, off-resonance detector current, with minimum attenuation and the auxiliary plunger set for maximum response, was held to less than 10 microamperes. (More than 50 were usually obtainable.) When the attenuator in the plunger arm of the directional coupler was set to maximum, the current dropped to two or three microamperes at most. Under these conditions, there appeared to be no indication of power saturation of the spectral lines.

The dc power supply was of commercial manufacture and was highly stabilized. It could be operated with either pole grounded. The measurements reported hereafter were the averages of data obtained with both polarities. When the response was properly symmetrized, the differences of the voltages of Stark resonance with the two polarities did not exceed one volt and were often considerably less.

The Fabry-Perot resonator which was used for the principal measurements reported herein was the third model built for this purpose. Earlier models suffered from mechanical instability and microphonics. Some of the instability was found to be due to fluctuations of atmospheric pressure acting upon the tuning knobs which controlled the spacing. In the third model, whose design is sketched in Fig. 3, the adjustments are made through three precision micrometers located entirely within the vacuum envelope, but whose scales can be read through glass tubes surrounding them. These micrometers are decoupled from the effects of atmospheric pressure by rotary vacuum feedthroughs. The coupling between the inner end of a shaft and the micrometer is slotted so that the shaft can slide parallel to the axis of the micrometer freely, and yet torque can be transmitted to the micrometer.

Three such micrometer mechanisms are employed. One controls the tilt of one reflector about its vertical diameter, the second controls the tilt of the other reflector about its horizontal diameter, and the third controls the spacing between the reflectors. The design is such that once the reflectors are made parallel by the use of the first two micrometers, they remain nearly parallel with a large change in the setting of the third micrometer.

With this arrangement, it is a matter of only a few minutes to adjust the reflectors for parallelism. The frequency stabilization of the klystron is disconnected, and a saw-toothed voltage is applied to its repeller. The phase sensitive detector is replaced by an oscilloscope, on whose screen is displayed the mode pattern of the resonator. As one of the tilt controls is varied, the pattern is observed to change. However, the pattern does not recognize the sign of the angle of tilt. Therefore, the correct setting corresponds to an extreme configuration of the mode pattern. In this way the tilt controls can be optimized by a process of successive approximation, but usually two cycles of adjustment are sufficient to obtain parallelism. Experimentally it was found that for a fixed frequency, the spacing is a maximum for good parallelism. For a given degree of tilt, the (absolute) shift in the spacing for resonance was smaller, the larger the spacing; that is, the greater the value of the mode number M. This is one of the reasons why the best accuracy is obtained with large mode numbers.

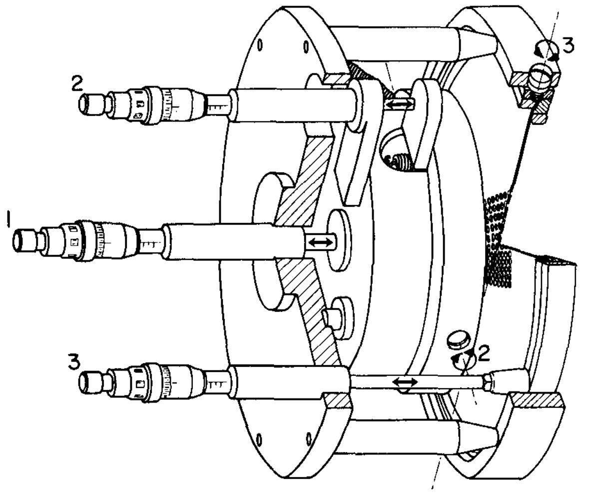

Fig. 3. Diagram of spectrometer. Micrometer No. 1 adjusts the spacing. Micrometers Nos. 2 and 3, which adjust the tilts of the reflectors about mutally orthogonal axes, are used for making the reflectors parallel. Micrometers are spring loaded.

II. Effect of Field Inhomogeneities

In principle, even assuming the plates are flat and uniform, the field can be supposed to lack uniformity because of two different causes, 1) fringing at the edges of the reflectors, and 2) effects due to the coupling holes. The first of these two effects can be disregarded. Experimentally, it is easily demonstrated that the RF field is almost entirely confined to the cross section of the pattern of the coupling holes, because the mode pattern is nearly undisturbed as large metal objects are inserted between the plates unless they come close to, say within about one-half inch, the edge of this cross section. Since the plate diameter is about eight inches, while the hole pattern is a square $2''\times2''$, it can be concluded that the effect of edge fringing is negligible within the active volume of the resonator.

The effect of the coupling holes is to give variations of the field in a region close to this reflector. Since the holes are smaller than a half wavelength, it can be supposed that the field is uniform at distances beyond one half wavelength. Therefore, for $M=1$, the average field is not given by the voltage divided by one half wavelength, but a small correction δ must be added to this distance to give the average field strength. However, as the spacing is increased, the additional volume does contain uniform field, and in the limit of large spacings one expects the effective plate spacing to approach the actual spacing. This argument provides one of two reasons for postulating that, when one of the Stark resonances is produced by applying a voltage V_M with the interferometer resonant with a nominal spacing M half wavelengths, the average field strength is given by

$$E_0 = \frac{V_M}{M\lambda/2 + \delta}. \qquad (1)$$

If it is assumed that δ is small compared to one half a wavelength and if one defines the apparent field strength E_M as V_M divided by $M\lambda/2$, it can be shown, approximately, that

$$E_M = E_0\left(1 + \frac{2\delta}{M\lambda}\right). \qquad (2)$$

Therefore, if E_M is observed at different values of M (by observing the same Stark components at different spacings) and if it is plotted against $1/M$, the points should lie upon a straight line, and the effective field strength E_0, which is to be used in reduction of Stark data, is obtained by extrapolating this line to $1/M = 0$.

A second reason for postulating (1) is that the first resonance does not occur exactly at one half wavelength because of the finite conductivity of the reflectors, but succeeding resonances occur at intervals of one half wavelength [4]. However, strictly speaking, the resonances of the interferometer are obtainable by solving the electromagnetic wave equation subject to three dimensional boundary conditions [4]. An exact solution gives not only the family of modes mentioned here, commonly called longitudinal modes, but other families as well, and near to each one of these longitudinal modes are members of these other families. We have generally observed these. Furthermore, the exact treatment indicates that even for the longitudinal modes, the spacing is not exactly M half wavelengths, but the correction is small when the transverse dimensions are large compared to the spacing. However, this correction is not constant. Therefore, if this effect were to predominate, δ would not be constant, and the points on the graph would not lie upon a straight line.

A plot of data of this type is shown in Fig. 4, and the points do lie very close to the straight line that is shown, which was determined by a least squares fit. The relative standard deviation of the intercept (i.e., of E_0) is 1.3×10^{-4}. Thus the validity of (1) is established, and it appears that the elementary resonance formula is valid within the accuracy of the experiment.

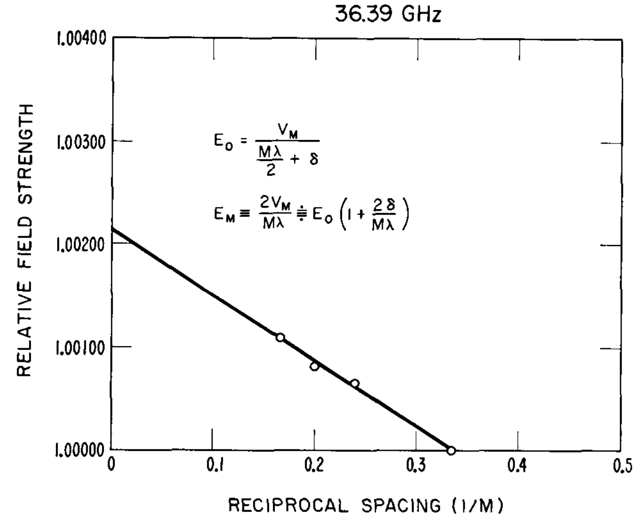

Fig. 4. Plot of field strength vs. the reciprocal of spacing. Field strength is expressed relative to the field strength at a spacing of three half wavelengths. The spacing is expressed in half wavelengths.

There is, however, one slightly unsatisfactory feature of this situation. Figure 1 represents the average of data obtained with three Stark lines. The data pertaining to the individual lines lie (with slightly larger deviations) close to straight lines, but the slopes of the three lines are slightly different. While the discrepancies in the slopes are hardly any larger than their standard deviations, the slopes have always ranked in the same order when measurements have been repeated: -7.92×10^{-3} for the No. 2 line, -6.21×10^{-3} for the No. 1 line, and -4.81×10^{-3} for the No. 3 line. (These are pure numbers based on a system of units where each E_M is expressed as a ratio to the respective E_3.) Further evidence that this effect is not a matter of statistics results from the observation of a gradual M dependence of the ratio of two voltages for which two lines come into resonance. These slopes appeared to be frequency independent.

The explanation for this anomaly is not clear, especially since (1) is a purely classical equation, and the effects associated with it can not be expected to recognize quantum numbers. Further confusion results from the fact these slopes are neither ordered with regard to the Stark coefficients nor with regard to the intensities of the lines. Had they been ordered with regard to either the linear or quadratic Stark coefficients, it might be supposed that the averaging process is slightly different because of differing amounts of non-linear contributions to the Stark coefficients. Had they been ordered with regard to the intensities of the lines, it might be supposed that the change in dielectric coefficient associated with the resonance of the gas was modifying the response of the interferometer. Had the slope of the No. 1 been intermediate between the other two, it might be supposed that the effect was due to residual distortions of the shapes of lines 2 and 3, since these occur at voltages which differ by only a few percent. Still further confusion results from the fact that if dipole moments are computed from the data using the average slope, the average deviation is slightly less than if individual slopes are used. As it is, no certain explanation can be given. It can be speculated that the effect is the result of two of these causes, possibly the dielectric effect and the residual distortion of lines 2 and 3. In the reduction of data presented in Table I, the average slope was used.

TABLE I

DIPOLE MOMENT OF CH_3CN

$(J=2) \leftarrow (J=1)$ Transition Debye Units

Orig. Freq. Shift Δf (MHz)	Line 1* $(0 \leftarrow -1)$ or $(0 \leftarrow 1)$	Line 2 $(-2 \leftarrow 1)$ or $(-1 \leftarrow 0)$	Line 3 $(1 \leftarrow 0)$ or $(2 \leftarrow 1)$	Ave. at Orig. Δf	Ave. at Corr. Δf**
−704.08	3.9192	3.9161	—	3.9177	3.9207
−404.08	3.9165	3.9145	3.9179	3.9163	3.9216
−284.08	3.9071	3.9044	3.9068	3.9061	3.9137
+315.92	3.9251	3.9224	3.9263	3.9246	3.9178
Average	3.9170	3.9144	3.9170	3.9162	3.9185
Stan. Dev. of Mean				0.0038	0.0017

* Numbers in parentheses give m_J values of spectral line. Number on left pertains to upper level. Upper pair pertains to negative Δf, and lower pair to positive Δf.

** Corrected values of Δf obtained by adding −0.55 GHz to numbers in first column respectively.

III. DETERMINATION OF THE DIPOLE MOMENT CH_3CN

Measurements were made upon the Stark resonances at four different frequency offsets from the zero field line, and the data were reduced by the use of Shirley's table, as stated earlier, to give values for the dipole moment as shown in Table I. Each of the numbers in the first three columns is based upon averages of readings made with both polarities and with a number of attempts (usually five) to reproduce the interferometer resonance.

For the reduction of these data it was necessary to employ the values of certain physical quantities and constants. In particular it was necessary to know at least a preliminary value of the zero field line, which was not observed directly in the present experiment. Using the value for the rotational constant [5] $B_0 = 9198.70 \pm 0.20$ MHz and for the centrifugal distortion constant [5] $D_{JK} = 0.178 \pm 0.100$ MHz, this frequency, neglecting hyperfine effects, was computed as being 36 795.08 ± 0.80 MHz, and the effective rotational constant was computed as 9198.52 MHz. The value for the velocity of light [6] $2.997\,925 \times 10^{10}$ cm/s was used, and with this a new value for the Stark effect constant of 0.503 447 MHz per Debye per (volt per cm) was computed. The standard deviations at the bottom of the last two columns are obtained by applying error analyses to the numbers above and do not represent the entire error of the experiment.

It is necessary to scrutinize the primary values of the dipole moment contained in the second, third, and fourth columns of Table I for four possible corrections.

1) *Error in the Zero Field Frequency.* The above computed value of this quantity has an assigned error of 0.8 MHz, and it is legitimate to try other values which will reduce the standard deviation of the mean, provided they do not differ from this value by amounts greater than this assigned error. It is to be noted that the offsets −284 MHz and +315 MHz are of comparable magnitude but of opposite sign, and that the average values given, respectively, on the fifth column do differ widely, suggesting that perhaps the zero field frequency should be lowered a little bit. Various new values were tried, the smallest steps being 0.05 MHz, and the standard deviation of the mean was found to be a minimum when the *zero field frequency is decreased by 0.55 MHz from the* computed value above. The corresponding values of the dipole moment are given in the last column of Table I. These values are given in Debye units, which are 10^{-18} cgs esu of charge multiplied by centimeters (or 3.33×10^{-30} coulomb meters).

Calculation of the hyperfine structure of this transition at zero field (see 4) below) indicates that the center of gravity of the line is shifted upward by 0.135 MHz. Therefore, the corrected value for the center of gravity of the zero field line is 36 794.67 ± 0.10 MHz, and the corrected value of the rotational constant $B_0 = 9198.56 \pm 0.10$ MHz, where this constant applies to hypothetical transitions without hyperfine splitting.

2) *Effect of Electrostatic Forces.* Electrostatic forces resulting from turning on the Stark field tend to pull the reflectors together, causing the spacing to be smaller than calculated and indirectly causing the computed value of the dipole moment to be too large. Since the field strengths giving resonances of the No. 2 and No. 3 lines are roughly three times as large as that for the No. 1, the electrostatic forces are nine times larger for lines Nos. 2 and 3 than for line No. 1. Therefore, if this effect were significant, the dipole moments computed from Nos. 2 and 3 should be systematically larger than that from No. 1, and the differences should become larger at large frequency deviations where the fields are larger. The data in Table I show no indication of this trend. Therefore, it can be concluded that this error is negligible.

3) *Effect of Induced Dipole Moment.* Were the molecule comprised of charged particles in a rigid structure, the dipole moment could be considered as being a true constant. However, since it is composed of a collection of charges in motion subject to mutual forces, it must be supposed that the application of any external field causes their motions to be modified with the result of a change in the dipole moment. Marshall and Weber [7] have considered this effect in their work upon the dipole moment of the molecule carbonyl sulfide (OCS) and have shown that the effect is approximately equivalent to increasing the Stark energy (which is the equivalent of a frequency shift) of the amount $\frac{1}{2}\alpha E^2 G$, where α is a parameter of the molecule defined more completely in their paper, E is the field strength, and G is a known function of the quantum numbers which is different for each line. With the modification of the method described in [7] appropriate to symmetric top molecules, the values of $\frac{1}{2}G$ for lines Nos. 1, 2, and 3 on the low-frequency side were computed as $-(1/70)$, $+(17/210)$, and $-(19/210)$, respectively. Therefore, if this effect is significant, the dipole moments from the No. 2 and No. 3 lines diverge as the frequency offset increases, and the value of that due to line No. 1 should be intermediate. No such trend is indicated by the values in Table I.

Therefore, this effect is negligible. Indeed, using values of the polarizabilities of other molecules, the greatest induced dipole moments which could be expected, with the field strengths used here, are between 10^{-5} and 10^{-4} Debye.

4) *Hyperfine Splitting.* The splitting of the zero field line due to the interaction of the N^{14} nucleus with the electric field of the molecule was computed by standard methods [8] and found to consist of seven lines (two of which coincide) spread out over a range of 2.75 MHz with their center of gravity, as stated previously, 0.135 MHz higher than the frequency of the hypothetical unsplit transition. In addition, there are splittings and displacements due to the nitrogen and hydrogen magnetic moments, which being only a few kHz, can be neglected.

The Stark energies involved in the present experiment are very much larger than the hyperfine energy splittings. The situation, commonly called "the Strong Field Case," which is analogous to the Paschen Back and Back-Goudsmit effects, is one where the spin of the nitrogen is decoupled from the rotational angular momentum J, and both precess independently about the field direction. The quantum numbers associated with the precession of the spin and of J are denoted m_I and m_J, the latter having been previously denoted by m with no subscript. The theory can be found elsewhere [8], [9]. In the general case where $|m_J| \neq 1$, the results are simple and indicate that there are only two distinct lines with a very small spacing between them and with the center of gravity having little or no shift from the frequency which would occur with no hyperfine splitting. However, there is some distortion of line shape. A special situation arises when one of the levels has $|m_J| = 1$. The transitions studied here fall into this special category.

In this special case, m_J is no longer a good quantum level because perturbations caused by off-diagonal matrix elements, connecting the state $m_J = +1$ with the state $m_J = -1$, mix these states up. The references state that the energy must be calculated by the solution of a second order secular equation. In this the two energy levels are perturbed by equal and opposite amounts equal to the square of the off-diagonal element of the quadrupole energy divided by the difference in the diagonal elements, including Stark energy. Explicit expressions for the matrix elements of the quadrupole Hamiltonian can be found in reference [10]. Numerical values of the off-diagonal elements were computed, and the largest was found to be about 0.7 MHz, when expressed in terms of frequency by the Bohr condition. The diagonal elements, expressed in frequency units are of the order of twice the Stark frequency shift; that is, with reference to the data of Table I, they have a minimum value of about 500 MHz. Thus, the shifts and splittings due to this effect cannot be expected to exceed about 200 kHz, and it is likely that these will be partly of opposite signs, and the shift of the center of gravity of the hyperfine structure of the Stark line is probably even less. Therefore, this effect should have been very small or negligible under the present conditions. Incidentally, these magnitudes are of the same order as those pertaining to the $|m_J| \neq 1$ cases. It appears, then, that the discussion in the references was aimed at the cases of linear molecules and $K=0$ states of symmetric tops, where in the first order the two $|m_J| = 1$ states are degenerate, and not to the present case where $K \neq 1$ and where the two $|m_J| = 1$ states are widely separated.

If this effect is appreciable, a plot of dipole moment vs. frequency shift should give a resonance maximum or minimum at zero frequency superimposed upon a horizontal straight line. Such a plot requires the evaluation of three constants. In the present experiment there were only four sets of points, and it seemed impractical to fit such a function. However, our colleagues G. E. Hudson and Marian Cord very kindly performed a least squares fit involving a parabolic correction as well as a shift in the zero field frequency. They obtained the best fit with almost exactly the same frequency as given above, and the inclusion of the parabolic correction reduced the standard deviation of a sample value by only 20 percent, which we do not consider significant. Therefore, we conclude that the effects of quadrupole splitting, aside from the small shift of the zero field frequency, are negligible, as suggested by the theory.

Error in the Average Value of the Dipole Moment

In view of the preceding discussion, we conclude that the value 3.9185 Debye, shown in the lower right corner of Table I, is the most probable value of the dipole moment. However, the standard deviation of the mean of 0.0017 Debye does not represent all of the errors of the experiment. There are, in addition, the errors associated with the extrapolation of the field based upon (1) of 0.0005 Debye and the error due to pulling of the interferometer resonance due to the horn of 0.0008 Debye. When these are combined by taking the square root of the sum of the squares, the total is 0.0020 Debye or a relative error of 5 parts in 10^4. Dipole moments are commonly quoted in the literature as having accuracies of the order of a few percent. Therefore, the present accuracy is out of the ordinary. However, the dipole moment of OCS has been measured by several authors, and the accuracy of the value obtained by Marshall and Weber [7], when expressed as a standard deviation is 3 parts in 10^4, which is slightly more accurate than the value for CH_3CN reported here.

In 1964, a less comprehensive set of data of the same type were obtained with an earlier model interferometer using one copper and one stainless steel reflector. The average of the corresponding values from the 1966 data, to which Table I refers, differs from the average of the 1964 data by 0.0006 Debye or 1.5 parts in 10^4.

The present value of 3.9185 ± 0.0020 Debye is in excellent agreement with the best previous [11] value of 3.92 ± 0.06 Debye.

IV. Evaluation of the Apparatus as a Voltmeter

There are at least three possible modes of operation of this apparatus as a voltmeter, and each one has a different evaluation of errors.

1) *The Standard Cell Mode.* In this application, the apparatus is used to reproduce a single reference voltage in a manner analogous to the use of standard galvanic cells. In this application it might be used as a sensing unit of a servo system used to stabilize a voltage source. For short term applications of this type, the errors are solely those associated with the precision of resetting on a Stark resonance, which is mainly determined by the linewidth and the signal-to-noise ratio. Using very conservative numerical parameters, including a one second averaging time, this relative error was estimated by theory [12] to be at worst 1 part in 10^5 and probably much better. Experimentally, if one, in rapid succession, alternately sets the voltage off resonance and then attempts to reset to resonance, the corresponding sample standard deviation of the potentiometer readings is better than 1 part in 10^4. However, if one merely throws the potentiometer off null and tries to reproduce the null, he obtains essentially the same result. Therefore the limit of short term precision of the present apparatus is apparently due to the potentiometer or to fluctuations in the power supply rather than due to the Stark phenomenon, and apparently the theoretical estimate is valid.

When long term reproducibility is concerned, changes in the plate spacing due to thermal expansion or mechanical instability come into play. The apparatus was located in a room where the temperature variation was less than 1°C. Data were examined to ascertain if any changes due to temperature could be found, but none were, probably because of the small temperature range. On the other hand, when all the controls were clamped and when the apparatus was left as undisturbed as possible, there was a gradual drift of about 2 parts in 10^4 per day in the sense consistent with a gradual decrease in the interferometer spacing. It seems logical to suppose that this may have been due to stretching of the thin foil reflector. Probably this could be eliminated or reduced by using a reflector deposited upon a dielectric slab, which might, incidentally, serve simultaneously as the window of the chamber.

2) *The Desert Island Mode.* By applying the reasoning of the dipole measurement experiment backwards, one can determine a voltage completely in terms of atomic and molecular constants: the dipole moment and rotational constant of CH_3CN, the resonant frequency of some substance such as cesium used to control an atomic frequency standard, and the speed of light in vacuum. The accuracy of the apparatus in this mode is, of course, given by the assigned error in the most probable value of the dipole moment; that is, 5 parts in 10^4.

It is probable that with further work, this accuracy could be improved somewhat. If the microwave interferometer were mechanically coupled with an optical Michelson interferometer so that the spacing could be determined in terms of the wavelength of light from some specified source (another atomic constant), many of the present errors would be eliminated or greatly reduced. In addition, the present coupling holes were selected to give optimum signal-to-noise ratio, but it has been shown that the accuracy has not been limited by this factor. Indeed, the accuracy obtained with the No. 1 line, which is considerably weaker than the other two, has been just as good as that obtained with the other two. Therefore, it is probable that with holes smaller by a few percent, the overall accuracy would improve as the result of smaller horn pulling, although the signal-to-noise ratio would be poorer. Furthermore, if a different transition occurring at higher frequency were used, the coupling holes would be appreciably smaller with the result of a smaller error due to field inhomogeneities. As this paper is being written, the apparatus is being modified to operate with another transition of CH_3CN at 55 GHz to test this hypothesis.

3) *The Voltage Divider Mode.* The apparatus may be used to measure the ratio of two voltages in terms of the theoretical Stark coefficients of two lines by bringing the two lines into resonance by applying the two voltages in turn. In the present case, the No. 1 and No. 2 lines, for example, could be used to measure the ratio of two voltages, when the ratio is about three. In principle, the accuracy associated with this mode is intermediate between the two which have been discussed. The precision should be essentially that of the standard cell mode, and errors in the two voltages, due to errors in the plate spacing, should compensate in part. Indeed, in a sequence of measurements of Stark resonances, when the attempts were made to reproduce the interferometer resonance, the standard deviation of ratio of the potentiometer readings is noticeably less than the computed standard deviations of the potentiometer readings themselves, but it is considerably poorer than suggested by the precision of the standard cell mode. Also, it is to be recalled that there is an unexplained M dependence of the ratio. Finally, the accuracy of the theoretical ratio can never exceed the accuracy of the input constants, and thus, ultimately, the accuracy must be nearly the same as for the desert island mode.

Finally, it must be mentioned that there are, of course, other types of apparatus which can be used to observe the Stark effect. One is the parallel plate absorption cell used by a number of workers including Marshall and Weber [7], which offers some advantages and some disadvantages over the present apparatus. Considerably smaller linewidths can be obtained by the use of masers and molecular beam electric resonance equipment, but the present work indicates that at present the accuracy is not limited by linewidth but by other causes, which are likely to produce comparable errors in apparatus of these types.

It is visualized that the greatest usefulness of the Stark method is with high voltages, in the hundred kilovolt region, where conventional measurements are disturbed by corona effects. The present apparatus, therefore, is to be considered a low voltage "pilot model." No fundamental difficulties are visualized in scaling up the apparatus to higher voltages. Of course, to avoid breakdown, the plate spacing must be made larger, and to maintain field uniformity, the other dimensions must be scaled accordingly, and thus the apparatus is likely to become rather large. At the same time the greater volume of gas will lead to greater signal-to-noise ratio.

ACKNOWLEDGMENT

The authors wish to express their thanks to R. L. Ehret for constructing some electronic equipment and taking some of the data, to Jean McKennan and J. H. Wilson for taking some data, to M. Humpal for construction and assistance in the details of design of the interferometers, and to R. C. Mockler for a helpful discussion.

REFERENCES

[1] Y. Beers and G. L. Strine, "The measurement of voltage by the use of the Stark effect," *IRE Trans. on Instrumentation*, vol. I-11, pp. 171–176, December 1962.

[2] See, for example, C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy*. New York: McGraw-Hill, 1955, Ch. 10.

[3] J. H. Shirley, "Stark energy levels of symmetric-top molecules," *J. Chem. Phys.*, vol. 38, pp. 2869–2913, June 1963.

[4] R. W. Zimmerer, M. V. Anderson, G. L. Strine, and Y. Beers, "Millimeter wave resonant structures," *IRE Trans. on Microwave Theory and Techniques*, MTT-11, pp. 142–149, March 1963.

[5] G. G. Weber, "On the *l*-type doubling and *l*-type resonance of molecules in the microwave region," *J. Molecular Spectrosc.*, vol. 10, pp. 321–347, May 1963.

[6] National Bureau of Standards, Washington, D. C., Misc. Pub. 253, November 1963.

[7] S. A. Marshall and J. Weber, "Microwave Stark effects measurement of the dipole moment and polarizability of carbonyl sulfide," *Phys. Rev.*, vol. 105, pp. 1502–1506, March 1, 1957.

[8] C. H. Townes and A. L. Schawlow [2], ch. 6 and sec. 10.4.

[9] W. Low and C. H. Townes, "Molecular dipole moments and Stark effects. I. Stark effects on symmetric top molecules with nuclear quadrupole coupling," *Phys. Rev.*, vol. 76, pp. 1295–1298, November 1, 1949.

10] N. F. Ramsey, *Molecular Beams*. London: Oxford University Press, 1956, p. 423, equations (C.28).

[11] S. N. Ghosh, R. Trambarulo, and W. Gordy, "Electric dipole moments of several molecules from the Stark Effect," *J. Chem. Phys.*, vol. 21, pp. 308–310, February 1953.

[12] Y. Beers, "Theory of the cavity microwave spectrometer and molecular frequency standard," *Rev. Sci. Instr.*, vol. 30, pp. 9–16, January 1959.