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THE MEASUREMENT OF VOLTAGE BY USE OF THE STARK EFFECT

by

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The Measurement of Voltage by Use of the
Stark Effect

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ABSTRACT

The Stark effect pertains to the splitting of a spectral line into components. Since the displacement of the components depends upon the electric field strength, the measurement of the frequency shift may be used to measure the electric field strength and, if the electrode spacing is known, to measure the voltage. Thus the method involves a modification of the principle of an atomic or molecular standard. However, the principal errors are due to geometry, and therefore a frequency standard of the highest accuracy is not required. With even a simple absorption spectrometer a precision of the order of one part in several million is obtainable. Another potentially useful feature is that this device works directly with high voltages, which are difficult to measure with reference to conventional standards. Unfortunately, it is not a primary standard but must be calibrated against some dc standard voltage. The method may be used to compare peak sinusoidal voltages with dc voltages with precisions approaching those of dc voltage measurements. However, to obtain uniform fields it is necessary to use large electrodes, and these cause impedance transformation errors. Except for these errors the method could be used with frequencies up to about 1000 Mc. The report contains a review of the results of the theory of the Stark effect and a review of the theory of the absorption spectrometer.

1. INTRODUCTION

In the present trend to replace the existing prototype standards of physical units by atomic standards, the obvious thought of employing the Stark effect to measure voltage or electric field strength seems to have occurred to many people, but this writer has not been able to find any record of any serious attempt to exploit this idea. The purpose of this memorandum is to present some of the possibilities which are available in the hope of provoking some interest in the subject and in the hope of ascertaining which of these possibilities should be considered in greater detail.

It should be recalled that with the Stark effect, the application of an electric field causes a spectral line to break into components whose frequency displacement is a function of the electric intensity. Thus the measurement of the frequency displacement can be used as a measurement of electric intensity. One of the possibilities to be considered is a special type of transition occurring with symmetric top molecules with the selection rules $\Delta J = 0$ and $|\Delta M| = 1$ in which the line at zero field is hypothetical: that is it occurs at zero frequency with zero intensity, and in this case the frequency, rather than a difference in frequency, is a measure of the electric field.

Thus such an apparatus is really a modification of the so-called atomic clock. There exist several types of atomic clocks; atomic and molecular beams, gas cells, beam masers, and absorption cells, and, in principle, all of these could be used in this application. However, since the Stark effects are small with monatomic gases (with the possible exception of hydrogen), the gas cell does not appear to be very practical in this application, and the most favorable type of beam apparatus is one employing diatomic or polyatomic molecules and electric resonance rather than magnetic resonance.

Since the Stark effect depends upon the electric field strength, its observation can be used to determine voltage only when the field is produced by electrodes of well-defined geometry. These must be precisely parallel. To obtain a uniform field the transverse dimensions of the electrodes should be large compared to the spacing. It appears that the largest errors result from defects in the geometry, or from thermal expansion or mechanical instability of the electrode structure. In the numerical examples which will follow, it appears that the precision of reproducibility of measurements of one second duration, if these effects are neglected, can be considerably better than one part in several million employing simple absorption techniques. While the more complicated and expensive beam technique is probably capable of giving a precision of reproducibility better than that of the absorption method, its use seems hardly justified because of the errors due to geometry.

Unfortunately, the Stark voltmeter has possibilities only as a secondary standard. The theory involves the ratio of the dipole moment of the molecule to the electrode spacing as a parameter. There appears to be no independent method of measuring the dipole moment with significant accuracy, and the accuracy with which the spacing can be determined is somewhat poorer than the precision of the frequency measurements.

The principal advantage of the Stark method is this high precision which can be of the order of one part in several million or better, and a second advantage is that the Stark effect is mainly useful in the direct measurement of high voltage. The present practical standard is the standard cell, which, of course, is a low voltage standard. Its emf is defined to one part in about a million, although Dr. C.H. Page, Chief of the Electricity Division of the National

Bureau of Standards, informed this writer that measurements can be made to a few parts in ten million. On the other hand, high quality potentiometers generally available commercially can be read to only about one part in a hundred thousand. Therefore, the precision of the Stark voltmeter compares very favorably with the existing methods, and it is more convenient for use with high voltages since no voltage divider is required nor is there any uncertainty in the voltage division ratio resulting from corona or leakage. Dr. Page stated that often it is difficult to measure high voltages with accuracies better than one per cent.

The Stark method may be used with high frequency alternating voltages as well as with static ones, and, while the accuracy is somewhat poorer than with static fields, it is capable of giving improvement over existing ac methods under some circumstances. At high frequencies there is the usual additional error resulting from the effects of leads. Another difficulty in using it for most high frequency measurements is that the theory requires that the less sensitive quadratic Stark effect be employed than the more sensitive linear effect, as will be shown.

The use of the Stark effect to measure an electric field is somewhat analogous to the use of nuclear magnetic resonance to measure a magnetic field. However, the magnetic case is much simpler in theory. The total angular momentum of the nucleus is of constant magnitude, and, to a very high degree of approximation, the only energy of interaction which need be considered is that between the nuclear magnetic moment and the field under measurement. Under these conditions only a single resonance line is obtained, and its frequency is very accurately proportional to the field strength. However, the Stark effect concerns an entire atom or molecule whose angular

momentum may take on an infinite number of values. Corresponding to each is a different effective value of the electric dipole moment. Furthermore, the interaction of the electric field upon the electric moment can indirectly affect the internal energy interactions, and this effect in turn causes the effective moment to change with field strength. Consequently, each spectral line is split by the action of the field into a number of components whose frequencies shift with field strength at their own individual rates. The variation of frequency of any component as a function of the field strength is given as a power series with an infinite number of terms, although, in principle, the coefficients may be calculated from theory with any desired accuracy. Only in the special case of comparatively low fields and with systems having degenerate pairs of energy levels is the frequency shift reasonably linear with field strength.

2. GENERAL CONSIDERATIONS

The first order behavior of any type of atomic molecular frequency standard is given by the following equation^[1]

$$\varepsilon = 1.54 (\Delta\nu)/S, \quad (1)$$

wherein ε is the r m s fluctuation in the frequency, ν is the frequency, $\Delta\nu$ is the half width of the line at half maximum, and S is the voltage signal-to-noise ratio at the maximum response of the line. In the evaluation of S the existence of a detecting system of noise bandwidth B and noise figure F is implied. The interval of time to which ε is referred is approximately $1/B$.

The derivation of Eq. (1) has assumed that the line has a

Lorentz shape and that the determination of ν is obtained by averaging alternate measurements at the most favorable frequencies on either side of the maximum. These occur at the frequencies ν' given by

$$\nu' = \nu \pm (\Delta\nu)/(3)^{\frac{1}{2}} . \quad (2)$$

Also assumed is a detector whose output deflection is linear with the power response of the line. For the sake of definiteness, these conditions will be assumed in the remainder of this report.

The effect of replacing these assumptions by others is merely to change the numerical factors in Eqs. (1) and (2). The principal significance of Eq. (1) is that a narrow line width $\Delta\nu$ and a high signal-to-noise ratio S are equally important in obtaining high precision. In considering practical details, there is much to be said in favor of having a small $\Delta\nu$ and a proportionately smaller S rather than a large $\Delta\nu$ and a correspondingly larger S . At any rate, considerations of signal-to-noise ratio will play a major role in the present treatment.

If the Stark voltmeter is based upon a molecule with linear Stark effect, the voltage may be expressed, neglecting higher order terms, as

$$V = a (\nu_1 - \nu_0) , \quad (3)$$

wherein a is a constant, ν_1 is the frequency of some selected Stark component with the voltage on and ν_0 is the frequency of the unsplit line with the voltage off. (In some special cases to be discussed later ν_0 may be zero, but this situation can be covered in the theory by merely allowing appropriate quantities to go to zero.) In view of the

fact that a Stark component has only a fraction of the intensity of the unsplit line, the signal-to-noise ratios are respectively S_1 and S_o . Also, in general, the linewidth of the Stark component $\Delta\nu_1$ is larger than the linewidth of the unsplit line $\Delta\nu_o$ because of inhomogeneities in the field. Then by the use of Eqs. (1) and (3) and by application of standard error theory, the standard deviation in voltage is

$$g = 1.54 a \left[\frac{(\Delta\nu_1)^2}{S_1^2} + \frac{(\Delta\nu_o)^2}{S_o^2} \right]^{\frac{1}{2}}, \quad (4)$$

and the fractional standard deviation is

$$G = \frac{1.54}{(\nu_1 - \nu_o)} \left[\frac{(\Delta\nu_1)^2}{S_1^2} + \frac{(\Delta\nu_o)^2}{S_o^2} \right]^{\frac{1}{2}}. \quad (5)$$

With the quadratic Stark effect, since the frequency shift is proportional to the square of the electric field, Eq. (3) is replaced by

$$V = b(\nu_1 - \nu_o)^{\frac{1}{2}}, \quad (6)$$

in which b is a constant. Then

$$g = \frac{0.77 b}{(\nu_1 - \nu_o)^{\frac{1}{2}}} \left[\frac{(\Delta\nu_1)^2}{S_1^2} + \frac{(\Delta\nu_o)^2}{S_o^2} \right]^{\frac{1}{2}}, \quad (7)$$

and

$$G = \frac{0.77}{(\nu_1 - \nu_o)} \left[\frac{(\Delta\nu_1)^2}{S_1^2} + \frac{(\Delta\nu_o)^2}{S_o^2} \right]^{\frac{1}{2}}. \quad (8)$$

In comparing Eqs. (5) and (8) it would appear at first sight that the linear Stark effect would give twice the fractional standard deviation of the quadratic Stark effect. However, in practice the numerical values of the coefficients a and b are such that the values of $(\nu_1 - \nu_0)$, which can be obtained with the linear effect, are generally much larger than those obtainable with the quadratic effect, and, therefore, actually the linear effect is capable of giving the greater precision. Also it is generally desirable to employ an effect which varies linearly with the quantity which is to be measured. Therefore, for dc measurements, the linear effect is to be preferred. For most ac measurements, the quadratic effect must be used. Therefore, in later sections it will be considered also.

It is to be noted that the method employs a frequency difference. In principle this may be measured in two ways. One method employs a source of the frequency ν_0 and another source of frequency $(\nu_1 - \nu_0)$ which is mixed with ν_0 to give a "sideband" at the frequency ν_1 . In this case ν_0 need not be known accurately but its source should have sufficient stability such that it does not change between the ν_0 and ν_1 measurements. Only the $(\nu_1 - \nu_0)$ source need be known accurately. The second method uses a single source of high accuracy which is used first in the ν_0 and later in the ν_1 measurements. With the high precision measurements with which this report is concerned, the stability requirements on ν_0 in the first method are so high that the first method merges with the second. Then in these measurements ν_0 can be considered a constant which can be measured once very precisely. In such a case the first terms in the brackets in Eqs. (4), (5), (7), and (8) can be neglected in comparison with the second terms.

3. THE ABSORPTION METHOD

The calculation of the signal-to-noise ratio, of course, depends upon the type of frequency standard which is employed. The only one which will be considered in detail here is an absorption cavity spectrometer as this has the advantage of simplicity over the maser and molecular beam, and while its precision is not as great, it is more than adequate because of errors of geometry. A formula for the signal-to-noise ratio of such a device has been derived by the present author.^[1]

$$S = \frac{hc \gamma}{8 \pi \bar{\mu}} \left(\frac{\Delta \nu}{\nu} \right) \left(\frac{Q V_0 \nu}{2 F k T' B} \right)^{\frac{1}{2}}, \quad (9)$$

wherein γ is the power absorption coefficient of the gas, $\bar{\mu}$ is the dipole moment matrix element, Q is the unloaded quality factor of the cavity, V_0 is its volume, ν is the resonant frequency of the cavity and of the line, F is the noise figure of the detector, and T' is a reference temperature. h , c , and k have their usual definitions as fundamental constants.

In the derivation of Eq. (1) it has been assumed that the power level has been adjusted to cause the linewidth to be approximately the square root of 2 times the linewidth at low levels. Also it has been assumed that the cavity is a single port device whose impedance is matched to the detector and highly mismatched to the source. However, little error will result by applying this formula to transmission cavities under normal conditions. In the derivation it was assumed that $Q\gamma$ times the wavelength is small compared to 4π .

It is interesting to note that, if Eq. (9) is substituted into Eq. (1), $\Delta\nu$ cancels out. Thus, paradoxically, in this theory the precision is independent of the linewidth but depends mainly upon the strength of the line: that is, upon γ . However, if the general formula for the absorption coefficient^[2] is introduced, $\Delta\nu$ returns to the picture.

$$\gamma = \frac{8\pi^2 \nu^2 N f \bar{\mu}^{-2}}{3 c k T \Delta\nu} \quad , \quad (10)$$

wherein N is the number of molecules per unit volume, f is the fraction in the state from which the transition originates and T is the temperature of the gas. If Eqs. (1), (9), and (10) are combined,

$$\epsilon_o = \frac{D_o (\Delta\nu)_o}{\nu_o^{3/2} N f \bar{\mu}} \quad , \quad (11)$$

with

$$D_o \equiv 2.08 \left(\frac{kT}{h} \right) \left(\frac{k T' B}{Q V_o} \right)^{\frac{1}{2}} \quad (12)$$

wherein all of the constant and instrumental parameters are contained in D_o . Similar equations apply to ϵ_1 except that D_1 contains an additional multiplicative factor equal to the ratio of the intensity of the unsplit line to the intensity of the Stark component. In practice, transitions can be chosen in which this fraction is nearly unity. If the cavity is sufficiently large and if the pressure is sufficiently low, the linewidth is essentially the Doppler width. $\Delta\nu/\nu$ can be considered as a constant (about 1.5×10^{-6} for molecules of the mass of NH_3). Under these conditions the maximum value of N is proportional to ν . f varies with frequency in a manner which depends upon the specific molecule. However, as a working hypothesis which is roughly correct in most common situations, it will be taken proportional to the frequency.

Then it may be concluded that

$$\epsilon_0 = \frac{P}{\nu_0^{5/2} \bar{\mu}} \quad , \quad (13)$$

where P is a proportionality constant. Eq. (13) implies that $\bar{\mu}$ and ν should be selected to be as large as possible. ϵ_1 is of the same order of magnitude as ϵ_0 but somewhat larger. The fractional standard deviation in the Stark voltage is then roughly proportional to ϵ_0 and inversely proportional to the frequency shift. Then by examination of Eqs. (3), (6) and (13) it can be inferred that the following may be taken as figures of merit for spectral lines

$$M_a = \nu^{5/2} \bar{\mu}/a \quad (14)$$

for the linear effect, and

$$M_b = \nu^{5/2} \bar{\mu}/b \quad (15)$$

for the quadratic effect. When a and b are evaluated, other factors of $\bar{\mu}$ and ν appear explicitly.

4. MODULATION METHODS

An effective detection scheme requires the use of some form of modulation. The simplest method is to frequency modulate the source and observe the receiver output on an oscilloscope or with a phase sensitive detector and a recording meter. To obtain the maximum of sensitivity and also to present the opportunity of measuring the electrode separation by resonance measurements on the cavity, Q must be made as high as possible. In such a case the variation in response with frequency due to instrumental effects is very rapid and

can obscure the desired effect unless the resonant frequency of the cavity can be swept synchronously with that of the source. Technologically this is a difficult, but possibly not unsurmountable, problem. Alternatively it is necessary to utilize a compromise value of Q . It can be shown that the relative variation in response of the cavity over the full half power width of the line, assuming that both are resonant at the same frequency and that the cavity impedance is matched to the detector, is

$$\beta = \frac{1}{8} (Q/Q_\ell)^2 \quad , \quad (16)$$

where Q is the unloaded quality factor of the cavity and Q_ℓ is the quality factor of the line defined as $\nu/(2\Delta\nu)$. On the other hand the variation of response at resonance by the introduction of the sample is given by

$$\psi = \frac{c Q \gamma}{4 \pi \nu} \quad . \quad (17)$$

Eq. (17) is valid only under conditions when ψ is somewhat less than unity. If Eq. (16) is divided by Eq. (17) and if the result is solved, the maximum tolerable Q for a given β and ψ is obtained

$$Q_{\max} = \frac{2c}{\pi} \left(\frac{\beta}{\psi} \right) \frac{\gamma Q_\ell^2}{\nu} \quad . \quad (18)$$

Since Q_ℓ is essentially independent of frequency (about 2.5×10^5 for light molecules) and γ increases faster than the second power of the frequency, it is apparent that it is advantageous to use as high a frequency as possible.

Another modulation method would be to superimpose a small ac voltage on the dc voltage to be measured. Either the frequency is slowly swept, or the so-called "dc" voltage is swept. In the former

case some of the same difficulties of the previous method are encountered, but if the cavity tuning is to be synchronized to the oscillator, the technological problems are less severe than in the first method since the cavity tuning only has to follow a slow sweep rather than a periodic modulation. The method of sweeping the voltage eliminates this difficulty but does not allow measurement of arbitrary voltages. On the other hand, this method has the problem of decoupling the source of modulation from the dc voltage, which is likely to be difficult since high dc voltages will be used. With the quadratic Stark effect, corrections have to be applied for the asymmetry of line shape caused by modulation.

Another conceivable method is the application of a periodic field to produce Zeeman modulation. This method is not very attractive because most molecules which are stable and have favorable Stark effects are diamagnetic and have small coefficients of the order of one nuclear Bohr magneton: that is, about one kilocycle per gauss, and therefore it is necessary to use comparatively large fields, and these have to be maintained over large volumes. Furthermore, to keep eddy current losses down, the frequency must be limited.

Another method which should be mentioned for completeness is pressure modulation, which has been used in infrared spectrographs,^[3] but this is not very attractive as modulation frequencies greater than about 10 cps are impractical and also because it is impractical to seal the cell off permanently from a gas handling system.

Thus there appears to be no completely satisfactory modulation system, but with compromises the second and possibly the first method can be made to give acceptable performance. With regard to modulation, the maser and the electric resonance molecular beam methods offer advantages as the modulation can be applied to the deflecting electrodes.

5. THE LINEAR STARK EFFECT

Before proceeding with experimental considerations, it is necessary to present the theory of the Stark effect: that is, to evaluate the coefficients a and b which were introduced in Eqs. (3) and (6) respectively. The linear Stark effect is obtained only with atoms and molecules having doubly degenerate energy levels. The only monatomic gases of this type are hydrogen-like systems, which are not useful in the present application because of their difficulty of production. The only other molecules which have this effect are symmetric top molecules in states for which the quantum number $K \neq 0$. These are non-linear molecules having two of their principal moments of inertia equal.

For the sake of those readers who are concerned with details, this paragraph is inserted to qualify the previous remarks for the sake of rigor. A realistic definition of a double degeneracy is that there exist a pair of levels whose spacing can be considered smaller than any energy of interaction which tends to split or broaden them. Strictly speaking, all of these pairs of levels in symmetric top molecules are split by inversion, but in all molecules except ammonia the splittings are very small, in most cases much less than the linewidth. In ammonia, as is well known, this splitting is large compared to Stark energies at the field strengths usually obtainable, and, therefore, while from the point of view of geometrical structure, ammonia is a symmetric top, it does not display a linear Stark effect at ordinary fields. Conversely, linear molecules in an excited bending mode of vibration acquire the characteristics of a symmetric top molecule, and, if the Stark energy is large compared to their ℓ -type doublet splittings, their Stark effects become approximately linear. Also asymmetric top

molecules whose asymmetry splittings are small compared to their Stark energy give an approximately linear effect. The general theory of this intermediate case may be found in textbooks.^[4]

The energy of a symmetric top molecule is a function of three quantum numbers: J , which determines the total angular momentum; K , which determines the component of angular momentum along the figure axis; and M , which determines the component of angular momentum along some space fixed direction. The energy associated with the linear Stark effect is given by^[4]

$$W_1 = -\mu \frac{V M K}{d J(J+1)}, \quad (19)$$

where μ is the static dipole moment, V is the voltage, and d is the spacing.

In the following discussion, nuclear hyperfine splittings will be neglected. In practice it is desirable to choose molecules with few splittings as these generally tend to weaken the intensity of the lines and in the case of complex splittings, difficulties arise from troubles with identification. Also the presence of hyperfine effects will possibly require corrections to the theory. Therefore, molecules with small or no hyperfine effects are to be preferred.

Transitions are governed by the selection rules $\Delta J = 0, \pm 1$ (but not $0 \rightarrow 0$), $\Delta K = 0$, and $\Delta M = 0, \pm 1$. The $\Delta M = 0$ transitions (sometimes called σ transitions) are observed with the Stark field parallel to the rf field and are the ones which usually have been observed because it is easy to build an appropriate cell. The $\Delta M = \pm 1$ (or π) transitions have been observed only by the use of special techniques,^[5] but these are the transitions which normally will be observed when a Fabry-Perot cavity is used as a Stark cell. Then there are four cases

to be considered

Case I. $J \rightarrow J + 1$; $K \rightarrow K$; and $M \rightarrow M$.

The appropriate relations are as follows:^[4]

$$\nu_0 = 2 B (J+1) \quad , \quad (20)$$

$$a = \frac{d h J (J+1) (J+2)}{2 M K \mu} \quad , \quad (21)$$

and

$$\mu^{-2} = \mu^2 \frac{(J+1)^2 - K^2}{(J+1)(2J+1)} \quad . \quad (22)$$

Equation (20) is an approximation based upon the assumption that centrifugal distortion and nuclear effects may be neglected. The "constant" B is inversely proportional to the principal moment of inertia with respect to an axis perpendicular to the axis of symmetry.

Equation (22) pertains to the entire transition unsplit by the Stark effect. The intensity of an individual Stark component is proportional to the product of Eq. (22) and the factor

$$U = (J+1)^2 - M^2 \quad . \quad (23)$$

These relations may be used to evaluate M_a from Eq. (14). However, M_a is merely a figure of merit pertaining to the precision whereby it is possible to set upon the center of the line. It will be shown that in practice this type of error is likely to be very much smaller than errors of other types. Therefore, the effort required to evaluate it explicitly and to maximize it exactly with respect to the quantum numbers does not seem to be justified. Only rough conclusions obtained by inspection will be given.

M_a varies as $\nu^{5/2}$ and, because of Eq. (20) this in turn is proportional to $J^{5/2}$. On the other hand, since M and K are generally proportional to J , a is, according to Eq. (21), proportional to J , and thus M_a is proportional to $J^{3/2}$. Therefore a high J is desirable, and apparently to obtain operation at some specific frequency, it is better to use a heavy molecule with a small B and a high value of J rather than the reverse. Secondly, M_a is proportional to μ^2 , and, as one expects intuitively, it is desirable to use a molecule with a large dipole moment. Thirdly, values of K and M intermediate between zero and the maxima of J should be used, because if on one hand they are made zero, $1/a$ becomes zero. On the other hand, if they are placed equal to J , Eqs. (22) and (23) go nearly to zero.

Case II. $J \rightarrow J+1$; $K \rightarrow K$; and $M \rightarrow M \pm 1$.

Equations (20) and (22) apply again, but

$$a = \frac{dhJ(J+1)(J+2)}{\mu K (2M \mp J)} \quad , \quad (24)$$

and

$$U = (J \pm M + 1) (J \pm M + 2) \quad . \quad (25)$$

The upper signs are for $M \rightarrow M+1$, and the lower are for $M \rightarrow M-1$.

The same conclusions concerning the desirability of large values of J , B , and μ and an intermediate value of K of Case I apply here also. In the case of $M \rightarrow M+1$, the value of $M = +J/2$ should be avoided as $1/a$ goes to zero and values of M approximately equal to $-J$ should be avoided as U becomes very small. Similarly for $M \rightarrow M-1$, the values of $M = -J/2$ and $M \approx +J$ should be avoided. Otherwise, it is not clear without extensive analysis what value of M would be best.

Case III. $J \rightarrow J$; $K \rightarrow K$; and $M \rightarrow M$.

If hyperfine splittings are neglected, this case is trivial because, since none of the quantum numbers change, there is no transition.

However, if nuclear hyperfine interactions are considered, J is not the total angular momentum. A fourth quantum number F is the resultant of J and nuclear angular momentum, and the selection rules allow this to change giving transitions between the sublevels which are split by the nuclear interactions. Such transitions have been observed^[6] with some iodine compounds where they are large compared to other compounds but with which they occur at low frequencies, of the order of 400 Mc. Because they occur at low frequencies and because they have small matrix elements, their intensities are poor, and they appear to be unsuited for precise voltage measurements. Therefore, this case will not be considered further.

Case IV. $J \rightarrow J$; $K \rightarrow K$; and $M \rightarrow M \pm 1$.

This case, as has been stated previously, is the nearest analog to the measurement of a magnetic field by magnetic resonance since $\nu_0 = 0$. a is given by

$$a = \frac{dh J(J+1)}{\mu K} \quad . \quad (25A)$$

$$\mu^{-2} = \mu^2 \frac{K^2}{J(J+1)} \quad , \quad (26)$$

and

$$U = (J \mp M)(J \pm M + 1) \quad . \quad (27)$$

In cases I and II, ν and ν_0 were assumed so nearly equal that they did not have to be distinguished except where their difference appeared. There ν_0 was used in Eq. (14). Here, however, $\nu_0 = 0$, and, if M_a is to be evaluated explicitly, it is appropriate to employ $\nu = V/a$. In Eq. (19) one of the factors of ν came from the assumption that the fraction f of the molecules in the desired state is proportional to the frequency. Here, however, this assumption is not valid, and this factor should be omitted. f is roughly proportional to $\sqrt[3]{AB^2}$, where A is the rotational constant with respect to the axis of symmetry. (In Cases I and II the frequency is roughly proportional to this quantity, and, for this reason, the earlier assumption was made.)

By inspection it may be seen that the relative figure of merit depends upon $\mu^{7/2}$. Since $1/a$ and $\bar{\mu}$ increase with K , the maximum value of $K(K=J)$ should be employed and then $\bar{\mu} \approx \mu$. It follows from Eq. (25A), since a small value of a is desired, that the lowest possible value of J should be used. However, $J = 0$ is to be excluded since then K must also be equal to zero. Apparently the following situation is optimum or near to optimum: $J = 1$, $K = 1$, and $M = -1 \rightarrow M = 0$ and $M = 0 \rightarrow M = +1$. These two occur at the same frequency in this approximation, which from Eq. (24) may be seen to be

$$\nu = \frac{\mu V}{2 dh} \quad (28)$$

$\mu V/dh$ has the value of 0.503 Mc for one volt per cm and for a dipole moment of one debye (10^{-18} esu cm). It is unlikely that the value of μ greater than 3 debye is to be employed, and a field much greater than 10^4 volts per cm is not likely to be practical. With these values Eq. (28) gives about 7500 Mc. Since this frequency is compara-

tively low, the intensity is not as great as with the conventional $\Delta J = 1$ transitions.

A much more serious difficulty arises from the fact that the rf and dc fields must be at right angles. There appears to be no practical way of building a sample cell satisfying this requirement and giving a highly uniform dc field at low frequencies.

6. THE QUADRATIC STARK EFFECT

It is to be recalled that the frequency displacement resulting from the Stark effect is given in terms of a power series expansion in terms of the electric field V/d . Only in the special cases which have been mentioned is the linear (first order) effect finite, and more usually the quadratic (second order) is the lowest order which must be considered. Where the linear effect exists, the quadratic effect usually must be considered as a correction, and, in turn, higher order effects in principle must be considered as corrections to the quadratic effect.

In general, the second order Stark displacement of the m th energy level may be calculated from

$$W_{2m} = \sum_n \frac{\bar{\mu}_{mn}^{-2} V^2}{d^2 (W_m - W_n)}, \quad (29)$$

where $\bar{\mu}_{nm}$ is the dipole moment matrix element connecting the states n and m (which contains the static moment μ as a factor). W_m and W_n respectively are the energies of the m th and n th levels. In principle, n is summed over all states except m , but usually $\bar{\mu}_{nm}$ is finite for only finite number of states n . Frequently this number is so large that it is not practical to carry out the entire summation, and only a

few terms are taken as an approximation. In the case of two levels whose spacing is small compared to the spacings between these levels and all other levels, W_{2m} is well approximated by a single term. It is to be noted that in this case $W_{2n} = -W_{2m}$, and the two levels are pushed apart by an amount $2|W_{2m}|$, and the quadratic Stark effect causes the frequency to increase $2|W_{2m}|/h$. This splitting is inversely proportional to the magnitude of the energy denominator $|W_m - W_n|$, and thus the quadratic Stark effect becomes larger as the spacing between an isolated pair of levels decreases.

One case where this approximation is useful is with ammonia where the energy denominator is the inversion energy difference. The approximation is better with ND_3 than with NH_3 because the inversion splitting is about 15 times smaller. Another situation where this approximation is valid is in the case of some transitions of asymmetric top molecules, and some of these transitions are capable of giving some of the largest quadratic Stark splittings. Particularly favorable cases are HDO and formaldehyde H_2CO , where transitions between comparatively closely spaced and otherwise well-isolated levels exist. At the same time these molecules, have fairly large dipole moments, and, being light, have favorable partition functions. They are capable of giving relatively strong lines. However, the selection of asymmetric top molecule transitions of this type must be done by inspection since the theory cannot be put in closed form, and the energy denominators in the last analysis must be determined experimentally from measured frequencies at zero field.

In the case of a symmetric top molecule, the result of the summation can be given in closed form.

$$W_2 = \frac{\mu^2 V^2}{2d^2 h B} \left\{ \frac{(J^2 - K^2)(J^2 - M^2)}{J^3 (2J - 1)(2J + 1)} - \frac{[(J+1)^2 - K^2][(J+1)^2 - M^2]}{(J+1)^3 (2J+1)(2J+3)} \right\}. \quad (30)$$

The first term is due to the upward displacement due to interaction with the levels $J-1$ below, while the second term is due to the downward displacements due to the levels $J+1$ above. As J becomes large, these effects approach equality, and the net shift vanishes. Hence the shifts are greater at low values of J . Also the effect nearly vanishes when K has the maximum value $K=J$ and is greatest with $K=0$. At the same time it is to be noted from Eq. (19) that the linear effect vanishes for $K=0$. This quadratic theory may be made to apply to linear molecules by merely allowing $K=0$. It is also to be noted that the effect is greatest for $M=0$.

Strictly speaking, because of centrifugal distortion effects, B is not truly constant, and to be exact, different values should be used in the two terms of Eq. (30). With reference to Eq. (20), the value which should be used in the first term is the experimental value of the frequency of the $J-1 \rightarrow J$ transition at zero field divided by $2J$, while the value used in the second term should be the experimental value of the $J \rightarrow J+1$ transition divided by $2(J+1)$. For the purpose of calculating the second order Stark coefficients, it is possible to deal with these quantities determined directly from experiment and fortunately not necessary to deal with an explicit evaluation of the centrifugal distortion constants and a formula giving B as a function of the quantum numbers.

By comparison of Eqs. (19) and (30), it will be noted that the quadratic effect may be considered as a small correction to the linear effect when $\mu V/d$ is small compared to hB , and therefore light molecules with large B 's give more linear Stark effects for any given volt-

age than heavy molecules with small B 's. Conversely, if it is desired to select a linear molecule to have a large quadratic Stark effect, one with a large μ/B should be chosen.

The third order Stark effect for linear molecules is identically zero.^[4] The fourth order contains in the expression for the energy the parameter $[\mu V/(d h B)]^4$. Therefore, it can be inferred that $[\mu V/(d h B)]^n$, in general, can be taken as a measure of the magnitude of the n th order Stark effect.

The constant b defined by Eq. (6) may be evaluated by evaluating Eq. (30) for the upper and lower states, subtracting and solving. Because of the algebraic complexity of the result, this calculation will not be carried out in detail here. Therefore, the figure of merit M_b given by Eq. (15) will not be evaluated explicitly. Since b is inversely proportional to μ , M_b is proportional to μ^2 . $\nu^{5/2}$ is proportional to $B^{5/2}$ and to $J^{5/2}$. On the other hand, $1/b$ increases rapidly with J , and the effects tend to compensate.

As reported earlier, asymmetric top molecules are capable of having very large quadratic Stark coefficients and it is possible that some asymmetric top rotational transitions with large figures of merit can be found. HDO and H_2CO are likely candidates, but the selection must be made by inspection.

Of the molecules more amenable to theory, the alkali halides, in principle, are by far the most favorable choices. They have very large dipole moments, most being between 10 and 12 debye units, while a wide range of B values is available. Also their simplicity makes them amenable to calculation of high order corrections. Unfortunately their vapor pressures are negligible at low temperatures and therefore they cannot be used with conventional absorption spectrometers but require molecular beam or special maser techniques. Next

avored of the simpler molecules are some of the linear cyanogen compounds and some of the symmetrical tops.

7. DC STARK VOLTAGE MEASUREMENTS

It is to be noted from preceding remarks that the frequency shift produced by the Stark effect, in general, is given by an expression of the form

$$\nu_1 - \nu_0 = \sum_{n=1}^{\infty} a_n \left(\frac{\mu V}{d}\right)^n \quad (32)$$

wherein the a_n 's are functions of the quantum numbers which can be calculated from the theory and where, except for a_1 , they are functions of the rotational energy level splittings, which can be determined from experiment with high accuracy. However if the voltage V is to be determined from the measurement of $\nu_1 - \nu_0$, the factor μ/d must be determined. With the exception of the hydrogen atom, μ can be calculated from theory only with an accuracy poorer than that desired here. μ can be determined from dielectric constant measurements on bulk material but not with the accuracy desired. In view of the fact that Eq. (32) contains the quantities μ , d , and V solely through the single parameter $\mu V/d$, there is no possibility of determining any one of the three quantities separately by frequency shift measurements. μ can be found only if V and d are known from independent measurements, and in fact, this method, where applicable, gives the most accurate values of μ . Of course, this situation is the reverse of what is desired here. Therefore, it must be concluded that the conventional Stark effect measurements on molecules can only be used as a secondary standard of voltage, wherein μ/d is determined by measuring the

frequency shift at some voltage known by other methods. If the same cell is used for further voltage measurements, the spacing need not be measured. If the spacings in the original and some second cell are measured, then the use of the same molecule in the second cell also can lead to voltage measurements.

Before this subject is expanded, it is desirable briefly to consider the possibility of atomic hydrogen which has been mentioned. Strictly speaking, the Stark effect is not linear in the excited states but is intermediate between linear and quadratic since the Lamb shift breaks up the degeneracy between levels of the same j but different l . However, the Stark effect is large, and in principle it can be calculated, but, if high accuracy is desired, the calculation is likely to be formidable as numerous corrections must be included. The effective moment includes as a parameter the product of the electronic charge and the first Bohr radius, and therefore if the calculated Stark coefficient is to be used as the basis of voltage measurement, the accuracy will be limited by the accuracy in these constants among other things. Since this accuracy is likely to be considerably poorer than the precision obtainable when the device is used as a secondary standard, the principal outcome of a well designed experiment is likely to be a determination of the product of the electronic charge multiplied by the first Bohr radius, $\hbar^2/(me)$, which in itself might be very significant from the point of view of evaluation of fundamental constants. Unfortunately, the ground state exhibits the quadratic effect, and to obtain a quasi-linear effect, excited states must be used. All of the excited states, at least with the Stark field present, have large widths since they may make spontaneous downward transitions with frequencies corresponding to the visible and ultraviolet regions. Nevertheless, with the use of a suitable optical pumping double resonance method and with the use

of atomic beam techniques it may be possible to obtain results with sufficient accuracy to be of interest.

To return to molecular Stark effects, the molecule whose dipole moment is best known is OCS. The latest of several measurements gave a value of 0.7124 debye (10^{-18} esu cm) with an assigned error of about 3 parts in ten thousand.^[7] As a standard this molecule is not a favorable choice in all respects. Being a linear molecule, its lowest order effect is the quadratic one and therefore the reduction of data is less convenient than with a symmetric top. In addition its dipole moment is only moderate in size.

In a procedure of this type, the accuracy is likely to be limited by measurements in the spacing in either the first or second cell or both. The measurements of Marshall and Weber^[7] to which reference was just made, employed a nonresonant cell with a spacing of only 1 mm to obtain a uniform field and a high field strength for moderate voltages. Their cell was four feet long and six inches wide, and, being so large, its spacing could not be measured by optical interferometric methods.

If, by some means the uniformity of field could be preserved, even though the area is cut down and if the spacing is increased, the accuracy in the measurement of the spacing can be greatly improved. For example, if the spacing is made about 5 cm and if this could be measured by the methods of optical interferometry with an accuracy of one-tenth of a fringe, this distance could be known with an accuracy of about 2.5 parts in a million. Alternatively, these plates might form a Fabry-Perot interferometer for a frequency near 50,000 Mc. It should be practical^[8] to obtain a Q of about 35,000. Since it should be possible to set upon the resonance with a precision of about one hundredth of its width, the resonant frequency, and therefore the spacing, should be known with a precision of about 3 parts in ten million. Unfortunately, however, the distance obtained from the microwave

resonance is an effective distance and not the actual distance, and a correction must be made for skin depth and, if coupling holes are present, for their phase shift. The details of how the latter correction could be made have not been worked out.

Since the ratio μ/d is required rather than knowledge of μ and d individually, obviously the procedure can be improved by using the same cell for calibration and for measurement. In such a situation, the only errors which occur other than the errors of the standard which is used in the calibration are due to the lack of precision of setting on the resonance and errors resulting from variation of the spacing in time.

The direct error resulting from setting up on the resonance can be made very small. For example, consider the case of $J = 1 \rightarrow 2$, $K = 1 \rightarrow 1$, $M = 1 \rightarrow 2$ transition in methyl fluoride CH_3F . This molecule has the following parameters, approximately: $\mu = 1.79$ debye, $A = 1.53 \times 10^5$ Mc, $B = 2.55 \times 10^4$ Mc, and, for this transition, which occurs at about 1.01×10^5 Mc, Eq. (10) yields a value of $\gamma = 2 \times 10^{-3}$ cm. It is difficult to estimate the performance of Marshall and Weber's cell at this frequency, but it can be roughly estimated that under practical conditions the signal-to-noise ratio S should be at least 10^5 , with a noise bandwidth of 1 cps.

With a Fabry-Perot cavity with plates $30 \text{ cm} \times 30 \text{ cm}$ and a spacing of 15 cm, it is possible to obtain a Q of the order of one hundred thousand.^[8] Assuming a noise figure of 20 db (100) and a bandwidth of one cps, Eq. (9) gives a value of $S = 2.2 \times 10^8$. However, using Eq. (1) and $S = 10^5$, the relative precision in the unsplit line theoretically (for $\Delta\nu/\nu = 2 \times 10^{-5}$) is about 3 parts in 10^9 , and except for the inhomogeneity in the field, the relative precision in one of the Stark components would be only a little poorer, perhaps one part in

10^8 , or about 1 kc. If the field is 10,000 volts per cm, Eq. (24) gives $\nu_1 - \nu_0 = 4500$ Mc. Thus the precision in the frequency shift which in this case is equal to the precision in the voltage is about 3 parts in 10^7 .

This example does not represent the optimum in several respects. 10,000 volts per cm is not the maximum possible field. Marshall and Weber reported using up to 25,000 volts per cm. Also, CH_3F may not be the optimum molecule for this purpose. CH_3CN , for example, has a dipole moment more than twice as large, although its B value is less favorable. The common isotopic species has a quadruple splitting due to N_{14} , but this complication could be avoided by using a sample enriched in N_{15} . Unfortunately this material is poisonous and corrosive. At any rate precisions of the order of one part in 10^7 or better are obtainable.

The preceding paragraph neglected the effect of inhomogeneity of the field, which tends to broaden the Stark components and spoil the precision. With the cell used by Marshall and Weber, there was the effect of fringing fields, which not only gives a broadening but an asymmetry of the line, causing a systematic error. The Fabry-Perot resonator offers a potential advantage in this regard. If the coupling antennas are made considerably smaller in transverse dimensions than the reflectors, the rf field attenuates more rapidly radially than the dc field, and therefore the dc field can be held fairly uniform over the effective volume. The outer portions of the reflectors serve as the equivalent of guard rings. On the other hand, present Fabry-Perot techniques employ coupling holes, and their presence is a source of inhomogeneity, for which a correction must be made. For this purpose the sensitivity is so good that the highest available reflectivities and Q's are not required. In fact, a very high Q, although aiding

sensitivity presents difficulties. One is the difficulty of modulation which was mentioned earlier.

Another is the so-called "pulling" effect, which arises from the distortion of the line shape a result of the variation of response of the resonator. Gordon, Zeiger, and Townes,^[9] have shown that the shift in the maximum of the line $\delta\nu$ resulting from the detuning of the cavity from the line frequency by an amount D is given by

$$\frac{\delta\nu}{\nu} = \frac{Q_L}{Q_l} \left(\frac{D}{\nu}\right), \quad (31)$$

where Q_L is the loaded Q of the cavity and where Q_l is the Q of the line, equal to $\nu/(2\Delta\nu)$, which for most molecules is about 2.5×10^5 .

Thermal expansion can cause errors directly as the result in the change in the spacing d , and, in the case of cavity spectrometers, indirectly by the pulling effect. If it is possible to build a cell with a linear coefficient of expansion of 10^{-6} per C° (approximately equal to invar and about one tenth of that of common metals), and if it is possible to hold the temperature constant to one-hundredth of a centigrade degree, the direct effect can be kept to less than one part in 10^8 . If the cell is a resonant cavity, there is a resulting proportionate shift in the resonant frequency. If Q_L is 10^5 , then the pulling effects are one-fifth as much. With lower Q_L 's, of course, it is proportionately smaller.

The previous discussion has mentioned only two types of cells: the transmission line cell of Marshall and Weber and the Fabry-Perot resonator. Actually the type of cell used by Marshall and Weber was first devised by Professor Gordy's group at Duke University and was used earlier by Trambarulo and Luck,^[10] and it has been used to study $\Delta M = \pm 1$ transitions.^[5] Parallel plate cavities for high

precision dipole moment measurements have been described by Verdier^[11] and Dyamus,^[12] but these suffer from fringing effects and are not capable of giving the results which are desired here.

The transmission cell, although giving a poorer sensitivity and therefore poorer precision than the various types of resonators, is capable with fixed spacing of operating at arbitrary frequencies and therefore with arbitrary voltages, while with fixed spacing the resonators can operate only at a discrete set of frequencies corresponding to their modes.

Because of its academic interest, some mention should be made as to what precision should be obtainable using $\Delta J = 0$, $\Delta M = \pm 1$ (Case IV) transitions if the seemingly impossible job designing a cavity with a uniform electric field at right angles to rf field could be surmounted. Consider the $J = 1 \rightarrow 1$, $K = 1 \rightarrow 1$, $M = 0 \rightarrow \pm 1$ transitions in the same molecule considered previously, CH_3F . With the same 10,000 volts per cm, Eq. (28) gives $\nu = 4500$ Mc. Then Eq. (10) gives $\gamma = 4.2 \times 10^{-6}$ cm. With $F = 10$, $B = 1$ cps, $V = 10^4$ cm, and $Q = 10^4$, Eqs. (1) and (9) give for ϵ a relative value of about one part in 10^8 , which is comparable with that obtainable using the conventional transitions.

At any rate, accuracies of one part in a few million appear to be feasible, and this is comparable to what can be obtained with the best standard cells and potentiometers. As stated in the introduction, this accuracy is obtained with high voltages rather than with low voltages. It would be especially useful, therefore, with van der Graaff accelerators and in X-ray work. The Stark voltmeter may be used as a sensing element in a servo system used to stabilize the voltage.

These Stark voltmeters are useful to basic science for making very accurate measurements of dipole moments of either the same

molecule in various states or measurements of the dipole moment of one molecule relative to another. These data would serve as important experimental checks on theories of molecular structure.

8. AC STARK VOLTAGE MEASUREMENTS

The conventional Stark spectrograph employs a low frequency square wave voltage: that is, ideally one which is accurately zero during half of the cycle and accurately constant at some finite voltage during the other half. The output is observed on a synchronously swept cathode ray oscilloscope, and the pattern which is observed is essentially that which would be obtained at the corresponding dc voltage. If the square wave is replaced by a sinusoidal voltage, the pattern is a superposition of distorted Lissajous figures, from which it would be possible to determine the peak voltage once the deflection resulting from a frequency shift caused by a known dc voltage had been determined. However, this method of comparing ac and dc voltages employs the Stark effect in a redundant manner since the original ac frequency is applied to the oscilloscope.

If the Stark effect is to be used in a nontrivial way in ac measurements, it must be used in a way that the original frequency is, in the language of electronics, "detected": that is, it does not appear at the oscilloscope terminals.

Two methods appear possible in principle. However, first it should be pointed out that these procedures suffer one difficulty which is common with many other high frequency measurements: namely, the effect of impedance transformation produced by leads of finite length so that the electric field at the sample does not correspond to the actual voltage which is to be measured. This problem is serious in

the case where high precision is desired because then the electrodes must be large to produce a uniform field. Thus it may be necessary to compromise precision to reduce these effects. On the other hand, the Stark effect might be useful for measuring field strength rather than voltage inside of resonating cavities in cases where the impedance transformation cannot be determined. While the transformation question may be of prime importance, here it will be neglected for simplicity. It is quite possible that the molecular beam electric resonance method could be advantageous in this application since it may be possible to work with electric fields confined to a smaller volume.

The theory of ac Stark effects is given in Townes and Schawlow's book.^[13] With a conventional Stark spectrometer, if the frequency increases until it is comparable to the line width, the Stark component broadens and ultimately breaks up into additional components, which are the analogs of sidebands. With the linear effect they are displaced from the original line at zero field by amounts $\nu_0 + n\nu_m$, where ν_m is the modulation frequency and n is an integer. The intensity of the component $\nu_0 + n\nu_m$ is given for a sinusoidal voltage by

$$I_n = I J_n^2 \left(\frac{\delta\nu}{\nu_m} \right), \quad (32)$$

where I is the intensity with a dc field, $\delta\nu = \nu_1 - \nu_0$ is the frequency displacement for a dc voltage equal to the peak voltage, and J_n is the Bessel function of the first kind for order n .

With the quadratic effect at high Stark modulation frequencies there is a pattern of sidebands associated with each of the original Stark components. The frequencies in one of these patterns are given by

$$\nu_0 + \frac{1}{2}(\nu_1 - \nu_0) + 2n\nu_m \quad (33)$$

where ν_1 is the frequency of the respective Stark component as measured with a dc voltage equal to the peak ac voltage. The intensity is given by

$$I_n = I J_n^2 \left(\frac{\delta\nu}{4\nu_m} \right) . \quad (34)$$

Note that with the quadratic effect the sidebands are spaced by $2\nu_m$ while with the linear effect they are spaced by ν_m . Eqs. (32) and (34) remind one very much of the expression for the intensities of the sidebands of a frequency modulated signal. The similarity is not surprising since a Stark component can be considered as being frequency modulated.

Eqs. (32) and (34) are not valid when the Stark modulation frequency approaches resonance: that is, not when it closely corresponds to the energy separation between one of the levels involved in the transition and some other level. The situation of resonance [11] is scientifically interesting since it provides the possibility of observing some transition frequencies not normally observed, but since it appears to have no application to measuring voltage, it will not be considered further here.

Eqs. (32) and (34) can serve as the basis of two methods of comparing a peak sinusoidal voltage to a dc voltage. One method uses the variation in intensity of the lines as an indication of the voltage. Probably this method is potentially effective only when used as a null method: that is, when the voltage and frequency correspond to one of the roots of the Bessel function causing one of the lines to disappear. Thus in practice, at any one frequency, the method can be used effectively only with a discrete set of voltages, and, to be practical, it must be supposed that either the frequency or the voltage can be varied a little so that, so to speak, it is possible to set right upon the zero of a Bessel function.

For example, the lowest voltage at which, with the linear Stark effect, the carrier ν_0 disappears is when $\delta\nu/\nu_m = 2.405$, and

$$V = 2.405 a \nu_m, \quad (35)$$

where a has the meaning in Eq. (3). a can be determined from dc measurements. The constant is the first root of J_0 . In the examples which were given in Section 7 it was seen that $\delta\nu$'s at least up to 3000 Mc could be produced. Therefore, measurements based upon Eq. (35) up to about 1200 Mc can be made.

It was shown that, with dc measurements, signal-to-noise ratios of 10^7 or better are obtainable. Under these conditions the precision in the setting upon the null must be such that the magnitude of J_0 is less than 10^{-7} . From the numerical value of the derivative of J_0 with respect to its argument, it can be shown that the precision in the voltage under ac conditions can be at least as good as 2 parts in 10^7 . To this must be added the errors in calibration and the effects of impedance transformation to get the total error. The quadratic effect could be used instead of the linear effect except that the accuracy potentially is not as great because the frequency shifts are smaller.

The last three paragraphs have neglected the fact that the linear Stark effect always has the higher order effects superimposed upon it. Without these higher order effects, a true null cannot be obtained at the frequency ν_0 , since the response at that frequency is due to the combined effects of all of the Stark components. In general, they have different values of $\delta\nu$, and therefore the separate contributions will not all go to zero with the same value of ν_m . However, the higher order effects separate these responses so that it should be possible to observe only one. On the other hand, because of the higher order effects, it is necessary to correct Eq. (35) to obtain the exact condition for a null. Such corrections can be made.

The second method employs frequency measurements rather than intensity measurements. The frequencies given by high frequency modulation of the linear Stark effect are only those given by the expression $\nu_0 + n\nu_m$. Since this expression is independent of the voltage, nothing precise concerning the voltage can be learned by measuring the frequencies in the pattern. However, with the quadratic effect there is a pattern of side bands associated with each of the original Stark components with frequencies given by the expression

$\nu_0 + \frac{1}{2}(\nu_1 - \nu_0) + 2n\nu_m$, and since ν_1 is linearly related to the peak voltage, there exists a basis of determining the voltage from measurements of the frequency. As ν_m is increased, the side bands get farther and farther apart until ultimately the nearest ones ($n = \pm 1$) are outside the immediate range of observation, and the only observable lines are those given by the expression $\nu_0 + \frac{1}{2}(\nu_1 - \nu_0) = \frac{1}{2}(\nu_0 + \nu_1)$, where ν_1 takes on values corresponding to the various Stark components. In other words, the pattern is qualitatively identical with that obtained with dc fields. Furthermore, under these conditions, the J_0 approaches unity while all the other J_n 's approach zero. Therefore the respective intensities become identical with those in the dc pattern. Thus in every respect the two patterns become identical when the ac peak voltage equals the dc voltage multiplied by the square root of two. This fact has been demonstrated experimentally.

The first method which employs intensity measurement, or more specially, a null observation of the carrier, is capable of giving higher precision than the second method since it may employ the linear Stark effect which gives greater frequency displacements, while the second or frequency measurement method is restricted to the quadratic effect. On the other hand, the first method, at a given modulation frequency and electrode spacing, is restricted to discrete voltages

and cannot be used at frequencies above about 1200 Mc, while the second method may be used with arbitrary voltages sufficient to split the original line and with all frequencies which are large compared to the reciprocal of the linewidth, although the latter advantage is probably of academic importance.

The ac Stark effect then can be used to measure peak sinusoidal voltages with high precision for all frequencies up to where impedance transformation errors become serious. Also it can be used as a sensing element in a servo system used to stabilize the voltage. It is conceivable that in some devices, such as high energy nuclear machines, the latter feature may be very useful.

The theory of the ac Stark effect has been worked out only for sinusoidal voltages, and before much practical use is made of it, the theory should be worked out for other types of wave forms.

The high precisions approaching a few parts in 10^5 which appear to be feasible with ac Stark measurements compare most favorably with what can be obtained by conventional techniques. In 1949 Selby^[14] called precisions of one percent in the radio frequency region as good. No doubt, during the years which have followed, the conventional techniques have improved, but it seems unlikely that they have improved so much as to give precisions as good as are potentially possible by the Stark method.

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