considers a new set

$$x^n;\quad n=n_0,\, n_0+1,\, n_0+2,\, \cdots, \tag{A.21}$$

it can be shown easily that this is also complete.[29] We have therefore two complete sets where one is a subset of the other. Such a situation may occur because the x^n's of (A.20) are not orthogonal to each other and thus the removal of some x^n's does not necessarily diminish the dimensions of the Hilbert space constructed on the set (A.20).

The orthonormal complete sets constructed from (A.20) and (A.21) may, however, look quite different. Thus a function $f(x)$ may be expanded in different ways in the different sets. Which set is more convenient will depend on the function we want to expand. It will be obvious however that the set (A.20) is more convenient than (A.21) when we expand a function which may be approximated easily by a linear combination of x^n with $n \leqq n_0$.

As is seen immediately, the relation of the Hylleraas expansion to our expansion is quite similar to that of (A.21) to (A.20). Thus the above argument suggests strongly that the actual eigenfunction of He atom will be approximated more easily and quickly by the generalized expansion (2.11) than the ordinary Hylleraas expansion (2.7), if it is possible at all.

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[29] The completeness of the set $\{x^n; n=0, 1, 2, \cdots\}$ may be expressed as follows: If $\int_0^1 f(x)x^n dx=0$ for $n=0, 1, 2, \cdots$, $f(x)$ must be identically zero. Therefore, to prove the completeness of (A.21), we have only to show that $f(x)=0$ derives from the relation $\int_0^1 f(x)x^n dx=0$ for $n=n_0, n_0+1, n_0+2, \cdots$. Now, since this relation can be rewritten as $\int_0^1 f(x)x^{n_0}x^n dx=0$ for $n=0, 1, 2, \cdots$, we obtain $f(x)x^{n_0}=0$. Thus $f(x)=0$ for $x\neq 0$. We may not have to worry about the value of $f(x)$ at $x=0$ since it does not contribute to the integral.

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Microwave Stark Effect Measurement of the Dipole Moment and Polarizability of Carbonyl Sulfide

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An improved microwave spectrograph has been developed which permits measurements of electric field intensity to one part in ten thousand. The instrument is employed to make precise Stark effect measurements. A method is also given for measuring the polarizability of polar molecules in a given rotational state. The transition $J=1\rightarrow 2$, $\Delta M=0$ for the ground vibrational state of carbonyl sulfide (OCS) was studied and the electric dipole moment was determined to be (0.7124 ± 0.0002) Debye units. In addition the polarizability anisotropy $(\alpha_{zz}-\alpha_{xx})$ was measured and found to be $(2.4\pm 3.0)\times 10^{-24}$ cm^3.

Effects caused by the fourth-order term in the perturbation expansion for the Stark Effect were observed and found to be in good agreement with theoretical predictions.

I. INTRODUCTION

THIS work was motivated by the need for improvement of the precision of Stark effect measurements in microwave molecular spectra in order to study higher order effects. The splitting of degenerate rotational energy levels through the Stark field interaction with nonvanishing electric dipole moments is in general many times greater than that caused by other Stark field interactions. Consequently, Stark displacements of rotational spectral lines are taken to be the result of dipole interactions even though other interactions are recognized and known to be present. For the most part, these weak interactions present no serious problems to the determination of electric dipole moments because of their very small effects; in addition the determination of field strengths in most microwave Stark cells is not sufficiently precise to establish their presence conclusively.

Because of its uncomplicated rotational spectrum and its lack of nuclear quadrupole coupling, carbonyl sulfide (OCS) has in recent years been the object of a number of microwave investigations.[1–3] Dakin, Good, and Coles[1] reported the first microwave Stark investigation of the molecule and later, Shulman and Townes[3] investigated its various vibrational state electric dipole moments. By using a set of carefully selected Stark

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* Part of a dissertation submitted by S. A. Marshall in partial fulfillment of the requirements for a Ph.D. at the Catholic University of America.

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[1] Dakin, Good, and Coles, Phys. Rev. **71**, 640 (1947).

[2] Strandberg, Wentink, and Kyhl, Phys. Rev. **75**, 270 (1949).

[3] R. G. Shulman and C. H. Townes, Phys. Rev. **77**, 500 (1950).

wave guide cells, the latter investigators were able to report dipole moments of OCS having probable errors of the order of 0.004 Debye unit. Precision measurements of the dipole moment will enable subsequent workers to use a particular molecule as a standard in order to calibrate new spectrographs where cell dimensions and field configurations are not known or are difficult to measure.

Molecular polarizability interaction with an electric field produces rotational energy level splitting which is quadratic in the field and several orders of magnitude below the splitting caused by electric dipole moments. To detect this effect in the class of molecules having the linear Stark effect would indeed be a formidable task. However, in molecules exhibiting a quadratic Stark effect the dipole splitting of energy levels is small enough to make an attempt at polarizability determinations feasible..

Molecular dipole moment determinations involve the measurement of electric field strengths and frequency shifts of spectral line components. It would be desirable if these two measurements could be made to within the same degree of precision. For example, OCS exhibits a second-order Stark splitting with part of its rotational spectrum in the 24 000 Mc/sec region. Assume electric field strengths of the order of 20 statvolts/cm to cause OCS spectral line displacements of roughly 50 Mc/sec. Present techniques make it possible to measure frequencies of lines to 1 part in 10^7, so that it is not unreasonable to say that Stark shifts of the order of 50 Mc/sec can be determined to within a few parts in 10^4. To put electric field strengths and spectral line displacements on a nearly equal footing of measurement, we would like to be able to determine field strengths to within 1 part in 10^4 or better.

Wave guide absorption cells having Stark septums are clearly undesirable in attempting this order of precision because of the nonuniformity of wave guide dimensions and the field uncertainties associated with edge and corner regions of the septum and guide. In an effort to reduce these uncertainties, a special silver-coated polished glass microwave absorption cell has been put into operation. Two sets of plates separated by quartz spacers give the configuration of a plane parallel plate transmission line. The separation of the plates is 1 millimeter having a uniformity of 1 part in 10^4 over a four-foot absorption path length, and the plate width is six inches.

Using this cell[4] and a frequency standard having a stability of 1 part in 10^8, we have measured the dipole moment of OCS in its ground vibrational state by observing the Stark splitting in the $J=1\rightarrow 2$, $\Delta M=0$, rotational transition. The observed energy level splittings indicated the need for approximations to be carried out to fourth order in the Stark perturbation and for the inclusion of effects due to molecular polarizability.

II. APPARATUS

The instrument used in this investigation is a Stark square wave modulated spectrograph.[5] The cell is inclosed in a six-foot steel vacuum chamber fitted with vacuum tight flanges. One of these flanges is used to bring in the Stark voltage through a glass-to-metal seal and two other flanges have accommodations for bringing in the microwave radiation. The radiation oroginates from a $2K33$ klystron oscillator and is coupled to the absorption cell by means of an electromagnetic horn having a 6-inch H-plane flare with a one millimeter E-plane opening matching the separation of the cell plates. A more detailed description of the instrument will be given elsewhere.

The spectrograph has two oscilloscope displays, one for the presentation of the absorption and another to monitor the oscillator mode pattern. This second display makes it possible to locate the absorption line on a flat region of the mode.

A saw-tooth sweep generator used to frequency-modulate the klystron oscillator is equipped with an inverting stage of amplification having a gain adjustable to unity. The oscillator can thus be swept in a forward and reverse direction for the purpose of averaging out errors due to time delay in the frequency measurements. By sweeping in both directions and at the same time keeping the frequency and amplitude of the sweep voltage as low as possible, we were able to reduce time delay errors to less than the uncertainty in placing a frequency marker on the peak of the absorption line.

III. EXPERIMENTAL PROCEDURE

Stark frequency displacements for a rigid linear rotor without nuclear quadrupole couplings are given by a relation having the form

$$\Delta\nu = A(J,M)\mu^2E^2/h^2\nu_0, \tag{1}$$

where μ is the permanent electric dipole moment, E is the Stark field strength, ν_0 is the frequency of the undisplaced rotational line, $\Delta\nu$ is the frequency difference between the Stark displaced and the undisplaced line, h is Planck's constant,[6] and $A(J,M)$ is given by[7]

$$\frac{3M^2(16J^2+32J+10)-8J(J+1)^2(J+2)}{J(J+2)(2J-1)(2J+1)(2J+3)(2J+5)}. \tag{2}$$

The selection rules are $J\rightarrow J+1$ for the angular momentum quantum number and $\Delta M=0$ for the magnetic

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[4] The electromagnetic horns discriminate against radiation from the edges of the cell. No line broadening due to edge effects was observed at field strengths up to 7500 volts per cm.

[5] R. H. Hughes and E. B. Wilson, Jr., Phys. Rev. **71**, 562 (1947).

[6] J. W. M. DuMond and E. R. Cohen, Revs. Modern Phys. **25**, 691 (1953).

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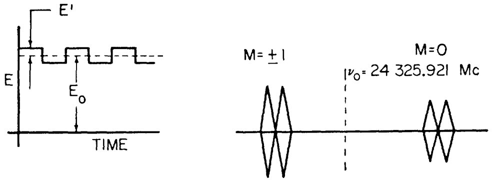

FIG. 1. Relation between Stark field and absorption display.

quantum number when the Stark and microwave electric vectors are parallel as is the case here.

Following Shulman and Townes,[3] we apply a Stark field to the cell which is the sum of a dc bias field E^0 and a small 100-kc square-wave field E' for modulation. From Fig. 1 we see that when E^0 and E' are first turned on, the field applied to the cell for the first 5 microseconds is (E^0+E') which produces a Stark frequency displacement in the OCS spectrum given by

$$\Delta\nu_+ = A(J,M)\frac{\mu^2}{h^2\nu_0}(E^0+E')^2.$$

During the next 5 microseconds, E' changes sign, causing a slightly different displacement given by

$$\Delta\nu_- = A(J,M)\frac{\mu^2}{h^2\nu_0}(E^0-E')^2.$$

Taking the average of these two displacements, we get

$$\Delta\nu = A(J,M)(\mu^2E^0/h^2\nu_0)^2[1+(E'/E^0)^2]. \quad (3)$$

Although both $\Delta\nu_+$ and $\Delta\nu_-$ vary linearly with E', their average cancels this dependence and reduces considerably inevitable uncertainties associated with the square-wave field. If now the ratio (E'/E^0) is maintained in the neighborhood of (1/100), then fluctuations in E' amounting to as much as 10% will affect the correction term $[1+(E'/E^0)^2]$ by not more than a few parts in 10^5, provided E^0 is held constant.

The simple geometry of the cell makes it possible to define the field within the interior regions by the relation $E=V/d$, where V is the potential difference in statvolts[6] applied to the plates of the cell and d is the plate separation distance. Since the width is six inches and the separation is one millimeter, the inhomogeneous field regions near the edges of the cell plates can be shown to cause only a slight broadening of the absorption line with no observable shift in the peak. For the quadratic Stark effect the broadening increases linearly with the field strength, and it is interesting to note that the plate separation in this particular instrument was sufficiently uniform to cause less than a 50-kc increase in the line breadths for field strengths of up to 25 statvolts/cm.

In determining the dipole moment of OCS, frequency displacements for the two Stark components $M=0$ and $M=\pm1$ were measured for a number of electric field strengths. The frequency of the undisplaced line was taken to be 24 325.921 Mc/sec.[8]

Frequency shifts for each of the Stark components were measured individually since the dipole moment measurements for the two M states were expected to differ slightly. This prediction was based on an estimated frequency displacement resulting from polarizability interaction.

IV. THEORY

The energy level splitting in a rigid linear rotor resulting from second order electric dipole Stark field interaction is given by[7]

$$\mathcal{H}_{J,M}{}^{\mu} = -\frac{\mu^2E^2}{2hB}F(J,M), \quad (4)$$

where B is the rotational constant defined as $h/8\pi^2I$, I is the moment of inertia about the molecular axis of rotation and

$$F(J,M) = [3M^2-J(J+1)]/[J(J+1)(2J-1)(2J+3)]. \quad (5)$$

We now consider another second order field-dependent energy contribution, that arising from the interaction of molecular polarizability with the Stark field. Classically, the energy of an electric dipole induced by a field E operating on a charge distribution is given by $-\frac{1}{2}\alpha'E^2\cos^2\theta$ where α' is the effective polarizability of the distribution and θ is the angle between the space fixed electric vector and the direction of the induced dipole moment. In OCS, the three elements of the diagonalized polarizability tensor are given by $\alpha_{xx}=\alpha_{yy}$ and α_{zz} so that the classical energy due to polarizability is given by

$$\mathcal{H} = -\tfrac{1}{2}(\alpha_{zz}-\alpha_{xx})E^2\cos^2\vartheta - \tfrac{1}{2}\alpha_{xx}E^2. \quad (6)$$

From this expression we can find the energy contribution due to polarizability by calculating the average of $\cos^2\theta$ over the rigid linear rotor wave functions. This energy is

$$\mathcal{H}_{J,M}{}^{\alpha} = -\tfrac{1}{2}\alpha E^2G(J,M) - \tfrac{1}{2}\alpha_{xx}E^2, \quad (7)$$

TABLE I. Experimental values of μ_e^2 *vs* E^2 for the two states $M=0$ and $M=\pm1$ with E measured in statvolts/cm and μ_e in Debye units.

E^2	μ_e^2 $(M=0)$	E^2	μ_e^2 $(M=\pm1)$
351	0.49969	479	0.50657
317	0.50057	425	0.50675
292	0.50110	383	0.50670
245	0.50204	339	0.50681
212	0.50281	310	0.50684
190	0.50324	253	0.50696
141	0.50427	211	0.50711
		177	0.50725

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[8] *Microwave Molecular Spectra Tables*, National Bureau of Standards Circular 518, 1952.

where

$$G(J,M)=\left(\frac{(J+1)^2-M^2}{(2J+3)(2J+1)}+\frac{J^2-M^2}{(2J+1)(2J-1)}\right)$$

and $\alpha=\alpha_{zz}-\alpha_{xx}$ is the polarizability anisotropy term. From here on, the term $-\frac{1}{2}\alpha_{xx}E^2$ is dropped since it does not contribute to energy level differences.

For fields of sufficient intensity, higher order electric dipole interaction terms become necessary to interpret the data properly. Since third-order terms can be shown to yield a vanishing energy contribution,[9] the next highest nonvanishing energy contribution is a fourth order term. Second-, fourth-, and sixth-order perturbations in $-\mu E\cos\theta$ for the rigid linear rotor have been worked out in a dissertation by Brouwer.[10] Hughes,[11,12] has confirmed most of this work and has applied it to a molecular-beam investigation of cesium fluoride.

The rotational energy level expressions given by Hughes (Brouwer's work was unavailable) appear as series expansions in even powers of the Stark field, the second term of the series being just what one would get by substituting the numerical values of J and M in the function $F(J,M)$ of Eq. (5). The third terms in the expansions vary as E^4 and are given by $(\mu^4E^4/h^3B^3)\times K(J,M)$, where the values of the function $K(J,M)$ are given by[11,12]

$$K(1,0)=-73/7000,$$

$$K(1,\pm1)=19/56\,000,$$

$$K(2,0)=1/3000,$$

$$K(2,\pm1)=-1/3000.$$

Combining Eqs. (4) and (7) with this fourth-order electric field-dependent term, we get

$$\mathcal{H}_{J,M}=-\frac{\mu^2E^2}{2hB}F(J,M)-\tfrac{1}{2}\alpha E^2G(J,M)+\frac{\mu^4E^4}{h^3B^3}K(J,M). \quad (8)$$

This equation gives us the Stark splitting in the rotational energy levels resulting from second and fourth order perturbation due to electric dipole interaction and the second order perturbation due to polarizability interaction. Taking energy differences for the transition $J\rightarrow J+1$ and $\Delta M=0$, using the Bohr frequency condition, and clearing the μ^2 term in the final result by dividing through by its coefficient, we get

TABLE II. Parameters of Fig. 2.

Parameters	$M=0$	$M=\pm1$
Theoretical slope	-0.224×10^{-40}	-0.0172×10^{-40}
Experimental slope	$-(0.214\pm0.01)\times10^{-40}$	$-(0.0205\pm0.003)\times10^{-40}$
Intercept (based on theoretical slope)	$(0.50756\pm0.00006)\times10^{-36}$	$(0.50743\pm0.00009)\times10^{-36}$
Intercept (based on experimental slope)	$(0.50732\pm0.00006)\times10^{-36}$	$(0.50754\pm0.00009)\times10^{-36}$

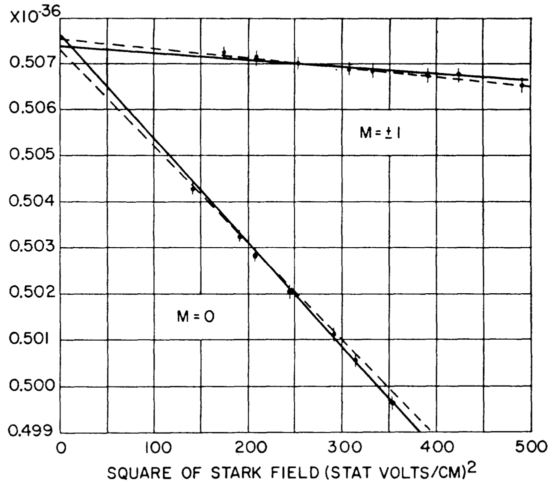

FIG. 2. Plot of the square of the effective dipole moment *versus* the square of the Stark field.

$$\mu_e^2=\mu^2+\alpha hB\left(\frac{G(J,M)-G(J+1,M)}{F(J,M)-F(J+1,M)}\right)-2\frac{\mu^4E^2}{h^2B^2}\left(\frac{K(J,M)-K(J+1,M)}{F(J,M)-F(J+1,M)}\right), \quad (9)$$

where $E^2=(E^0)^2[1+(E'/E^0)^2]$ and μ_e^2 (the effective dipole moment) is defined by

$$\mu_e^2=\left(\frac{2h^2B}{F(J,M)-F(J+1,M)}\right)\frac{\Delta\nu}{E^2}.$$

Since Eq. (9) is a linear relation between μ_e^2 and E^2, one can determine the sum of the first two terms on the right by extrapolation of μ_e^2 *vs* E^2 data to $E=0$. This sum, which is the μ_e^2 intercept, will of course depend on the quantum numbers J and M so that its determination for two different values of either J or M will enable one to solve for both μ^2 and α. This is our method for determining the polarizability of polar molecules.

In order to determine μ^2 and α, two sets of μ_e^2 *vs* E^2 data were taken, one for the transition $J=1\rightarrow2$ with $M=0$ and another for $J=1\rightarrow2$ with $M=\pm1$. The data were taken for nearly equal intervals of E^2 and best linear fits were determined by least squares (see Table I and Fig. 2). Table II gives the two sets of slopes and intercepts along with their probable errors and the slopes theoretically predicted by evaluation of the coefficient of E^2 in Eq. (9).

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[10] F. Brouwer, dissertation, Amsterdam, 1930 (unpublished).

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V. DISCUSSION

The absorption cell used in this investigation has made it possible to obtain data of sufficient reliability to establish a linear relation between μ_e^2 and E^2 which is interpreted to be the result of a fourth-order electric field term in the interaction Hamiltonian. Using this relation, the dipole moment of OCS in its ground vibrational state has been measured to be (0.7124 ± 0.0002) Debye and the agreement between experimental and theoretical fourth-order field dependence is shown to be 5% and 16% for the $M=0$ and $M=\pm1$ components. The dipole moment reported here is somewhat higher than that reported in earlier investigations; this is interpreted to be a consequence of the fact that μ_e^2 is a decreasing function of E^2. If the fourth-order contribution to μ_e^2 were averaged out by simply taking the mean of the $M=0$ and $M=\pm1$ values of μ_e^2 near a field strength of say 15 statvolts/cm the value of μ would turn out to be roughly 0.710 Debye units which is in fair agreement with the value (0.7085 ± 0.0040) Debye units obtained by Shulman and Townes.[3]

Figure 2 represents a curve fitting for 7 and 8 groups of 12 observations for the components $M=0$ and $M=\pm1$, respectively. The lengths of the short vertical lines in the figure correspond to the dispersion of 12 observations which have a common value of electric field strength. In determining the $E^2=0$ intercepts of μ_e^2, the theoretical slopes to the straight lines (solid lines in Fig. 2) were used in preference to the experimentally determined slopes (dashed lines). This choice was made because, in the writers' opinion, the theory is sufficiently adequate to give better slope values than can be obtained from these experimental measurements. As Fig. 2 shows, the theoretically predicted slopes are contained within the probable errors of the experimental slopes. The differences in the μ_e^2 intercepts, which result from the theoretical slope curve fitting of the data, lead to a polarizability anisotropy having the value $(2.4\pm3.0)\times10^{-24}$ cm^3 for OCS which is in fair agreement with the results obtained in the Appendix.

If the data were subjected to a statistical analysis assuming no theoretical information for the slopes, the order of the μ_e^2 intercepts would reverse (see Fig. 2) and cause the anisotropy to take the value $(-4.1\pm3.0)\times10^{-24}$ cm^3. Although the order of magnitude of this value is reasonable, its negative sign would imply that α_{xx} is greater than α_{zz} which is not consistent with known data for CO_2 and CS_2. This lack of agreement in the two methods of treating the data is a result of the fact that this measurement depends on the difference between two quantities evaluated by extrapolation treatment, the μ_e^2 intercepts. Since these quantities are very nearly equal, a small percentage error in their determination can lead to a large percentage error in their difference and hence in the value of the anisotropy. For this reason, a less ambiguous determination of the anisotropy will require more precise measurements of μ_e^2 than have been carried out here.

In conclusion, the authors wish to acknowledge the stimulating discussions and valuable advice from the late Dr. C. H. Schlesman, Dr. R. K. Wangsness, and Dr. E. C. Noonan.

APPENDIX

An approximation to polarizability originating from distortion of electronic distribution in the OCS molecule can be made by either a direct calculation[13] based on bond moment interactions or by use of molar refraction and depolarization factor data. The two methods give nearly the same results $\alpha_{zz}=8.7\times10^{-24}$ cm^3 and $\alpha_{xx}=4.0\times10^{-24}$ cm^3, which are intermediate to the corresponding polarizabilities[14] of CO_2 and CS_2. Another polarizability contribution (atomic polarization) originates from internuclear bond distortion. A relation for this polarization[15] based on a one dimensional oscillator is given by

$$P=(4\pi N/q)(e^2/f), \tag{10}$$

where N is Avogadro's number, e is the charge of the oscillator, and f is the force constant. If we assume e to be the same for both bond bending and bond stretching vibrations, the ratio of the two polarizations becomes the reciprocal of the ratio of the force constants. These constants are 13.7×10^5 dynes/cm for stretching and 0.49×10^5 dynes/cm for bending so that the bending polarization is roughly 28 times greater than the stretching polarization. If we now arbitrarily assume e to be one electronic charge unit and make use of the relation $P=(4/3)\pi N\alpha$ along with Eq. (10), we get 1.6×10^{-24} cm^3 for the bending polarizability. This increases the value of α_{xx} from 4.0 to 5.6×10^{-24} cm^3. Since the bond stretching polarizability is 1/28 that of bond bending, the value of α_{zz} will remain practically unchanged. These approximate calculations combine to give a value of 3.1×10^{-24} cm^3 for the anisotropy of OCS which is roughly 20% above the value obtained by the treatment in the text.

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