

comparable with the over-all efficiency of the most efficient phosphors, indicating that its lower over-all efficiency is due to a small percentage of radiative recombinations.

C. General

While this work was in progress, two other papers reporting the evaluation of the electron mobility in cadmium sulfide by combined photometric and photoelectric measurements appeared.^{12,13} In each of these the analysis depends upon the assumption of detailed models incorporating the bimolecular recombination law. By measuring the ac component of the photocurrent produced by modulated ultraviolet excitation,

¹² J. Fassbender and H. Lehmann, *Ann. Physik* **6**, 214 (1949).

¹³ I. Broser and R. Warminsky, *Ann. Physik* **7**, 289 (1950).

Fassbender and Lehmann found mobility values between 20 and 40 cm²/volt-sec, for which they claim only an order-of-magnitude accuracy because of the approximate nature of the theoretical representation. An investigation of the complete current decay curve led Broser and Warminsky to conclude that the mobility is of the order 5 cm²/volt-sec. Our method differs from these primarily in that it does not require a detailed model. The ultimate accuracy of the method is not limited by the validity of assumptions as to details of the mechanism or by the degree of approximation of the theoretical development.

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Centrifugal Distortion in Asymmetric Top Molecules. I. Ordinary Formaldehyde, H₂C¹²O*

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A semiclassical approach is used to develop a simple expression for the centrifugal distortion correction in asymmetric top molecules. The general expression for the shift of any given energy level involves five experimentally determined distortion coefficients and a knowledge of the dependence of the term value as a function of asymmetry. A useful simplified expression for the frequency correction in $\Delta J=0$ transitions involves only two effective rigid rotor parameters and four distortion coefficients. The method is applied to the microwave spectrum of H₂C¹²O; the results show excellent internal consistency. The resulting rigid-rotor parameters are: $a=282,106$ Mc/sec, $b=38,834$ Mc/sec, and $c=34,004$ Mc/sec. The electric dipole moment is determined to be 2.31 ± 0.04 debye and the line breadth parameter as 97 ± 10 microns Hg per Mc/sec.

I. INTRODUCTION

THE problem of handling the effects of centrifugal distortion in rotational spectra is not one of theory, which has been extensively discussed by several authors; rather, it is one of finding convenient and direct means of relating the experimental data to the theoretical parameters. With the high precision now available through microwave spectroscopy this central problem has acquired renewed urgency. In a series of papers by various authors from this Laboratory it is proposed to develop and apply two simplified methods for calculating the frequency shifts due to centrifugal distortion.

The general theory of vibration-rotation energies was first formulated by Wilson and Howard,¹ and several

other similar analyses² have since appeared. For our purposes the analysis given by Nielsen is the most convenient. His paper gives explicitly to second order the matrix elements for the hamiltonian of a general vibrating-rotating polyatomic molecule.³ The analysis proceeds in conventional fashion; the matrix elements for the rotational energies are developed in terms of symmetric top wave functions which have the quantum numbers J , K , and M . The matrix has off-diagonal elements in K only, namely, $(K|H|K\pm 2)$ and $(K|H|K\pm 4)$. The elements are expressed in terms of the three equilibrium-molecule principal moments of inertia, the variation of these moments with vibrational state, and six centrifugal distortion coefficients which involve the equilibrium structure and the vibrational potential constants through cubic terms. When the

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¹ E. B. Wilson, Jr., and J. B. Howard, *J. Chem. Phys.* **4**, 260 (1936).

² A list of these publications, mostly dealing with specific molecular symmetries, is given in H. H. Nielsen, *Phys. Rev.* **60**, 794 (1941); **61**, 540 (1942).

³ The treatment excludes molecules with internal rotation and those with tetrahedral symmetry. For accidental degeneracies see H. H. Nielsen, *Phys. Rev.* **68**, 181 (1945).

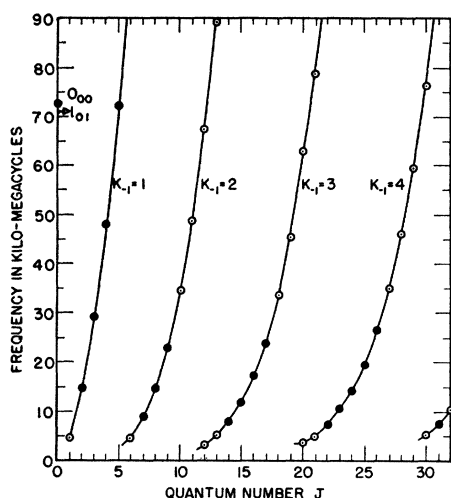


FIG. 1. The microwave absorption frequencies of $\text{H}_2\text{C}^{18}\text{O}$ as functions of J and K_{-1} . The solid circles represent the presently known spectrum.

centrifugal distortion terms are neglected, the matrix can be expressed in terms of the single asymmetry parameter κ (or the simply related parameter δ); hence, the matrix can be diagonalized once a numerical value for κ has been specified.

In short, the general procedure involves setting up the complete energy matrix and then diagonalizing it. A basic difficulty in the former operation is the inevitable lack of precise initial knowledge of the equilibrium molecular structure and the potential constants. Thus, the initial coefficients can be only estimates, although these estimates can be successively refined by reiterating the calculations after comparison with experimental data. However, the first diagonalization is generally tedious enough to discourage successive approximation even though a method of approximate diagonalization is available for some high J terms.⁴

Simplifications occur for certain classes of molecules and for certain types of transitions. The general analysis has been carried out for H_2O and H_2S .⁵ The second paper of the present series will give the development and application of a simple analytical expression with which the transition frequencies may be simply analyzed and the amount of distortion shift evaluated.

Alternately, a different attack may be used, which is presented in this paper. As shown by Wilson and Howard the exact calculation involves three "effective" reciprocal moments of inertia. These represent the equilibrium constants modified in a complicated fashion by the presence of zero point and excited vibration. The true levels are those of a fictitious rigid rotor corrected finally for the effects of centrifugal distortion.

⁴ S. Golden, *J. Chem. Phys.* **16**, 78 (1948); **16**, 250 (1948).

⁵ E. B. Wilson, Jr., *J. Chem. Phys.* **4**, 526 (1936); **5**, 617 (1937); B. T. Darling and D. M. Dennison, *Phys. Rev.* **57**, 128 (1940); P. C. Cross, *Phys. Rev.* **47**, 7 (1935); B. L. Crawford, Jr., and P. C. Cross, *J. Chem. Phys.* **5**, 621 (1937); Grady, Cross, and King, *Phys. Rev.* **75**, 1450 (1949).

The distortion correction can be expressed as a Taylor's series in the quantum numbers. In the following section we present a semiclassical analysis whose result is to indicate which in the terms in this expansion may be expected to be important.

II. DEVELOPMENT OF EXPRESSION FOR THE DISTORTION CORRECTION

In this section the notation adopted is that of King, Hainer, and Cross.⁶ In the interest of brevity we shall carry out the development for the case of a nearly prolate-symmetric molecule, but the method and many of its results are much more general than this. At the end of the derivation we indicate its wider application.

The following symbols and definitions are assigned:

a, b, c	Effective rigid-rotor rotational constants expressed in frequency units (Mc/sec). By convention $a \geq b \geq c$.
δ	Dimensionless asymmetry parameter defined by $\delta = (b-c)/(a-c)$. For nearly prolate-symmetric molecules $0 < \delta \ll 1$.
κ	Dimensionless asymmetry parameter defined by $\kappa = (2b-a-c)/(a-c) = -1 + 2\delta$.
W	Term value, a function of quantum numbers and asymmetry, expressed in frequency units (Mc/sec).
E_i , or $E(\kappa)$, $E(\delta)$	A dimensionless quantity, essentially a reduced energy. It contains the entire effect of asymmetry on the term value W .
J, M	Usual angular momentum quantum numbers.
K_{-1}	An index which for a limiting prolate-symmetric top becomes the quantum number K (projection of J on the molecule-fixed principal axis of least moment of inertia). In a slightly asymmetric top this significance is partially retained, partially lost. ⁷ In this paper K_{-1} will sometimes be abbreviated to K , where this can be done without confusion.
γ	A symmetry-indicating index which is $+1$ or zero. An asymmetric top state is specified by the quantum numbers J, K, M, γ .
K_1	An index having the same significance for an oblate-asymmetric top as K_{-1} does for a prolate-asymmetric one. See KHC for the relation between J, K_{-1}, K_1 , and γ .

The term value is

$$W_i = \frac{1}{2}(a+c)J(J+1) + \frac{1}{2}(a-c)E(J, K_{-1}, \gamma_i, \delta) + \text{distortion terms.} \quad (1)$$

We may temporarily confine ourselves to the transitions between states of the same J and of the same K_{-1} : states which in the prolate-symmetric top are degenerate. For these transitions we have

$$\nu_{ij} = \left[\frac{1}{2}(a-c) \{ E(J, K_{-1}, \gamma_i, \delta) - E(J, K_{-1}, \gamma_j, \delta) \} \right] + [\text{difference of distortion terms}]. \quad (2)$$

When $(a-c)$, δ , and the quantum numbers have been specified, the rigid-rotor transition frequency represented by the first bracketed expression can be calculated as accurately as desired.⁸

⁶ King, Hainer, and Cross, *J. Chem. Phys.* **11**, 27 (1943); Cross, Hainer, and King, *J. Chem. Phys.* **12**, 210 (1944). We shall refer to these as KHC and CHK, respectively.

⁷ The correct expression is given later in Eq. (4).

⁸ The continued fraction development given in KHC is extremely convenient and can give any required accuracy; useful

Before developing an expression for the distortion correction, we write down a simple approximate expression for the rigid-rotor frequency. Figure 1, which shows the absorption frequencies for formaldehyde, suggests that the variation with J involves a factor such as $[J(J+1)/K^2]^K$. A good approximate expression has been given by Wang;⁹ in our notation it is

$$\nu = \frac{a-c}{2} \frac{(J+K)!}{(J-K)!(K-1)!(K-1)!} \frac{\delta^K}{16^{K-1}(1-\frac{1}{2}\delta)^{K-1}}. \quad (3)$$

Noting that if $J \gg K$, then only a small error is incurred when $(J+K)!/(J-K)!$ is replaced by $J^K(J+1)^K$, we find that for our purposes adequate accuracy is obtained with the simple form¹⁰

$$\nu = \frac{1}{2}(a-c)[\delta J(J+1)/K^2]^K(f), \quad (3a)$$

$$f \approx 1.00, 1.00, 0.71, 0.44, 0.26, \dots$$

for $K=1, 2, 3, 4, 5, \dots$, respectively.

In this expression the factor f is substantially independent of J and δ , but does assume different values, as shown, for various K .

It is well known that for a nonrigid diatomic molecule, the term values are

$$W = BJ(J+1) - DJ^2(J+1)^2, \quad D > 0.$$

Thus, the correction acts to decrease the term value and is proportional to the square of the angular momentum of the molecule.

For an asymmetric top, with its three principal moments of inertia instead of one, we must generalize this result. We shall assume that the distortion correction involves terms, nine in all, containing the average-squared values of angular momenta as projected along the three principal axes. We calculate these average-squared momenta by a method discovered and applied to this type of problem by Cross;¹¹ the proof appears in a paper by Bragg and Golden.¹² The expression is $\langle P_a^2 \rangle = \partial W / \partial a$. Since W and a are both expressed as frequencies, the P 's are accordingly dimensionless momentum numbers.

If now we consider the effect on an energy level of small independent changes da, db, dc in the rotational constants a, b, c , we obtain easily the first-order change in the term value:

$$dW = da \left[\frac{1}{2}J(J+1) + \frac{1}{2}E - \frac{1}{2}\delta dE/d\delta \right] + db \left[\frac{1}{2}dE/d\delta \right] + dc \left[\frac{1}{2}J(J+1) - \frac{1}{2}E - \frac{1}{2}(a-b)/(a-c)dE/d\delta \right]. \quad (4)$$

approximate calculations can be made by a modification of Golden's method (reference 4, first paper).

⁹ S. C. Wang, Phys. Rev. **34**, 243 (1929). A discussion of this splitting formula, together with numerical tables, is given by Hainer, Cross, and King, J. Chem. Phys. **17**, 826 (1949) (referred to as HCK).

¹⁰ Here and above K is used as shorthand for the index K_{-1} .

¹¹ P. C. Cross, Phys. Rev. **47**, 7 (1935). In some respects our development of the centrifugal distortion correction is similar to that of Cross.

¹² J. K. Bragg and S. Golden, Phys. Rev. **75**, 735 (1949).

The brackets are easily identified as $\langle P_a^2 \rangle$, $\langle P_b^2 \rangle$, and $\langle P_c^2 \rangle$. We are now prepared to formulate our theory. Consider two states whose rotational constants have undergone small changes $da_1, db_1, dc_1; da_2, db_2, dc_2$, and whose energies are thus changed by increments dW_1, dW_2 . Focusing our attention on one of these states and using Eq. (1), we write for the first-order distortion correction

$$dW_1 = \langle P_a^2 \rangle_1 da_1 + \langle P_b^2 \rangle_1 db_1 + \langle P_c^2 \rangle_1 dc_1. \quad (5)$$

Next we postulate that

$$\begin{aligned} \frac{1}{2}da_1 &= A_a \langle P_a^2 \rangle_1 + A_b \langle P_b^2 \rangle_1 + A_c \langle P_c^2 \rangle_1, \\ \frac{1}{2}db_1 &= B_a \langle P_a^2 \rangle_1 + B_b \langle P_b^2 \rangle_1 + B_c \langle P_c^2 \rangle_1, \\ \frac{1}{2}dc_1 &= C_a \langle P_a^2 \rangle_1 + C_b \langle P_b^2 \rangle_1 + C_c \langle P_c^2 \rangle_1. \end{aligned} \quad (6)$$

The nine coefficients $A_a \dots C_c$ represent constants of the molecule. After some manipulation we find

$$dW_1 = L(dE_1/d\delta)^2 + M(dE_1/d\delta)E_1 + N(dE_1/d\delta)J(J+1) + QE_1^2 + RE_1J(J+1) + SJ^2(J+1)^2, \quad (7)$$

where the new constants $L \dots S$ involve only $a, b, c, A_a \dots C_c$ and are hence independent of quantum numbers.

The desired frequency correction is the difference of two such term-value corrections. At this point we may specialize, both for brevity and because it is appropriate to H_2CO , to the case of $\Delta J=0, \Delta K_{-1}=0$ transitions. Expressing the energy levels in terms of their average reduced energy, E , and the rigid-rotor frequency ν_{12} , we arrive at the distortion correction¹³

$$\begin{aligned} d\nu_{12} &= L \left[\frac{4K\nu_{12}}{(b-c)} \frac{dE}{d\delta} \right] + M \left[\frac{2\nu_{12}}{(b-c)} \left(KE + \delta \frac{dE}{d\delta} \right) \right] \\ &+ NJ(J+1) \left[\frac{2K\nu_{12}}{(b-c)} \right] + Q \left[\frac{4\nu_{12}}{(a-c)} E \right] \\ &+ RJ(J+1) \left[\frac{2\nu_{12}}{(a-c)} \right]. \end{aligned} \quad (8)$$

All these terms contain ν_{12} as a factor, which is the first important result of our analysis.

We can now also insert the explicit dependence of E and $dE/d\delta$ on J, K , and δ :

$$E = [-J(J+1) + 2K^2] + \delta[J(J+1) - K^2] + \dots \quad (9)$$

The final expression, simplified by introducing four new constants, is

$$d\nu_{12} = -\nu_{12} [(X_j + X_{jk}K)J(J+1) + (X_k + X_{kk}K)K^2]. \quad (10)$$

Thus, we have arrived at the following point: six adjustable constants—the two rigid-rotor parameters

¹³ Also used is the expression (3a) and the easily verified fact that f is sufficiently constant so that $d\nu_{12}/d\delta \cong (K/\delta)\nu_{12}$.

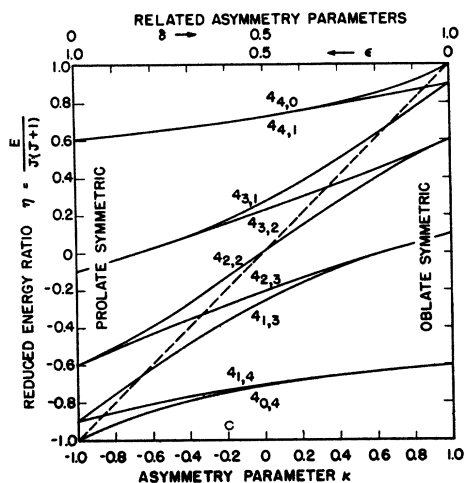


FIG. 2. Reduced energy levels of an asymmetric top for $J=4$ versus asymmetry parameters κ , δ , and ϵ .

($a-c$) and ($b-c$), and the four centrifugal distortion constants $X_{j \dots} X_{kk}$ —are available for fitting the measured frequencies of the $\Delta J=0$, $\Delta K_{-1}=0$ (“ a ”-type) transitions of a slightly asymmetric top molecule. Since in particular cases many more than six such transitions can be studied, the accuracy of the formula can be critically tested. The application of this analysis to the microwave absorption spectrum of formaldehyde is given in the next section.

It was indicated above that the analysis given is valid for many asymmetric tops other than nearly prolate-symmetric ones, assuming that it is valid at all. Since the experimental evidence confirms this latter point, it is worth while to indicate the appropriate extensions.

The various exact and approximate methods for calculating asymmetric top energy levels have recently been discussed by King¹⁴ and by Hainer, Cross, and King.⁹ They introduce the convenient ratios $\lambda = [K^2/J(J+1)]^{1/2}$ and $\eta = E(\kappa)/J(J+1)$; these quantities range between 0 and +1 and between -1 and +1, respectively. The familiar diagram of Fig. 2 shows the variation of a typical set of energy levels over the complete range of asymmetry. Several remarks can be made with reference to this diagram. First, the energy levels are perfectly symmetrical about the dashed diagonal line; the prolate-asymmetric treatment using the asymmetry parameter $\delta = (1+\kappa)/2$ is exactly paralleled by the oblate-asymmetric treatment using a parameter $\epsilon = (1-\kappa)/2$. Replacement of δ by ϵ hence adapts all formulas presented here to the oblate case.

Second, our general expression [Eq. (7)] gives the distortion correction to a level in terms of its reduced energy E and the rate of change, $dE/d\delta$. Owing to the simple linear relationship between δ , κ , and ϵ , however, Eq. (7) can be written with its derivatives in terms of whichever asymmetry parameter is convenient; it is

perfectly general and applies over the entire range of asymmetry. The problem is thus reduced to one of finding adequate expressions for $E(\kappa)$ and $dE/d\kappa$. As pointed out by King, an expansion of E in terms of δ or ϵ diverges when carried to the dashed diagonal line, so that such expansions are useful only in the rather large upper left and lower right corner regions. Suitable approximations are also discussed in reference 12.

A third remark applies to the more specific case of those $\Delta J=0$ transitions between adjacent levels for which the Wang formula [Eq. (3)] is applicable. The same considerations of remoteness from the dashed diagonal apply, and for high values of λ (i.e., high K_{-1} for prolate-asymmetric or high K_1 for oblate-asymmetric) the Wang formula is useful to surprisingly large values of δ (or ϵ). This point is thoroughly discussed in HCK.

III. APPLICATION TO THE MICROWAVE SPECTRUM OF $H_2C^{12}O$

To test the six-constant formula developed above we have measured the frequencies of seventeen $\Delta J=0$, $\Delta K_{-1}=0$ absorption transitions of ordinary monomeric formaldehyde gas $H_2C^{12}O$. The values of J range from 2 to 31 and those of K_{-1} from 1 to 5.

The constants are evaluated according to the following procedure. Define the symbols

ν_t = true frequency (measured),

ν_c = calculated rigid-rotor frequency,

ν_d = distortion correction to rigid-rotor frequency

(this is called $d\nu_{12}$ in the derivation above).

For much of the calculation it is convenient to deal with the readily recognized dimensionless quantities obtained when the above frequencies are divided by

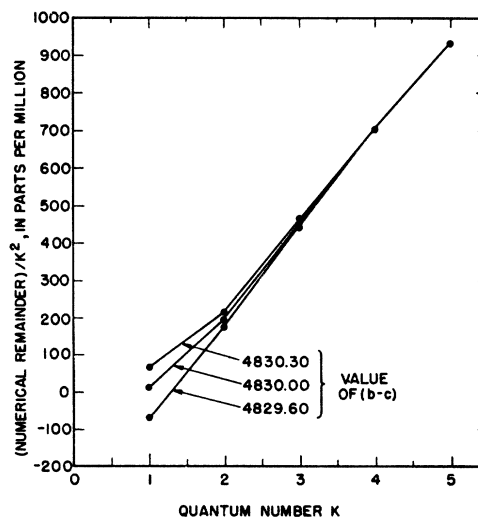


FIG. 3. Effect on K correction when ($b-c$) and ($a-c$) are simultaneously varied, their ratio δ being kept constant. Calculated for $\delta=0.019,466,39$.

¹⁴ G. W. King, J. Chem. Phys. 15, 820 (1947).

$(a-c)/2$. These root-differences will be referred to simply as "roots."

$$\begin{aligned} r_i &= 2\nu_i/(a-c), \\ r_c &= 2\nu_c/(a-c), \quad (r_c \text{ is exactly the quantity } E_2 - E_1 \\ r_d &= 2\nu_d/(a-c). \end{aligned}$$

from the rigid-rotor calculation),

The steps are as follows:

1. Assume a value of $\delta = (b-c)/(a-c)$. The energy level expansions in powers of δ , as given in Table III of KHC can be used for a first crude estimate of δ . A feedback method for refining this value in Appendix A. The initially chosen value of δ should be a rounded number of two or three significant figures.

2. Calculate the rigid-rotor quantities r_c corresponding to all the measured transitions. Even for this first computation the continued-fraction method of solving the secular equations is about as easy as the Mathieu approximation and has the advantage that its accurate values can be useful in later interpolation calculations. The frequency calculations should preferably be made to at least seven places.

3. Pick a likely value for $(a-c)$. If some low J and $K_{-1}=1$ transitions are available, these have the smallest possible distortion correction and can hence be used to estimate $(b-c)$ initially to three or four significant figures; $(a-c)$ is obtained by combining this value with the assumed value of δ .

4. Calculate all the "true" roots r_i . These are simply the measured true frequencies ν_i divided by $(a-c)/2$.

5. Form all the quantities $r_d/r_c = (r_c - r_i)/r_c$. All subsequent manipulations are performed with these quantities, which may be given the symbol $T_{J,K}$.

6. Within each family of the same K , form first differences $T_{J+1,K} - T_{J,K}$, and divide by $2(J+1)$. These are the provisional values of $(X_j + X_{jk}K)$ for the various values of K .

7. Calculate X_j and X_{jk} either graphically or, preferably, by a

TABLE I. Rigid-rotor constants and distortion coefficients of $\text{H}_2\text{C}^{18}\text{O}$.

$\delta = (b-c)/(a-c) = 0.019,466,6 \pm 5$
$b-c = 4829.7 \pm 0.3$ Mc/sec
$a-c = 248,102 \pm 12$ Mc/sec
$X_j = 7.74, X_{jk} = +2.33$ } all $\times 10^{-6}$, and all estimated
$X_k = -277, X_{kk} = +242$ } accurate to ten percent

TABLE II. Calculated distortion-corrected spectrum compared with measurements.

Transition	Correction used (Mc/sec)	Calc. freq. (Mc/sec)	Meas. freq. (Mc/sec)	Error (Mc/sec)
$0_0, 0 \rightarrow 1_0, 1$	not calc.	not calc.	72,838.14	...
$2_1, 2 \rightarrow 2_1, 1$	- 0.37	14,488.74	14,488.65	+0.09
$3_1, 3 \rightarrow 3_1, 2$	- 2.49	28,975.07	28,974.85	+0.22
$4_1, 4 \rightarrow 3_1, 3$	- 8.04	48,284.39	48,284.60	-0.21
$5_1, 5 \rightarrow 5_1, 4$	- 19.35	72,407.81	72,409.35	-1.54
$7_2, 6 \rightarrow 7_2, 5$	- 13.55	8884.44	8884.87	-0.43
$8_2, 7 \rightarrow 8_2, 6$	- 25.38	14,725.97	14,726.74	-0.77
$9_2, 8 \rightarrow 9_2, 7$	- 44.73	22,964.53	22,965.71	-1.18
$14_3, 12 \rightarrow 14_3, 11$	- 56.71	7892.49	7892.03	+0.46
$15_3, 13 \rightarrow 15_3, 12$	- 89.73	11,753.88	11,753.13	+0.75
$16_3, 14 \rightarrow 16_3, 13$	- 138.15	17,028.65	17,027.60	+1.05
$17_3, 15 \rightarrow 17_3, 14$	- 207.53	24,069.98	24,068.31	+1.67
$22_4, 19 \rightarrow 22_4, 18$	- 147.87	7362.77	7362.60	+0.17
$23_4, 20 \rightarrow 23_4, 19$	- 216.68	10,366.87	10,366.51	+0.36
$24_4, 21 \rightarrow 24_4, 20$	- 312.44	14,361.53	14,361.54	-0.01
$25_4, 22 \rightarrow 25_4, 21$	- 443.78	19,595.83	19,595.23	+0.60
$26_4, 23 \rightarrow 26_4, 22$	- 621.42	26,359.16	26,358.82	+0.34
$31_5, 27 \rightarrow 31_5, 26$	- 347.94	7827.25	7833.20	-5.95

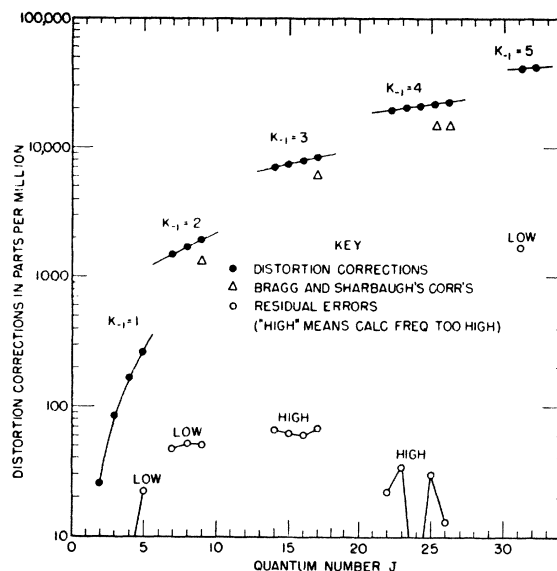


FIG. 4. Distortion corrections and residual errors.

least-squares solution. It will be found that this result is relatively insensitive to errors in the initial choice of δ , and the values obtained will probably not require drastic modification. On the basis of the calculated X_j and X_{jk} calculate the J corrections $(X_j + X_{jk}K)J(J+1)$ for each line.

8. Subtract these J corrections from the total corrections $T_{J,K}$ to obtain the provisional K corrections for each line. These quantities are the "numerical remainders" referred to in the Appendix.

9. Divide these K corrections by K^2 and examine whether the trend with K is linear. In making a least-squares evaluation of X_k and X_{kk} it is advisable to average the quantities within each value of K and then weight the averages equally. This prevents overemphasis of the data associated with any particular K value.

10. Correct the value of $(a-c)$, if necessary, by the method of the Appendix. Compute a new value of δ rounded to four significant figures.

11. Repeat steps 2 through 9; the result should be a much improved K -fit. Having computed the r_c for the new value of δ , it is now appropriate to vary $(b-c)$. The quantity $(a-c)$ will, of course, vary proportionally, giving rise to new values of r_i . These can rapidly be made to give new approximations to the K correction, as shown in Fig. 3, where δ is near the correct value.

From this point the procedure is essentially one of successive refinings and will not be further described. Note that when $(b-c)$ is varied the change of K correction is greatest for $K=1$ with dilutions of $1/4, 1/9, \dots$ for the successively higher K 's. This provides a means for straightening the K -fit. By carrying out the fitting procedure outlined above we have arrived at the results shown in Tables I and II.

As indicated earlier, the distortion corrections are proportional to the rigid-rotor frequencies ν_c , and it is hence natural to carry out the fitting process in terms of the fractional quantities $(r_c - r_i)/r_c$ or $(\nu_c - \nu_i)/\nu_c$. Figure 4 shows the values of distortion correction and residual error expressed in parts per million of the calculated rigid-rotor frequency. Figure 4 and Table II thus display the corrections in fractional parts and in terms of frequency, respectively.

Since the test of any theory is its ability to predict, the computations were based entirely on the sixteen lines with K equal to one through four, and the frequency of the previously unobserved $31_{5,27} \rightarrow 31_{5,26}$ transition was predicted with the use of the best-fit constants. This transition was subsequently searched for and found very nearly at the predicted frequency. The error amounts to only 1.7 percent of the distortion correction applied, or one part in 1300 of the measured frequency. The sixteen lines used in evaluating the constants are fitted to one part in 20,000. It seems evident that a useful amount of truth resides in the simplified distortion theory.

In obtaining the values set forth in Table I a total of eight complete fitting processes were carried out involving four slightly different values of δ and four slight variations of $(b-c)$ and $(a-c)$. The limits of error stated in Table I are estimates based on the sensitivity of the residual errors to variation of the respective parameters. Slight variations in δ , for instance, can be accommodated by corresponding variations of the other parameters, particularly the distortion coefficients. Variations in the rigid-rotor parameters δ , $(b-c)$, and $(a-c)$ greater than those indicated give rather pronounced deviations from the required form; and it is on this basis that these limits of error are assigned.

The individual values of the distortion coefficients are purposely assigned rather large uncertainties, although the three-figure values shown result quite definitely when the stated values of δ , $(b-c)$, and $(a-c)$ are used. The striking fact is that for every value of rigid-rotor constants in the narrow range where a reasonable fit can be obtained, the net values of the distortion corrections are predicted with great consistency. Even though the individual values of $X_j \cdots X_{kk}$ do vary appreciably as shown in Table III, their combination to give the distortion correction results in a highly stable value.

We conclude that although the individual values of $X_j \cdots X_{kk}$ are not known with great certainty the distortion corrections can be taken as quite accurate.

For the three lines of Table III, Bragg and Sharbaugh¹⁵ have published approximate values of the

TABLE III. Distortion corrections for some typical lines calculated with three slightly different sets of constants.

Identifi- cation	δ	$(b-c)$	$(a-c)$	X_j	X_{jk}	X_k	X_{kk}
A	0.019,466,60	4829.7	248,102	7.74	2.33	-277	242
B	0.019,466,39	4829.6	248,099	8.94	1.97	-310	251
C	0.019,466,68	4829.8	248,106	7.75	2.33	-242	232

Identifi- cation	$9_{2,8} \rightarrow 9_{2,7}$ (Mc/sec)	$17_{3,15} \rightarrow 17_{3,14}$ (Mc/sec)	$25_{4,21} \rightarrow 25_{4,21}$ (Mc/sec)
A	44.7	207.5	443.8
B	44.3	206.9	441.3
C	46.2	208.9	442.7

¹⁵ The first microwave measurements of formaldehyde were reported by J. K. Bragg and A. H. Sharbaugh, in *Phys. Rev.* **75**,

TABLE IV. The rotational constants of $H_2C^{18}O$, and the corresponding effective moments of inertia.

Rotational constant	Value (Mc/sec)	Moment of inertia
a	282,106	1.792 amu-A ²
b	38,834	13.015
c	34,004	14.864

distortion correction calculated by the method of Wilson and Howard. These corrections were given as 30, 147, and 305 Mc/sec, respectively, which are uniformly less than our values in the ratio of about 0.68 to one. This agreement is considered very satisfactory.

IV. THE ROTATIONAL CONSTANTS OF $H_2C^{18}O$

From the analysis just given we have obtained values of the effective rigid-rotor rotational constants in the form $(a-c)$ and $(b-c)$. An additional piece of information, permitting individual evaluation of a , b , and c , is the measured value of the $0_{0,0} \rightarrow 1_{0,1}$ transition frequency, which is simply $(b+c)$. We must remember that the a , b , and c are approximately, although not exactly, reciprocal moments of inertia averaged with respect to the zero-point vibrations. If we assume that centrifugal distortion is negligible for the $0_{0,0} \rightarrow 1_{0,1}$ transition (it vanishes identically for the initial level), then we obtain a , b , and c immediately. These values, together with the effective moments of inertia to which they correspond, are given in Table IV.

Table IV shows two points of importance. First, the values obtained from the ultraviolet work of Dieke and Kistiakowsky¹⁶ are rather spectacularly confirmed. They obtained for a and $(b+c)$ the values 281,900, and 72,850 Mc/sec, respectively, to four significant figures. These agree excellently with our more accurate values of 282,106 and 72,838 Mc/sec.

The second point is that although the molecule is planar its largest moment of inertia, I_c , is not equal to the sum of the other two. This "inertia defect" is a well-known consequence of zero-point vibration and can be calculated.² The fact that it is so large makes those structure calculations which appear in the literature¹⁷ much less accurate than indicated.

We have made extensive measurements of the microwave spectrum of the isotopic molecule $H_2C^{18}O$, which we intend to report later. With the aid of these

1774 (1949). In this excellent work they measured and correctly identified the four transitions $9_{2,8} \rightarrow 9_{2,7}$, $17_{3,15} \rightarrow 17_{3,14}$, $25_{4,21} \rightarrow 25_{4,21}$ and $26_{4,23} \rightarrow 26_{4,22}$. Their fifth unidentified line we have shown to be the $9_{2,8} \rightarrow 9_{2,7}$ transition of the isotopic molecule $H_2C^{18}O$. Other early unpublished work was done by R. L. Kyhl and M. W. P. Strandberg, who are responsible for the $0_{0,0} \rightarrow 1_{0,1}$, $3_{1,3} \rightarrow 3_{1,2}$, $4_{1,4} \rightarrow 4_{1,3}$, and $5_{1,5} \rightarrow 5_{1,4}$ measurements here reported.

¹⁶ G. H. Dieke and G. B. Kistiakowsky, *Phys. Rev.* **45**, 4 (1934). They resolved the rotational fine structure of an electronic transition with six vibration bands between 3530 and 3260A. Infrared work by H. H. Nielsen and collaborators has confirmed certain of the results but not improved their accuracy.

¹⁷ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 440.

measurements, approximately corrected for the effects of zero-point vibration, we have estimated the equilibrium structural parameters of formaldehyde to be the following: C-H distance $1.12 \pm 0.01 \text{ \AA}$, C-O distance $1.21 \pm 0.01 \text{ \AA}$, H-C-H angle $118^\circ \pm 2^\circ$. While these figures are tentative, we feel that they represent the best values available.

Finally, we show in Fig. 5 a map of the microwave spectrum of $\text{H}_2\text{C}^{12}\text{O}$. The intensities are calculated according to the Van Vleck-Weisskopf formula, but all quantities entering into the calculation are experimentally known. In particular, the dipole moment has been measured as 2.31 ± 0.04 debye and the line-width parameter P/Δ^1 is 97 ± 10 microns Hg per Mc/sec. In a recent letter (Phys. Rev. **82**, 95 (1951)) J. N. Schoolery and A. H. Scharbaugh give a precision measurement of the formaldehyde dipole moment. The two values are 2.339 ± 0.013 , and 2.340 ± 0.019 debye units, for the $9_{2,8} \rightarrow 9_{2,7}$ and $3_{1,8} \rightarrow 3_{1,2}$ transitions, respectively. This supersedes the earlier, and lower, result of Bragg and Scharbaugh and is in excellent agreement with our less precise results.

The method of preparation of formaldehyde developed for these experiments is due to Dailey.¹⁸ Well-dried calcium formate was decomposed at temperatures in excess of 150°C to form solid calcium carbonate and monomeric formaldehyde.

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APPENDIX

FEEDBACK METHOD FOR CORRECTING ASSUMED VALUES OF δ AND $(a-c)$

Say that the calculation has been carried through step 8, but that the results are known to be incorrect. Differentiate between these incorrect and the as yet unknown correct values by superscripts i and c , respectively: $\nu_c^c, \nu_i^c, \nu_d^c$, correct values (unknown); $\nu_c^i, \nu_i^i, \nu_d^i$, incorrect values from first calculation:

$$\nu_c^c = \nu_c^i - \nu_d^i.$$

But ν_i is a measured frequency and cannot be incorrect; hence, drop its superscript:

$$\nu_c^c = \nu_c^i - \nu_d^i = \nu_c^c - \nu_d^c. \quad (1a)$$

Define the Δ 's of various quantities as the increment in going from incorrect to correct values:

$$\Delta\nu_c = \nu_c^c - \nu_c^i, \text{ similarly for } \Delta\text{'s of } \nu_d, (a-c), (b-c).$$

Also, by Eq. (1a), we have $\Delta\nu_c = \Delta\nu_d$, so again we drop subscripts and refer simply to $\Delta\nu$.

The quantity $(b-c)$ can be taken as known (see step 3) and so

¹⁸ B. P. Dailey, private communication.

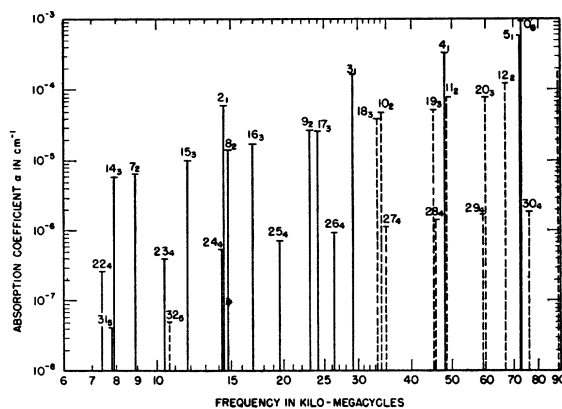


Fig. 5. Map of the $\text{H}_2\text{C}^{12}\text{O}$ spectrum between 6000 and 90,000 Mc/sec. The intensities are calculated, but the quantities entering into the calculation have been measured. Solid lines represent observed absorption frequencies; dashed lines are computed.

can $(X_j + X_{jk}K)J(J+1)$. Unknown are $(a-c)^c$ and δ^c .

$$\nu_c^i = \frac{1}{2}J[J(J+1)/K^2]^{K-1}[(b-c)^i]^{K-1}/[(a-c)^i]^{K-1}.$$

Taking logarithmic derivative and applying to the finite changes Δ , we obtain

$$\Delta\nu/\nu_c^i = K\Delta(b-c)/(b-c)^i - (K-1)\Delta(a-c)/(a-c)^i. \quad (2a)$$

As stated above, however, the first term can be taken as zero, giving

$$\Delta(a-c)/(a-c)^i = [-1/(K-1)]\Delta\nu/\nu_c^i. \quad (3a)$$

But $\Delta\nu = \nu_d^c - \nu_d^i$ and we have

$$\begin{aligned} \nu_d^c &= \nu_c^c[(X_j + X_{jk}K)J(J+1) + (X_k + X_{kk}K)K^2] \\ &= (\nu_c^i + \Delta\nu)[(X_j + X_{jk}K)J(J+1) + (X_k + X_{kk}K)K^2], \\ \nu_d^i &= \nu_c^i[(X_j + X_{jk}K)J(J+1) + \text{numerical remainder}]. \end{aligned}$$

In this the $X_j \cdots X_{kk}$ are all the correct values; the numerical remainder is, for each transition, the quantity left when $(X_j + X_{jk}K)J(J+1)$ is subtracted from the $(r_i - r_c^i)/r_c^i$. See step 8.

We obtain

$$\begin{aligned} \frac{\Delta\nu}{\nu_c^i} &= \frac{[\text{numerical remainder} - (X_k + X_{kk}K)K^2]}{1 - [(X_j + X_{jk}K)J(J+1) + (X_k + X_{kk}K)K^2]} \\ &= -[\text{num. rem.} - (X_k + X_{kk}K)K^2]\nu_c^c/\nu_i. \end{aligned} \quad (4a)$$

Thus, finally, we have

$$\frac{\Delta(a-c)}{(a-c)^i} = \frac{[\text{numerical remainder} - (X_k + X_{kk}K)K^2]}{K-1} \frac{\nu_c^c}{\nu_i}. \quad (5a)$$

For initial correction purposes the factor ν_c^c/ν_i may be taken as unity: refined values can be used in later applications of the formula. The presence of $K-1$ in the denominator compels the numerator to vanish for $K=1$, hence the average value of the numerical remainders for $K=1$ is equal to $X_k + X_{kk}K$. At this point it is possible to estimate the variation of $(X_k + X_{kk}K)K^2$ with K 's greater than 1, but it is usually better to neglect this quantity compared with the numerical remainder and form a best estimate of the required correction $\Delta(a-c)$. With this information a new value of δ , rounded to perhaps four significant figures, can be used to recompute the complete set of roots r_c .

For later application the complete expression obtained by combining Eqs. (2a) and (4a) can be used instead of Eq. (5a).