

## Resolution of the Discrepancies Concerning the Optical and Microwave values for $B_0$ and $D_0$ of the $X^3\Sigma_g^-$ State of $O_2$

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The discrepancies concerning the optical and microwave values of  $B_0$  and  $D_0$  for the  $X^3\Sigma_g^-$  state of  $O_2$  have been removed by a nonlinear least-squares fit to all of the lines of the  $O_2$   $b^1\Sigma_g^+ - X^3\Sigma_g^-$  Red Atmospheric bands recorded by Babcock and Herzberg (*Astrophys. J.* **108**, 167, 1948). The resulting values for  $B_0''$  and  $D_0''$  are in excellent agreement with the Raman and microwave values. Improved values are determined for  $B_1''$ ,  $D_1''$ ,  $\gamma_1''$  (spin-rotation), and  $\epsilon_1''$  (spin-spin). Both  $\gamma_0''$  and  $\epsilon_0''$  increase in magnitude from  $v'' = 0$  to  $v'' = 1$ . Improved Dunham  $Y_{10}$  and  $Y_{11}$  expansion coefficients are determined for the  $b^1\Sigma_g^+$  state, from which the Rydberg-Klein-Rees potential is constructed.

### I. INTRODUCTION

In 1948 at the Mt. Wilson Observatory, Babcock and Herzberg (1) photographed seven absorption bands of the  $b^1\Sigma_g^+ - X^3\Sigma_g^-$  Red Atmospheric band system of the oxygen molecule between the vibrational levels  $v'' = 0$  and 1 of the  $X^3\Sigma_g^-$  state and  $v' = 0$  through 3 of the  $b^1\Sigma_g^+$  state. This electric-dipole-forbidden transition was recorded with the Snow telescope using air absorption paths up to 100 km. In addition, these measurements were supplemented in the laboratory with interferometric studies using 30 m air absorption paths. The resulting combination differences  $\Delta_2 F_2''(N) = {}^R R(N-1) - {}^P P(N+1)$  from the better-measured (0,0), (1,0), and (2,0) bands agree typically within  $0.005 \text{ cm}^{-1}$ , a remarkable accomplishment for electronic band spectra measurements. From these combination differences, Babcock and Herzberg obtained highly precise values of the rotational constants for  $v'' = 0$  namely,  $B_0'' = 1.43777_0 \pm 0.000015 \text{ cm}^{-1}$  and  $D_0'' = (4.91_3 \pm 0.020) \times 10^{-6} \text{ cm}^{-1}$ .

Burkhalter, Anderson, Smith, and Gordy (2), in their 1950 microwave study of the Zeeman effect in oxygen, suggested that the optical value of  $B_0$  is most likely an order of magnitude less accurate than the error limits stated by Babcock and Herzberg. In 1968, McKnight and Gordy (3) measured the  $N = 1 \rightarrow 3$ ,  $J = 2 \rightarrow 2$  submillimeter-

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wave oxygen line, which was the first microwave measurement of a purely rotational transition in  $O_2$  (or, for that matter, in any molecule without a permanent electric dipole moment). McKnight and Gordy also remeasured with improved accuracy the fine-structure transitions within the  $N = 1$  and  $N = 3$  rotational levels. Using Babcock and Herzberg's value of  $D_0$  and an estimate of their own for  $H_0$ , McKnight and Gordy determined  $B_0 = 1.437681 \pm 0.000001 \text{ cm}^{-1}$ , where here and throughout this paper we have converted from MHz to  $\text{cm}^{-1}$  using  $c = 2.9979250 \times 10^{10} \text{ cm/sec}$  (4).

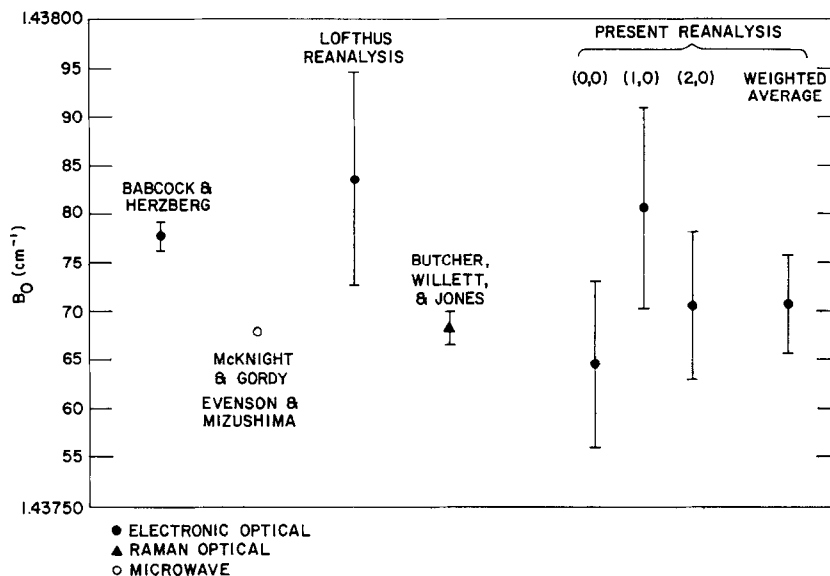
The quoted uncertainties on these values represent "limits of error" placed by the investigators on their respective values. Note that the difference between the optical and microwave values reported for  $B_0$  is about six times larger than the combined limits of error. Despite attempts by Lofthus (5) and Welch and Mizushima (6) to reconcile this difference by reanalyzing the optical and microwave data, respectively, this discrepancy has not been removed. Although McKnight and Gordy's microwave value has a significantly lower error limit, not surprisingly, optical spectroscopists have continued to use the optical value, and microwave spectroscopists, the microwave value. In fact, all absorption spectra of  $O_2$  taken subsequent to the work of Babcock and Herzberg have been analyzed using the optical values of  $B_0$  and  $D_0$  (7).

Recently, Butcher, Willetts, and Jones (8) have investigated the Raman spectrum of oxygen and Evenson and Mizushima (9) have extended the microwave spectrum of this molecule. The resulting  $B_0$  and  $D_0$  values agree remarkably well with each other and the microwave value of  $B_0$ , but not with the electronic optical values of  $B_0$  and  $D_0$ . In order to determine the origin of these discrepancies, we have carried out a reanalysis of Babcock and Herzberg's data, whereby we utilize, for the first time, *all* of their observed rotational lines, rather than just the combination differences associated with the  $F_2$  component of the  ${}^3\Sigma_g^-$  state. We find that the electronic optical values of  $B_0$  and  $D_0$  determined in this manner are in good agreement with the Raman optical and microwave values.

## II. PREVIOUS ANALYSES OF THE RED ATMOSPHERIC BANDS

The time-honored approach to the rotational analysis leading to  $B_v$  and  $D_v$  values for  ${}^3\Sigma$  states is to disregard the  $F_1$  and  $F_3$  components because the spin-spin and spin-rotation interactions cause the expressions for these components to be algebraically complex and nonlinear (10). It is only the  $F_2$  components that can be developed as a power series in  $N(N + 1)$  to determine the rotational constants  $B_v$ ,  $D_v$ , etc. For the  $O_2$  molecule this procedure can utilize only the  ${}^P P$  and  ${}^R R$  Red Atmospheric lines, which terminate on the  $F_2$   ${}^3\Sigma_g^-$  component, and not the  ${}^R Q$  and  ${}^P Q$  lines, which terminate on  $F_1$  and  $F_3$ , respectively. Thus, in determining values for the rotational constants, half of the observed line positions must be ignored. Furthermore, when a line is missing or blended and its position cannot be determined accurately, then the two combination differences involving this line must be omitted from the analysis. For Babcock and Herzberg's data, a loss of another several percent occurs because of this reason. Thus, all together, the traditional method of determining the rotational constants ignores well over half of the measured line positions in this application.

Prior to the advent of high-speed digital computers, it was necessary to reduce spectroscopic data by graphical methods (Ref. 10, pp. 175-191) and it was, therefore,


 FIG. 1.  $B_0$  values for the  $X \ ^3\Sigma_g^-$  state of  $O_2$ .

difficult to obtain a meaningful estimate of the statistical uncertainty associated with the calculated values of  $\nu_o(v', v'')$ ,  $B_v$ , and  $D_v$ . Babcock and Herzberg's determination of values for these parameters suffered from all of the above difficulties. Lofthus (5) eliminated the latter of these three difficulties by making a linear least-squares fit to Babcock and Herzberg's  $\Delta_2 F_2''(N)$  combination differences. He obtained  $B_0'' = 1.43784 \pm 0.00011(2\sigma) \text{ cm}^{-1}$  and  $D_0'' = [4.99 \pm 0.10(2\sigma)] \times 10^{-6} \text{ cm}^{-1}$ .<sup>2</sup> In Fig. 1, this  $B_0''$  value and its  $2\sigma$  uncertainty are compared to Babcock and Herzberg's and McKnight and Gordy's values. In Fig. 2, a similar comparison is made between Lofthus' and Babcock and Herzberg's  $D_0''$  values. (Recall that McKnight and Gordy could not determine a value of  $D_0''$ .) Since Lofthus fit the same data with the same analytical form used in the graphical analysis, it is clear that Babcock and Herzberg overestimated the accuracy of their  $B_0''$  value. The same conclusion applies to their  $D_0''$  value. Note also that Lofthus'  $B_0''$  value (which we have verified) *increases* the difference between the electronic optical and microwave values. It would require a  $3\sigma$  uncertainty, (i.e.,  $\approx 100$  percent confidence limits) for Lofthus' value to "agree" with the microwave value.

Butcher, Willetts, and Jones (8) recorded ten  $O_2$  Raman lines to an accuracy of about  $\pm 0.0015 \text{ cm}^{-1}$ . Their fit to these values gives  $B_0 = 1.437682 \pm 0.000018(2\sigma) \text{ cm}^{-1}$  and  $D_0 = [4.85_2 \pm 0.02_4(2\sigma)] \times 10^{-6} \text{ cm}^{-1}$ .<sup>3</sup> Figure 1 shows that this value of  $B_0$  is in excellent agreement with the microwave value and hence is in disagreement with the

<sup>2</sup>  $2\sigma$  denotes two standard deviations and probably corresponds more closely with the "limits of error" given by Babcock and Herzberg (1) and McKnight and Gordy (3) than  $1\sigma$ . Except for a few clearly indicated exceptions,  $2\sigma$  is used throughout.

<sup>3</sup> Welch and Mizushima (6) maintain that Butcher, Willetts, and Jones (8) only accounted for the first order spin-spin and spin-rotation parameters in their calculations and the inclusion of second order effects would alter the Raman values to  $B_0 = 1.437681$  and  $D_0 = 4.850 \times 10^{-6} \text{ cm}^{-1}$ . This is a decrease of only one and two units in the last place. Since the  $2\sigma$  uncertainty is ten times larger, we only make note of these proposed changes here.

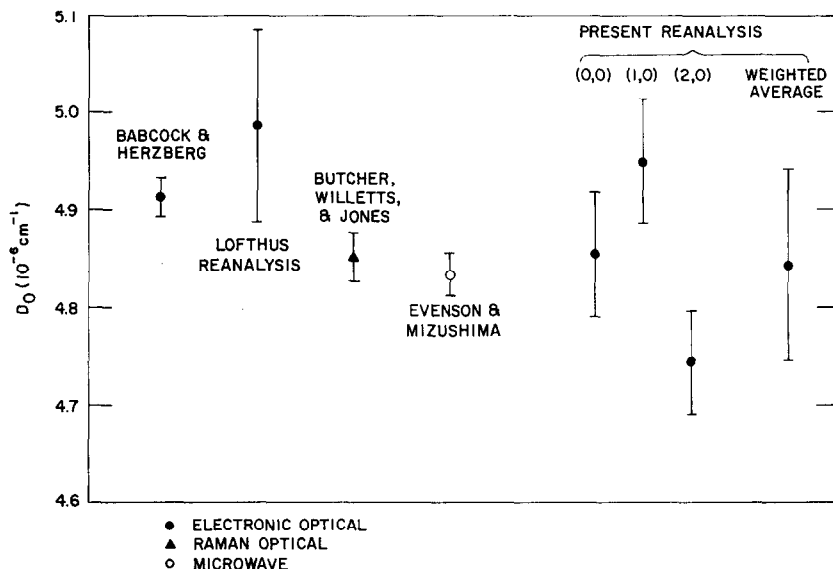


FIG. 2.  $D_0$  values for the  $X^3\Sigma_g^-$  state of  $O_2$ .

electronic optical values. Furthermore, this Raman value of  $D_0$  differs significantly from the optical electronic values.

Evenson and Mizushima (9) obtained the  $N = 13 \rightarrow 15$  and  $N = 21 \rightarrow 23$  transitions using a new laser magnetic resonance technique. Combining these data with McKnight and Gordy's value for the  $N = 1 \rightarrow 3$  transition, gave  $B_0 = 1.4376783 \pm 0.0000016(2\sigma) \text{ cm}^{-1}$  and  $D_0 = [4.835 \pm 0.020(2\sigma)] \times 10^{-6} \text{ cm}^{-1}$ .<sup>4</sup> On the scale of Fig. 1, this  $B_0$  value is coincident with McKnight and Gordy's value, and as shown in Fig. 2, this  $D_0$  value is in very satisfactory agreement with the Raman value. Welch and Mizushima (6) have combined McKnight and Gordy's and Evenson and Mizushima's measurements with numerous other microwave and infrared fine structure data to determine a consistent set of molecular parameters for  $v = 0$  of  $O_2 X^3\Sigma_g^-$ . Their values of  $B_0$  and  $D_0$  are the same as those of Evenson and Mizushima<sup>5</sup> and hence are not repeated here. Their values for the spin-spin and spin-rotation parameters are presumably the best now available for  $v = 0$ .

### III. PRESENT ANALYSIS

In a previous paper (11), we describe an alternative procedure for the determination of mechanically significant spectroscopic parameters from measured line positions.

<sup>4</sup> The uncertainty in the microwave values include the 0.66 ppm  $2\sigma$  error in the speed of light (4) and the (assumed) independent experimental error in the microwave measurements, where the two errors have been combined in the standard way.

<sup>5</sup> Welch and Mizushima quote one- and three-order-of-magnitude lower uncertainties on  $B_0$  and  $D_0$ , respectively, than Evenson and Mizushima. However, the uncertainties of Evenson and Mizushima are based on the variation of these parameters with the various current values for the set of  $g$ -factors, which must be assumed to be known in the reduction of their data. Thus, the larger uncertainties of Evenson and Mizushima are probably the more reasonable and are used here.

TABLE I  
The Molecular Constants<sup>a</sup> of the  $b^1\Sigma_g^+$  and  $X^3\Sigma_g^-$  States of  $O_2$  Determined by a Full Line Fit to the Measurements of Babcock and Herzberg (1) on the Red Atmospheric Bands

(v', v'')	degrees of freedom	$\delta$ cm <sup>-1</sup>	$\nu_0(v', v'')$ cm <sup>-1</sup>	$b^1\Sigma_g^+$		$X^3\Sigma_g^-$			
				$B_v'$ cm <sup>-1</sup>	$D_v'$ 10 <sup>-6</sup> cm <sup>-1</sup>	$B_v''$ cm <sup>-1</sup>	$D_v''$ 10 <sup>-6</sup> cm <sup>-1</sup>	$\gamma_v''$ 10 <sup>-3</sup> cm <sup>-1</sup>	$e_v''$ b cm <sup>-1</sup>
(0,0)	56	0.005	13 122.239(2)	1.391228(89)	5.383(70)	1.437644(85)	4.854(63)	-8.52(13)	1.3250(18)
(1,0)	45	0.005	14 526.992(3)	1.373105(105)	5.526(63)	1.437807(103)	4.949(62)	-8.40(18)	1.3235(21)
(2,0)	49	0.004	15 903.750(2)	1.354653(77)	5.385(57)	1.437705(75)	4.745(56)	-8.38(12)	1.3235(14)
(3,0)	26	0.006	17 252.427(5)	1.33572(21)	5.27(31)	1.43713(21)	4.45(32)	-8.26(34)	1.3255(29)
(1,1)	39	0.010	12 970.615(6)	1.37286(26)	4.93(26)	1.42184(25)	4.48(26)	-8.56(38)	1.3281(38)
(2,1)	13	0.04	14 347.392(42)	1.3557(23)	8.2(5.8)	1.4229(23)	7.5(6.6)	-9.3(4.0)	1.349(27)
(3,1)	7	0.15	15 696.11(39)	1.3349(76)	5(21)	1.4203(79)	≈0(20)	-13(20)	1.31(12)

<sup>a</sup> The number(s) in parentheses are the uncertainty in the last digit(s) that corresponds to two standard deviations (2σ).

<sup>b</sup> See footnote 6.

TABLE II  
 $B_0$  and  $D_0$  Values for the  $X^3\Sigma_g^-$  State of  $O_2$  <sup>a</sup>

	Source	$B_0$ ( $\text{cm}^{-1}$ )	$D_0$ ( $10^{-6} \text{ cm}^{-1}$ )
Electronic Optical	[present reanalysis of Babcock and Herzberg's (1) data]	1.437708(49)	4.842(98)
Raman Optical	[Butcher, Willetts, and Jones (8)]	1.437682(18) <sup>b</sup>	4.852(24) <sup>b</sup>
Microwave	[Evenson and Mizushima (9)]	1.4376783(16) <sup>c</sup>	4.835(20) <sup>c</sup>

<sup>a</sup> The numbers in parentheses are the uncertainty in the last digits that corresponds to two standard deviations.

<sup>b</sup> See footnote 3.

<sup>c</sup> See footnote 5.

TABLE III

Correlation Coefficients of the (0,0) Red Atmospheric Band

		$\nu_0(v', v'')$	$b^1\Sigma_g^+$		$X^3\Sigma_g^-$			
			$B_0'$	$D_0'$	$B_0''$	$D_0''$	$\gamma_0''$	$\epsilon_0''$
$\nu_0(v', v'')$		1						
$b^1\Sigma_g^+$	$B_0'$	-0.20	1					
	$D_0'$	-0.08	0.78	1				
$X^3\Sigma_g^-$	$B_0''$	-0.13	0.995	0.77	1			
	$D_0''$	-0.03	0.78	0.996	0.77	1		
	$\gamma_0''$	-0.19	0.25	-0.20	0.26	-0.21	1	
	$\epsilon_0''$	0.26	-0.07	0.18	-0.07	0.18	-0.41	1

Briefly, this method employs a nonlinear least-squares fit of the measured lines to energy levels given by the phenomenological Hamiltonians for the  $b^1\Sigma_g^+$  and  $X^3\Sigma_g^-$  states,

$$\mathcal{H}_{v'} = \nu_0 + B_{v'}N^2 - D_{v'}N^4 \tag{1}$$

$$\mathcal{H}_{v''} = B_{v''}N^2 - D_{v''}N^4 - \gamma_{v''}N \cdot S - \epsilon_{v''}(S^2 - 3S_z^2), \tag{2}$$

where  $\mathbf{N}$  and  $\mathbf{S}$  are nuclear rotational angular momentum and electronic angular momentum operators,  $\nu_0$  is the band origin of the  $v' \leftarrow v''$  transition, and  $\gamma_{v''}$  and  $\epsilon_{v''}$  are the so-called spin-rotation and spin-spin coupling constants.<sup>6</sup> The centrifugal distortion constants  $H_{v'}$  and  $H_{v''}$  could not be statistically determined from the measured lines and were, therefore, omitted from the fit. The mixing of the  $b^1\Sigma_g^+$  and  $X^3\Sigma_g^-$  through the spin-orbit interaction is discussed by Kayama and Baird (12). The effect of this mixing is largely to alter the meaning of  $\gamma_{v''}$  and  $\epsilon_{v''}$ , not  $B_{v''}$  and  $D_{v''}$ , because the off-diagonal spin-orbit interaction that connects these two states is  $J$ -independent (11). Since our interest is in the rotational constants, we do not incorporate this mixing in the present study. Thus, for each of the seven Red Atmospheric bands recorded by Babcock and Herzberg, values of  $\nu_0(v', v'')$ ,  $B_{v'}$ ,  $D_{v'}$ ,  $B_{v''}$ ,  $D_{v''}$ ,  $\gamma_{v''}$ , and  $\epsilon_{v''}$  are sought. Table I gives the results.

The  $B_{v''}$  and  $D_{v''}$  values from the (0,0), (1,0), and (2,0) bands are clearly superior to those from the rest of the bands and it is on these more accurate values that we con-

<sup>6</sup> The spin-spin constant is often written as  $\frac{2}{3}\lambda_v$  (6,9,10). We have omitted this numerical factor from the Hamiltonian by defining  $\epsilon_v = \frac{2}{3}\lambda_v$ .

TABLE IV  
 $\nu_0(v',0)$ ,  $B_{v'}$ , and  $D_{v'}$  Values for the  $b\ ^1\Sigma^+$  State of  $O_2$  with  
 Fixed Lower State Constants in the Fit to the (0,0), (1,0),  
 (2,0), and (3,0) Bands <sup>a</sup>

$(v',0)$	degrees of freedom	$\hat{\sigma}$ cm <sup>-1</sup>	$\nu_0(v',0)$ cm <sup>-1</sup>	$B_{v'}$ cm <sup>-1</sup>	$D_{v'}$ 10 <sup>-6</sup> cm <sup>-1</sup>
(0,0)	59	0.005	13 122.2381(21)	1.391262(9)	5.3623(61)
(1,0)	43	0.003	14 526.9909(17)	1.372982(10)	5.418(10)
(2,0)	47	0.003	15 903.7509(16)	1.354609(11)	5.446(13)
(3,0)	30	0.012	17 252.4285(88)	1.336244(104)	5.62(22)

<sup>a</sup> The numbers in parentheses are the uncertainty in the last digits that corresponds to two standard deviations ( $2\sigma$ ).

centrate our attention. The three values and  $2\sigma$  uncertainties obtained for  $B_0''$  are plotted on Fig. 1. Note that they cluster about the microwave and Raman-optical values, rather than the older electronic-optical values. The weighted average<sup>7</sup>  $1.437708 \pm 0.000049(2\sigma)$  cm<sup>-1</sup> agrees with these microwave and Raman optical values to within a small percentage of its  $2\sigma$  uncertainty. Figure 2 compares the various  $D_0''$  values. Again the value obtained from the present reanalysis agrees much better with the microwave and Raman optical values than with the older electronic-optical values.

The conclusion appears inescapable. When a least-squares fit is made to *all* of the measured lines, not just those that are simple to describe algebraically, there is no discrepancy between the optical and microwave  $B_0''$  and  $D_0''$  values. These values are summarized in Table II. In the Appendix, the best of these values are used to obtain improved values for  $B_{v'}$  and  $D_{v'}$  of the  $b\ ^1\Sigma^+$  state.

<sup>7</sup> We have followed the simple methods given by Worthing and Geffner (13) for computing weighted means and associated uncertainties from values with consistent or inconsistent uncertainties.



IV. APPENDIX

As indicated in Table I, the best of the Red Atmospheric bands have  $v'' = 0$  as the lower vibrational level. In this Appendix, we use the accurate microwave values for the constants of this vibrational level to improve the values for the constants of  $v' = 0, 1, 2,$  and  $3$  of the  $b^1\Sigma_g^+$  state and those associated with  $v'' = 1$  of the  $X^3\Sigma_g^-$  state.

One hindrance in determining accurate  $B_v', D_v', B_v'',$  and  $D_v''$  values from bands between the electronic states is the strong correlation between these four constants. Table III shows the correlation coefficients for the (0,0) band. Other bands are similar. Complete correlation would be indicated by  $\pm 1$  and complete independence would be indicated by zero. Since the values for  $B_v''$  and  $D_v''$  are much more accurately known from the microwave spectra (see Table II), then these can be used to break the correlation and improve the remaining constants. Thus, to determine improved values for the

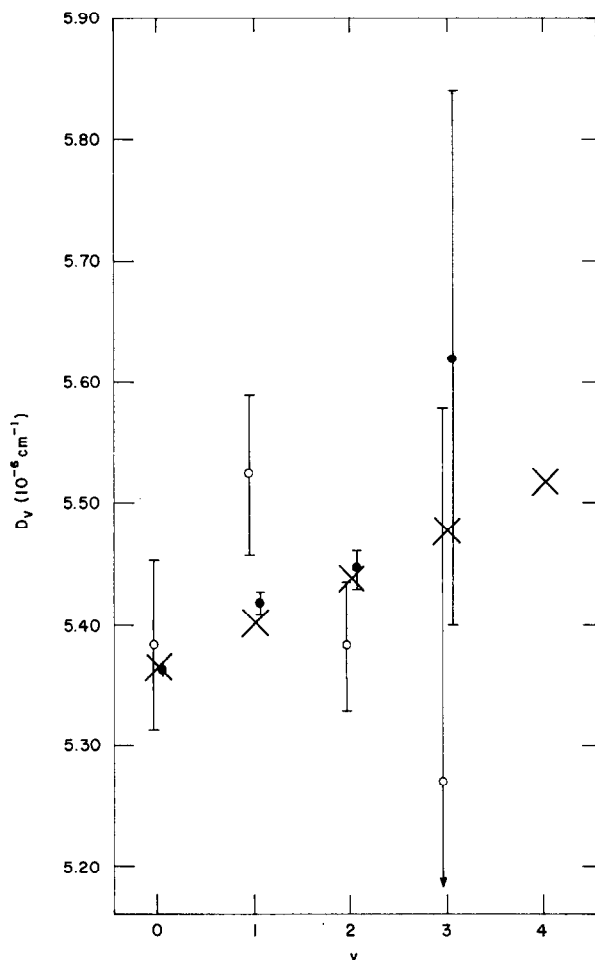


FIG. 3.  $D_v$  values for the  $b^1\Sigma_g^+$  state of  $O_2$ . The open circles are experimental values from the Red Atmospheric bands with both upper and lower state constants free (Table I) and the closed circles are similar values with the lower state constants fixed (Table IV). The crosses are calculated  $D_v$  values.

TABLE V  
The  $\nu_0(v', 0)$  and  $B_v$  Values for the  $b^1\Sigma_g^+$  of  $O_2^a$

Calculation of $Y_{i0}$				
$v'$	Exp. $\nu_0(v', 0)$ cm <sup>-1</sup>	Calc. $\nu_0(v', 0)$ cm <sup>-1</sup>	Exp. - Calc. cm <sup>-1</sup>	$2\sigma$ cm <sup>-1</sup>
0	13 122.2381	13 122.2351	0.0030 *	0.0021
1	14 526.9909	14 526.9968	-0.0059 *	0.0017
2	15 903.7509	15 903.7456	0.0053 *	0.0016
3	17 252.4285	17 252.4815	-0.0530 *	0.0088
Calculation of $Y_{i1}$				
$v'$	Exp. $B_v'$ cm <sup>-1</sup>	Calc. $B_v'$ cm <sup>-1</sup>	Exp. - Calc. 10 <sup>-3</sup> cm <sup>-1</sup>	$2\sigma$ 10 <sup>-3</sup> cm <sup>-1</sup>
0	1.391262	1.391263	-0.001	0.009
1	1.372982	1.372980	0.002	0.010
2	1.354609	1.354612	-0.003	0.011
3	1.336244	1.336159	0.085	0.104

<sup>a</sup> The calculated values in this table and the associated coefficients in Table VI are obtained from a weighted least-squares fit to the experimentally obtained values. The assigned weights are equal to the inverse square of the standard deviations. The residuals between the experimentally obtained and calculated values are then compared to the estimated experimental uncertainties ( $2\sigma$ ). An asterisk denotes that the absolute value of the residual exceeds the  $2\sigma$  estimate.

constants of the  $b^1\Sigma_g^+$  state, we fixed  $B_0''$  and  $D_0''$  to the microwave values of Evenson and Mizushima ( $\varrho$ ) and  $\gamma_0''$  and  $\epsilon_0''$  to the values of Welch and Mizushima ( $\delta$ ),  $-8.425378 \times 10^{-3}$  and  $1.3231672$  cm<sup>-1</sup>, respectively. The fixing of the latter two constants is certainly not essential because of the low correlation between these and the  $B_v'$  and  $D_v'$  constants (see Table III). The resulting values for  $\nu_0(v', v'')$ ,  $B_v'$ , and  $D_v'$  are given in Table IV. Figure 3 shows the improvement in the  $D_v'$  values. The open circles identify the values from Table I (free lower state constants) and closed circles identify the values from Table IV (fixed lower state constants). The crosses show the  $D_v'$  values calculated using the vibrational wavefunctions computed from our rotationless

potential (described below) with a method described in an accompanying paper (14):  $D_0' = 5.3673 \times 10^{-6}$ ,  $D_1' = 5.4016 \times 10^{-6}$ ,  $D_2' = 5.4380 \times 10^{-6}$ ,  $D_3' = 5.4771 \times 10^{-6}$ , and  $D_4' = 5.5190 \times 10^{-6}$  cm<sup>-1</sup>. The agreement between the experimental  $D_v'$  values determined with fixed lower state constants and the calculated values is very good.

A weighted least-squares fit is made to the  $\nu_o(v', 0)$  and  $B_v'$  values in Table IV to determine the Dunham expansion coefficients  $Y_{i0}$  and  $Y_{i1}$ , respectively, for the  $O_2 b^1\Sigma_g^+$  data. The details of the fit are given in Table V and the expansion coefficients are listed in Table VI. The selection of the number of  $Y_{i0}$  coefficients to represent the  $\nu_o(v', 0)$  values required careful consideration. Two  $Y_{i0}$  coefficients give residuals a few times larger than the  $2\sigma$  uncertainties. On the other hand, three  $Y_{i0}$  coefficients require an exact fit and hence may be seriously degraded due to the relatively inaccurate value for  $\nu_o(3,0)$ . It is believed that the disadvantages of the latter are greater than the oversized residuals, which are by no means excessive. Furthermore, as will be noted below, two  $Y_{i0}$  produce a more consistent potential. The fit to the  $B_v'$  values was straightforward; three  $Y_{i1}$  coefficients were an obvious choice.

Table VII lists the rotationless potential constructed for the  $b^1\Sigma_g^+$  state from the  $Y_{i0}$  and  $Y_{i1}$  coefficients using the Rydberg-Klein-Rees procedure (15). The uncertainty in the turning points corresponds approximately to that in the  $B_v'$  values. The internal consistency of this potential is tested in Table VIII. The eigenvalues  $E_{v0}$  of the potential and the expectation value  $\langle B(r) \rangle_v \equiv \langle v | \hbar/8\pi^2\mu r^2c | v \rangle$  calculated from the vibrational wavefunctions are compared in Table VIII to the values of  $E(v, J = 0) = Y_{00} + G(v)$

TABLE VI

Expansion Coefficients for the  $b^1\Sigma_g^+$  State of  $O_2$  for  $v \leq 3$ <sup>a</sup>

$\nu_o(v', 0) = T_{0e} + \sum_{i=1}^2 Y_{i0} (v + \frac{1}{2})^i \text{ cm}^{-1}$		$B_v = \sum_{i=0}^2 Y_{i1} (v + \frac{1}{2})^i \text{ cm}^{-1}$	
$T_{0e} = 12\ 409.\underline{3494}$ <sup>b</sup>		$Y_{01} = 1.400372$	
$Y_{10} = 1\ 432.\underline{7747}$		$Y_{11} = -0.0181982$	
$Y_{20} = -14.00647$		$Y_{21} = -0.0000424$	

<sup>a</sup> The standard deviation (1σ) of each coefficient is less than 5 units in the last non-underlined digit. It should be realized that this is the statistical uncertainty in the present fit and may not reflect the absolute accuracy of the coefficients.

<sup>b</sup>  $T_{0e}$  is the separation between  $v''=0$  and  $G'(v' = -\frac{1}{2})$ .

TABLE VII  
 Numerical Rotationless Potential for the  $b\ ^1\Sigma_g^+$  State of  $O_2$

$v$	$E(v,0)^a$ cm <sup>-1</sup>	$r_{\min}$ Å	$r_{\max}$ Å
-0.50008		1.2268901	
-0.25	357.4375	1.1903817	1.2672641
0.0	713.0050	1.1762940	1.2852362
0.5	1418.8875	1.1573290	1.3120271
1.0	2117.7667	1.1435027	1.3337560
1.5	2809.6428	1.1323157	1.3529242
2.0	3494.5155	1.1228035	1.3704973
2.5	4172.3851	1.1144733	1.3869697
3.0	4843.2514	1.1070333	1.4026348
4.0	<u>6163.974</u> <sup>b</sup>	<u>1.094125</u> <sup>b</sup>	<u>1.432248</u> <sup>b</sup>
5.0	<u>7456.684</u>	<u>1.083137</u>	<u>1.460292</u>
6.0	<u>8721.381</u>	<u>1.073550</u>	<u>1.487300</u>
7.0	<u>9958.065</u>	<u>1.065040</u>	<u>1.513612</u>
8.0	<u>11166.737</u>	<u>1.057388</u>	<u>1.539461</u>

$$A1 = 28\ 850.983^c$$

$$A2 = 2\ 769.9653$$

$$A3 = 644.75308$$

$$D = 1.137037$$

<sup>a</sup>  $E(v,0) = G(v) + Y_{00}$ , where the  $G(v)$  values are given by the  $Y_{10}$  coefficients in Table VI and  $Y_{00} = 0.1192$  cm<sup>-1</sup>.

<sup>b</sup> The underlined numbers are the extension of the potential to the vibrational level at which the Hulbert-Hirschfelder function is spliced on and are considerably less accurate than the other numbers.

<sup>c</sup>  $A1$ ,  $A2$ ,  $A3$ , and  $D$  are the parameters of the Hulbert-Hirschfelder extension function  $E(v,0) = A1(1 - \exp(-X))^2 + A2(X^3 \exp(-DX)) + A3(X^4 \exp(-DX))$ , where  $X = \omega_e(r - r_e) / 2r_e(B_e D_e)^{1/2}$ .

and to  $B_v$ , respectively. For  $v \leq 3$ , the remarkably good agreement demonstrates the high degree of consistency between the potential and the  $Y_{i0}$  and  $Y_{i1}$  coefficients that were used to create it. Note that if  $G(v)$  alone, rather than  $Y_{00} + G(v)$ , had been compared to the eigenvalues  $E_{v0}$ , i.e., if  $Y_{00}$  had been ignored, then there would have been a nearly constant  $0.119 \text{ cm}^{-1}$  discrepancy, attesting to the reality and need for  $Y_{00}$ . This internal consistency is nearly an order of magnitude better than that for a potential based on Babcock and Herzberg's original  $\nu_o(v', 0)$  and  $B_v'$  values, thus demonstrating the improvements available using the reanalysis and other techniques described above.

The underlined numbers in Table VIII correspond to the less accurate portion of the potential constructed by extending the  $Y_{i0}$  and  $Y_{i1}$  coefficients beyond their strict validity, i.e., an extension of five vibrational levels beyond the last level for which there are experimental values. Since the  $Y_{i0}$  and  $Y_{i1}$  coefficients are no longer coupled through the experimental values for these extended vibrational levels, they yield an increasingly inconsistent potential. These underlined numbers are included in Table VIII

TABLE VIII  
Consistency Test of the  $O_2$   $b^1\Sigma_g^+$  Potential

$v$	<sup>a</sup> $E(v, 0) - E_{v0}$ $\text{cm}^{-1}$	<sup>b</sup> $B_v - \langle B(r) \rangle_v$ $10^{-3} \text{ cm}^{-1}$
0	-0.0025	0.006
1	-0.0041	0.006
2	-0.0006	0.005
3	-0.0022	0.002
4	<u>-0.000</u> <sup>c</sup>	<u>0.002</u> <sup>c</sup>
5	<u>0.014</u>	<u>-0.001</u>
6	<u>0.023</u>	<u>-0.002</u>
7	<u>0.050</u>	<u>0.003</u>
8	<u>0.115</u>	<u>0.038</u>

<sup>a</sup> See note (a) in Table VII.

<sup>b</sup>  $\langle B(r) \rangle_v = \langle v | h/8\pi^2 \mu r^2 c | v \rangle$ .

<sup>c</sup> The underlined numbers correspond to the extension portion of the potential [see note (b) in Table VII].

TABLE IX  
 $\nu_0(v', l)$ ,  $\Delta G_{1/2}''$ ,  $B_1''$ ,  $D_1''$ ,  $\gamma_1''$ , and  $\epsilon_1''$  Values for the  $X^3\Sigma_g^-$  State with  $B_V'$  and  $D_V'$  of the  $b^1\Sigma_g^+$  State Fixed to the Values in Table IV<sup>a</sup>

$(v', v'')$	degrees of freedom	$\hat{c}$ cm <sup>-1</sup>	$\nu_0(v', v'')$ cm <sup>-1</sup>	$\Delta G_{1/2}''^b$ cm <sup>-1</sup>	$B_1''$ cm <sup>-1</sup>	$D_1''$ 10 <sup>-6</sup> cm <sup>-1</sup>	$\gamma_1''$ 10 <sup>-3</sup> cm <sup>-1</sup>	$\epsilon_1''^c$ cm <sup>-1</sup>
(1,1)	40	0.010	12 970.614(6)	1556.377(8)	1.421925(54)	4.859(90)	-8.98(30)	1.3288(41)
(2,1)	15	0.040	14 347.39(4)	1556.36(4)	1.42186(88)	4.7(3.2)	-8.9(2.8)	1.346(25)
(3,1)	9	0.14	15 696.17(41)	1556.26(41)	1.4227(70)	4(26)	-10(11)	1.31(11)
$D_1''$ fixed to $4.8402 \times 10^{-6}$ cm <sup>-1</sup>								
(1,1)	41	0.010	12 970.613(5)	1556.378(7)	1.421914(15)	-	-8.97(30)	1.3287(40)
(2,1)	16	0.038	14 347.39(3)	1556.36(4)	1.42188(19)	-	-8.9(2.3)	1.346(23)
(3,1)	10	0.13	15 696.18(21)	1556.25(21)	1.4229(14)	-	-9.9(9.9)	1.31(10)

<sup>a</sup> The number(s) in parentheses are the uncertainty in the last digit(s) that corresponds to two standard deviations (2 $\sigma$ ).

<sup>b</sup>  $\Delta G_{1/2}''$  was computed using the  $\nu_0(v', 0)$  values in Table IV. The uncertainties were added.

<sup>c</sup> See footnote 6.

TABLE X  
Spin-Rotation  $\gamma_V$  and Spin-Spin  $\epsilon_V$  Constants  
for the  $X^3\Sigma_g^+$  State of  $O_2^a$

$\gamma_V$ (spin-rotation) $10^{-3}$ $\text{cm}^{-1}$		
	microwave	present optical
$v = 0$	-8.425378(33) <sup>d</sup>	-8.436(79) <sup>b</sup>
$v = 1$	-	-8.97(30) <sup>c</sup>

$\epsilon_V$ (spin-spin) <sup>e</sup> $\text{cm}^{-1}$		
$v = 0$	1.3231672(5) <sup>d</sup>	1.3239(10) <sup>b</sup>
$v = 1$	-	1.3287(40) <sup>c</sup>

<sup>a</sup> The number(s) in parentheses are the uncertainty in the last digit(s) that corresponds to two standard deviations ( $2\sigma$ ).

<sup>b</sup> From the (0,0), (1,0), and (2,0) bands in Table I.

<sup>c</sup> From the (1,1) band in the lower part of Table IX.

<sup>d</sup> See footnote 4.

<sup>e</sup> See footnote 6.

to give an indication of the risks of constructing a potential by extending the  $Y_{i0}$  and  $Y_{i1}$  coefficients. In many cases, particularly where higher-order coefficients are involved, the inconsistency is many times worse than that given here.

A few last bits of information can be gleaned from the Red Atmospheric data. The (1,1), (2,1), and (3,1) bands, although much less accurate than the (0,0), (1,0), (2,0), and (3,0) bands, afford the only accurate information currently available about the  $v'' = 1$  level of the  $X^3\Sigma_g^-$  state. Table I shows that these bands, particularly the more accurate (1,1) band, can furnish values for  $\Delta G_{\frac{1}{2}}''$ ,  $B_1''$ ,  $D_1''$ ,  $\gamma_1''$ , and  $\epsilon_1''$ . Improved values for these constants are given in the upper part of Table IX, where the least-square fits were made with  $B_v'$  and  $D_v'$  fixed to the values listed in Table IV. A comparison of Tables I and IX shows that the  $B_1''$  and  $D_1''$  values improved substantially and the  $\Delta G_{\frac{1}{2}}''$ ,  $\gamma_1''$ , and  $\epsilon_1''$  values somewhat, as expected from the correlation matrix in Table III.

Using the method described in an earlier paper (14) the *RKR* potential for the  $O_2 X^3\Sigma_g^-$  state yields the following theoretical values for the  $D_v''$  values of the first three levels of the  $X^3\Sigma_g^-$  state:  $D_0'' = 4.8400 \times 10^{-6}$ ,  $D_1'' = 4.8402 \times 10^{-6}$ , and  $D_2'' = 4.8408 \times 10^{-6}$   $\text{cm}^{-1}$ . This value for  $D_0''$  is in very good agreement with the electronic, Raman, and microwave values listed in Table II. However, the value just obtained for  $D_1''$  from the (1,1) band in the upper part of Table IX differs substantially from the theoretical value above. This is undoubtedly due to the weakness of the (1,1) band. To improve the value of  $B_1''$ , the (1,1), (2,1) and (3,1) bands (the latter two for completeness only) were refit with  $D_1''$  fixed to the theoretical value and  $B_v'$  and  $D_v'$  fixed as before. The results are given in the lower part of Table IX. The values listed here for the (1,1) band are the preferred values.

These values of  $\gamma_1''$  and  $\epsilon_1''$  are the only values for these quantities since there are no microwave values for  $v'' > 0$ . Table X compares the values of  $\gamma_v''$  and  $\epsilon_v''$  for the  $X^3\Sigma_g^-$  state. The agreement between the present optical values and the much more accurate microwave values for  $v'' = 0$  is very satisfactory. Furthermore, the optical values for  $v'' = 1$  imply that  $\gamma_v''$  increases in magnitude from  $v'' = 0$  to  $v'' = 1$  and strongly suggest that  $\epsilon_v''$  does also.

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