

MEASURED OSCILLATOR STRENGTHS FOR THE  $2p^4\ ^3P - 2p^33s\ ^3S^o$  TRANSITION IN ATOMIC OXYGEN\*

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Directly calibrated absorption of resonance line emission by atomic nitrogen and oxygen has been used in this laboratory in studies of flowing afterglows. Doppler line profiles were assumed in determining the oscillator strength of the nitrogen ( $2p^3\ ^4S^o - 2p^33s\ ^4P$ ) transition near 1200 Å, giving results two orders of magnitude smaller than expected.<sup>1,2</sup> Similar measurements have now been performed on the corresponding resonance triplet in oxygen ( $2p^4\ ^3P - 2p^33s\ ^3S^o$ ) at 1302, 1305, and 1306 Å, using a more general line-profile function in the data reduction, and good agreement with theory is found.

Oxygen atoms were produced by adding NO to the pure nitrogen afterglow; the rate of production was very nearly equal to the flow rate of NO, and the concentration was adjusted by varying this flow.<sup>3</sup> Recombination was negligible at speeds greater than 1000 cm/sec. The absorption cell was isolated by LiF windows and placed between a one-meter vacuum spectrometer and a He-O<sub>2</sub> microwave discharge. The resolved resonance emission lines were used as the background light to be absorbed. In this manner of operation the resolution is determined by the width of the background lines, not by the spectrometer.

In the analysis of the measured absorption as a function of atomic concentration, the more general Voigt line profile was used, which in special cases reduces to the Doppler shape. If the oxygen concentration is  $n$ , and  $I(n)$  is the observed intensity of one of the lines, then

$$I(n) = \text{const} \int_{-\infty}^{\infty} V(A_e, \omega) \exp[-K_r x_r V(A_r, B\omega) - K_a x_a V(A_a, C\omega)] d\omega, \quad (1)$$

where  $e$ ,  $r$ , and  $a$  refer to the emission, self-reversing, and absorption lines, respectively.  $K$  is the absorption coefficient,  $x$  the effective path length, and  $V(A, \omega)$  the Voigt profile:

$$V(A, \omega) = \frac{A}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-y^2)}{A^2 + (\omega - y)^2} dy; \quad (2)$$

$$A = \frac{\Delta\nu_N + \Delta\nu_C}{\Delta\nu_D} (\ln 2)^{1/2}; \quad \omega = \frac{(\nu - \nu_0)}{\Delta\nu_D} 2(\ln 2)^{1/2}. \quad (3)$$

$\Delta\nu_N$  is the natural linewidth,  $\Delta\nu_C$  the collision

width, and  $\Delta\nu_D$  the Doppler width.  $B$  and  $C$  are ratios of Doppler widths:

$$B = \Delta\nu_{De} / \Delta\nu_{Dr}, \quad C = \Delta\nu_{De} / \Delta\nu_{Da}. \quad (4)$$

Equation (1) is limited by the assumption that there is no shift or other asymmetry of the emission, self-reversing, and absorption lines. In

Table I. The parameters and derived physical quantities which yield the best fit to the experimental points.

$\lambda$ (Å)	1302	1305	1306
$A_e$	7.39 - 03 <sup>a</sup>	4.50 - 03	1.50 - 03
$A_r$	1.05 - 02	6.37 - 03	2.13 - 03
$A_a$	1.28 - 02	7.73 - 03	2.58 - 03
$B$	1.45 + 00	1.47 + 00	1.47 + 00
$C$	1.81 + 00	1.84 + 00	1.84 + 00
$K_r x_r$	7.21 + 01	4.39 + 01	1.46 + 01
$K_a x_a / (10^{14} \text{ cm}^{-3})$	2.17 + 01	1.32 + 01	4.39 + 00
$T_e$ (°K)	982	1015	1015
$T_r$ (°K)	465	470	470
$\Delta\nu_{De}$ (cm <sup>-1</sup> )	4.29 - 01	4.35 - 01	4.35 - 01
$\Delta\nu_{Dr}$ (cm <sup>-1</sup> )	2.95 - 01	2.96 - 01	2.96 - 01
$\Delta\nu_{Da}$ (cm <sup>-1</sup> )	2.37 - 01	2.37 - 01	2.37 - 01
$\Delta\nu_{Ce}$ (cm <sup>-1</sup> )	1.68 - 03	1.09 - 03	3.63 - 04
$\Delta\nu_{Cr}$ (cm <sup>-1</sup> )	2.25 - 03	1.38 - 03	4.59 - 04
$\Delta\nu_{Ca}$ (cm <sup>-1</sup> )	2.45 - 03	1.49 - 03	4.96 - 04
$n_r x_r$ (cm <sup>-2</sup> )	1.36 + 15	1.37 + 15	1.37 + 15
$gf$	1.69 - 01	1.03 - 01	3.43 - 02
$M^b$	32	21	32
$\Delta^c$	6.3 - 03	1.4 - 02	1.0 - 03
$\sigma^d$	1.57 - 02	9.44 - 03	1.92 - 02
$gf$ ratio	4.9	3.0	1.0

<sup>a</sup>The numbers following the ( $\pm$ ) sign indicates the exponent (e.g., 7.4 - 03 =  $7.4 \times 10^{-3}$ ).

<sup>b</sup> $M$  is the number of experimental points used in the fit.

$$\Delta = \sum_{i=1}^M \left[ \frac{I(n_i)}{I(0)} \exp \left( -\frac{I(n_i)}{I(0)} \text{calc} \right) \right].$$

$$\sigma = \left[ \left\{ \sum_{i=1}^M \left[ \frac{I(n_i)}{I(0)} \exp \left( -\frac{I(n_i)}{I(0)} \text{calc} \right) \right]^2 \right\} / (M-1) \right]^{1/2}.$$

the present experiment, however, these approximations should be valid, since the calculated collision broadening is much less than the Doppler broadening, and each line of the multiplet is calculated to be strongly self-reversed.

The experimental points  $I(n)/I(0)_{\text{exp}}$ ,  $0.7 \times 10^{14} \leq n \leq 15 \times 10^{14} \text{ cm}^{-3}$  were fitted to the  $I(n)/I(0)_{\text{calc}}$  of Eq. (1) with  $A_e$ ,  $A_r$ ,  $A_a$ ,  $K_r x_r$ ,  $K_a x_a/n$ ,  $B$ , and  $C$  as independent parameters, using an iterative search routine on an IBM-709 computer. Convergence of fit was obtained for each of the resonance lines at several combinations of parameters. Of these, only one set was consistent with the requirements that the oscillator strengths be approximately in the ratio 5:3:1 for 1302, 1305, and 1306 Å, respectively, and that  $B$  and  $C$  each be about the same for the three lines. The values of these parameters and the associated physical quantities are given in Table I.

Since an atom makes only about  $10^5$  collisions between the formation region and the absorption cell, the results in Table I are calculated on the assumption that the  $J=2, 1, 0$  lower states are populated according to statistical weights. If a Maxwellian distribution is assumed, the calculated oscillator strengths increase by only 35%, but the standard deviation of the best fit increases by a like amount.

Theoretical values for  $gf$  have been calculated by Garstang<sup>4</sup> to be 0.23, 0.14, and 0.046 for the three transitions, using a value of  $\sigma^2 = 0.15$  for

the radial integral. These numbers are about 25% greater than the experimentally determined values but could be brought into agreement by a not unreasonable reduction of  $\sigma^2$  to 0.11. On the other hand, experimental error is estimated at about 25%, limited largely by the possibility of appreciable quantities of atoms in the metastable states or in transient distributions other than that assumed.

This improved technique of analysis is being applied to the previous data on nitrogen. With the assumption of a strongly self-reversed Voigt profile, an improved fit can be obtained yielding  $\sum gf = 0.53$ , which is consistent with theory.<sup>2</sup> Details of these studies applying to measurements of resonance absorption in oxygen and nitrogen will be reported soon.

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### ANALYTIC SCF OSCILLATOR STRENGTH FOR THE OI $2p^4(^3P) - 2p^33s(^3S)$ TRANSITION\*

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A direct measurement of the oscillator strength of the OI  $2p^4(^3P) - 2p^33s(^3S)$  transition has recently been reported by Prag and Clark.<sup>1</sup> Since the value they obtained is slightly lower than the estimate suggested by Garstang<sup>2</sup> (mainly on the basis of the Coulomb approximation<sup>3</sup>) and since no Hartree-Fock value has been reported to date (due to the previous unavailability of a Hartree-Fock wave function for the <sup>3</sup>S upper state), it is appropriate to present the results of our analytic Hartree-Fock computations for this transition. In spite of the fact that these results were obtained in strict *LS* coupling, our theoretical value is in closer agreement with the Prag-Clark experimental result than is Garstang's suggested value.

For this multiplet, our value of the radial dipole integral  $\sigma^2$  is 0.0974. This yields an (absorption)  $f$  number of 0.0303 and is substantially smaller than the value  $\sigma^2 = 0.15$  suggested by Garstang. It is also in relatively closer agreement with the experimental value  $\sigma^2 = 0.11$  obtained by Prag and Clark.

The wave functions used for the  $1s^22s^22p^4(^3P)$  and  $1s^22s^22p^33s(^3S)$  states of neutral oxygen were obtained by use of computer programs designed by Roothaan and his co-workers.<sup>4</sup> The programs are based on the expansion method for self-consistent-field solutions to the wave equation. Our wave functions represent exact solutions to the restricted Hartree-Fock equations to at least