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KINETIC SPECTROSCOPY IN THE FAR VACUUM ULTRA-VIOLET

PART 3.—OSCILLATOR STRENGTHS FOR THE 3s, 4s, AND 5s ^3S–$2p^4$ $^3P_2$ TRANSITIONS IN ATOMIC OXYGEN

Kinetic Spectroscopy in the Far Vacuum Ultra-violet

Part 3.—Oscillator Strengths for the 3*s*, 4*s* and 5*s* ^3S–$2p^4$ $^3P_2$ Transitions in Atomic Oxygen

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Line absorption measurements for ns $^3S-2p^4$ ^3P_J transitions have been made as a function of ground state oxygen O $2p^4$ ^3P_J atom concentration. The results gave the following values for the oscillator strengths (f_{ik}) of the ns $^3S-2p^4$ $^3P_2$ transitions of oxygen:

$(4.5 \pm 1.0) \times 10^{-2}$ ($n = 3$, λ 130.22 nm); $(5.9 \pm 1.4) \times 10^{-3}$ ($n = 4$, λ 103.92 nm); $(1.5 \pm 0.4) \times 10^{-3}$ ($n = 5$, λ 97.65 nm).

The agreement with the literature of the *f*-value for $n = 3$ is good; no previous measurements for the $n = 4$ and $n = 5$ transitions appear to have been reported.

Atomic oscillator strengths (*f*-values) or the associated transition probabilities (such as A_{ki}, the Einstein coefficient for spontaneous emission) are necessary basic data in a number of different areas. Well-known oscillator strengths provide the required correlation between observed intensities of absorption (or of fluorescence), and the density of absorbing or emitting atoms. Thus, for example, quantitative chemical kinetic measurements may be performed, or the composition of planetary atmospheres may be modelled. Also, experimental *f*-values provide data both for theoretical work involving semi-empirical calculations, and for verification of *ab initio* calculations of oscillator strengths.

Most resonance transitions of atoms of aeronomic interest occur in the vacuum ultraviolet spectrum, with its concomitant experimental difficulties. Therefore, only recently has a significant body of data on such resonance transitions begun to accumulate. Studies of transition probabilities at wavelengths shorter than the LiF cut-off (*i.e.*, $\lambda < 105$ nm) are quite rare because of acute experimental problems, although it is in this wavelength region that theoretically important, resonance-Rydberg series can be studied.

In order to begin to fill the void of information concerning transition probabilities below the LiF cut-off, and more specifically those for resonance-Rydberg transitions, we have measured *f*-values for the 3*s*, 4*s* and 5*s* ^3S–$2p^4$ $^3P_2$ transitions in O(I) which appear at 130.22, 103.92 and 97.65 nm respectively (see table 1). We have used the line-absorption method for the determination of the *f*-value for all three transitions. (The method is applicable to the many other resonance transitions of O which lie between 92 and 110 nm). The apparatus employed collimated hole structures in lieu of windows to separate the source, absorber and detector. The source was a microwave discharge through a flow of helium with a trace of molecular oxygen. The 130.22 nm *f*-value was the same within experimental error as other recent experimental and theoretical results. The shorter wavelength Rydberg transitions ($n = 4, 5$) show a trend in *f*-value consistent with theoretical expectations.

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TABLE 1.—WAVELENGTHS AND ENERGIES OF *ns* $^3S-2p^4\ ^3P_J$ TRANSITIONS OF O(I)

		ground state $2p^4$					
		$^3P_2$		$^3P_1$		$^3P_0$	
excited state		λ/nm	$\bar{\nu}$/cm^{-1}	λ/nm	$\bar{\nu}$/nm	λ/nm	$\bar{\nu}$/cm^{-1}
3*s*	$^3S^\circ$	130.217	76 795	130.487	76 636	130.603	76 568
4*s*	$^3S^\circ$	103.923	96 226	104.094	96 067	104.168	95 999
5*s*	$^3S^\circ$	97.645	102 412	97.796	102 253	97.862	102 185

In this paper, we first consider the processes contributing to line broadening of the emitters and absorbers. A brief formulation of the line absorption method is then presented. The results section includes a description of the methods used to establish the optical density and temperature in the oxygen atom resonance lamp, followed by the results of the *f*-value measurements. Finally, our experimental *f*-values are compared with previous work.

THEORETICAL

LINE ABSORPTION METHOD FOR O *ns* ^3S–$2p^4\ ^3P_J$ TRANSITIONS

The raw data from which *f*-values were derived were measurements of fractional absorption, A, as a function of ground state O $2p^4\ ^3P_J$ atom concentration, N, using a resonance lamp. The method is based on well-established principles,[1-5] and it utilizes the relationship between the integral of the absorption coefficient at frequency ν, k_ν, and the oscillator strength, f, for the corresponding transition:

$$f = (mc/\pi e^2 N)\int_{-\infty}^{\infty} k_\nu \,\mathrm{d}\nu. \tag{I}$$

The expression relating A to k_ν is eqn (II),

$$A = (I_0 - I_{\mathrm{trans}})/I_0 = \left\{\int_{-\infty}^{\infty} I(\nu)[1-\exp(-k_\nu l)]\,\mathrm{d}\nu\right\}\bigg/\int_{-\infty}^{\infty} I(\nu)\,\mathrm{d}\nu \tag{II}$$

where l is the path length for absorption, and $I(\nu)$ is the frequency distribution of the source emission line. The analysis used to determine values of f from measurements of A using eqn (I) and (II) has been given in full elsewhere [1, 2, 4] and will be merely summarized here (in a section to follow).

BROADENING OF OXYGEN ATOM LINES

The definition of the line shapes of the emitters [$I(\nu)$] and absorbers, (k_ν), and knowledge of the magnitudes of the line widths (FWHM), is central to the correct evaluation of *f*-values in the line absorption method [see eqn (I) and (II)]. In some cases, such as the halogens F, Cl, Br, I, hyperfine nuclear splitting can broaden the lines and can lead to resolved multiplet structure; [6] this leads to an underestimate of *f*-values if the hyperfine splitting is ignored.[1, 7] In other cases, such as Ne, hyperfine isotopic splitting of lines [8] can have the same effect. The oxygen ^{16}O atom lines are free from both nuclear and isotopic hyperfine effects.

The observed profile of any non-reversed atomic line is considered to be intermediate between the limiting cases of a Gaussian, or Doppler profile, and a Lorentzian profile. In the present work, the experimental conditions were such that all factors leading to Lorentzian broadening were much less than those leading to Doppler broadening. The basis for this conclusion is briefly summarized as follows.

The Doppler width ($\Delta\nu_D$) due to thermal motions of atoms having mass M and at temperature T is given by eqn (III),[1]

$$\Delta\nu_D/\text{cm}^{-1} = (2/\lambda_0 c)(2RT \ln 2/M)^{\frac{1}{2}} \tag{III}$$

λ_0 is the wavelength of the line centre. Values for $\Delta\nu_D$ at 298 K for the oxygen atom lines of interest are: 0.238 cm^{-1} (4.03×10^{-4} nm) for λ 130.22 nm, 0.299 cm^{-1} (3.23×10^{-4} nm) for λ 103.92 nm, and 0.318 cm^{-1} (3.03×10^{-4} nm) for λ 97.65 nm.

The phenomena leading to a Lorentzian line profile can be divided into two groups. These are: (i) natural broadening, which arises from the Heisenberg Uncertainty Principle; and (ii) the several types of collision broadening, which include Lorentz, Holtzmark and Stark broadening.[1] For the case of a resonance transition (where the lower state has an infinite lifetime), the natural line width ($\Delta\nu_N$) reduces to the simple form of eqn (IV),[9]

$$\Delta\nu_N = 1/2\pi\tau c = (4\pi e^2/mc^2)\sum_i g_i f_{iu}/g_u \lambda_{iu}^2 \tag{IV}$$

τ is the lifetime of the upper state (u) with respect to all transitions to all lower states (i), and m is the electron rest mass. In the case of the 130.22 nm transition ($3s-2p^4$), we need consider only transitions to the three J levels of the ground state. In conjunction with the well-established f-value (0.048—see table 2), the value $\Delta\nu_N = 3.01 \times 10^{-3}$ cm^{-1} for the 130 22 nm line is then obtained. The f-value results given in table 3 and in ref. (10) established that the natural widths were $\Delta\nu_N = 6.80 \times 10^{-4}$ cm^{-1} for λ 103.92 nm and 2.27×10^{-4} for λ 97.65 nm. It is clear, therefore, that even for the strongest 130.22 nm line, $\Delta\nu_N$ is two orders of magnitude less than $\Delta\nu_D$ at 298 K. Contributions to the absorption from the natural line width can be safely neglected for all save extremely large absorbances involving radiation trapping ($k_0 l > 10$).

TABLE 2.—OSCILLATOR STRENGTHS FOR THE 130.22 nm, $3s-2p^4$, TRANSITION

f-value	method	reference
0.045 ± 0.010	line absorption	this work
0.047 ± 0.009	line absorption	3
0.046 ± 0.001	lifetime (time-resolved)	27
0.050 ± 0.009	lifetime (phase shift)	28
0.049 ± 0.011	wall-stabilized arc	29
0.047 ± 0.005	beam foil	30
$0.050 \pm 0.005_5$ *		
$0.047_5 \pm 0.00_5$	beam foil	31
0.052 ± 0.005	line absorption	32
0.050 ± 0.004	beam foil	33

* measured at 130.5 nm.

The magnitude of Holtzmark or self-broadening, $\Delta\nu_H$, is dependent upon the f-value of the relevant line, as well as on the density of like atoms in the system[11]:

$$\Delta\nu_H{}^{\dagger} = 0.0229(8\pi e^2/mc^2)(g_i/g_u)Nf\lambda_0. \tag{V}$$

The maximum value for $\Delta\nu_H$ in our work was for the λ 130.22 nm line with $N \simeq 10^{13}$ cm^{-3}, where its magnitude was 2×10^{-6} cm^{-1}. This value is clearly negligible compared with $\Delta\nu_D$ (or $\Delta\nu_N$), and Holtzmark broadening can be neglected in this work.

Lorentz or foreign-gas collisional broadening arises from perturbations to the energy levels of the emitting species by van der Waals interactions with the perturbing molecule or atom. Its magnitude is given approximately by the simple expression (IV)[12]:

$$\Delta\nu_L = 8.34 \times 10^2 (T/\mu)^{0.3} (\Delta C_6)^{0.4} N \tag{VI}$$

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† In ref. (4) this quantity ($\Delta\nu_H$) was inadvertently given as a factor of 2 greater.

where μ is the reduced mass of the colliding species, and ΔC_6 (erg cm^6) is the difference between the dispersion coefficients for the upper-state perturber system and the lower-state perturber system. The small ground-state interaction was neglected, and the excited state broadening was estimated by calculating dispersion coefficients based upon the Slater–Kirkwood approximation. Since excited-state physical properties are not well known, we have had to make estimates of the excited oxygen atom polarizabilities by the method of Slater orbitals.[13] Although the accuracy of this method for excited states is expected to be low, the calculated line widths should be reasonably accurate, since $\Delta\nu_L$ depends upon the polarizability only to the 0.4th power. Our calculated polarizabilities for the $3s$, $4s$ and $5s$ excited ^3S oxygen atoms are 1.16×10^{-29}, 4.82×10^{-27} and 8.53×10^{-27} m^3 respectively. These values lead to Lorentz line widths of about 9.7×10^{-4}, 4.0×10^{-3} and 4.3×10^{-3} cm^{-1} in the absorption cell ($N \simeq 8 \times 10^{16}$ helium atoms cm^{-3}) for the $3s$, $4s$ and $5s$ states respectively. In the lamp ($N \simeq 1.4 \times 10^{17}$ helium atoms cm^{-3}) the values of $\Delta\nu_L$ are 1.5×10^{-3}, 6.7×10^{-3} and 7.7×10^{-3} cm^{-1} in the same order. The results of these calculations show that although Lorentz broadening was always much less than Doppler broadening in our work, $\Delta\nu_L$ and $\Delta\nu_N$ become comparable in magnitude at helium pressures in the order of 65 000 Pa (500 Torr). In fact, in flash photolysis—atomic resonance studies at λ 130.22 nm with much higher total pressures, the Lorentzian tail of the absorption coefficient curve (*i.e.*, k_ν as a function of ν) is expected to modify appreciably resonance absorption phenomena based on Doppler line models. For instance, at 1 atmos. pressure of He, $\Delta\nu_L/\Delta\nu_D = 1.2$ for λ 130.22 nm.

Stark broadening results when the local electric field near an electron or ion leads to a splitting in the energy levels of an atom with which the electron or ion is colliding. Most neutral atoms show a quadratic Stark effect, which is only of large magnitude for plasmas with high charged-particle densities. Unfortunately, the Stark effect gives line shapes which are difficult to describe analytically. But for weakly-ionized plasmas, such as in low-power microwave discharges, one may employ the impact approximation for electrons and ignore contributions from ions. The Stark broadening then gives rise to a Lorentzian whose width, $\Delta\nu_S$, is given by (VII),[14]

$$\Delta\nu_S = (38.8/2\pi)C_4{}^{2/3}\, V_e{}^{1/3}\, N_e \qquad \text{(VII)}$$

where $C_4 = 6.15 \times 10^{-15}$ times the Stark displacement (in cm^{-1}) for a field of 10^5 V cm^{-1}. The Stark displacement is $5.6 \times 10^{20}\ \alpha$,[15] where α (cm^3) is the polarizability of the species of interest. N_e (cm^{-3}) is the electron density and V_e (cm s^{-1}) is the mean electron velocity. Eqn (VII) and the polarizabilities, as estimated above, give Stark widths of 8.3×10^{-7}, 4.7×10^{-5} and 7.0×10^{-5} cm^{-1} for the $3s$, $4s$ and $5s$ transitions, respectively. These results assumed an electron temperature of 5000 K, which is not a critical parameter, since T enters the formula for $\Delta\nu_a$ only to the one-sixth power. The electron density was taken to be 10^{12} cm^{-3}, which is the maximum value expected for a low-power microwave discharge. We conclude that the estimates for $\Delta\nu_S$ thus obtained are two to three orders of magnitude less than the Lorentz line widths, $\Delta\nu_L$.

In summary, the only parameter determing the spectral distributions of the emission line and of the absorption coefficient is Doppler broadening, with a small (often negligible) contribution from Lorentz and natural broadening.

DOPPLER LINE MODELS IN ABSORPTION MEASUREMENTS

The determination of *f*-values from line absorption measurements with Doppler line models has been discussed previously.[1-5] We have used a computer program developed previously for this purpose.[4, 5] This program takes account of a limited contribution to the line profile from Lorentzian broadening, and includes integration by Gaussian quadrature using the form of the Voigt profile given by Reiche.[7] The object of the program is to evaluate the optical depth in the absorber, k_0l, as a function of fractional absorption, A, and absorber concentration, N. f-values may then be directly determined from eqn (VIII),

$$k_0l = \frac{2}{\Delta\nu_D}\left(\frac{\ln 2}{\pi}\right)^{\frac{1}{2}} \frac{\pi e^2}{mc} Nfl. \qquad \text{(VIII)}$$

k_0l is a function not only of A and of N, but also of the optical depth k_0m in any self-reversing layer in the lamp, and in addition, of the ratio α^2 of source and absorber temperatures; $\alpha^2 = T_s/T_a$. The parameters of importance in the present problem are summarized in eqn (IX):

$$k_0l = g(A, N, k_0m, \alpha). \qquad \text{(IX)}$$

Minor variables are B and C, equal to $[\surd(\ln 2).\Delta\nu_D/(\Delta\nu_N+\Delta\nu_L)]$ for the absorber and emitter respectively; these were included to account for small amounts of Lorentzian broadening. Neglect of Lorentzian broadening terms would amount to, at most, a 2 % reduction in the f-value; they will not be discussed further.

The experimental measurements were sets of values of A and N. The objective was thus first to determine the best values of the secondary parameters k_0m and α, and then to compute the corresponding k_0l value for each pair of A, N values [see eqn (IX)]. The two-layer model was used to calculate k_0m, based on final values of the oscillator strength. Since the self-reversal in the source was always minimized, k_0m was always <1, and the function of eqn (IX) was, therefore, rather insensitive to k_0m. This matter is discussed more fully below.

The parameter α, equal to $\surd(T_s/T_a)$, is a more important one in determining k_0l (and hence f-values), and this quantity is additionally very uncertain for absorption experiments with most resonance lamps. It was practicable in our work to develop a technique for determining α, as described below.

No physical significance is attached to α in this analysis, the object of which was to parameterize the frequency distribution of the source.[1] An analogy with this approach is the common use of an equivalent Boltzmann temperature to characterize an energy distribution which may not be an equilibrium distribution.

EXPERIMENTAL

The apparatus for studies of atomic resonance phenomena in the far vacuum ultraviolet has been described previously.[16] In outline, it consisted of a resonance lamp, an absorption cell through which known concentrations of O ^3P_J atoms flowed, and a monochromator. The lamp was a 2.45 GHz discharge in helium, to which was added a trace of oxygen for the studies on the weaker 103.92 nm and 97.65 nm lines. Traces of residual oxygen or water in the helium left after purification with a refrigerant trap at 77 K, sufficed for the studies on the strong 130.22 nm line. The monochromator was a 1 m normal-incidence type (Hilger and Watts E760) and the grating was a Pt-overcoated replica blazed at 90 nm in the first order, with 600 line mm^{-1} and three equal, separately-ruled areas in total 96 × 56 mm (Bausch and Lomb). The detector was an E.M.I. 9789Q photomultiplier cell, and a sodium salicylate phosphor, showing a mean dark count of 1.5 s^{-1} at 290 K and at 850 V e.h.t.

All solid window materials absorb strongly below 105 nm; hence collimated hole structures (Brunswick Corporation) were used to separate the lamp from the absorption cell, the absorption cell from a buffer volume, and the buffer volume from the monochromator [see fig. 1 of ref (16)]. The narrow parallel channels of the collimated hole structures [16] restricted the diffusion of gas between the sections of the apparatus, whilst allowing 40 % transmission of on-axis light. Off-axis light (>5° off-axis) is not transmitted, thus reducing scattered light from the lamp below detectable limits.

Ground state oxygen atom concentrations were determined by using the N+NO reactions to produce O ^3P_J atoms in the presence of a large excess of N ^4S atoms (from a microwave discharge in N_2+Ar). With [N ^4S] $> 2\times10^{13}$ cm^{-3}, the reaction, $N+NO \rightarrow N_2+O$, was >99 % complete within 10 ms under the conditions used. The concentration of O ^3P_J absorbers, N, was then simply taken to be $(F_{NO}/\Sigma F)\times[M]$; where F_{NO} is the flow (mol s^{-1}) of nitric oxide added, ΣF is the total mass flow rate, and $[M]$ the total concentration in the absorption cell.

A small correction to N was required because there was some gas flow into the absorption cell, from the lamp and from the buffer volume. All these flows could be measured, but there remained some uncertainty regarding the appropriate total mass flow rate to be used in the absorption cell, which uncertainty we estimate to be ±13 %. A second correction was necessary, in this case, for the path length over which absorption took place. This arose because of the existence of a small dead volume in the absorption path, and once again some uncertainty, in this case about the true path length, remained. We took the path length to be the diameter of the flow tube (3.4 cm) plus one-half of the length of the side-arm (0.75 cm). The maximum error introduced was ±18 %. It appears, from the excellent agreement with the literature of our f-value for the 130.2 nm transition, that neither of these uncertainties introduced serious error, or alternatively, that the errors cancelled out.

Fig. 1 shows part of the spectrum of the oxygen atom resonance lamp, between 95 and 105 nm, using FWHM resolution of 0.07 nm. As well as the very strong $3s\ ^3S-2p^4\ ^3P_J$ triplet near 130 nm, and the much weaker $4s\ ^3S-2p^4\ ^3P_J$ and $5s\ ^3S-2p^4\ ^3P_J$ triplets, many other (some fairly intense) resonance multiplets were observed. Most of these would be feasible for f-value determination, although complete spectral resolution within the $^3D-^3P$ multiplets would not be practicable.

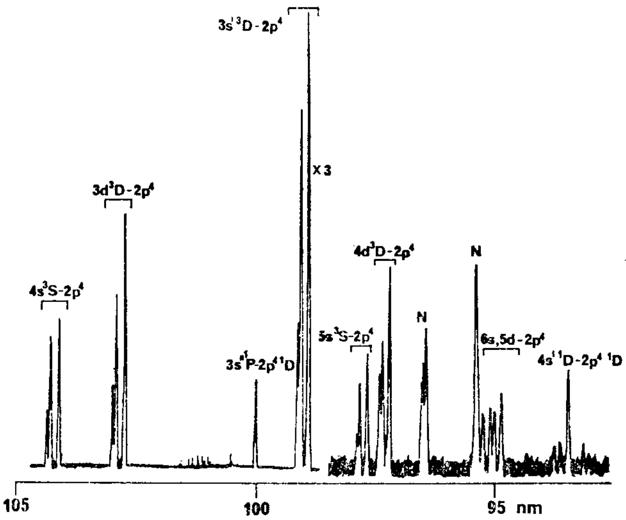

FIG. 1.—Spectrum of far-u.v. oxygen atom resonance lamp, showing $3s$–$2p^4$, $4s$–$2p^4$, $5s$–$2p^4$ and other resonance multiplets of O. λ 93 to 98 nm (300 Hz full-scale); λ 98 to 105 nm (1000 Hz full-scale).

RESULTS

LINE REVERSAL AND THE DETERMINATION OF k_0m

The extent of self-reversal in the lamp, as measured by k_0m, could be determined experimentally. The observed oxygen atom emission ($ns\ ^3S$–$2p^4\ ^3P_{2,1,0}$) are triplets, with a single upper state emitting to a ground state consisting of three separate J sublevels. The intensity ratio of this triplet is 5 : 3 : 1 for emission to $J = 2, 1, 0$ in the absence of self-reversal. Small amounts of self-reversal will reduce the intensity ratios ($^3P_2 : {}^3P_1 : {}^3P_0$), since the lowest $J = 2$ level possesses a much greater Boltzmann population (74 %) at 300 K than the intermediate $J = 1$ level (20 %) and the highest $J = 0$ level (6 %). Thus the fractional absorption is greatest for the $J = 2$ transition and least for the $J = 0$ transition.

The computer program based on the two-layer model was used to calculate relative lamp intensities ($^3P_2 : {}^3P_1 : {}^3P_0$) as a function of k_0m. The results were then compared with experiments and the appropriate k_0m value for the $J = 2$ transition was determined. (The procedure is similar in principle to that described by Braun and Carrington [17] and Kaufman and Parkes [2]). The lamp temperature was taken to be 1000 K, in accordance with the present results for α (see below), and the f-value for the 130 nm multiplet was the mean value of table 2.

The experimental intensity ratio for the $3s\,{}^3S$–$2p^4\,{}^3P_J$ (130 nm) was 4.6 : 2.9 : 1, which corresponded to $k_0m = 0.15$ for the ^3S–$^3P_2$ line. Anticipating the results of the following sections, we found that inclusion of this amount of self-reversal in the analysis resulted in a 6 % upwards correction to the final f-value.

Because of lack of intensity, we were able to fully resolve only the triplet of the $3s\,{}^3S$–$2p^4\,{}^3P_J$ transition between 130.2 and 130.6 nm. Therefore, to determine k_0m values for the weaker $4s$–$2p^4$ and $5s$–$2p^4$ triplets, measurements of k_0m for the $3s$–$2p^4$ triplet were made. This value of k_0m was then multiplied by the appropriate ratio of f-values to obtain k_0m for the other triplets; *e.g.*, for the $4s$–$2p^4$ triplet, k_0m (103.92 nm) $= k_0m\,(130.22) \times (f(103.92)/f(130.22))$.

For the 103.92 nm studies, higher concentrations of oxygen atoms in the lamp than for the 130.22 nm work were used, resulting in a measured $^3P_2 : {}^3P_1 : {}^3P_0$ intensity ratio for the $3s$–$2p^4$ triplet equal to 3.5 : 2.7 : 1. This gave $k_0m = 0.6$ for the 130.22 nm line, and hence $k_0m = 0.08$ for the 103.92 nm line. At still higher lamp oxygen atom concentration, similar results for the 97.65 nm line, $5s$–$2p^4$, gave $k_0m = 0.07$ derived from the datum $k_0m = 2.2$ for the 103.22 nm line. The small amounts of self-reversal for the two higher energy transitions led to negligible corrections in the final f-values for the 103.92 nm and the 97.65 nm transitions.

f-VALUE FOR THE 130.22 nm LINE, AND THE DETERMINATION OF α

In fig. 2, we have plotted values of k_0l (derived from measurements of A via computation—see above), against N, for the 130.22 nm line; N is equal to $\Sigma[\mathrm{O}\ {}^3P_J]$. According to eqn (VIII), this plot should be linear over the whole range of k_0l, if the correct choice of α has been made. As shown in fig. 2, the plot of k_0l against N is linear for $\alpha = 1.8$, but not for $\alpha = 2.5$ (positive curvature), nor for $\alpha = 1.5$ (negative curvature). Since direct measurement of α is inappropriate, we used the linearity of k_0l against N plots to determine α. The value of α was chosen by minimizing the quadratic term in least squares polynomial fits of k_0l against N which were generated for different choices of α. Our data extended to sufficiently high k_0l that α could be determined to better than ± 0.1. It was found unnecessary to correct the results for self-reversal in the lamp.

One effect that could invalidate analysis would be significant contributions to the light signal in the presence of absorbing O atoms from fluorescent scattering.[2] Some of the light absorbed by the O atoms in the absorption cell would be re-emitted in the direction of the detector, thus increasing the transmitted light signal. This re-emission would have an increasingly large effect on the absorption measurements as the optical depth is increased. The determination of A would thus be low, leading to an underestimate of the optical depth, k_0l, in the absorption cell. The effect of fluorescent scattering is readily observed in plots of k_0l against N, for data taken using a non-collimated lamp, at optical depths as low as 1.5 to 2.0.[2] The collimated hole structures used in our apparatus so severely restricted the fields of view from the lamp, and of the detector, that an insignificant number of re-emitted photons is expected at the detector. This expectation was verified directly: no resonance fluorescence could ever be seen under conditions similar to those of the absorption experiments.

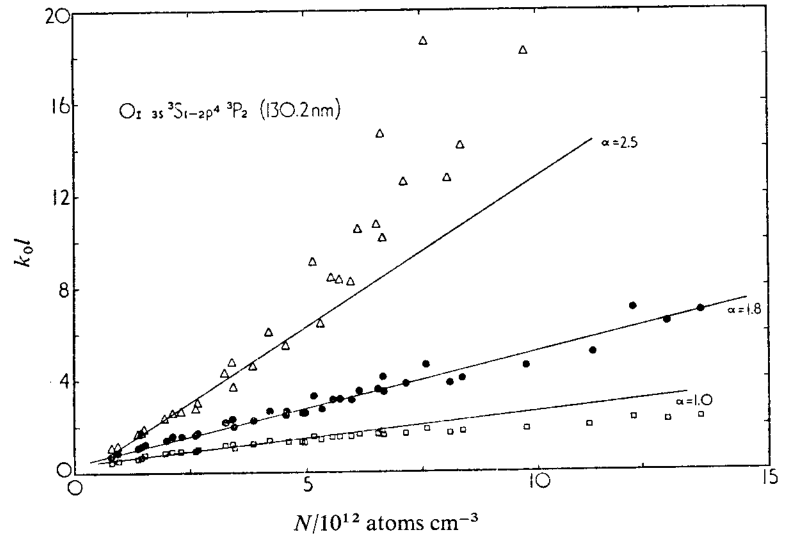

FIG. 2.—Variation of optical depth k_0l with atom concentration for the 130.22 nm line, showing various choices of α.

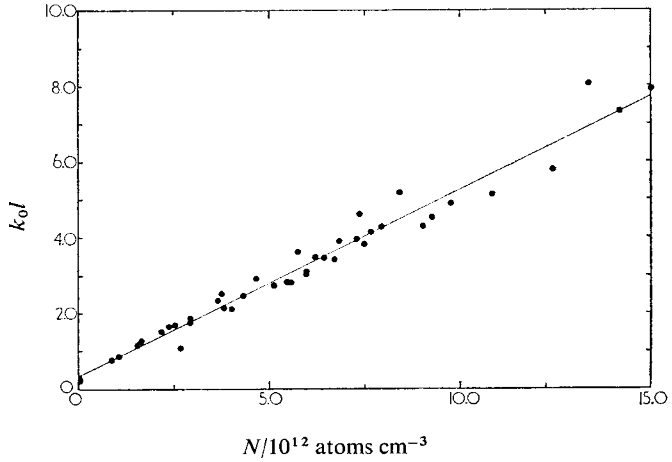

FIG. 3.—Variation of k_0l with N for the 130.22 nm line: determination of f-value. ($\alpha = 1.8$). $f = 0.045 \pm 4$ %.

The present value, $\alpha = (1.8 \pm 0.1)$, is, therefore, likely to be free from major systematic errors. When this value of α was used with our experimental absorption results at λ 130.2 nm (see below), the resulting f-value was within 10 % of most of the other recent determinations of f (see table 1). This finding adds extra weight to our method for determining α.

Fig. 3 shows a plot of k_0l against N, with $\alpha = 1.8$, for the absorption experiments at 130.22 nm. The plot is a composite of six independent experiments, each including about 20 data points. Some of the scatter in the data shown (fig. 3, 4 and 5) results from slight changes in the residual O-atom concentration present in the N atom flow before NO is added. The small positive intercepts in fig. 3 (also in fig. 4) are attributed to the residual O atom concentrations. The final result, $f = (0.045 \pm 0.004)(2\sigma)$[†], was the mean value obtained from least mean squares fits (of k_0l against N plots) to each of the six separate experiments.

f-VALUES FOR THE 103.92 nm AND 97.65 nm LINES

Fig. 4 and 5 show plots of k_0l against N, with $\alpha = 1.8$, for the absorption experiments at 103.92 nm and at 97.65 nm. Seven independent sets of experiments in each case were carried out. The analysis for the $4s$–$2p^4$ 103.92 nm line was exactly as described for the 130.22 nm line, and the result was $f = (0.0059 \pm 0.0007)$[*].

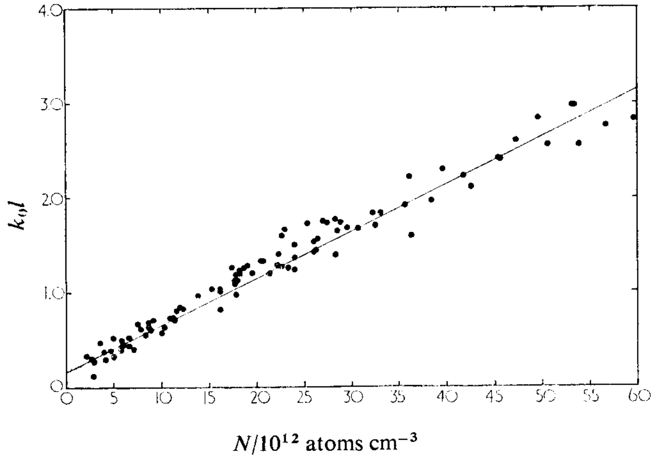

FIG. 4.—Variation of k_0l with N for the 103.92 nm line: determination of f-value. ($\alpha = 1.8$). $f = 0.0059 \pm 5.5$ %.

The scatter of the 97.65 nm, $5s$–$2p^4$ data, was considerably greater than that of the 130.22 nm and 103.92 nm results, as expected on account of the low count rates used ($I_0 \simeq 22$ Hz at 97.65 nm). In this case, the data were analyzed in two ways. First, the residual O atom concentration was measured using the (already calibrated) 130.22 nm absorption, and all the O atom concentrations in the 97.65 nm studies were corrected accordingly. This results in the full line through the origin shown in fig. 5. However, there appeared to be a slight deviation, marginally significant, of our data from this line at high N. Therefore, we fitted the data by a linear least squares procedure, to give the broken line (and finite intercept) also shown in fig. 5. This intercept, if significant, suggests that the residual N may have been slightly overestimated.

[†] This is the statistical uncertainty. The overall uncertainty is taken to be the square root of the sum of squares of the uncertainties in l (±18 %), N (±13 %) and in the gradient k_0l ($2\sigma = \pm 8$ %). Thus the overall uncertainty for the 130.22 nm f-value is ±23 %.

[*] Overall uncertainty is ±25 %.

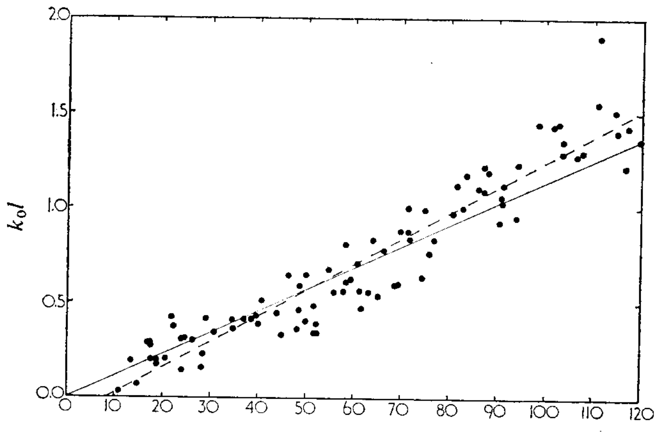

FIG. 5.—Variation of k_0l with N for the 97.65 nm line: determination of f-value. ($\alpha = 1.8$). $f_{\text{slope}} = 0.0016 \pm 11$ %, $f_{k_0l}/[\text{O}] = 0.0014 \pm 5$ %.

However, since the error limits of the gradients of both lines (fig. 5) overlapped, we took the mean of these gradients to give the best estimate of f for the 97.65 nm line:

$$f = (0.0015 \pm 0.0004).^{\dagger}$$

DISCUSSION

The final f-values for the $3s$–$2p^4$, $4s$–$2p^4$ and $5s$–$2p^4$ ^3S–^3P_J transitions are summarized in table 3. The quoted error limits include allowance for uncertainty in mass flow rate and absorption path length (see Experimental section). They are probably unduly conservative, in view of the excellent agreement of the f-value for the $3s$–$2p^4$ transition with recent literature (table 2). The relative f-values should be reliable to within the statistical uncertainties given above. Table 2 lists our value for the oscillator strength of the 130.22 nm transition, along with a comparison of nine other recently reported values for this quantity. The mean of the ten values listed is (0.048 ± 0.004) (2σ), where the mean was obtained by weighting each value by the inverse of the reported error limits. The f-value for the 130.2 nm transition is thus known to good precision. The results listed in table 2 were obtained by a number of different methods, but no one method appears to show a consistent difference from the results obtained by other methods. Transition probabilities obtained by various lifetime

TABLE 3.—COMPARISON OF f-VALUES BETWEEN EXPERIMENT AND THEORY

n	f/experiment	inverse cube extrapolation of expt.	Kelley [21] [a]	Kelley [21] [b]	Kazaks *et al.*[20]	Armstrong and Purdum [22]	Wilson and Nicolet [25]
3	0.045 ±0.010	0.049	0.059	0.047	0.056	0.030	0.047
4	0.0059±0.0015	0.0054	0.0066	0.0067	0.008	0.0063	0.0022
5	0.0015±0.005	0.0015	0.0017	0.0017_5	0.003	0.0029	5.8×10^{-4}
6		6.4×10^{-4}	6.6×10^{-4}	6.8×10^{-4}	0.0015	0.0017	2.2×10^{-4}
7		3.2×10^{-4}	3.2×10^{-4}	3.3×10^{-4}	8×10^{-4}	7×10^{-4}	
8		1.8×10^{-4}	1.9×10^{-4}	1.9×10^{-4}	5×10^{-4}	1.3×10^{-4}	

[a] based on calculated transition energies; [b] based on true transition energies.

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† Overall uncertainty is ±33 %.

measurement methods have at times been regarded with a certain scepticism [18] since cascade from longer-lived upper states sometimes masks the true lifetime of the state under study. Thus, the measured lifetime may be too long, resulting in an oscillator strength which is too small. This cascade problem evidently does not affect the more recent lifetime determinations, since they yield results consistent to within a few per cent with values obtained from other methods.

In the hydrogen atom, oscillator strengths for any Rydberg series fall off as n^{-3}.[19] For hydrogen-like transitions in a series, the oscillator strengths would vary with n as indicated by eqn (X),[20]

$$f_n = f_1^*/(n-\delta_1)^3 \tag{X}$$

where f_n is the oscillator strength of the transition from the state with principal quantum number n, f_1^* is a constant and δ_1 is a quantum defect. This equation can be rearranged to give a linear relationship (XI) between the inverse cube root of the f-value and the principal quantum number:

$$f_n^{-\frac{1}{3}} = f_1^{*-\frac{1}{3}}\delta_1 + f_1^{*-\frac{1}{3}}n. \tag{XI}$$

Our experimental data are plotted according to eqn (XI) in fig. 6. The straight line through the points is derived from least squares fit, which gave values of $f^* = 0.0384$ and $\delta_1 = 2.08$. Our experimentally-determined parameters of the inverse cube law, allowed the calculation of the oscillator strengths of the higher-lying transitions in the series. Since oxygen has been the subject of several theoretical studies, an experimental check is provided for the calculated values of f for the principal resonance series of oxygen.

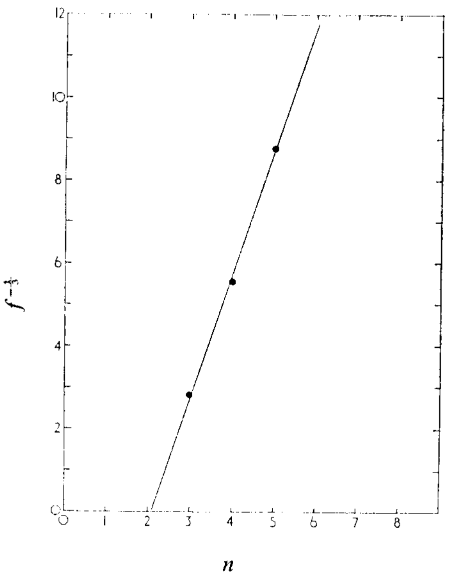

FIG. 6.—Rydberg series oscillator strength (f) $ns\ ^3S$–$2p^4\ ^3P_2$. Variation of $f^{-\frac{1}{3}}$ with principal quantum number n.

Table 3 lists our experimental f-values, the values corresponding to our best-fit parameters to the inverse cube law, and those from several theoretical studies. Both Kelley [21] and Armstrong and Purdum [22] list values of σ^2, rather than the f-value for the transition. The f-values listed in table 3 from these authors were calculated according to eqn (XII):[23]

$$f = 0.333\Delta E.\mathbf{S}/g, \qquad \text{(XII)}$$

where ΔE is the energy difference between the two states involved in the transition in Rydbergs, g is the statistical weight of the lower state, and $\mathbf{S}$ is the absolute line strength of the transition, which is given by

$$\mathbf{S} = S(L)S(M)\sigma^2. \qquad \text{(XIII)}$$

In eqn (XIII), $S(L)$ is the relative line strength of the particular line, $S(M)$ is the multiplet strength, and σ^2 is the term which accounts for overlap in the radial matrix elements of the two states involved in the transition. $S(L)$ and $S(M)$ were taken from the tables of Shore and Menzel which are based upon L–S coupling.[24]

The results of Kelley [21] are in excellent agreement with the present results, based upon the inverse cube root extrapolation, especially if one takes the true transition energies rather than those calculated from Kelley's Hartree–Fock–Slater wave functions. The values of Kazaks *et al.*[20] based upon an independent particle model, are too large. For $n > 5$ their values are about a factor of 2.5 larger than our own numbers. The results of Armstrong and Purdum [22] based in part upon the Coulomb approximation, are about a factor of two larger than the present results for $n > 5$. Wilson and Nicolet,[25] on the other hand, report values which are about a factor of 2.5 smaller than the present results. Their values are taken from a report by Armstrong, Johnston and Kelley.[26]

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