Transition probabilities for the 3s $^3S^0-4p$ ^3P and 3s $^5S^0-4p$ ^5P multiplets in O I

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We have measured the atomic transition probabilities of two weak $E1$ multiplets in neutral oxygen for which advanced atomic structure calculations have encountered problems due to severe cancellation of positive and negative parts of the transition integrand. Measurements were made in emission from a wall-stabilized arc. Our results differ significantly from those of all recent calculations. [S1050-2947(98)05206-8]

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INTRODUCTION

The $3s$ $^3S^0-4p$ ^3P and $3s$ $^5S^0-4p$ ^5P multiplets in neutral oxygen are attractive for diagnostic studies of laboratory and astrophysical plasmas because they are fairly well isolated from other oxygen lines and appear, under typical laboratory conditions, as single features with their component lines almost coinciding. However, theoretical calculations for the radiative transition probabilities of these multiplets have encountered considerable problems due to appreciable cancellation of positive and negative parts of the transition integrand. Recent sophisticated calculations by Hibbert *et al.* [1], Butler and Zeippen [2], Bell and Hibbert [3], and Pradhan and Saraph [4] all contain detailed configuration-interaction treatments. Hibbert *et al.* [1] calculated their wave functions with the CIV 3 atomic structure code and included about 450 configuration state functions for both upper and lower states in their configuration-interaction approach. The calculations by Butler and Zeippen [2] were part of the International Opacity Project [5] and were carried out with the R-matrix code. This as well as the CIV 3 code was also utilized by Bell and Hibbert [3] in their calculations of selected O I multiplets. Pradhan and Saraph [4] performed their calculations with the frozen-core approximation, an approach similar to the R-matrix method, but they constructed their wave functions on a less elaborate scale. Due to the cancellation problem encountered by all calculations for these two weak transitions, accurate experimental measurements are desirable, first for testing the reliability of the recent calculations in handling cancellations in the transition integral and second to get values with improved accuracy for diagnostic studies. We report here on such accurate measurements.

EXPERIMENT

The experiment has been carried out with a wall-stabilized arc discharge and the spectra were taken photoelectrically with a 2-m Czerny-Turner monochromator equipped with a photomultiplier. The arc source and experimental setup have been previously described in detail [6,7], so only a brief description is given here. The arc plasma is confined within a cylindrical channel, 50 mm long and 4 mm in diameter, formed by water-cooled copper plates. The arc was operated with several mixtures of oxygen and other gases in different proportions as discussed below. These gas mixtures are obtained by controlling flow rates of the respective gases into the arc chamber. Maintaining constant flow rates at atmospheric pressure results in stable operating conditions. Oxygen was added only to the midsection of the arc, well away from the electrodes. In this region the arc is approximately homogeneous along its axis (within a small cylindrical volume). The arc plasma was observed "end on," along the axis, with a solid angle of 3×10^{-4} sr (f/50). Spectral scans were made of each spectral line. Signals were recorded at wavelength intervals spaced to get 20 or more measurements on each line profile. To obtain the line intensities, the continuum background was first subtracted, a spline function was fitted to the line profile, and the spline function was integrated. The omission of small fractions of the line intensities in the far wings of each line was estimated to not significantly affect the *relative* line intensities since all investigated lines are treated in the same manner. A tungsten strip lamp calibrated by the Optical Technology Division at NIST was used as a radiometric standard to calibrate the relative response with wavelength of the spectrometer and optical system. All spectral lines were checked for self-absorption by a method using a concave mirror behind the arc [8]. This mirror reflected the light back along its path, focusing it at the position of the plasma. The light intensity in the forward beam thus would be doubled were it not for that portion of the reflected beam lost by imperfect reflection and window transmission as well as possible self-absorption. The optical depth $\tau(\lambda)$ of the plasma is determined from the ratio of the signal with the mirror included to that with the mirror blocked. Losses from mirror reflection and window transmission are determined from the same ratio measured at a nearby wavelength where self-absorption is negligible for the continuum radiation emitted from the plasma. If the optical depth τ is small, i.e., $\tau<1$, the amount of self-absorption may be accurately calculated and the intensity that would have been emitted from the same plasma if it were optically thin (the intensity related to the transition probabilities in the equations below) could be determined.

METHOD

We have measured the intensities of the weak $3s$ $^3S^0-4p$ ^3P and $3s$ $^5S^0-4p$ ^5P multiplets at 436.8 and 394.7 nm relative to five strong multiplets of O I: $3s$ $^5S^0-3p$ ^5P at 777.3 nm, $3p$ ^5P-5s $^5S^0$ at 645.5 nm, $3p$ ^5P-4d $^5D^0$ at 615.7 nm, $3s$ $^1D^0-3p$ ^1D at 715.6 nm, and $3p\ ^3P-5s\ ^3S^0$ at 725.4 nm. These strong multiplets were chosen as reference lines since their transition probabilities have been accurately determined by sophisticated calculational methods, mainly in Refs. [1,2]. The results are in close agreement, their calculations are not subject to significant cancellation effects, and the uncertainties of the averaged transition probabilities are estimated to be smaller than ±10% [9].

We have measured the relative intensities I_M of the above-noted multiplets and utilized them to construct a Boltzmann plot. This technique is usually applied to determine the excitation temperatures of plasmas that are (at least) in partial local thermodynamic equilibrium (PLTE) [10], but we have used it to derive transition probabilities as discussed below. For LTE plasmas, the population of excited atomic levels of energies E_k follow Boltzmann statistics. Emission multiplet intensities may thus be expressed as [10]

$$I_M=[hcg_k l/4\pi\lambda_0 U(T)]AN\exp(-E_k/k_BT),$$

where I_M denotes the measured multiplet intensity, g_k the statistical weight of the upper term k, l the length of the emitting plasma, λ_0 the average multiplet wavelength, $U(T)$ the partition function, T the temperature, A the transition probability, N the atomic density, and E_k the energy of level k. Rearrangement and logarithmization of this relation yields

$$\ln(I_M\lambda_0/Ag_k)=-E_k/k_BT+\ln[hclN/4\pi U(T)]$$
$$=-E_k/k_BT+C. \quad (1)$$

For a specific plasma of given length l and fixed temperature T, the quantities collected in the second term on the right-hand side of the equation are a common constant for all lines of a given species. Equation (1) may be considered as the equation for a straight line, with the quantities $\ln(I_M\lambda_0/Ag_k)$ and E_k as variables, and a slope of $-1/k_BT$. Thus the determination of intensities I_M for several multiplets of different excitation energies E_k will yield the excitation temperature from such a ''Boltzmann plot.'' Full equilibrium to the ground state is no longer required since the magnitude of N is immaterial and only PLTE among the atoms in excited states E_k is required.

DISCUSSION OF MEASUREMENTS

We have constructed Boltzmann plots from the five O I multiplets listed above. These yield the excitation temperature, but also allow us to derive the A values of the two weak multiplets at 394.7 and 436.8 nm by fitting them to the Boltzmann plot utilizing their measured intensities. Measurements of the transition probabilities of the two weak $3s$-$4p$ multiplets were undertaken with three different operating conditions.

(a) The first experiments were made with a mixture composed of mostly helium, containing about 2% oxygen by volume. A few percent of argon was also added to increase the arc stability at the electrodes. The high concentration of helium gave a lower electron density, with a corresponding smaller value of continuum intensity and narrower emission lines than would be the case for a predominantly argon or oxygen arc. This condition was chosen for better line-to-

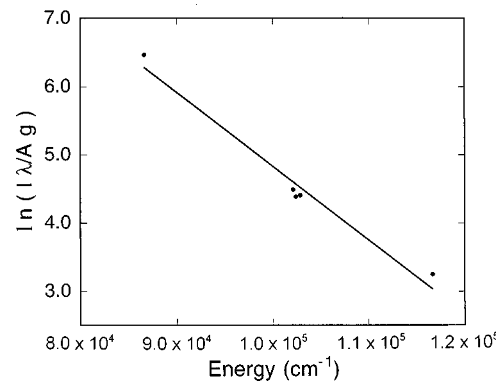

FIG. 1. Boltzmann plot for O I multiplets in helium-oxygen plasma, containing 2% oxygen by volume.

continuum ratios, allowing for more accurate relative line intensity measurements. The lines were determined to be optically thin except for the multiplet at 777.3 nm. For this strong multiplet, only the weakest component, which was well separated from the other components, was measured. The oxygen concentration was limited to an amount such that the self-absorption correction for this line was only a few percent in all runs in which it was included. For smaller concentrations of oxygen, the weaker lines could not be accurately measured. After measuring the relative multiplet intensities, a Boltzmann plot was constructed for the five multiplets for which the A values are accurately known from calculations. The resulting plot for a measurement made with the above conditions is shown in Fig. 1. The straight line is a least-squares fit to the points. Clearly, the points do not lie on a straight line, as should be the case for a Boltzmann distribution of excited-state populations. According to a criterion independently established by Wilson [11] and Griem [12], a state of partial local thermodynamic equilibrium should exist for atomic states with $n\geqslant 3$ in plasmas with ionization potentials similar to that of hydrogen if the electron density is 2×10^{14} cm^{-3} or higher. In order to determine the electron density N_e, we admixed a small amount of hydrogen, about 1%, to measure the width of the line H_β, for which Stark broadening is the predominant broadening mechanism. Using calculated results [13] for this linewidth as a function of N_e, a value of 7×10^{15} cm^{-3} is obtained for the electron density, which is well above the value required for PLTE according to Wilson's and Griem's criterion. However, for stationary but inhomogeneous plasmas, Griem has also established another requirement that the spatial variation of the electron temperature be small over the diffusion length of the plasma atoms [14] which in this case are predominantly helium. An estimate of the diffusion length in the arc plasma according to Ref. [14] reveals that this condition is not satisfied: The average distance between equilibrating collisions is indeed greater than the arc diameter.

(b) Additional measurement were made in which appreciable amounts of nitrogen were added to the arc plasma. A typical mixture was about 60% helium, 2% oxygen, 10% argon, and 25% nitrogen by volume. The addition of nitrogen, having a lower ionization potential than helium, yields a considerably higher electron density and a smaller diffusion length, which are, for similar arc conditions, more likely to result in a Boltzmann distribution for the atomic level popu-

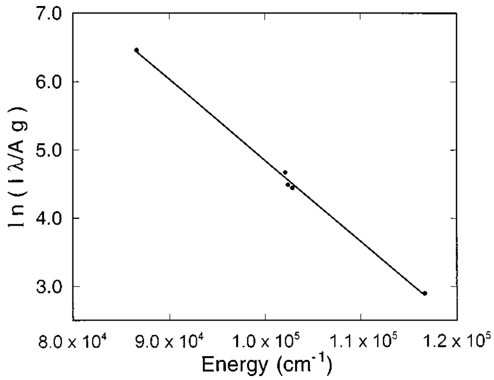

FIG. 2. Boltzmann plot for O I multiplets in plasma composed of 60% helium, 2% oxygen, 10% argon, and 25% nitrogen by volume.

lation densities. The oxygen line intensities were approximately the same as before. Figure 2 is a Boltzmann plot resulting from measurements on the oxygen lines from this plasma. In this case, the multiplets essentially do fall on a straight line, confirming that for this plasma a Boltzmann distribution indeed exists among the upper atomic levels of the measured multiplets. In order to determine the electron density in this plasma, again about 1% hydrogen was added and the width of H_β was measured as before. A density of 5×10^{16} cm^{-3}, a factor of 7 times greater than that for the previous gas mixture, was obtained. Also, the atomic diffusion length for this arc plasma, which is essentially determined by the argon and nitrogen contributions, was estimated to be 0.2 mm, a distance over which the temperature near the arc axis is approximately constant. Thus, for these conditions both equilibrium requirements are fulfilled. The transition probabilities of the multiplets at 436.8 and 394.7 nm could therefore be determined from the corresponding $\ln(I_M\lambda/Ag)$ values that fell exactly on the fitted line.

(c) Measurements were also undertaken with a higher concentration of oxygen: typically a gas mixture of about 70% helium, 15% argon, and 15% oxygen. Thus the oxygen concentration was increased by about a factor of 10 relative to the above conditions. With this condition, even the weakest line for the multiplet at 777.3 nm was appreciably self-absorbed and was therefore omitted from the analysis. Also, the multiplet at 715.6 nm became slightly self-absorbed. The mirror test, described earlier, was applied to determine this qualitatively and a correction of a few percent was required. Otherwise, the A values of the multiplets at 436.8 and 394.7 nm were determined in the same manner as described above. Excluding the line at 777.3 nm, the upper levels of the multiplets other than that at 715.6 nm do not cover a wide range, so that the fit of a straight line could not be used as evidence for PLTE. However, since the electron density and the atomic diffusion lengths are approximately equal to that in the gas mixture discussed immediately above a state of PLTE may be assumed for these operating conditions too.

TABLE I. Contributions to uncertainties in measured multiplet transition probabilities.

Contribution	436.8 nm	394.7 nm
standard deviation of mean	1.1%	1.9%
measurement of relative areas	4.0	4.0
A values of ''standard lines''	5.9	5.9
radiometric calibration	2.0	2.3
total uncertainty 1σ (root of sum of squares of above contributions)	7.5	7.7

RESULTS

Our final values were obtained by averaging the results of six independent measurement taken under conditions (b) and (c). The experiments with condition (a), which did not yield good Boltzmann plots, were not utilized. The results for the two different oxygen concentrations were in agreement within 2% and 4%, respectively, for the 436.8-nm and 394.7-nm multiplets. The contributions to the estimated uncertainties in our values are given in Table I. The total uncertainties given in the table are from combining these in quadrature.

TABLE II. Calculated and measured transition probabilities (in 10^5 s^{-1}) for two weak O I multiplets showing near cancellation in the $E1$ transition integral.

Source	$3s\ ^3S^0-4p\ ^3P$ (436.8 nm)	$3s\ ^5S^0-4p\ ^5P$ (394.7 nm)
Calculations		
Hibbert *et al.* (CIV 3) [1], dipole length	5.86	5.06
dipole velocity	9.48	3.92
Bell and Hibbert (R matrix) [3], dipole length	10.1	4.10
dipole velocity	2.52	0.542
Pradhan and Saraph (R matrix) [4], dipole length	11.2	4.67
Butler and Zeippen (Opacity Project, R matrix) [2], dipole length	9.01	4.55
Experiments		
Solarski and Wiese [15]	6.55	
Veres *et al.* [16]	7.58	
Present work	7.62±7.5%	3.64±7.7%

In Table II we present the results of our measurements and compare them with the results of several calculations and the data available from two other experiments. When available, we have listed the theoretical data obtained in both the ''dipole length'' and ''dipole velocity'' approximations [1,3]. It is seen that the differences between these two formulations of the transition integral, which should ideally produce the same result, are considerable. In general, the dipole length calculation is the preferred choice [2,3,4]. Our value for the multiplet at 436.8 nm is close to the average value of the two most recent dipole length calculations [1,2]. For the multiplet at 394.7 nm, all dipole length calculations are in fair agreement with each other, but all these results are higher than our value by factors ranging from 1.13 to 1.4. Experimental data are only available for the 436.8-nm multiplet from two earlier wall-stabilized arc experiments by Solarski and Wiese [15], who applied a different plasma analysis technique, and Wiese and co-workers [9,16], who applied a diagnostic method similar to ours. Their results are different from our value by 14% and 1%, respectively.

SUMMARY

The transition probabilities of the $3s\ ^3S^0 - 4p\ ^3P$ and the $3s\ ^5S^0 - 4p\ ^5P$ multiplets in O I have been measured relative to several strong O I multiplets for which the transition probabilities are accurately known. The data for the latter are all from recent advanced calculations [1–4] and have been estimated to be uncertain by amounts from $\pm 3\%$ to $\pm 10\%$, largely judged from their generally excellent agreement with each other as well as with experimental data. Another result of our experiment is evidence for the lack of PLTE among atomic oxygen levels in a wall-stabilized arc operated essentially in helium, but with a small oxygen admixture. This is apparently due to the small diameter of the arc discharge. However, Boltzmann plots of excellent quality are obtained from such arc plasmas when nitrogen, argon, or oxygen is present in significant quantities. Also, the good agreement between results obtained from two distinctly different arc plasmas give confidence in the accuracy of our results.

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