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Measurement of the Oscillator Strength of the O I(^1S-$^1P^o$) Transition at 1217.6 Å[*]

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The oscillator strength for the ^1S-$^1P^o$ transition in atomic oxygen has been measured using resonance-absorption techniques. The metastable absorbing atoms were formed in a weak dc discharge at a pressure of a few Torr, and their concentration determined by absolute photometry of the auroral green line arising in the ^1D-^1S transition. The light source for the emission line was a water-cooled hollow-cathode discharge operated in pure oxygen at a pressure of 0.25 Torr and a current of 70 mA; self-reversal was negligible. A pure Gaussian line profile was assumed to describe the shapes of the emission and absorption lines. Treating f as a parameter and using measured values for emission and absorption temperatures and absorber concentration, a computer search was made to find that f which gave the best fit of the absorption integrals to the experimental data. The experimental oscillator strength of 0.051 ± 0.018 compares satisfactorily with the theoretical estimate of 0.13 ± 0.06, but is at least 50% smaller than other experimental values reported.

I. INTRODUCTION

The experimental determination of atomic transition probabilities is important both for its direct application to emission and absorption of radiation and as a check on the theoretical methods used to calculate unmeasured values. Atomic oxygen, because of its importance in aeronomic processes, has been the subject of much recent experimental and theoretical study of this kind. This paper is a report on the measurement of the oscillator strength for the transition O I $2p^4\ {}^1S$-$2p^3({}^2P^0)3s''\ {}^1P^0$ with wavelength 1217.6 Å in the vacuum ultraviolet. The transition, studied here in absorption, takes place between a weakly autoionizing upper state and a metastable lower state. The line-absorption method used in this measurement was similar to that used for the study of the resonance transitions in oxygen and nitrogen by Prag, Fairchild, and Clark[1] in this laboratory, and by Lin, Parkes, and Kaufman[2] elsewhere. The results are compared to the emission-probability measurements for the same transition by Ott[3] and by Boldt and Labuhn,[4] to the theoretical calculations of Garstang[5] and Kelly,[6] and to the direct lifetime measurements of Lawrence.[7] Additional details of the investigation can be found in the doctoral dissertation of the author.[8]

II. METHOD

The resonance-absorption technique, clearly described by Mitchell and Zemansky,[9] obviates the need for high instrumental resolution in line-absorption measurements, but does require consideration of emission and absorption line shapes. The intensity of an emission line transmitted through an absorption column of length X is expressed mathematically by the integral

$$I = \int_{-\infty}^{\infty} I_0(\nu)e^{-k(\nu)X}d\nu\ , \qquad (1)$$

where $I_0(\nu)$, the incident intensity per frequency interval, and $k(\nu)$ the linear-absorption coefficient, are functions describing the emission and absorption line shapes. These functions depend on the line-broadening mechanisms in the emission and absorption regions, respectively.

In the absence of extreme broadening, the central portion of the line is broadened almost exclusively by the ordinary Doppler effect arising in the random motion of the atoms. Then, if self-absorption in the light source is negligible, most of the absorption takes place near the line center where the emission intensity and absorption coefficient are greatest, and the line shapes are adequately described by Gaussian functions whose widths are proportional to the square roots of the emission and absorption temperatures. If self-absorption is severe, however, the intensity is low near the emission line center, and much of the measured absorption takes place near the edges of the line where the line shape is largely determined by broadening mechanisms other than simple Doppler broadening. In that case, the Voigt line shape must be used in the calculation of the absorption integral.[1]

Parkes, Keyser, and Kaufman,[10] measuring line absorption by atomic oxygen in the ground state, found as expected that self-absorption is negligible only when the emitting region is physically very thin. Since the oscillator strength for the transition studied here is not greatly different from that for the resonance transitions, the emitting region can be increased in thickness by a factor approximately equal to the ratio of ground-state-to-metastable concentrations without an increase in the optical depth for the 1218-Å line. At the operating pressure of the hollow-cathode light source used in the present experiment, the mean free path of the metastable atoms was approximately equal to the cavity diameter, so deactivation at the metal walls prevented a significant buildup of $O(^1S)$ population. It was not possible to monitor the amount of self-absorption directly as in the case of the resonance lines; however, a comparison to the measured absorption of Parkes *et al.* indicated strong absorption, as would be expected for absorption taking place near the line center. Even if the metastable-to-ground-state concentration ratio in the light source was as high as 10^{-3}, calculations indicate that the resulting distributed self-absorption is adequately accounted for in the calculation of the absorption integrals by including an additional absorbing layer at or near emission temperature.

Since both emission and absorption pressures were never more than a few Torr, pressure broadening was negligible and the assumption of simple Doppler-broadened lines is justified. By virtue of the assumed Gaussian shape and the integral expression relating the absorption coefficient and oscillator strength,

$$\int_{-\infty}^{\infty} k(\nu)\,d\nu = (\pi e^2/mc)Nf\ , \tag{2}$$

the absorption coefficient has a peak value given by

$$k_0 = \frac{2}{\Delta\nu_a}\left(\frac{\ln 2}{\pi}\right)^{1/2}\frac{\pi e^2}{mc}Nf\ , \tag{3}$$

where $\Delta\nu_a\ (\mathrm{sec}^{-1}) = (8kT\ln 2)$, ν_0/c is the Doppler width of the absorption line, $N\ (\mathrm{cm}^{-3})$ is the absorbing atom concentration, and f is the oscillator strength for the transition. Using measured values for temperatures and absorber concentration, and an assumed value for the oscillator strength, the transmission of the absorption column, I(transmitted)/I(incident), can be calculated as the ratio of integral (1) to the same integral with N set equal to zero. A series of calculated curves of transmission versus absorber concentration with f as a parameter, called curves of growth, are compared to the experimentally measured curve of growth. That value for f which provides the best fit to the experimental curve is the oscillator strength for the transition.

The principal difficulty in an experiment such as the present is that of determining the absolute concentration of atoms in the lower state. Because of the transient existence of the $O(^1S)$ metastable atoms, a steady-state population capable of producing measurable absorption can be maintained only under conditions of continuous excitation. The absorption cell developed for this experiment provided an absorption path which was the positive column of a weak dc discharge through a mixture of oxygen in argon. The $O(^1S)$ concentration could be varied continuously by simply changing the current through the discharge.

Fortunately, for the transition in atomic oxygen being studied here, the metastable-atom concentration can be determined directly. The concentration of $O(^1S)$ atoms is related to the absolute volume-emission rate for 5577-Å photons arising in the transition $\mathrm{O\,I}(^1S - {}^1D)$ through the Einstein spontaneous-emission coefficient A_{5577},

$$[O(^1S)] = \frac{I_{5577}\ (\mathrm{cm}^{-3}\,\mathrm{sec}^{-1})}{A_{5577}\ (\mathrm{sec}^{-1})}\ . \tag{4}$$

The absolute-intensity measurements were carried out by calibrating an optical system against the light from the chemiluminescent reaction of O atoms and NO molecules in the absorption cell. This intensity standard, established by Fontijn, Meyer, and Schiff,[11] is better suited to the weak discharge and cylindrical geometry of the absorption column than would be the case for a tungsten-ribbon standard lamp. The spontaneous-emission coefficient, following Weise, Smith, and Glennon,[12] is assigned the value 1.34 sec^{-1}. This is the mean of the 1.43 sec^{-1} determined by Omholt[13] from lifetime measurements of the $O(^1S)$ state in rapidly fluctuating auroras and the 1.25 sec^{-1} from the refined calculations of Garstang.[14]

An effect which might negate the previous assumption of spontaneous emission is collisional stimulation of the 5577-Å line. At pressures near atmospheric, a discharge through xenon or argon containing traces of O_2 results in the emission of a diffuse molecular-band emission spectrum in the vicinity of the 5577-Å line.[15,16] After extensive study of this emission, Herman and Herman[17] attributed it to emission from quasimolecules formed during the

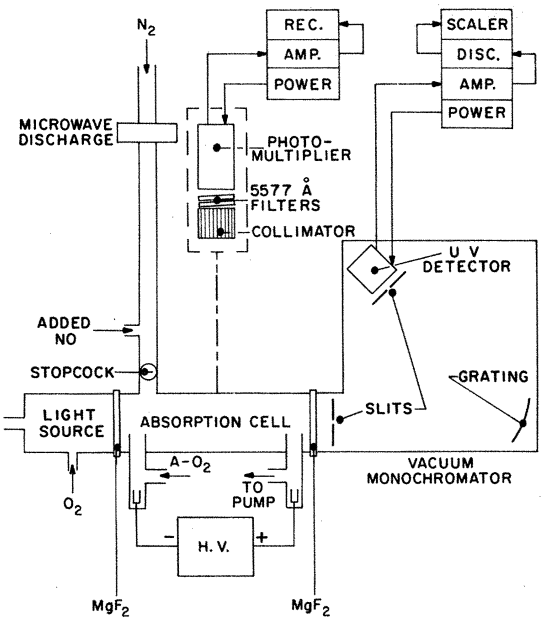

FIG. 1. Schematic diagram of the experimental apparatus.

collisions of rare-gas and oxygen atoms. In the collision complex, molecular selection rules governing electronic transitions come into play. Some transitions which are metastable in the isolated atom become allowed in the perturbed atom. The transition corresponding to the $^1D-^1S$ atomic transition is no longer forbidden by the $\Delta J = 0, \pm 1$ rule, although the transition to the ground state, a triplet state, remains forbidden by the rule $\Delta S = 0$. The importance of collisional stimulation can thus be estimated experimentally by observing the relative intensities of the 5577-Å line and the 2972-Å line of the O I($^3P - ^1S$) transition as the argon partial pressure is increased. Since both transitions have the common ^1S upper level, in the absence of collisional stimulation the relative intensities should remain constant, independent of discharge conditions. However, if collisional stimulation preferentially enhances the 5577-Å line, it should appear relatively brighter than the 2972-Å line as the argon partial pressure increases.

A measurement of the intensity ratio of the 5577- to 2972-Å lines was carried out over the range of argon pressures from 1 to 18 Torr. The constancy of the measured ratio is in agreement with the more recent measurements of Cunningham,[18] who found that although the 5577-Å line plus its associated band becomes relatively more intense than the 2972-Å line as the argon pressure increases, the 5577-Å line alone does not. The measured 5577-Å line intensity thus corresponds to photons arising in spontaneous emission only.

III. EXPERIMENTAL

A schematic diagram of the resonance-absorption apparatus is shown in Fig. 1. The absorption cell, separated from the emission line source and from a vacuum monochromator by MgF_2 windows, served in the dual role as discharge cell for the dc discharge used to produce O(^1S) atoms and as a reaction chamber for the chemiluminescent reaction employed to calibrate the photomultiplier for the absolute photometry of the 5577-Å emission.

The light source designed for this experiment was a water-cooled hollow-cathode discharge tube with a molybdenum-lined aluminum cavity 1.4 cm in diameter and 4.2 cm deep. The molybdenum liner reduced the intensity drifts caused by oxide formation to a few percent per hour. The discharge was operated in pure flowing O_2 at a pressure of 0.25 Torr and a discharge current of 70 mA. The emission temperature in the light source was determined while the light source was operated under normal conditions of pressure and discharge current, but with a small nitrogen impurity added to the oxygen flow. Standard rotational analysis of the (0, 0) band of the N_2^+ first negative system yielded a temperature of 610 °K within about 15%. This temperature was used to determine the Doppler width of the emission line.

A Bendix magnetic electron multiplier, mounted behind the exit slit of a 1-m normal-incidence vacuum monochromator, served as a high-gain (10^7) low-dark-current (10^{-12} A) detector for photons with wavelengths below 1500 Å. The monochromator, which acted only as a narrow bandpass filter to isolate the line being studied (the high resolution is provided by the atoms involved in the emission-absorption process), was operated in second order to separate the 1217.6-Å oxygen line from the nearby hydrogen Lyman-α line at 1215.7 Å (see Fig. 2). The output from the electron multiplier could be switched between analog and digital recording systems. The analog system, a microvolt ammeter and a chart recorder, was used to locate the line center in spectral scans. The digi-

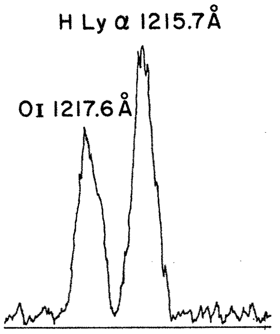

FIG. 2. Spectral scan of O I 1218-Å and H Lyman-α lines from the emission line source.

tal system—a pulse amplifier, discriminator and shaper, and a scaler—was used to count the single-photon pulses when absorption data were taken.

The absorption cell, a 5-cm-i.d. Pyrex tube, provided an absorption path of roughly 30 cm. During absorption measurements, the entire length of the cell was occupied by the positive column of a dc discharge through a flowing oxygen-argon mixture. The argon gas, which made up more than 98% of the mixture, served as a buffer to prevent diffusion of the metastable atoms to the walls. The optimum mixture of 1.9% oxygen in argon was determined by a series of measurements of 5577-Å intensity as the oxygen-to-argon ratio and total pressure were varied.

The Ar-O_2 discharge was operated at a pressure of 2.5 Torr and with discharge currents between 5 and 140 mA to produce $O(^1S)$ concentrations between 9×10^9 and 2×10^{11} cm^{-3}. The temperature in the absorption region was measured with a calibrated, glass-enclosed thermistor probe inserted into the center of the discharge. The temperature was found to vary with discharge current from slightly above room temperature at the lowest currents to approximately 200 °C at the highest currents. This temperature variation, which led to variations in the Doppler width of the absorption line, was taken into account in the data reduction.

The concentration of $O(^1S)$ atoms was found to increase slightly from the cathode end to the anode end of the positive column, as determined by the measured intensity of the 5577-Å emission. Since the important quantity in absorption measurements is the total number of atoms per cm^2 in the absorption path, the integral

$$NX = \int_0^X N(x)\,dx \tag{5}$$

was evaluated graphically from the 5577-Å intensity distribution and the absolute concentration of $O(^1S)$ atoms at the midpoint of the cell.

The chemiluminescent reaction used to calibrate the photomultiplier tube for absolute photometry of the 5577-Å emission produces a continuous emission of radiation with total intensity proportional to the product of concentrations of the reacting species according to the scheme

$$O + NO \rightarrow NO_2 + h\nu \text{ (continuum)}, \tag{6}$$

$$O + NO_2 \rightarrow NO + O_2\,, \tag{7}$$

$$I(\text{photon cm}^{-3}\,\text{sec}^{-1}) = k\,[O][NO]\,, \tag{8}$$

where k was found by Fontijn, Meyer, and Schiff[11] to be 6.4×10^{-17} cm^{-3} molecule^{-1} sec^{-1}. Reaction (7) is much faster than reaction (6), so the overall scheme represents an NO-catalyzed recombination of O atoms, the concentration of O atoms decreasing only slowly, while the NO concentration remains essentially constant.

Known concentrations of O and NO were established by adding NO to a flowing nitrogen afterglow as described in Ref. 1. The very rapid reaction $N + NO \rightarrow N_2 + O$ converts essentially all of the NO to O in a one-to-one fashion. Beyond that point where all N atoms have reacted with NO molecules, any additional NO molecules begin to react with O atoms to produce NO_2 and the continuum radiation. Since the volume flow rate of the nitrogen afterglow and the inflow of NO were measured, both [NO] and [O] were determined.

Light from either the Ar-O_2 discharge or from the O-NO reaction passed first through a collimator, then through a pair of tuned, 17-Å FWHM interference filters before reaching the photomultiplier tube. With known concentrations of O atoms and NO molecules in the absorption cell, and with the spectral distribution of emitted radiation and interference-filter transmission profile taken into account, the photomultiplier was calibrated for the specific geometry of the absorption cell. The slight differences in geometry between the NO_2 continuum emission and that from the $O(^1S)$ atoms arose because of wall deactivation of $O(^1S)$ metastable atoms. The resulting radial distribution of $O(^1S)$ atoms and the corresponding radial intensity distribution of 5577-Å radiation was determined experimentally by means of the Abel inversion technique described by Wiese.[19] The absorber concentration was then the $O(^1S)$ concentration on the axis of the cell.

The presence of weak molecular emission due to a nitrogen impurity in the argon was noted in the passband of the filters. This weak background, along with any possible emission arising in the collisional stimulation of the $O(^1S)$ atoms discussed earlier, was measured during each absorption run and subtracted from the measured intensity of the

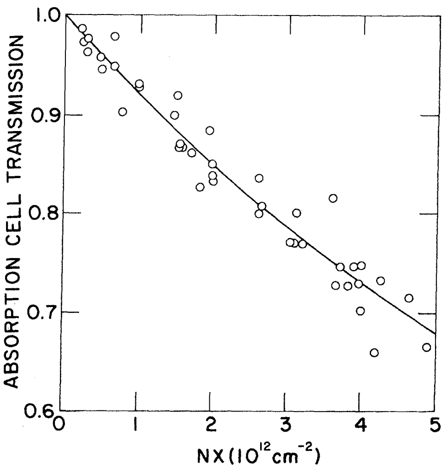

FIG. 3. Absorption data and best-fit curve of growth.

5577-Å radiation.

Absorption of the 1218-Å line by undissociated molecular oxygen in the absorption-cell discharge was not significant as the well-known Lyman-α "window" in the absorption spectrum of O_2 includes the 1218-Å line. The absence of this absorption was experimentally verified by monitoring the intensity of the 1218-Å emission line as the Ar-O_2 pressure was increased from zero without a discharge in the cell.

IV. RESULTS

The measurements of absorption-column transmission versus the number of absorbing atoms per cm^2 in the absorption path are shown by the points in Fig. 3. The curve shown with the data is the least-squares-fit transmission curve calculated with the absorption integral (1) having f as a parameter. The least-squares fitting, done by a systematic search routine on a CDC-6400 computer, produced a best-fit oscillator strength of 0.051 when self-absorption in the light source was assumed negligible and emission and absorption temperatures were assigned their measured values. Of the approximately 75 absorption measurements made, only 41 are shown in Fig. 3. The first 30, rejected because of unreliable supporting data, yielded an approximate f number within 20% of the above value.

In addition to the inevitable uncertainties arising in the experimental measurements and data analysis, the uncertainty in the measured oscillator strength includes the 30% quoted uncertainty in the rate constant for the production of the NO_2 continuum and the 15% uncertainty in the O I(^1D-^1S) transition probability. Since both of these constants are used in the measurement of the absorber concentration, and hence in the product Nf, the effect of future possible revisions in the constants and/or their estimated uncertainties can be readily accounted for.

The uncertainty in f due to possible errors in the measured temperatures was estimated by calculating best-fit f numbers with the temperatures at the limits of their respective uncertainties. The effect of possible self-absorption in the light source, estimated by calculating the f number when an absorbing layer capable of producing up to 40% absorption at line center was included in the integrals, proved to be small. The uncertainty in f because of temperature errors, possible self-absorption, and scatter in the data is set at ± 10%. Other sources of uncertainty in f include those arising in experimental measurements: absorption path length (± 5%), radial-intensity distribution in the Ar-O_2 discharge (± 3%), afterglow volume flow rate (± 4%), NO-flow rate (± 4%) and 5577-Å detector calibration (± 2%). When these estimates of error are combined with the quoted uncertainties in supporting data, the over-all rms uncertainty in f becomes ± 36%.

TABLE I. Comparison of present results with recent experimental and theoretical determinations of the oscillator strength for the O I(^1S-$^1P^o$) transition.

Authors	Method	f
Forsman (this work)	Line absorption	0.051 ± 0.018
Ott (Ref. 3)	Wall-stabilized arc	0.12 ± 0.028
Boldt and Labuhn (Ref. 4)	Wall-stabilized arc	0.29
Garstang (Ref. 5)	Theory	0.15
Kelly (Ref. 6)	Theory	0.114
NBS Data Center (Ref. 12)	Critical review	0.13 ± 0.06

Table I compares the measured O I(^1S-$^1P^o$) oscillator strength with the most recent data from the literature. The present result is seen to be a factor of 2 or more lower than either the experimental or theoretical values reported. The very large discrepancy between the present result and that of Boldt and Labuhn[4] can probably be attributed to a systematic error in their work discussed in detail by Ott.[3] Both the measurements of Ott and those of Boldt and Labuhn were direct experimental measurements of the transition probability in emission using a wall-stabilized arc discharge in a mixture of argon and oxygen. Although Ott repeated the experiment of Boldt and Labuhn using a simpler and more direct approach, he points out that an error of only 1% in his determination of the arc temperature would produce a corresponding error of 9 to 12% in the calculation of the blackbody intensity standard. The over-all estimated rms uncertainty in the 1218-Å oscillator strength measured by Ott, set at ± 23%, is not consistent with the value reported here.

Lawrence[7] recently used a pulsed electron beam to measure the decay lifetime of the upper $^1P^o$ state in the 1218-Å transition. His measured lifetime of $(0.9 \pm 0.2) \times 10^{-9}$ sec is consistent with the present result if the effect of forbidden autoionization is taken into account. Using the measured lifetime of Lawrence and the theoretical branching ratio of 0.34 for the 1218-Å transition out of the $^1P^o$ state[12] together with the present transition probability of 0.75×10^8, the autoionization transition rate for the $^1P^o$ state becomes 8.9×10^8 sec^{-1}, a result roughly four times the radiation rate.

Garstang[5] used the Coulomb approximation to calculate transition integrals for several transitions in the $2p^4$-$2p^3 3s$ transition array, then used the average value $\sigma^2 = 0.15$ in his calculation of the oscillator strengths. Kelly[6] used self-consistent field (SCF) wave functions with exchange effects included in an approximate way to calculate σ^2 for each individual multiplet, then assumed LS coupling to obtain oscillator strengths. In both sets of calculations, configuration interaction was neglected. The NBS Data Center[12] lists the average of the two theoretical values, but estimates the uncertainty at greater than 50%.

It is apparent that the results reported here are somewhat smaller than those given by other methods. A resolution of the disparities, however, is with one exception possible through overlap of estimated experimental and theoretical uncertainties or allowance for autoionization. The measurement by Ott remains at least 50% larger than the present.

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Transition Probabilities of Neutral and Singly Ionized Germanium[*]

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Absolute transition probabilities are measured for 24 prominent Ge I and Ge II lines between 3200 and 6500 Å. Spectroscopic plasmas are generated by the shock heating of neon or argon containing (0.2-2.0)% GeH_4 to temperatures 10 200–12 600 °K at pressures of (6–32) × 10^6 dyn cm^{-2}. To reduce possibilities for bias, the state of the light source and the integrated energy of emitted lines were determined redundantly. A values were measured by methods inherently insensitive to possible temperature errors. Ionic transition probabilities [estimated accuracies (23–50)%] are compared with central-field approximations and are tested for conformity with quantum-mechanical sum rules. Neutral germanium data [accuracies (30–$>$50)%] are compared with other experimental results.

I. INTRODUCTION

The spectrum of neutral germanium has been described as being prototypical of medium weight two-electron systems.[1,2] Experimental line strengths should be helpful for testing[2] the calculated trend[1] wherein LS coupling prevails for the deepest levels, pair coupling (LK and jK) becomes important at moderate principle quantum numbers, and jj coupling dominates in the highly excited states. Data on the strengths of visible lines should be useful for refining interpretation of spectra from remote plasmas, germanium being among the more astrophysically abundant of the elements beyond the iron group.[3]

The leading transition arrays in the visible ionic spectrum are well suited for evaluating the applicability of Coulomb-approximation radial wave integrals to systems of moderate ($Z = 32$) atomic number. Moreover, a quantitative understanding of the second spectrum may have technological implications related to the lasing action[4] of some Ge II transitions.

This paper presents the first experimental transition probabilities for Ge II.[5] The majority of the Ge I data involve transitions originating in 6p or