Measured Oscillator Strengths for the Allowed 2p-3s Transitions from the Ground State in Oxygen and Nitrogen*

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Oscillator strengths for the $2p^4\,^3P_{2,1,0}-3s\,^3S_1$ transitions in oxygen and the $2p^3\,^4S_{3/2}-3s\,^4P_{5/2,3/2,1/2}$ transitions in nitrogen were obtained from measurements of the absorption of resonance radiation by O and N atoms in their ground states. The N atoms were produced in a flowing nitrogen afterglow; calibrated titration of this afterglow with NO was used to produce O atoms and to measure concentrations of both N and O. The measured oscillator strengths for the individual multiplet transitions are in the expected ratios and the values of Σgf are 0.30 ± 0.08 and 0.39 ± 0.12 for the OI and NI transitions, respectively; these are both in good agreement with recent calculations.

INTRODUCTION

THE available methods of measuring atomic transition probabilities for which the associated radiation is in the extreme ultraviolet are limited primarily by the transmission and reflection properties of existing optical materials. Additional limitations are imposed upon measurements involving oxygen and nitrogen because of the transient existence of these atoms. This paper contains an expanded description of the reported[1,2] use of resonance line absorption to determine oscillator strengths for the NI $2p^3\,^4S_{3/2}-3s\,^4P_{5/2,3/2,1/2}$ transitions near 1200 Å and for the OI $2p^4\,^3P_{2,1,0}-3s\,^3S_1$ transitions near 1300 Å. In addition, improved data are presented for the NI transitions and experimental results for both NI and OI are compared with the calculations of Kelly and Armstrong.[3,4]

RESONANCE ABSORPTION

A detailed treatment of the atomic absorption of resonance radiation has been given by Mitchell and Zemansky[5]; it will be extended[1,2] here to include a wide variety of experimental conditions.

With atomic absorption of resonance line emission, wavelength resolution is provided naturally by the emission lines; therefore, the measured transmission of an absorbing gas is related to the gas absorption coefficient through the integral of transmitted intensity per unit frequency over the full width of the emission line. For a beam of parallel light consisting of one emission line the intensity transmitted through an absorption cell of length x_a is given by

$$I = \int_{-\infty}^{\infty} I_{0\nu} \exp[-K(\nu)x_a]d\nu,$$

where $I_{0\nu}$ is the incident intensity per unit frequency and $K(\nu)$ is the linear absorption coefficient of the gas. If the emission and absorption lines are symmetrical it is convenient to express the line shapes in terms of the variable

$$\omega = 2(\ln2)^{1/2}(\nu-\nu_0)/\Delta\nu_{De}$$

and the parameters

$$A = \frac{\Delta\nu_N+\Delta\nu_C}{\Delta\nu_D}(\ln2)^{1/2}, \quad B = \Delta\nu_{De}/\Delta\nu_{Dr},$$

and

$$C = \Delta\nu_{De}/\Delta\nu_{Da}.$$

In these expressions, ν_0 is the central frequency of the lines, $\Delta\nu_N$ is the natural linewidth, $\Delta\nu_C$ is a collision broadening width, $\Delta\nu_D$ is a Doppler width, and subscripts a, e, and r refer, respectively, to the absorption line, to the emission line, and to the effective absorption line produced by self-reversing atoms in the light source. In terms of these quantities,

$$I = C_0 \int_{-\infty}^{\infty} V(A_e,\omega) \exp[-K_{0r}x_r V(A_r,B\omega)$$
$$-K_{0a}x_a V(A_a,C\omega)]d\omega, \quad (1)$$

where K_0 is the absorption coefficient at $\omega=0$ when Doppler broadening alone is present, x_r is the effective reversing path length, and $V(A,\omega)$ is the Voigt profile[5]:

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

The transition oscillator strength f appears in K_{0r} and K_{0a} through the relation

$$K_0 = \frac{2}{\Delta\nu_D}\left(\frac{\ln2}{\pi}\right)^{1/2}\frac{\pi e^2}{mc}nf,$$

[1] C. E. Fairchild and K. C. Clark, Phys. Rev. Letters **9**, 100 (1962).

[2] A. B. Prag and K. C. Clark, Phys. Rev. Letters **12**, 34 (1964).

[3] P. S. Kelly and B. H. Armstrong, Phys. Rev. Letters **9**, 426 (1962); **12**, 35 (1964).

[4] P. S. Kelly, Astrophys. J. **140**, 1247 (1964).

[5] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, New York, 1934), Chap. 3.

where m is the electron mass and n is the concentration of absorbing atoms.

Determination of f is made by experimentally measuring the transmission coefficient I/I_0 versus n_a or x_a. Because of the need to evaluate seven parameters in Eq. (1), it is necessary to obtain a wide range of data with a minimum of scatter and to corroborate the uniqueness of a fit by using light sources of differing characteristics. For the OI and NI transitions of interest here, each line is a member of a multiplet, and known relations between individual parameters for the different lines of a multiplet are used to restrict the allowable solutions for f. Also, in the present experiment, the restriction $1 \leq B \leq C$ can be imposed, and C can be independently verified by measuring the rotational temperature of molecular nitrogen ions in the source.

APPARATUS

A schematic diagram of the resonance absorption apparatus is shown in Fig. 1. The absorption cell is located between a light source and a vacuum monochromator, and the separate regions are isolated by thinly cleaved lithium fluoride windows. The transmission of these windows limited absorption measurements to resonance transitions at wavelengths greater than 1150 Å; however, windows of some type are necessary to define the absorption cell and to prevent its contamination by the light source. The use of collimating lenses was circumvented by insuring that light accepted by the vacuum monochromator is essentially parallel.
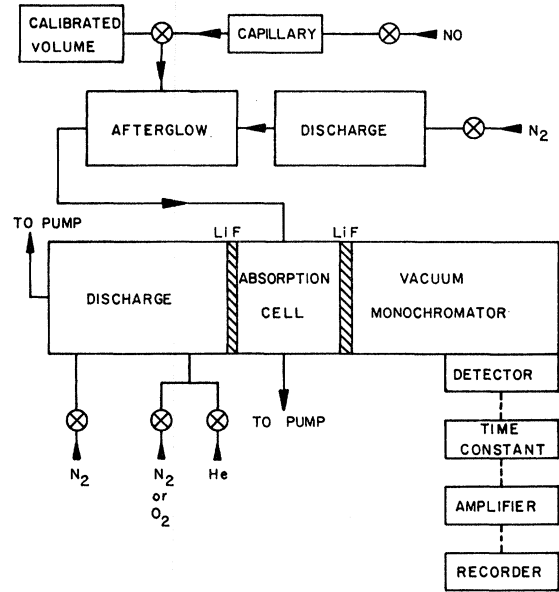

FIG. 1. Block diagram of the experimental arrangement.

Light Sources

Four different light sources were used, two each for the NI and OI experiments. These sources will be referred to as NA, NB, OA, and OB. As shown by the line shape parameters of Tables I and II, these sources provided considerable variety in the amounts of strong self reversal.

Sources NA and OA are nearly identical and are

TABLE I. The parameters and derived physical quantities giving best agreement with the oxygen data. Indicated ranges of error in calculated parameters of Tables I and II relate only to deviations among tabulated values.

	Multiply by	Source OA 1302.2 Å	1304.9 Å	1306.0 Å	Source OB 1302.2 Å	1304.9 Å	1306.0 Å	Average Source OA	Source OB
A_e	10^{-3}	7	5	2	7	4	1		
A_r	10^{-3}	11	6	2	8	5	2		
A_a	10^{-3}	12.8	7.73	2.58	13.8	7.77	2.59		
B	10^0	1.45	1.47	1.47	1.18	1.03	1.02		
C	10^0	1.81	1.84	1.84	1.80	1.78	1.96		
K_0 $_r x_r$	10^1	7.21	4.39	1.46	3.35	1.99	0.69		
K_0 $_a x_a / n_a$ (cm^3)	10^{15}	2.17	1.32	0.44	2.19	1.26	0.42		
T_e (°K)	10^2	9.82	10.15	10.15	9.73	9.46	11.49	10.04 ±0.07	10.23 ±0.43
T_e (°K) (exp.)	10^2							10.26 ±0.65	
T_r (°K)	10^2	4.65	4.70	4.70	7.03	8.98	10.95	4.68 ±0.01	8.99 ±0.76
T_a (°K) (exp.)	10^2							3.00 ±0.10	3.00 ±0.10
$\Delta\nu_{De}$ (cm^{-1})	10^{-1}	4.29	4.35	4.35	4.27	4.20	4.63	4.33 ±0.01	4.37 ±0.09
$\Delta\nu_{Dr}$ (cm^{-1})	10^{-1}	2.95	2.96	2.96	3.63	4.09	4.52	2.96 ±0.00	4.08 ±0.17
$\Delta\nu_{Da}$ (cm^{-1})	10^{-1}	2.37	2.37	2.37	2.37	2.37	2.37	2.37 ±0.00	2.37 ±0.00
$\Delta\nu_{Ca}$ (cm^{-1})	10^{-3}	2.47	1.49	0.50	2.75	1.54	0.51	0.496±0.001[c]	0.526±0.008[c]
$\Delta\nu_N$ (cm^{-1})	10^{-4}	11.8	7.14	2.37	11.7	6.71	2.22	0.237±0.000[c]	0.227±0.003[c]
gf	10^{-2}	16.9	10.3	3.43	16.8	9.68	3.21	3.414±0.026[c]	3.266±0.023[c]
M[a]	10^0	32	21	32	14	17	18		
σ[b]	10^{-2}	1.57	0.94	1.92	1.19	2.48	4.13		

[a] M is the number of experimental points used in the fit.

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

[c] Items averaged after division by statistical weight of lower state.

TABLE II. The parameters and derived physical quantities giving best agreement with the nitrogen data.

	Multiply by	Source NA 1199.6 Å	1200.2 Å	1200.7 Å	Source NB 1199.6 Å	1200.2 Å	1200.7 Å	Average Source NA	Source NB
A_s	10^{-3}	4	4	4	5	5	5		
A_r	10^{-3}	2	2	2	2	2	2		
A_a	10^{-3}	6.00	6.18	5.98	5.77	5.75	5.57		
B	10^0	1.23	1.23	1.22	1.04	1.03	1.01		
C	10^0	1.51	1.51	1.52	1.43	1.45	1.49		
$K_{0r}x_r$	10^1	9.03	5.90	2.97	1.94	1.30	0.67		
$K_{0a}x_a/n_a$ (cm³)	10^{15}	5.10	3.35	1.65	4.89	3.27	1.61		
T_e (°K)	10^2	6.84	6.84	6.97	6.12	6.32	6.70	6.88±0.03	6.38±0.12
T_e (°K) (exp.)	10^2							6.85±0.10	6.65±0.10
T_r (°K)	10^2	4.52	4.52	4.69	5.68	6.01	6.57	4.58±0.04	6.09±0.18
T_a (°K) (exp.)	10^2							3.00±0.10	3.00±0.10
$\Delta\nu_{De}$ (cm⁻¹)	10^{-1}	4.16	4.15	4.19	3.93	3.99	4.11	4.17±0.01	4.10±0.04
$\Delta\nu_{Dr}$ (cm⁻¹)	10^{-1}	3.38	3.38	3.44	3.79	3.89	4.07	3.40±0.01	3.92±0.06
$\Delta\nu_{Da}$ (cm⁻¹)	10^{-1}	2.75	2.75	2.75	2.75	2.75	2.75	2.75±0.00	2.75±0.00
$\Delta\nu_{Ca}$ (cm⁻¹)	10^{-3}	1.15	1.23	1.18	1.11	1.10	1.04	1.19±0.01	1.09±0.01
$\Delta\nu_N$ (cm⁻¹)	10^{-4}	8.29	8.16	8.01	7.96	7.96	7.98	8.15±0.06	7.97±0.00
gf	10^{-1}	2.02	1.33	0.65	1.94	1.30	0.64		
M	10^0	28	16	24	20	16	23		
σ	10^{-2}	3.74	4.79	4.43	2.78	4.15	4.23		

excited by establishing an air-cooled electrodeless 2450-Mc/sec discharge in a mixture of a few percent N_2 or O_2 in He at a total pressure of 1–10 Torr. This discharge is contained in a 25-mm-diam Vycor tube and has a length of 25–50 mm. Maintenance of a continuous flow of the gas mixture through the discharge region and away from the absorption cell serves to enhance the stability of the discharge and to reduce self reversal of the observed atomic emission. These sources are very clean in the sense that their emission in the extreme ultraviolet consists almost entirely of the desired atomic lines.[6] Figure 2 shows a monochromator scan of the OI emission lines from source OA.

Source NB differs externally very little from source NA. Here N_2 is added downstream from the discharge instead of being premixed with the reverse flowing He, and the total source pressure is maintained between 0.5 and 1.0 Torr. With this arrangement, the discharge length is about 150 mm and the source of the visible emission changes continuously from nearly pure nitrogen at the downstream end to nearly pure helium at the upstream end. The NI emission from this source is shown in Fig. 2.

Source OB is a hollow cathode dc discharge excited in flowing oxygen with no admixture of helium. The pressure is kept near 0.2 Torr; higher pressures or the addition of foreign gases decreases still further the already weak resonance lines. The relative intensities of the three lines of interest are much nearer to the unreversed values of 5:3:1 than in source OA, indicating directly that source OA and source OB are significantly different.

The Absorption Cell

The absorption cell is a Pyrex tube 25 mm in diameter and 33 mm long. A steady, uniform concentration of nitrogen atoms is produced in this cell by passing a flowing nitrogen afterglow through it as indicated in Fig. 1. The nitrogen afterglow is excited in a long 9-mm-diam Vycor flow tube by establishing a 2450-Mc/sec electrodeless discharge in flowing nitrogen gas at a pressure of a few Torr and at a volume flow rate between 0.1 and 1.2 liter/sec. Nitrogen afterglows of this type are known to contain nitrogen atom concentrations up to about 10% of the total gas pressure.[7–9] They also contain unknown concentrations of various states of the nitrogen molecule and possibly small
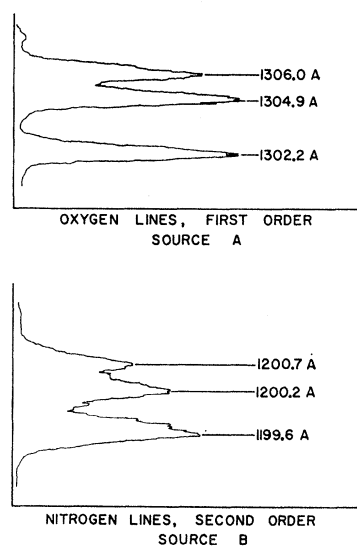
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                      1306.0 A
                      1304.9 A
                      1302.2 A

OXYGEN  LINES,  FIRST  ORDER
        SOURCE   A


                      1200.7 A
                      1200.2 A
                      1199.6 A


NITROGEN  LINES,  SECOND  ORDER
          SOURCE  B
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FIG. 2. Examples of instrumental wavelength resolution and of relative intensities of emission lines.

[6] For a typical spectrogram, see C. E. Fairchild, A. B. Prag, and K. C. Clark, J. Chem. Phys. 39, 794 (1963).

[7] R. Harteck, R. R. Reeves, and G. Mannella, J. Chem. Phys. 29, 608 (1958).
[8] D. S. Burch and K. Evenson (private communication).
[9] A. A. Westenberg and N. de Haas, J. Chem. Phys. 40, 3087 (1964).

traces of molecular ions; however, absorption by molecular constituents was undetectable throughout the range of wavelengths used.

Since molecular oxygen does have a relatively large absorption coefficient throughout the extreme ultraviolet, an oxygen afterglow was not used to produce oxygen atoms; instead, titration of a nitrogen afterglow with nitric oxide[7] was used to give a steady, uniform concentration of oxygen atoms in the absorption cell. The NO titration technique utilizes the strong predominance of the reaction

$$NO+N \rightarrow N_2+O$$
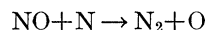
over other afterglow reactions[10,11] to provide nearly complete replacement of N atoms by O atoms, which is determined by photometric detection of the accompanying minimum in the visible afterglow emission. In addition to nitrogen atoms in the ^4S ground state the nitrogen afterglows used here contained detectable concentrations of nitrogen atoms in the metastable ^2D and ^2P levels.[1] Resonance absorption from these metastable levels has been used to show that the concentrations of metastable atoms are relatively small, to the extent that their inclusion in the titration reaction is not necessary.[12] With only ground-state nitrogen atoms involved in the titration reaction, the formation of oxygen atoms in the metastable ^1S and ^1D levels is prohibited, respectively, by conservation of energy and by conservation of net electronic spin; therefore it is concluded that concentrations of metastable oxygen atoms are of negligible effect.

Calibrated NO titration of nitrogen afterglows at a point upstream from the absorption cell (Fig. 1) was used throughout this work for the production of oxygen atoms and for the measurement of atom concentrations in the absorption cell. The NO was admitted to the afterglow through a capillary tube which was periodically calibrated in place. The concentration of nitrogen atoms at the titration position was determined by measuring simultaneously the input flow of NO required for titration, and the afterglow pressure, temperature, and flow speed.[12] Samples of the NO used for titration were analyzed with a mass spectrometer and found to contain about 10% impurities, which were largely N_2, O_2, and oxides of nitrogen other than NO. These impurities are allowed for in the data analysis.

For all the measurements reported here, the afterglow flow rates were large enough that atomic recombination between the titration position and the absorption cell was established to be negligible[13]; therefore atom concentrations at the absorption cell were

equal to their measured concentrations at the titration position. The distribution of atoms in the absorption cell was always essentially uniform, as determined by photometry of the afterglow emission from the cell.

Two different methods were used to vary atom concentrations at the absorption cell. During the oxygen experiment atom concentrations in the titrated afterglow were changed by varying the power level of the afterglow discharge and by varying the afterglow pressure and flow rate. During the recent nitrogen experiment, partial titration of the afterglow was used to vary atom concentrations. The recent measurements of Westenberg and de Haas show that when atomic recombination is negligible in a partially titrated afterglow, the relations

$$[NO]_i=[O]=[N]_0-[N]$$

hold over a wide range of partial titration. In this expression, $[NO]_i$ is the concentration of NO in the unexcited stream and $[N]_0$ is the concentration of N in the untitrated afterglow. The flow conditions established here and the fact that the O atoms present in this situation have negligible absorption at the NI wavelengths allowed use of this convenient technique to produce known adjustable changes in the N atom concentrations at the absorption cell.

Monochromator and Detectors

The vacuum monochromator used in this work has a one-meter concave aluminum reflection grating with 600 lines/mm and 63 000 lines total; the instrument is operated at nearly normal incidence with slit-limited first-order resolution of about 0.4 Å. For the oxygen experiment, the light detector was an EMI 9502S 13-stage photomultiplier, which viewed fluorescent radiation from an internal coating of sodium salicylate on a Pyrex exit window. For the recent nitrogen experiment a significant improvement in signal-to-noise ratio and in the consistency of transmission data was achieved by using a Bendix resistance strip magnetic multiplier mounted inside the monochromator.

RESULTS

Typical measurements of transmission coefficient versus atom concentrations are shown by the points in Fig. 3 and Fig. 4. The data for each line of a multiplet were separately analyzed by fitting the experimental points with calculated transmission curves having A_e, A_r, A_a, $K_{0r}x_r$, $K_{0a}x_a/n_a$, B, and C as independent parameters. Calculated least-squares fits were obtained by using an iterative search routine on an IBM 709 computer to determine the set of parameter values within likely regions which would give least standard deviation. The criterion for the acceptability of such a calculated transmission curve was that the standard deviation of the experimental points from the curve be small enough to be consistent with estimated random

[10] G. B. Kistiakowsky and G. G. Volpi, J. Chem. Phys. **27**, 1141 (1957).

[11] F. Kaufman and J. R. Kelso, J. Chem. Phys. **27**, 1209 (1957).

[12] C. E. Fairchild and K. C. Clark, Physics Department, University of Washington, Seattle, Technical Report 62-2, 1962 (unpublished).

[13] A. B. Prag, Ph.D. dissertation, University of Washington, Seattle, 1964 (unpublished).
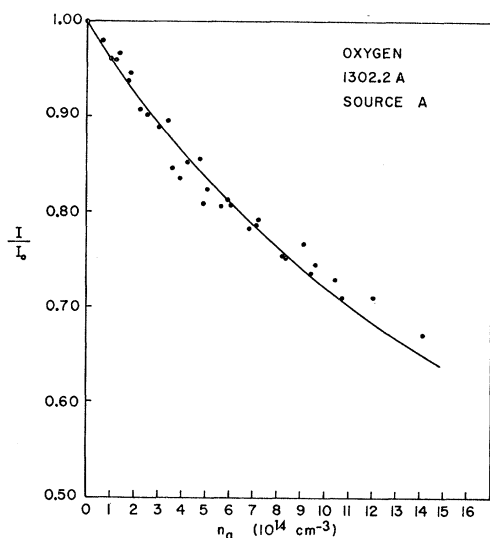
FIG. 3. Transmission of strongest multiplet line versus concentration of absorbing oxygen atoms. Curve shows best functional fit to experimental points.

errors in the measurement of I/I_0 and n_a. The curves shown in Figs. 3 and 4 are representative of acceptable fits to the data. The correct fit to the data was taken to be the set of three curves (one each for the three lines of a multiplet) which had acceptably small standard deviation and which also most nearly satisfied the following restrictions on line shape parameters:

(1) Since the reversing atoms can be no hotter than the emitting atoms and no colder than the atoms in the absorption cell, the condition $1 \leq B \leq C$ must hold.

(2) For a given source all three lines must be characterized by the same emission temperature and by the same reversing temperature; therefore a given source must have only one value of C and one value of B.

(3) The parameter C must be compatible with independently measured values of temperature in the source and in the absorption cell. The gas temperature in the source was determined by measuring the rotational temperature of the (0,0) N_2^+ first negative band. This measurement was made in source OA by adding a trace of N_2, but was impossible in source OB because even a trace of N_2 drastically lowered the intensity of this discharge.

(4) The derived oscillator strengths for the three lines of a multiplet are required to be in approximately the ratio predicted by theory.

(5) For a given line, the same value of f and of $\Delta\nu_{Ca}$ must be obtained using the two different light sources. Since the absorption cell pressure was changed by as much as 20% during the experiment, the restriction on $\Delta\nu_{Ca}$ is correspondingly less stringent.

(6) The $J = 2, 1, 0$ states of the ^3P oxygen atoms are required to be populated according to statistical

weights both in the reversing layer and in the absorption cell. An attempt to fit the data using a Boltzmann population distribution in these states was unsuccessful.[2]

Parameter values and associated physical quantities for the most probably correct calculated fits are listed in Tables I and II. Also listed are the measured values of T_a and T_e. The errors given for T_a and T_e are probable experimental uncertainties, and the errors for the calculated quantities are probable errors of the mean of the values shown. Errors and associated collision widths are not listed for A_e and A_r because in all cases the calculated fits are not significantly affected by variations of a factor of two in A_e and A_r; this is not true for the remaining parameters, in which a variation of a few percent significantly increases the standard deviation. If an emission line is self reversed to the extent that it has a cut off Lorentz profile, I/I_0 is independent of A_e; therefore the insensitivity of the calculated fits to A_e is consistent with the relatively large amount of self reversal listed in all cases. Although the sensitivity of I/I_0 to A_r cannot similarly be estimated, it is clear that the observed insensitivity to this parameter is not unreasonable. It may also be mentioned that because I_0 alone is quite sensitive to variation in either A_e or A_r, a comparison of the calculated I_0 ratios within a multiplet with the measured ratios is not itself a useful indication of the correctness of a fit. Finally, it is pointed out that the individual values obtained for the absorption collision width are in the ratio of the statistical weights of the lower states in both oxygen and nitrogen.

The calculated fits represented by Tables I and II were judged correct only after a wide range of values of $K_{0r}x_r$, $\Delta\nu_{Ca}$, and f had been tested for possible
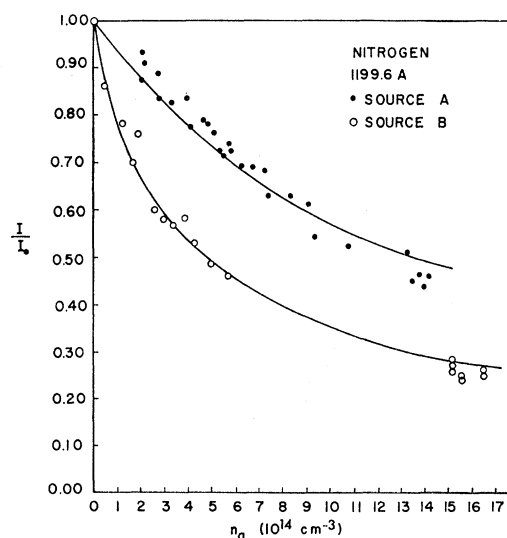

FIG. 4. Transmission of strongest multiplet line versus concentration of absorbing nitrogen atoms. Curve shows best functional fit to experimental points.

acceptable fits. The complexity of the calculation prohibits an exhaustive search except in the region $K_{0r}x_r \leq 4.0$. If either or both of $K_{0r}x_r/f$ and f are so small that $K_{0r}x_r \leq 4.0$, then I/I_0 can be expressed in terms of Gauss profiles[5] and a complete search for fits can be made. The region with $K_{0r}x_r \geq 4.0$ was searched by first systematically varying the parameters in rather large steps until an indication of a fit was found; the computer then searched this general region until a minimum standard deviation was obtained. Once a possible fit was obtained, the direction of further search was dictated by the general dependence of I/I_0 on the parameters. It is not surprising that many shallow minima of standard deviation can exist; a strong minimum indicating a very good fit will appear only if the data points have small scatter.

The only acceptable fit found for oxygen is shown in Table I. The resulting values of gf are in the ratio 5.1:3.0:1.0, in good agreement with the predicted 5:3:1 ratio. For nitrogen the fit represented in Table II and one additional fit were obtained. Parameter values from this second fit were also acceptable within limits of the experimental data but differed from those shown in the table approximately as follows: (1) Oscillator strengths were smaller by a factor of 4. (2) $\Delta\nu_{Ca}$ was larger by a factor of 8. (3) $K_{0r}x_r$ was smaller by factors of 2 and 1.5 for sources NA and NB, respectively. The standard deviations of the two fits do not differ significantly; therefore the results shown here are recommended only by the close agreement with theory (see Table III) and the nearness of $\Delta\nu_{Ca}$ to the analogous collision width in oxygen. A preliminary study[1] of the nitrogen transitions previously assumed Gauss profiles, yielding an average oscillator strength of 1.2×10^{-4}, but this also gave an oscillator strength ratio of 2.5:2.0:1.6, in poor agreement with the predicted ratio of 3:2:1. A ratio of 3.0:2.0:1.0 is obtained from the present results in Table II. A subsequent fit to the previous data

using Voigt profiles gives oscillator strengths in agreement with the values obtained from the new data and yields the predicted ratio of f values.

In Table III the average experimental values of

TABLE III. Comparison of the present experimentsl results with calculations by Kelly and Armstrong.

Source	Σgf	Final Σgf	Theoretical Σgf
OA	0.307		
OB	0.297	0.30±0.08	0.27
NA	0.400		
NB	0.387	0.39±0.12	0.40

Σgf for the O$\textsc{i}$ and N$\textsc{i}$ multiplets are seen to compare closely[14] with values calculated by Kelly and Armstrong.[3,4] The accuracy assigned to the experimental numbers is estimated both from scatter of the data and from possible systematic errors in the determination of I/I_0, NO and afterglow flow rates, the input flow of NO required for titration, constancy of the NO purity, the absorption cell length, and the absorption cell temperature. Since sources A and B differed significantly for both oxygen and nitrogen, any appreciable errors in the assumption of symmetric lines should have appeared as inconsistencies in the derived values of f and $\Delta\nu_{Ca}$.

Although other fits to the data have been found, extensive searching has indicated that these fits occur only for discrete, widely separated, and unrealistic values of the parameters; therefore the results presented here may be regarded as supporting the calculations of Kelly and Armstrong.

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[14] Additional experimental support has been obtained by F. A. Morse and F. Kaufman, J. Chem. Phys. (to be published). Conversations with F. Kaufman and with B. H. Armstrong and R. H. Garstang have been appreciated.