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Oscillator Strength of the Resonance Transitions of Ground-State N and O[*]

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Abstract

Multiplet oscillator strengths, $\Sigma g_L f_{LU}$, for the resonance triplets of N and O were determined using the line absorption method and measuring atom concentrations by chemical "titration". For the NI triplet at 1200Å, $\Sigma g_L f_{LU} = 0.87 \pm 0.20$, and excellent internal agreement was obtained among the separately measured f_{LU} of the three lines. A value of $(3 \pm 1) \times 10^{-11}$ cm^3 sec^{-1} is required for the rate constant of the N + NO $\rightarrow$ N$_2$ + O reaction in the analysis of the data. For the OI triplet near 1300Å, the apparent $\Sigma g_L f_{LU}$ increased sharply and reproducibly from 0.19 to 0.42 when the diluent gas in the discharge light source was changed from Ar to He, which indicates that excitation transfer is a major source of excitation in such Ar-O$_2$ resonance lamps. The larger oscillator strength obtained with He-O$_2$ light sources is in excellent agreement with results of lifetime measurements by other workers.

Introduction

Stimulated by aeronomic interest and by needed comparison with theory, experimentalists have continued to study the allowed radiative transitions among the principal electronic states of atomic air species. Three very dif-

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ferent techniques have been used principally: (1) Direct lifetime measurements using either pulsed or sinusoidally varying excitation[1,2]; (2) Emission intensity measurements in high temperature arcs in thermal equilibrium[3,4,5]; (3) Absorption measurements in partly dissociated flowing gases near 300°K using line sources[6,7,8]. The first two of these have the advantage of being applicable to a large number of transitions, whereas the third is limited to those whose lower states are sufficiently long-lived to be prepared in known concentration, and is therefore restricted to ground states or metastable states resistant to de-excitation. Nevertheless, the absorption technique is worth pursuing for several reasons: It necessitates the development and testing of (resonance) light sources possessing known line shapes; such sources become useful tools in atom reaction studies because of their high selectivity and sensitivity for atom concentration measurements; it further confirms the correctness of widely used atom "titration" reactions; and, lastly, it helps resolve present discrepancies among the results of other methods.

The present paper first describes the successful measurement of the f-value for the NI resonance triplet at 1200Å resulting in good agreement with lifetime and some arc data, but in disagreement with earlier absorption results; it then re-examines and largely removes existing discrepancies between lifetime and absorption results for the aeronomically important case of the OI triplet near 1300Å, and points up a complication caused by excitation transfer in rare gas type light sources.

Although both determinations use the same titration reaction

$$N + NO \xrightarrow{k_1} N_2 + O \tag{1}$$

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for the quantitative measurement of the atom concentration in the absorption flow cell, the NI experiment is much the more difficult, because (a) the f-value is larger, which requires very small, known atom concentrations; (b) the wavelength region is closer to the cutoff for MgF_2 windows; and especially because (c) reaction (1) must be used as a quantitative atom removal step, i.e. at the very small concentrations of 1 to 3 x 10^{12} atoms cm^{-3}, which are required for optimum absorption, N-atoms react slowly with the variable, added NO, so that the rate constant k_1 must enter the data analysis. In the OI case, on the other hand, the titration produces the desired species; reaction (1) can therefore be carried out with great excess of N, and added NO is quantitatively and rapidly transformed into O.

Recent determinations of the absorption oscillator strengths, f_{LU}, and related radiative quantities are summarized for the NI resonance triplet in Table I and for the OI resonance triplet in Table II. It can be seen that for nitrogen there is fair agreement between lifetime and some arc results, but that earlier measurements using the absorption-titration method have given values which are lower by a factor of three.

For oxygen, the disagreement is worse. Some arc results are a factor of four larger than those of lifetime studies which, in turn, are a factor of two higher than our earlier absorption results. Several of these existing discrepancies are removed by the present work.

Experimental

The apparatus whose basic diagram is shown in Fig. 1 was similar to that described earlier[8] except for the following modifications: The original plane

reflectance grating of the 0.5 meter monochromator (1180 grooves/mm) was re-
placed with one having 3600 grooves/mm, blazed at 2400Å (Bausch and Lomb)
which greatly improved spectral resolution. For the light source discharge,
a well-regulated high voltage power supply (Kepco, Model 1520-B) was used in
conjunction with the magnetron oscillator of a Raytheon Microtherm unit (2450
MHz, 100 watt) in order to increase the stability of the light source. For
best results, the voltage was pulsed by a square wave generator at 500 Hz.
Either Ar or He were used with trace addition of O_2 to produce the OI reso-
nance triplet, and with 1 to 5% addition of N_2 to produce the NI emission.
For He + N_2, a second microwave source had to be placed directly in front of
the MgF_2 window to provide enough intensity of the 1200Å triplet.

Cylinder grades of He, Ar, N_2, and O_2 were used without further purifi-
cation. Cylinder grade NO was extensively purified by slow passage over sup-
ported NaOH at atmospheric pressure, condensation at 77°K, and repeated sub-
limation.

Results

A. NI Resonance Triplet.

The lines at 1199.55, 1200.22, and 1200.71Å are due to the transitions
from the J = 5/2, 3/2, and 1/2 members of the $2p^2 3s$ ^4P upper state to the
$2p^3$ $^4S_{3/2}$ ground state. The Einstein A-coefficients of the three lines are
therefore equal and the emitted intensities should be in the ratio 3:2:1 due
to the statistical weights of the upper states (their energy differences are
too small to affect their relative population) as long as the source is optic-
ally thin. Since the absorption f-values also stand in the ratio 3:2:1, large

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optical depths in the light source lead to lower line intensity ratios in emission. This criterion was used as a diagnostic for small optical depth. Typical NI sources used in this work had emission ratios of 2.7:1.9:1.

N atoms were produced in the absorption flow system by a microwave discharge (Raytheon Micortherm) in helium or argon containing less than 0.4% N_2 at total pressures of 1.1 to 2.7 Torr. The discharge exciter was placed well upstream of the NO addition point in order to let metastable atomic or molecular species decay, and the flow velocity was kept low (100 to 300 cm sec^{-1}) to let reaction (1) go as far to completion as possible, while keeping the N-atom loss due to surface recombination small.

In a typical experiment the monochromator was set at the peak of any one of the three lines, the emission intensity, I_0, was recorded in the absence of N, followed by several readings, I, in the presence of a certain amount of N and variable amounts of added NO. For each fractional absorption, $A_\alpha = (I_0-I)/I_0$, the corresponding $k_0\ell$ was obtained graphically on the assumption of Doppler-shaped emission and absorption lines[10] using $\alpha = \sqrt{2}$ as described earlier[8]. A typical plot of $k_0\ell$ vs. $[NO]_0$, the initial concentration of added NO before its partial reaction with N, is shown as line 1 in Fig. 2. If reaction (1) were infinitely fast this would be a straight line and its intercept, $[NO]_{0i}$, the "titration endpoint", would equal the initial N-atom concentration. The absorption oscillator strength, f_{LU}, is then given by $(\Pi/4 \ \ell n \ 2)^{1/2} \ mck_0 \ \Delta\nu_a/\Pi e^2 [N] = 3.34 \ x \ 10^{11} \ k_0/[N]$, where $\Delta\nu_a$ is the Doppler width of the absorption line, $(8 \ RT \ \ell n \ 2/M)^{1/2} \ \nu_0/c$.

The slowness of the titration reaction is shown by the curvature of line 1. The correct endpoint is obtained from the integrated second-order rate equation, $B(A-x)/A(B-x) = exp[k_1 t(A-B)]$, where A and B are the initial

concentrations of N and NO, x is the concentration of N reacted, k_1 the rate

constant for reaction (1) and t the reaction time from the NO inlet to the

absorption region, a distance of 11 cm. If the flow is sufficiently slow,

the initial, linear part of the $k_0 \ell$ vs. [NO] plot can be extrapolated to yield

$[NO]_{0i}$ which equals A in the above equation. Then, with A, k_1, and t given or

assumed, the concentration of N-atoms remaining, A-x, is calculated and plot-

ted as four sets of points in Fig. 2 (using two different values each for A

and k_1). A correct choice of all parameters must lead to a straight line plot,

lines 2 and 3, ending at the (preselected) "endpoint" where all N has been re-

moved (requiring, of course, the addition of an infinite amount of NO). It

can be seen in Fig. 2 that a lower value of k_1 (2×10^{-11} cm^3 sec^{-1}) is more

consistent with a smaller A (2.3×10^{12} cm^{-3}) by giving a better fit to line 2,

whereas the larger k_1 (4×10^{-11} cm^3 sec^{-1}) is more consistent with a larger A

(2.6 c 10^{12} cm^{-3}), giving a better fit to line 3 and thereby a lower f-value.

Published values of k_1 near 300°K in the 2 to 4×10^{-11} cm^3 sec^{-1} range[11] are

supported by the present results. Line 3 is a better tangent to the experi-

mental curve at small $[NO]_0$ and so the larger A of 2.6×10^{12} and a k_1 close

to but somewhat smaller than 4×10^{-11} are slightly preferred. The error in-

troduced by the present extrapolation should be about $\pm$ 10%. Data were col-

lected separately for each of the three lines and repeatedly for the strongest

line using either He or Ar diluent in the absorption cell and in the light

source as shown in Table III.

The substitution of He for Ar in the light source is particularly signi-

ficant for OI as discussed below, but it apparently has no effect in the ni-

trogen case. The uncorrected values of $\Sigma g_L f_{LU}$ obtained as 8, 16, or 24 times

the f_{LU} of the strongest, middle, or weakest line are next corrected for

broadening in the source and for scattering in the absorption cell, as described in some detail elsewhere[12]. The source broadening correction is quite small, requiring an increase of 6, 4, and 2%, respectively, for $\Sigma g_L f_{LU}$ of the three lines, based on the observed deviation from the theoretical 3:2:1 emission intensities. The scattering correction amounts to approximately 10% and is based on the geometry of the flow-cells of 2.35 or 2.10 cm length, an effective radius of 0.5 cm defined by the size of light beam traversing the cell, and an optical depth, $k_0\ell$, of 1 to 2. These conditions correspond fairly closely to curve C in Fig. 5 of reference 12, where it is seen that the scattering correction is not very sensitive to the optical depth.

In fourteen experiments, the f-values for the three lines were found to be in the expected 3:2:1 ratios, i.e. $\Sigma g_L f_{LU}$ is indeed constant and equals 0.87 (Table I). The exact agreement is, of course, fortuitous, and a single standard deviation of $\pm$ 20 to 25% is estimated, i.e. $\pm$ 0.17 to 0.22, which takes account of the difficulties of the corrected "titration" and of all other systematic errors. The present analysis requires a k_1 of $(3 \pm 1) \times 10^{-11}$ cm^3 sec^{-1}, in good agreement with more direct measurements[12].

B. OI Resonance Triplet.

The absorption measurements of the OI triplet at 1302.17, 1304.87, and 1306.04 need not be described in great detail as they are very similar to the earlier ones[8]. Following a suggestion by Lawrence that the Ar-O_2 light source could have emitted broadened lines due to the excitation transfer process

$$Ar(^3P_{2,0}) + O \rightarrow Ar + O(^3S) + Ar + 2.03 \text{ to } 2.23 \text{ eV}$$

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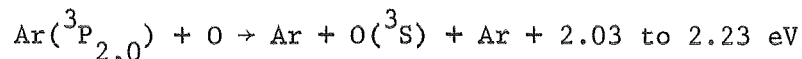
which would leave 1.45 to 1.60 eV of kinetic energy in the excited O-atom, additional experiments were performed. During its radiative lifetime of a few nanoseconds the de-excitation probability of $O(^3S)$ at a pressure of 1 Torr of Ar is entirely negligible and the emission line will be characteristically broadened as has been observed in studies of the dissociative recombination of molecular ions[13]. It is not possible to investigate such line shape problems in the vacuum u. v., and it was therefore decided to eliminate this complication as much as possible. Two different approaches were tried: (a) excitation in the presence of major amounts of a molecular gas (N_2, N_2O) such that excitation transfer does not occur at all because of the absence or very short lifetime of highly excited molecular precursor states. O-atoms would then be excited by electron impact, leaving them kinetically at ambient temperature and leading to Doppler-shaped emission lines. This was attempted repeatedly, but was unsuccessful due to interference from banded emissions; (b) excitation with He replacing Ar such that the energy mismatch in the excitation transfer process would be very much larger, 10.3 eV for He $2\ ^3S$, and the cross section very much smaller. Experimentally, this was accomplished by using two microwave discharges, one on the downstream side of the light source as normally placed[8], and a second one directly in front of the window. Table IV shows the striking and reproducible way in which the apparent f-value of the strongest line of the OI triplet depends on the inert diluent gas. Each entry in Table IV represents about 6 to 8 measurements of $k_0\ell$ and atom concentration, where each such pair defines an f-value. A plot of $k_0\ell$ vs. [O] is prepared for each set of points so that the onset of non-linear effects at large optical depths can be guarded against. Average f-values so obtained from linear plots at small $k_0\ell$ need not be corrected for scattering. The

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plots were found to be linear to higher $k_0\ell$ for He than for Ar diluent, as would be expected if the Ar-excited lines are especially broad. A self-absorption correction of 6% is made[12], based on the deviation of the observed 4.3:2.9:1 emission ratio from the theoretical 5:3:1, and the result in Table II for $\Sigma g_L f_{LU}$ is the average of the six entries for He light sources in Table IV, increased by 6%, and multiplied by 9 for Σg_L.

Discussion

For the NI resonance triplet there can be little doubt that $\Sigma g_L f_{LU}$ is 0.9 to 1.0 to within 15 to 20%. Labuhn's[3] result is high, but its larger probable error makes it compatible with the present work or with the results of lifetime measurements[9]. The very high result of Morris and Garrison[5] must be based on an incorrect assumption, whereas the low value of the earlier line absorption studies[6] is probably due to the difficulty of properly accounting for source self-absorption and scattering when $k_0\ell$ is very large, both in source and cell, as was the case there.

Calculated values of 0.40 by Kelly and Armstrong[14], 0.386 by Kelly[15], and 0.74 by Wilson and Nicolet[16] are based on self-consistent field theory without configuration interaction. The last value is surprisingly close when one considers the errors involved in this approximation.

For the OI resonance triplet it is reassuring that our absorption-titration result is in excellent agreement with lifetime measurements by Lawrence[1] and by Gaillard and Hesser[2]. In view of the small probable error ($\pm$ 2.5%) of the former, this problem can be considered resolved, and the value of 0.42 may be used to guide and appraise theoretical calculations.

Recent theoretical results include Garstang's[17] 0.46, Kelly and Arm-

strong's[14] 0.27, Kelly's[15] 0.23, Armstrong and Purdum's[18] 0.24, and Wilson and Nicolet's[16] 0.42. The f-values in Wilson and Nicolet's[16] compilation which come from a report by Armstrong, Johnston, and Kelly[19] are thus surprisingly close to the best present experimental results for the resonance multiplets in both N and O. The accuracy of these calculations does not appear to hold in general, however, as shown by their large discrepancies with the much more extensive and reliable calculations in the case of several CI transitions (1329, 1561, 1657, and 2478Å) by Weiss[20] using pseudonatural orbitals in the superposition of configuration method. An unpublished calculation by Weiss on oxygen using the latter technique has given 0.32 in the dipole length and 0.40 in the dipole velocity approximation. Such calculations are expected to be accurate to better than 25% and these most recent results are thus in good agreement with experiment.

Lastly, the excitation transfer process involving Ar metastables seems clearly, though indirectly, established as an important source of resonance radiation in the oxygen but not in the nitrogen case. In the latter, the reaction is less energetic (1.22 or 1.39 eV) which might favor its occurrence, but it would leave the radiating $N(^4P)$ with less kinetic energy (0.94 or 1.07 eV), i.e. produce a somewhat smaller deviation from a Doppler-shaped emission line, though still a substantial one. No satisfactory reason can be given for the apparently different optical properties of OI and NI discharge light sources.

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Table I. Experimental oscillator strengths, A-values, and radiative lifetimes for the NI resonance triplet.

Authors	Method	$\Sigma g_L f_{LU}$	A_{UL} (10^8 sec^{-1})	τ (10^{-9} sec)
Prag, Fairchild, Clark[6]	Line absorption titration	0.39 ± 0.12	1.5 ± 0.5	6.7 ± 2.0
Labuhn[3]	Cascade arc	1.41 ± 0.56	5.4 ± 2.2	1.85 ± 0.74
Morris and Garrison[5]	Gerdin arc	3.5 ± 1.5[a]	13.5 ± 6[a]	0.74 ± 0.33[a]
Lawrence and Savage[9]	Lifetime	1.04 ± 0.13	4.0 ± 0.5	2.5 ± 0.3
This work	Line absorption titration	0.87 ± 0.20	3.3 ± 0.8	3.0 ± 0.7

[a]Based on calculated Doppler and Stark half widths.

Table II. Experimental oscillator strengths, A-values, and radiative lifetimes for the OI resonance triplet.

Authors	Method	$\Sigma g_L f_{LU}$	ΣA_{UL} (10^8 sec^{-1})	τ (10^{-9} sec)
Prag, Fairchild, Clark[6]	Line absorption titration	0.30 ± 0.08	3.9 ± 1.0	2.6 ± 0.7
Parkes, Keyser, Kaufman[8]	Line absorption titration	0.19 ± 0.03	2.5 ± 0.4	4.0 ± 0.6
Boldt and Labuhn[4]	Cascade arc	1.5 ± 0.5	19.5 ± 7	0.51 ± 0.2
Morris and Garrison[5]	Gerdin arc	0.28 ± 0.11[a]	3.7 ± 1.5[a]	2.7 ± 1.1[a]
Savage and Lawrence[2]	Lifetime	0.32 ± 0.04	4.2 ± 0.5	2.4 ± 0.3
Gaillard and Hesser[2]	Lifetime	0.45 ± 0.08	5.9 ± 1.0	1.7 ± 0.3
Lawrence[1]	Lifetime	0.420 ± 0.011	5.50 ± 0.15	1.82 ± 0.05
This work	Line absorption titration	0.42 ± 0.08	5.5 ± 1.0	1.8 ± 0.3

[a]Based on calculated Doppler and Stark half widths.

Table III. Experimental f_{LU} for NI lines.

Strongest line, 1199.55Å.

Ar diluent in light source: 0.093, 0.093, 0.095, 0.096, 0.093, 0.094;

He diluent: 0.098, 0.091;

      average: 0.094.

Middle line, 1200.22Å.

Ar diluent: 0.063, 0.064, 0.064;

      average: 0.064.

Weakest line, 1200.71Å.

Ar diluent: 0.032, 0.032, 0.033;

      average: 0.032.

Table IV. Experimental f_{LU} for the OI line at 1302.17Å

with He or Ar diluent in light source.

He: 0.044, 0.041, 0.044, 0.045, 0.047, 0.045;

                                                    average: 0.044.

Ar: 0.020, 0.023, 0.021, 0.021, 0.020;

                                                    average: 0.021.

Fig. 1. Diagram of Apparatus.

Fig. 2. Plot of $k_0 \ell$ vs. added NO for absorption of strongest NI line at 1199.55Å.

and line 1 are experimental

calculated for $A = 2.6 \times 10^{12}$ cm^{-3}, $k_1 = 4 \times 10^{-11}$ cm^3 sec^{-1}

calculated for $A = 2.6 \times 10^{12}$ cm^{-3}, $k_1 = 2 \times 10^{-11}$ cm^3 sec^{-1}

calculated for $A = 2.3 \times 10^{12}$ cm^{-3}, $k_1 = 4 \times 10^{-11}$ cm^3 sec^{-1}

calculated for $A = 2.3 \times 10^{12}$ cm^{-3}, $k_1 = 2 \times 10^{-11}$ cm^3 sec^{-1}

Figure 1.

Figure 2.