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Lifetime of the N_2 Vegard–Kaplan System*

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The results of an experiment by Carleton and Oldenberg, designed for the measurement of the relative lifetimes of the N_2 $B\,^3\Pi_g$ and $A\,^3\Sigma_u^+$ states, have been reanalyzed. The reanalysis was prompted by the assumption, in the original analysis, that the N_2 first positive (1*PG*) (1, 0) band could be described as a Hund's case (b) transition in the levels contributing significantly to the emission. The $B\,^3\Pi_g$ state is in fact intermediate in coupling between Hund's cases (a) and (b), with a rather gradual change from case (a) to case (b) as a function of increasing J. The error in the calculation of the population of the $A\,^3\Sigma_u^+$ $(v=0)$ level from the measurement of self-absorption in the N_2 1*PG* (1, 0) band, assuming Hund's case (b) coupling, is significant. An additional error due to neglect of a degeneracy factor (Λ-type doubling) resulted in a relative lifetime differing by a factor of about 7 from the recalculated value. The lifetimes of the $A\,^3\Sigma_u^+$ $(v=0)$ level, calculated using the $B\,^3\Pi_g$ $(v=1)$ lifetime measured by Jeunehomme, are 1.36 sec for the $\Sigma=0$ substate and 2.7 sec for the $\Sigma=1, -1$ substates, with a probable error of about 20%.

I. INTRODUCTION

A considerable number of attempts to measure the lifetime of the metastable N_2 $A\,^3\Sigma_u^+$ state have been made as a consequence of the importance of the N_2 Vegard–Kaplan (VK) $(A\,^3\Sigma_u^+–X\,^1\Sigma_g^+)$ system to both auroral studies and laboratory work involving active nitrogen. The forbidden nature of the transition has made the measurements and analysis difficult; the published lifetimes vary over a three-orders-of-magnitude range. Part of the scatter in the estimates can be attributed to erroneous analysis, but more than an order of magnitude of the uncertainty is due to the difficulty in making the measurements (Shemansky[1]). The majority of the estimates stem from observations of various types of laboratory afterglows. The decay of $A\,^3\Sigma_u^+$ state population in nearly all cases is dominated by diffusion to the walls of the container. The extraction of the radiative lifetime from this and other competing processes of radiationless deactivation (and possibly reactivation) depends critically on the accuracy of the measurements. The disparity in the published lifetimes suggests an accuracy of only an order of magnitude for the afterglow method of measurement. The experimental approach of Carleton and Oldenberg[2] (see also Oldenberg *et al.*[3]) is in principle much more accurate, since the measurements are independent of the processes that critically affect the afterglow experiments. The prospect of a reasonably accurate measure of the lifetime has prompted a reanalysis of their work in this paper. The experiment involved the direct measurement of the $A\,^3\Sigma_u^+$ $(v=0)$ population and the volume emission rate of the VK (0, 6) band, with the excited gas in a steady state. Thus the transition probability of the band, and hence the lifetime of the $v=0$ level, obtained from the ratio of the two measured quantities, would be independent of the processes controlling the $A\,^3\Sigma_u^+$ population. The accuracy of the lifetime estimate is in direct proportion to the accuracy of the population and volume emission rate measurements, in contrast to the afterglow experiments in which an error of 10% in the measured decay rate, or pressure, could cause as much as a factor of 5 error in the estimate of radiative lifetime. Some of the details of the Carleton and Oldenberg experiment will now be discussed in order that the following reanalysis may be readily understood.

The population of $A\,^3\Sigma_u^+$ $(v=0)$ molecules was determined in an electric discharge by a measurement of the fractional self-absorption $(\Delta I/I)$ of the (1, 0) N_2 first positive (1*PG*) band; the $A\,^3\Sigma_u^+$ state forms the lower state of the 1*PG* $(B\,^3\Pi_g–A\,^3\Sigma_u^+)$. The measurement of $\Delta I/I$ required a special technique, since the ratio was of the order of 10^{-2}, and not easily measured by the usual method. The measuring instrument was a dual-beam photometer. The absorption tube containing the $A\,^3\Sigma_u^+$ molecules, excited by a dc discharge, was placed in the path of one of the beams, along with an interference filter to isolate the (1, 0) N_2 1*PG* band. A background tube also excited by a dc discharge (at the same pressure as the absorption tube, 8 torr) provided the beam of N_2 1*PG* radiation which was to be measured. The second beam of the photometer, which was used to null the instrument, was also provided by the background tube through the use of a beam splitter. The background beam was chopped in order to discriminate against the unwanted N_2 1*PG* radiation from the absorption tube. The

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[2] N. P. Carleton and O. Oldenberg, J. Chem. Phys. **36**, 3460 (1961).

[3] O. Oldenberg, D. G. Bills, and N. P. Carleton, J. Opt. Soc. Am. **51**, 526 (1961).

chopper also performed the function of alternating the two photometer beams on the surface of a photomultiplier tube, to produce a null dc signal, with the absorption tube turned off. Thus with the absorption tube turned on, a measure of ΔI was obtained as an ac unbalance in the photomultiplier signal. This procedure avoided the very large dynamic range that would have been required to measure the ratio $(\Delta I/I)$ directly. The system was calibrated, by stretching a wire of known diameter across the absorption beam, in order to calculate $\Delta I/I$ from the measured signal.

The volume emission rate of the (0, 6) VK band in the absorption tube was measured with a spectrograph calibrated with a standard tungsten-ribbon lamp.

The reanalysis presented below is concerned with the calculation of the relationship of the measured $\Delta I/I$ to the population (N) of the $A\,{}^3\Sigma_u{}^+$ state. The quantity $(\Delta I/I)\ (1/N)$ for a band depends on the variation of the absorption probabilities of the lines within each branch, as a function of the quantum number J or K. There is also a dependence on temperature (T), $(\Delta I/I)(1/N) \propto T^{-1}$, for Doppler broadened lines. $(\Delta I/I)(1/N)$ can be calculated if the line-strength factors for the $(B\,{}^3\Pi_g$–$A\,{}^3\Sigma_u{}^+)$ transition are known. Carleton and Oldenberg calculated $(\Delta I/I)(1/N)$ by assuming the transition could be adequately represented by Hund's case (b) coupling. The transition is in fact characterized by coupling intermediate between Hund's cases (a) and (b). It will be shown that the error in the calculated population, and hence the lifetimes, due to the assumption of case (b) coupling, is significant. The neglect of the degeneracy due to Λ-type doubling in the $B\,{}^3\Pi_g$ state, in the original analysis, contributes an additional factor of 2 to the error. The recalculated effective absorption probability, relative to the lifetime of the $B\,{}^3\Pi_g$ state, differs by a factor of 7 from that of the original analysis. However, the lifetime of the $A\,{}^3\Sigma_u{}^+$ state calculated by Carleton and Oldenberg (2 sec) is roughly the same as the values determined in the present work, because the earlier estimate of the $B\,{}^3\Pi_g$ state lifetime was also in error by about a factor of 7. The more recent estimates of lifetime for the $A\,{}^3\Sigma_u{}^+$ state (Wentink and Isaacson,[4] Brennen[5]) based on the Carleton and Oldenberg results, with more accurate lifetimes of the $B\,{}^3\Pi_g$ state, are about 12 sec. In addition to the factors discussed above, the analysis presented below takes into account the double lifetime of the $A\,{}^3\Sigma_u{}^+$ state (Shemansky[1]). The recalculated lifetimes of the $v=0$ level are 1.36 sec for the $\Sigma=0$ substate levels and 2.7 sec for the $\Sigma=1, -1$ substate levels.

II. THEORY: SELF-ABSORPTION FOR A BAND

The weak fractional self-absorption $(\Delta I/I)$ for a single Doppler broadened line can be written in the following form (Mitchell and Zemansky[6]),

$$\Delta I/I = h\nu BNl/\alpha_D(2\pi)^{1/2}, \tag{1}$$

where B is the absorption probability, N is the population of the lower state, l is the length of the absorbing path, and $\alpha_D=(\nu/c)(2kT/m)^{1/2}$ is the Doppler width of the line. This α_D differs by the factor $(\ln 2)^{1/2}$ from the definition given by Ref. 6. The symbol ν refers to wavenumber (cm^{-1}) throughout the discussion.

The generalized form of Eq. (1) for a band can be written

$$\frac{\Delta I}{I} = \frac{hl}{(2\pi)^{1/2}\alpha_D} \times \sum_{i,J''} N_{J''}{}^{i}\Big(\sum_{j,J'} I_{J'J''}{}^{ji} B_{J''J'}{}^{ij} \nu_{J''J'}{}^{ij}\Big)/I, \tag{2}$$

where j, i refer to the upper and lower substates, respectively, and

$$I = \sum_{i,J''}\sum_{j,J'} I_{J'J''}{}^{ji}$$

is the total intensity of the band.

In this case the desired quantity is the total population in a particular vibrational level of the $A\,{}^3\Sigma_u{}^+$ state,

$$N = \sum_{i,J''} N_{J''}{}^{i}. \tag{3}$$

It should be noted that the transition probability of the N_2 1*PG* band is related to the absorption probability by the equation

$$A_{J'J''}{}^{ji} = 8\pi hc(\nu_{J'J''}{}^{ji})^3(d_{J''}{}^{i}/d_{J'}{}^{j})B_{J''J'}{}^{ij}, \tag{4}$$

where $d_{J'}{}^{j}=2J'+1$ and $d_{J''}{}^{i}=2J''+1$, are the degeneracies of the upper and lower states.

The degeneracy of the upper state due to Λ-type doubling does not appear directly in Eq. (4), since the levels are actually separated by a small amount of energy. However, the summation of Eq. (4) over i and J'', for the determination of the total transition probability of a given level, must be made over the four or five transitions (rather than the total of nine), from either the symmetric or antisymmetric part of the level J'. The symmetry of the transition probabilities is such that the total transition probability

$$A_{J'}{}^{j} = \sum_{i,J''} A_{J'J''}{}^{ji} \tag{5}$$

is the same for the symmetric and antisymmetric parts of a given level J'. $A_{J'}{}^{j}$ varies only slightly as a function of J' and j. One can therefore define a single transition probability, $A_{v'v''}$, for a band of the N_2 1*PG*. The transition probability of the band is related to the absorption probability $(B_{v'',v'})$ by the equation

$$A_{v'v''} = A_{J'}{}^{j} = 4\pi hc(\nu_{v'v''})^3 B_{v''v'}. \tag{6}$$

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[4] T. Wentink and L. Isaacson, J. Chem. Phys. **46**, 822 (1967).

[5] W. Brennen, J. Chem. Phys. **44**, 1793 (1966).

[6] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, New York, 1961).

Equation (6) in contrast to Eq. (4) includes the degeneracy due to Λ-type doubling, since by definition $A_{v'v''}$ and $B_{v''v'}$ are the summations of all transitions from a given level; $A_{v'v''}$ is determined by the summation of an average of 4.5 transitions while $B_{v''v'}$ is determined by a summation of 9 transitions. In other words, Eq. (6) would remain the same whether the Λ-doubling components were degenerate or not; a change from nondegeneracy to degeneracy would produce no change in the $A_{J'}{}^j$, or $B_{J''J'}{}^{ij}$ values, but the $A_{J'J''}{}^{ji}$ values would be reduced by one-half, and the summation in Eq. (5) would take place over 9 transitions rather than 4 or 5.

III. EVALUATION

The volume emission rate for a band is given by the equation

$$I_{v'v''}=\sum_j N_{v'}{}^jA_{v'v''}{}^j. \qquad (7)$$

The object of the experiment was to measure $I_{v'v''}$ and $N_{v'}=\sum_j N_{v'}{}^j$, in order to calculate the $A_{v'v''}{}^j$, for the (0, 6) band of the N_2 VK system. $I_{0,6}$ was measured directly with a calibrated spectrograph. N_0 was calculated from a measurement of the fractional self-absorption $(\Delta I/I)$ of the $1PG$ (1, 0) band through the use of Eq. (2). Note that Eq. (7) differs from the corresponding equation in the original analysis; the total intensity is now separated into the contributions from each of the substates. This is due to the fact that the superscript j is not redundant in the case of the VK system, in contrast to most other electronic transitions [cf. Eq. (6)]; the lifetime of the VK system is double valued, with $A_{v'v''}{}^1=A_{v'v''}{}^3=\frac{1}{2}A_{v'v''}{}^2$ (Shemansky[1]).

Equation (2) can be evaluated provided one has knowledge of, or assumes, the relative populations of the rotational levels in the upper and lower states, and the relative transition probabilities of the lines of the band. This is where the major difference between the present and the original analysis arises. The $(B\,{}^3\Pi_g$–$A\,{}^3\Sigma_u{}^+)$ transition was originally assumed to be characterized by Hund's case (b) coupling for a significant portion of the band. This implies that the transition probabilities of the lines within each branch would be a constant. However, it will be shown that the transition is characterized by coupling intermediate between Hund's cases (a) and (b), with a significant variation in the transition probabilities of the lines within each branch. The relationship between $(\Delta I/I)$ and N, determined by Eq. (2), is sensitive to this variation, and the assumption of case (b) coupling results in a significant compound error. The error is compounded since both the line-strength factors and the energy values would be invalid, leading to an erroneous population distribution and temperature measurement.

The populations in the rotational levels within the $B\,{}^3\Pi_g$ and $A\,{}^3\Sigma_u{}^+$ states have been assumed to be distributed in thermal equilibrium. The validity of these assumptions will be discussed later. The populations of the levels are therefore given by the equations

$$N_{J'}{}^j=(N^j/Q_j)(2J'+1)\exp[-F_j(J')/kT], \qquad (8)$$

$$N_{J''}{}^i=(N^i/Q_i)(2J''+1)\exp[-F_i(J'')/kT], \qquad (9)$$

where Q_j, Q_i and F_j, F_i are the partition functions and rotational energies of the upper and lower states, respectively. The line-strength factors for the N_2 $1PG$ bands have been determined theoretically by Budó[7] for the coupling case intermediate between Hund's cases (a) and (b). The energy equations for the $B\,{}^3\Pi_g$ state are given by Budó,[8,9] and those for the $A\,{}^3\Sigma_u{}^+$ state, by Schlapp.[10] The molecular constants used in the computation are given by Shemansky and Vallance Jones.[11]

The absolute transition probability for the N_2 $1PG$ (1, 0) transition was determined by Shemansky and Vallance Jones from the lifetime measurements of Jeunehomme.[12] This value of $A_{1,0}$ was then used to calculate the vibronic matrix element (D_1) by combining Eqs. (5) and (6) with the relationship

$$A_{J'J''}{}^{ji}=\frac{(C2)(D_1{}^2)(\nu_{J'J''}{}^{ji})^3(S_J{}^{ji})}{(2J'+1)}, \qquad (10)$$

where $S_J{}^{ji}$ is the line-strength factor, and $C2=64\pi^4/3h$. Because of the fact that the lifetime of the $B\,{}^3\Pi_g$ state varies slightly as a function of J', $D_1{}^2$ was computed at the level $J'=8$, $j=3$, as a rough average value for the band.

The total population (N_0) of the $A\,{}^3\Sigma_u{}^+$ $(v=0)$ level was computed from Eq. (2) as a function of temperature with the aid of the K.P.N.O. CDC 3200 computer, using Carleton and Oldenberg's measured value of $(\Delta I/I)$. The transition probabilities of the N_2 (VK) (0, 6) band were then determined using the equations

$$A_{0,6}{}^2=(3/2)I(\text{VK})_{0,6}/N \qquad (11)$$

and

$$A_{0,6}{}^1=A_{0,6}{}^3=(3/4)I(\text{VK})_{0,6}/N, \qquad (12)$$

derived from Eq. (7), where $I(\text{VK})_{0,6}=1.35\times10^{10}$ $\text{cm}^{-3}\cdot\text{sec}^{-1}$, as given by Ref. 2.

The total transition probability $(A_0{}^i)$ for the $A\,{}^3\Sigma_u{}^+$, $(v=0)$ level can be determined from the relative transition probabilities given by Shemansky[1]

$$[\tau^i(0)]^{-1}=A_0{}^i=\sum_{v''}A_{0,v''}{}^i=4.80A_{0,6}{}^i. \qquad (13)$$

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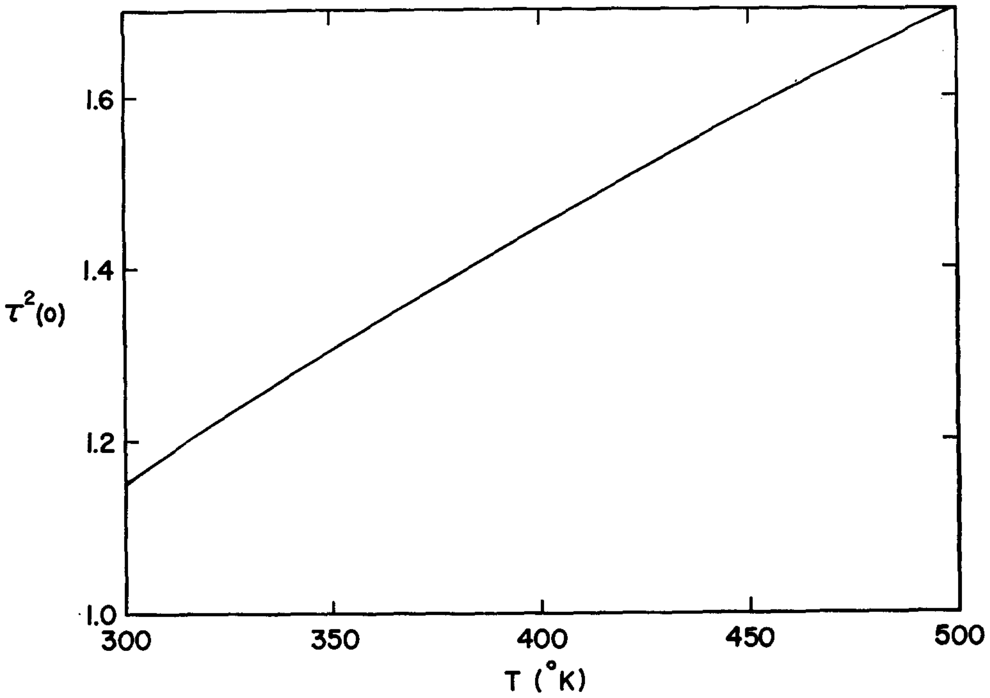

FIG. 1. Lifetime [$\tau^2(0)$ seconds] of the $A\ ^3\Sigma_u^+$ state as a function of temperature.

This does not imply a dependence on the absorption measurements of Ref. 1; the relative values of the electronic transition moment in the appropriate region of internuclear distance are determined largely by the emission measurements.

The lifetime of the $i=2$ levels [$\tau^2(0)$], calculated using Eqs. (2), (8), (9), (11), and (13), is plotted in Fig. 1 as a function of assumed temperature. The curve $\tau^2(0)$ vs T takes into account the instrumental transmission function. This curve differs by less than 15% from the curve calculated assuming a constant instrumental transmission function, independent of wavelength.

As Fig. 1 illustrates, the kinetic temperature of the gas must be taken into account in the analysis. Carleton and Oldenberg measured the temperature by doing a rotational analysis of a high-resolution spectrogram of the (1, 0) 1*PG* band, obtained from the background tube. However, the assumption of case (b) coupling for the transition leads to an erroneous temperature, since the relative populations of the rotational levels would not be properly separated from the transition probabilities of the lines. The temperature was therefore recalculated by comparing theoretical spectra with the original high-resolution spectrogram. The remeasured temperature was 370°±20°K, 50°K lower than the original estimate. This corresponds to lifetimes of $\tau^1(0)=\tau^3(0)=2.7$ sec and $\tau^2(0)=1.36$ sec.

IV. DISCUSSION

The experimental conditions were such that the assumptions involved in Eq. (2) should be valid. The pressure in both the emission and absorption tubes was 8 torr, and the temperatures of the tubes were roughly equal. Pressure broadening should be negligible at 8 torr, and Doppler broadening would be the dominant mechanism. The absorption was certainly weak, since the measured fractional absorption was $\Delta I/I=8\times10^{-3}$.

The validity of Eq. (9) is virtually a certainty even though the emission process, due to the double lifetime of the $A\ ^3\Sigma_u^+$ state, would tend to disturb the equilibrium; the very large number of collisions between excitation and emission, and between emissions, ensures that the population distribution would be very nearly thermal (Shemansky[1]). The validity of Eq. (8) also appears to be fairly certain, since one would expect about 10^8 kinetic collisions between excitation and emission; there is experimental evidence that rotational relaxation in the $B\ ^3\Pi_g$ state takes place at roughly the kinetic rate. This evidence is shown in Figs. 2(a)–2(c), which compare experimental and computed spectra. The experimental spectra in Figs. 2(b) and 2(c) were obtained with a $\frac{1}{2}$-m Ebert–Fastie-type scanning spectrometer, using pulse-counting techniques. The system is described by Broadfoot and Hunten.[13] The theoretical spectra were computed with a triangular instrumental function of half-width $\Delta\lambda=3.00$ Å. The wavelength mismatch of some of the features is due to nonuniformity in the grating drive. The experimental spectrum of Fig. 2(a) is an unpublished spectrum obtained by Vallance Jones, using a scanning spectrometer with a lead sulfide detector. Figure 2(c) shows an

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[13] A. L. Broadfoot and D. M. Hunten, Planetary Space Sci. 14, 1303 (1966).

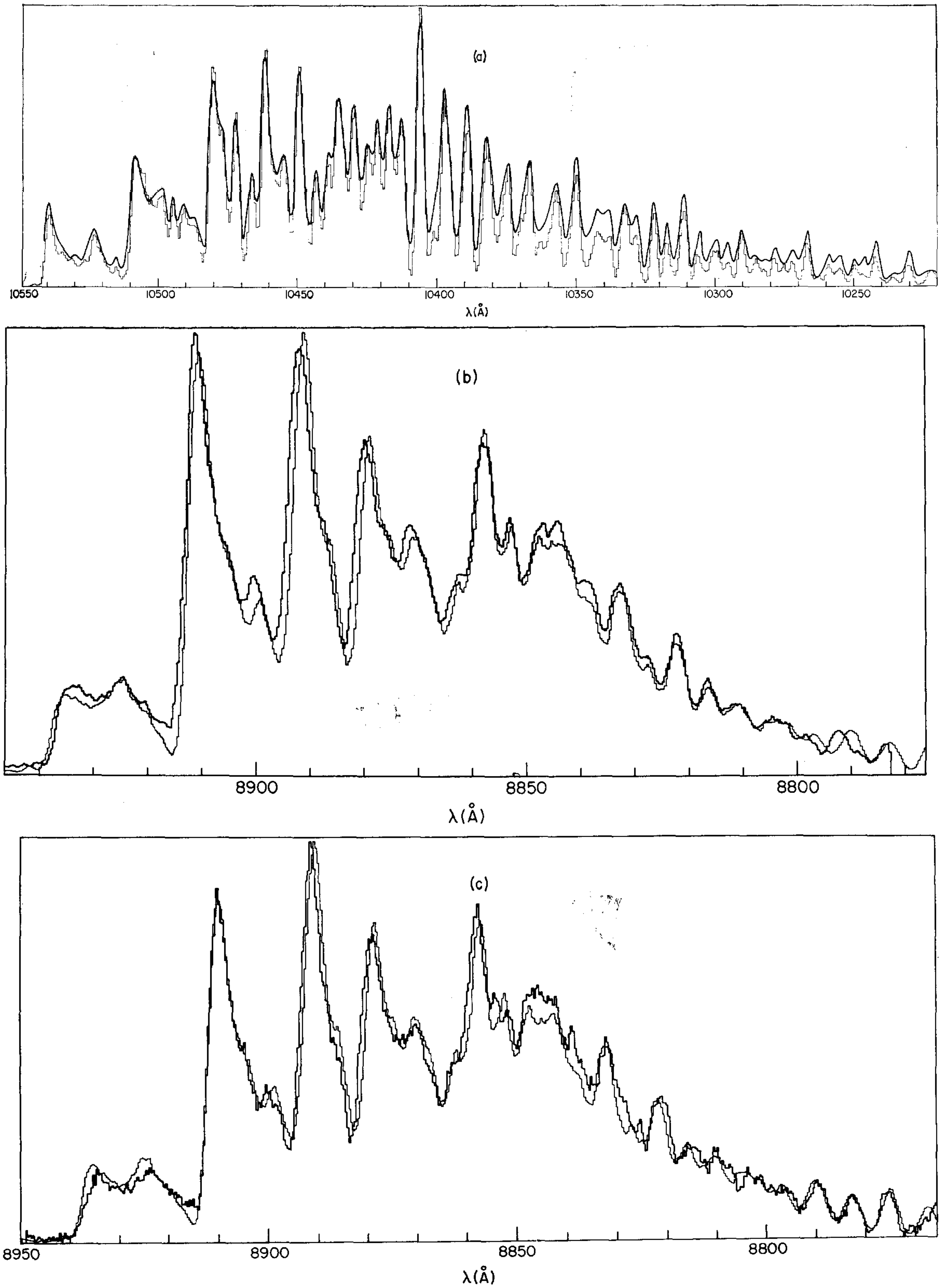

FIG. 2. Comparison of experimental and synthetic spectra of N_2 1*PG* (0, 0) and (1, 0) bands, with the rotational levels of the $B\ {}^3\Pi_g$ state in thermal equilibrium. Heavy traces are the experimental spectra; light traces are the synthetic spectra. (a) Experimental spectrum: from Vallance Jones (unpublished). Synthetic spectrum: (0, 0) band, $\Delta\lambda = 2.0$ Å, $T = 700$°K. (b) Experimental spectrum: Geissler discharge tube. Synthetic spectrum: (1, 0) band, $\Delta\lambda = 3.00$ Å, $T = 325$°K. (c) Experimental spectrum: Microwave discharge at 20 μ pressure. Synthetic spectrum: (1, 0) band, $\Delta\lambda = 3.00$ Å, $T = 400$°K.

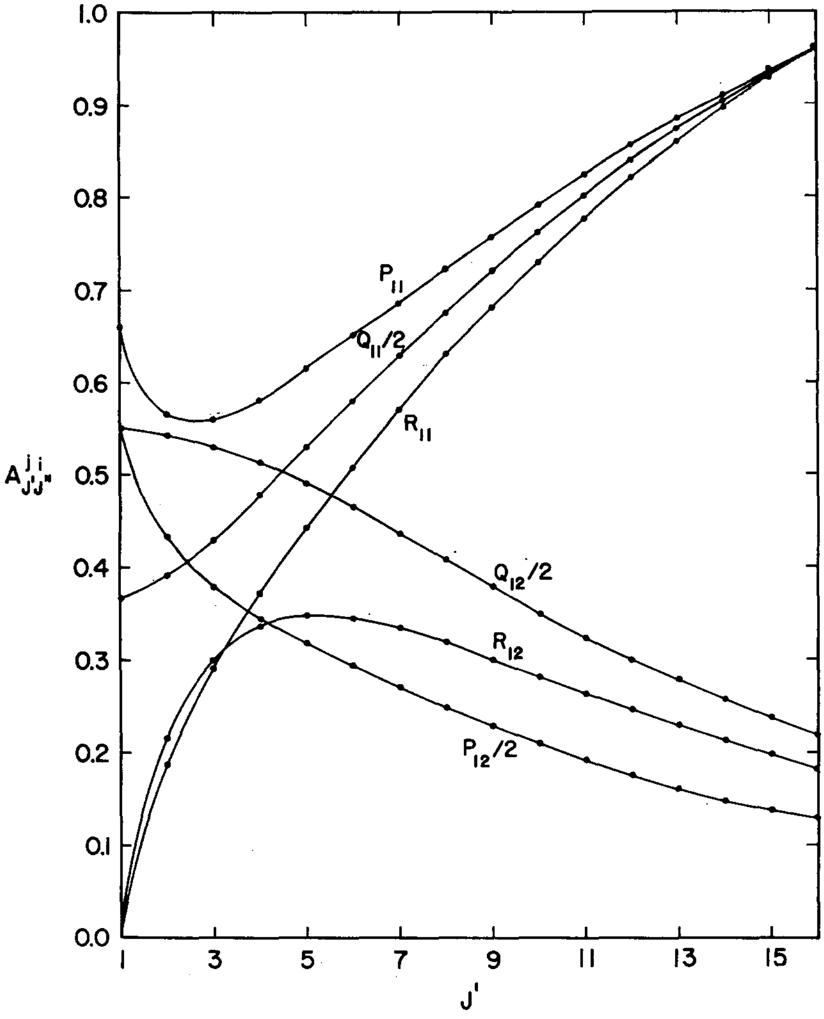

FIG. 3. Relative transition probabilities of branches of an N_2 1*PG* band.

experimental spectrum of the (1, 0) band obtained from a microwave discharge at about 20 μ pressure. The superposed theoretical spectrum, calculated for thermal equilibrium in the $B\,^3\Pi_g$ state, fits the experimental trace remarkably well. At 20 μ pressure the kinetic collision rate would be about 2 per lifetime. Although as many as one-half the collisions may be with the walls of the discharge tube, the remarkable agreement of the theoretical and experimental spectra suggests that rotational relaxation must be taking place at about the kinetic rate. Theoretical spectra, calculated with a rotational distribution in the $B\,^3\Pi_g$ state controlled by electron excitation, cannot be fitted to a spectrum in thermal equilibrium for any temperature. The nonthermal spectra are characterized by significant differences in the intensities of the features composed of the P_{11} head at 8912 Å, and the P_{32} and Q_{33} heads at 8858 and 8859 Å, relative to those for the thermal equilibrium case.

The accuracy of the population (N_0) of the $A\,^3\Sigma_u^+$ state calculated from ($\Delta I/I$) also depends on how accurately the theoretical line-strength factors and energy values reproduce the structure of the 1*PG* bands. Figure 2(a) shows theoretical and experimental spectra of the (0, 0) band. The spectra appear to be in very good agreement. The moderate amount of mismatch in the spectra is probably due mostly to the instrumental time constant, which was not taken into account in the computed spectrum. The complexity of the 1*PG* bands is well illustrated in this figure; the bands have 27 branches of comparable intensity, with 10 or 11 heads. Figure 2(b) shows an experimental spectrum obtained from a Geissler discharge tube in comparison with a theoretical spectrum computed for thermal equilibrium in the $B\,^3\Pi_g$ state. The pressure in the discharge tube was a few torr. Thus one would expect negligible error as a result of the use of the theoretical line-strength factors and energy values.

An estimate of the error due to the assumption of case (b) coupling can be made by applying the same transition probability for the N_2 1*PG* (1, 0) band to the original analysis. The lifetimes, for a temperature of 370°K, in this case are $\tau^1(0)=\tau^3(0)=19$ sec and $\tau^2(0)=9.5$ sec, a factor of about 7 larger than the present estimates. One-half of this factor is due to the assumption of case (b) coupling; a factor of 2 arises from the fact that the original analysis did not take Λ-type doubling into account in the relationship between $A_{v'v''}$ and $B_{v''v'}$ [Eq. (6)]. Case (b) coupling implies that there would be no differences in energy between the substates, and that the transition probability for most of the lines of a given branch would be constant, independent of the quantum number J or K. The ($B\,^3\Pi_g$–$A\,^3\Sigma_u^+$) transition is in fact intermediate in coupling between Hund's cases (a) and (b), with a very gradual transition to case (b) coupling with increasing J. Figure 3 illustrates this variation for three main branches and three satellite branches of an N_2 1*PG* band. The other 21 branches display a similar variation. The relative transition probabilities for case (b) coupling would be horizontal straight lines in the figure. The error one would expect as a result of neglecting the variation is significant since there is a $(B_{J''J'}{}^{ij})^2$ term in the equation for ($\Delta I/I$). That is, Eq. (2) can be reduced to the form

$$\Delta I/I \propto \sum\sum N_{J''}{}^{i} N_{J'}{}^{j} (B_{J''J'}{}^{ij})^2 \Big/ \sum\sum N_{J'}{}^{j} B_{J''J'}{}^{ij}. \tag{14}$$

An additional error results from the nonapplicability of the rotational energy equation, for case (b) coupling, to the energy levels of the $B\,^3\Pi_g$ state; the splitting of the substates is significant and the energy equations for the intermediate coupling case must be applied. Thus the error was a compound of erroneous relative rotational populations of the $B\,^3\Pi_g$ state and erroneous relative transition probabilities.

We judge that the analysis given here contributes a negligible error to the final result. Four measured quantities enter: the lifetime of the $B\,^3\Pi_g$ state, the self-absorption of the (1, 0) 1*PG* band ($\Delta I/I$), the temperature, and the volume emission rate of the (0, 6) VK band. The lifetime of the $B\,^3\Pi_g$ state measured by Jeunehomme[12] appears to be well established. The more recent measurements of Wentink and Isaacson,[4] and Peterson[14] are in good agreement, and the probable error (5%) given by Jeunehomme appears to be valid. Carleton and Oldenberg obtained a signal-to-noise ratio of about 10 in their measurement of ($\Delta I/I$) and estimate a probable error of 10%. Their error estimate for the measurement of the volume emission rate of the VK band is also about 10%. The accuracy of the temperature measurement is estimated to be 5%. Thus the probable error of the calculated lifetimes should be roughly 20%.

V. CONCLUSION

The Carleton and Oldenberg experiment for the measurement of the lifetimes of the N_2 $A\,^3\Sigma_u^+$ ($v=0$) level has been reanalyzed, using accurate theoretical line-strength factors and energy values for the ($B\,^3\Pi_g$–$A\,^3\Sigma_u^+$) transition. The original analysis was in error due to the use of line-strength factors and energy values based on Hund's case (b) coupling, and the neglect of the degeneracy of the $B\,^3\Pi_g$ state due to Λ-type doubling. The good agreement of the original lifetime estimate with the present values is due to a compensating error of a factor of 7 in the lifetime of the $B\,^3\Pi_g$ state.

Errors in the present work due to the asymptotic approximations implied by Eqs. (2), (8), and (9), and due to the use of the theoretical line-strength factors and energy values of the ($B\,^3\Pi_g$–$A\,^3\Sigma_u^+$) transition, are considered to be negligible. The experimental conditions were such that the line shapes would be dominated by Doppler broadening. The absorption was very weak ($\Delta I/I = 8\times10^{-3}$). There is little doubt that the rotational populations of the $B\,^3\Pi_g$ and $A\,^3\Sigma_u^+$ states were in thermal equilibrium. The spectra of Fig. 2 suggest a high degree of accuracy for the theoretical line-strength factors and energy values of the N_2 1*PG*. Thus the probable error of the calculated lifetimes is determined by the experimental measurements alone.

The lifetimes of the $A\,^3\Sigma_u^+$ ($v=0$) level are 1.36 sec for the $\Sigma=0$ substate levels, and 2.7 sec for the $\Sigma=1, -1$ substate levels, with a probable error of about 20%.

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