Oscillator strengths for the $W^3\Delta_u$-$X^1\Sigma_g^+$ band system of molecular nitrogen

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Bands of this highly forbidden transition have been observed thus far in absorption only. In fact, emission of the $W^3\Delta_u \rightarrow X^1\Sigma_g^+$ system is not to be expected from vibrational levels above $W(0)$, since these levels are more rapidly depleted by $W^3\Delta_u \rightarrow B^3\Pi_g$ transitions. For $W(0)$, however, the ν^3 factor so heavily favors the $W \rightarrow X$ that a progression of partially developed emission bands is to be expected in the 2000-Å region (when collisional deactivation is low.) These emissions are also favored by the circumstance that the $W^3\Delta_u$ is the N_2 state most readily excited by low-energy electrons so that the $v = 0$ level may attain a very large population. The present measurements consist of intercomparisons of absorption bands recorded photographically in the 1500-Å region to yield f numbers for several bands of the $W \leftarrow X$ system of N_2. From these, transition probabilities for absorption and emission between the various levels of the $W^3\Delta_u$ and the ground state $X^1\Sigma_g^+$ have been calculated. For the $W^3\Delta_u$ $v = 0$ level, however, the calculation of transition probabilities for emission and of a lifetime becomes a rather complicated procedure as a result of the competitive relationship between $W^3\Delta_u \rightarrow X^1\Sigma_g^+$ and $W^3\Delta_u \rightarrow B^3\Pi_g$ for this one level. It turns out that the forbidden vacuum ultraviolet emission becomes more probable than the permitted emission which falls in the infrared beyond 100 μm. The predominance of the ultraviolet is not clearcut, however, with one of the three spin components more directed to the infrared and with a J-dependent branching ratio all across the band. Thus the measured lifetime for the $W^3\Delta_u$ $v = 0$ must be given as an intricately averaged value for just two of the spin components. It is found to be 4 sec, a lifetime which can be realized only in low-collision environments. Parameters are favorable for lasing to the $B^3\Pi_g$ $v = 0$ level.

I. INTRODUCTION

We have previously measured transition probabilities for the $W^3\Delta_u - B^3\Pi_g$ system of molecular nitrogen and we have reported lifetimes for several vibrational levels of the $W^3\Delta_u$ state.[1] It is anticipated that such data will be useful in atmospheric radiative-transfer calculations, the construction of models for afterglow mechanisms in the presence of nitrogen, and, particularly, in the detailed study of excitation processes for the aurora. The extensive investigations of Cartwright,[2] Chutjian *et al.*,[3] and Cartwright, Trajmar, and Williams[4] serve to underline the importance of this kind of measurement to a thorough treatment of auroral excitation. Cartwright[5] has emphasized, for example, that a considerable portion of the auroral energy at the top of the atmosphere appears either as emission from N_2 or resides in low-lying N_2 electronic states such as the $W^3\Delta_u$ which then participate in energy-transfer processes with other atmospheric species. Furthermore, Cartwright *et al.*[6] have found that the total cross section for the excitation of the $W^3\Delta_u$ from the ground state by low-energy electrons is so large that no other N_2 state attains as high an excitation rate in either auroras or glow discharges.

In a preceding work,[1] it was pointed out that the natural lifelines of the $W^3\Delta_u$ levels could be realized only to rather specialized (low-collision-frequency) environments. Attention was further called to the fact that the $v = 0$ level, with a probability of transition to the $B^3\Pi_g$ several orders of magnitude lower than that for $v = 1$, is quite unique. This level, which has previously been characterized as confluently metastable,[7] is an upper level of both the $W^3\Delta_u \rightarrow B^3\Pi_g$ and the $W^3\Delta_u \rightarrow X^1\Sigma_g$ transitions. The potential curves for the states involved are given in Fig. 1. These are the four lowest electronic states of molecular nitrogen and encompass two permitted electronic transitions, $W^3\Delta_u \rightarrow B^3\Pi_g$ and $B^3\Pi_g \rightarrow A^3\Sigma_u^+$. The $W^3\Delta_u \rightarrow X^1\Sigma_g^+$ transition is dipole forbidden by virtue of the $\Delta\Lambda = 0, \pm 1$ selection rule and is spin forbidden as well. The enormous disparity in ν^3 in favor of $W \rightarrow X$ over $W \rightarrow B$, however, calls for an examination of relative transition probabilities for emission. To arrive at a lifetime for the $W^3\Delta_u$ $v = 0$ level, then, we must consider (at least) these two systems of transitions. The present work is concerned with a determination of the probability of the second type of transition, $W^3\Delta_u - X^1\Sigma_g^+$.

Since it is only the progression originating in the $v = 0$ level of the $W^3\Delta_u$ that is likely to be observed in transitions to the $X^1\Sigma_g^+$, the spectral domain of the electronic system is relatively narrow. It is to be sought within a few hundred angstroms of 2000 Å. The wavelengths and Franck-Condon factors for the bands of this progression have been tabulated by Saum and

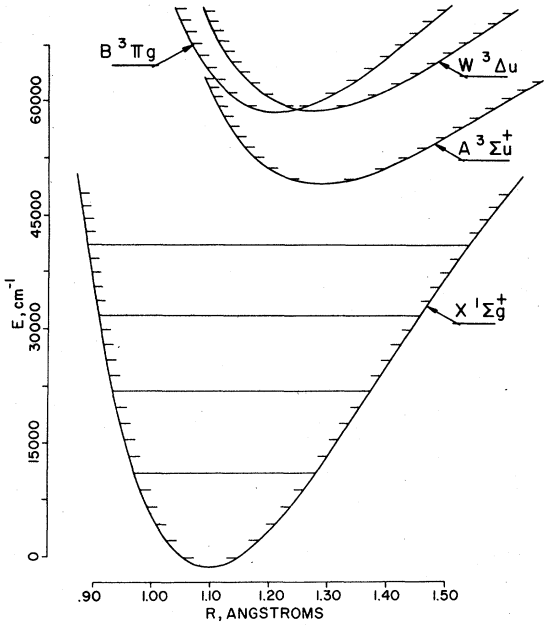

FIG. 1. Potential-energy curves for the four lowest electronic states of molecular nitrogen, with vibrational levels indicated. The present work is concerned with the lifetime of the $v=0$ level of the $W\,^3\Delta_u$. Note that $v=0$ levels of the W and B states apparently coincide in energy on this scale since the 73-cm^{-1} difference in favor of the $W\,^3\Delta_u$ is less than 1/100 of the distance between divisions on the vertical axis.

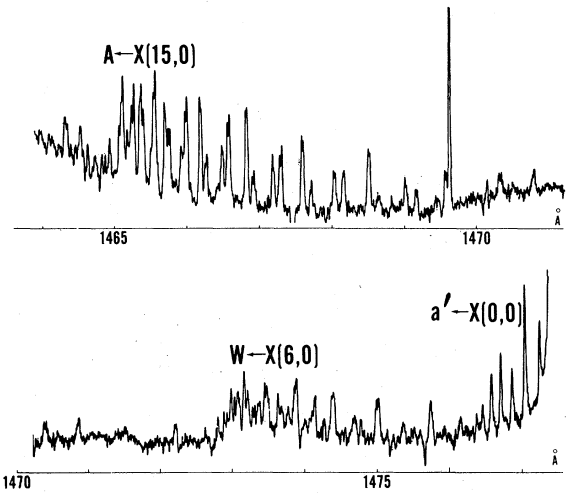

FIG. 2. Densitometer trace from which the principal measurements were made to determine the nitrogen $W\,^3\Delta_u - X\,^1\Sigma_g^+$ oscillator strength. The darkening of the photographic plate increases with increasing ordinate, the molecular lines being in absorption. The area of the $A-X(15,0)$ band is compared with the $W-X(6,0)$ band [and with the $a'-X(0,0)$ as a check]. Strong absorption by CO totally blackens the plate beyond 1478 Å. There is about 1 Å of overlap between the upper and lower traces.

Benesch.[8] One of the conclusions of the present investigation is that the progression will, in fact, be observed in competition with the $W-B(0,0)$ transition where collision frequencies are not high enough to impose a dominant quenching.

II. PROCEDURE FOR THE INTERCOMPARISON OF OSCILLATOR STRENGTHS

In the first studies of transition probabilities involving the $W\,^3\Delta_u$ state, Einstein coefficients were obtained for $W-B$ transitions through the direct comparison of two emission bands, one of whose transition probabilities was known.[1] Here, however, we are seeking the transition moments connecting the $W\,^3\Delta_u$ state with $X\,^1\Sigma_g^+$ rather than with $B\,^3\Pi_g$, and we must work with absorption intensities since the W-X system has not yet been identified in emission.

Again, the process will be that of comparing bands, one of known and one of unknown transition probability, which have the same *initial* state (now the ground state, $X\,^1\Sigma_g^+$). In particular, we have chosen to work principally with the 6-0 band at 1472 Å. It lies between the $A\,^3\Sigma_u^+ - X\,^1\Sigma_g^+$ (15-0) and the $a'\,^1\Sigma_u^- - X\,^1\Sigma_g^+$ (0-0). A photograph of the spectrum in this region has been presented by Saum and Benesch.[8] The working densitometer trace is displayed in Fig. 2 as it was by Tilford and Benesch (TB), where it was used to obtain the $a'\,^1\Sigma_u^-$ lifetime.[9]

The experimental process which produced the spectrogram from which Fig. 2 was taken has been detailed elsewhere.[10] Briefly, the source of continuum radiation was a low-pressure krypton lamp excited by the usual 100-W commercial microwave generator at 2450 MHz. The 21-ft spectrograph had a 30 000 groove/in. over-coated grating, which, in fifth order, yields a plate factor of 0.25 Å/mm. The entrance slit to the spectrograph was set at 12 μm and the photographs were made on Eastman SWR plates.

There are two complete bands at hand in Fig. 2 with which to relate the intensities of the systems W-X and A-X. In addition to those, the A-X(15-0) and W-X(6-0), we shall make a comparison of the A-X(14-0) with the W-X(5-0), which are likewise adjacent in wavelength with origins at 1487 and 1503 Å, respectively, and which have been photographed together on several plates.

The rationale for deducing absorption intensities from the ratios of band areas is based on Eqs. (1) and (2) below. The integrated absorption coefficient is related to the oscillator strength by the expression

$$\int k(\nu)\,d\nu = \frac{e^2}{mc} N f_{v'v''}\,, \qquad (1)$$

where e and m are the electronic charge and mass, respectively, and c is the velocity of light. N is the population of the initial level which for the present experiment is the $v=0$ level of the nitrogen $X\,^1\Sigma_g^+$ state for all bands under consideration. The oscillator strength $f_{v'v''}$ is also known as the absorption f number and is the central quantity of the present investigation.

Assuming that we may associate a measured band area with the integrated absorption coefficient on the left-hand side of Eq. (1), then to determine the oscillator strength for the W-X(6-0) band in Fig. 1, for example, we write

$$\frac{f[W\text{-}X(6\text{-}0)]}{f[A\text{-}X(15\text{-}0)]} = \frac{\text{Area}[W\text{-}X(6\text{-}0)]}{\text{Area}[A\text{-}X(15\text{-}0)]} \,. \qquad (2)$$

The remaining question in the justification of the outlined procedure is whether it is possible to obtain meaningful band areas from densitometer traces of the SWR photographic plates used to record the spectra.

We have made a number of tests and cross-checks to determine the functional relationship between the ordinates of Fig. 2 and the molecular absorption coefficients which must ultimately be related to the oscillator strengths as indicated in Eq. (1). Those preliminary investigations were laid out in some detail in TB. The simplifying conclusion of the analysis is that, in spite of the undoubted severe deviation from linearity for the general case, all of the densitometer trace ordinates with which we are presently concerned are proportional to the corresponding molecular absorption coefficients to within the experimental error of the measurement.

In the course of these subsidiary investigations it was established that all of the absorption lines under consideration fall on the linear (optically thin) segment of the curve of growth and that the background continuum radiation from the krypton lamp does not vary appreciably across a single photographic plate in this wavelength region. Furthermore, it has been possible to plot absorption-line peak heights against the theoretical rotational line intensities for easily measured bands in this region and to obtain a linear relationship which extends up to peak heights which are larger than any measured here. As a matter of fact, the curve was, in the course of the measurements, pursued through and beyond a knee which indicates the onset of the deviation from linearity, but present determinations do not impinge on that region.

The preceding considerations have given credence to the evaluation of oscillator strengths as outlined and they are presented in support of the validity of Eqs. (1) and (2).

III. CALCULATION OF $W\,^3\Delta_u$ LIFETIMES

The bands chosen as best suited to the present calculation are those of Fig. 1, the $A \leftarrow X(15 \leftarrow 0)$ and the $W \leftarrow X(6 \leftarrow 0)$. A parallel procedure has been carried out using the bands $A \leftarrow X(14 \leftarrow 0)$ and $W \leftarrow X(5 \leftarrow 0)$, and the $a'\,^1\Sigma_u^- \leftarrow X\,^1\Sigma_g^+(0 \leftarrow 0)$ has been included in the selection in order to provide a point of reference with previous results.[9]

Table I illustrates the relationships among the measured band areas. As argued in the previous section, the ratios of absorption f numbers (oscillator strengths) may be equated to the corresponding band area ratios as in Eq. (2). For present purposes, then, we apply Eq. (2) to the first row of Table I and, inserting the A-X(15-0) f number of 1.41×10^{-10} as given in TB, we arrive at an oscillator strength of 8.5×10^{-11} for the W-X(6-0) band.

The consistency of the present methods may be assayed through obtaining an independent f number for the W-X(5-0) band and comparing it with that just obtained for the (6-0). As a first step in this process, we test the variation in the band areas in going from one photographic plate to another. In particular, the two bands A-X(15-0) and A-X(14-0), with a rather well-established f number ratio,[9] are found to have a band area ratio which agrees with it to about 1%. Moving on to the next column, we find the area ratio of the W-X(6-0) to the (5-0) to be higher than that of the computed f number ratio. The latter is obtained from the following relation (assuming a constant transition moment).

$$f_1/f_2 = (\nu_1/\nu_2)(q_1/q_2) \qquad (3)$$

That is, the f numbers are directly proportional to the frequencies and the Franck-Condon factors. For the 6-0/5-0 case, the f number and area ratios

TABLE I. Measured nitrogen absorption bands and their areas. Plate 1 is that partially represented in Fig. 1 and containing the primary data for oscillator strength measurement. Plate 2 is an exposure encompassing the 1500-Å region which is used in an alternate determination of $W\,^3\Delta_u - X\,^1\Sigma_g^+$ f-numbers for comparison. All of the bands here have as their initial, lower level the $X\,^1\Sigma_g^+$ $v=0$. The area of the $a'\,^1\Sigma_u^- \leftarrow X\,^1\Sigma_g^+$ band has been corrected to take into account lines obliterated by the CO absorption which cuts off the long wavelength end of Fig. 1. Band areas are given in convenient arbitrary units; area ratios only are considered significant.

	$A\,^3\Sigma_u^+$		$W\,^3\Delta_u$		$a'\,^1\Sigma_u^-$	
Plate	Band	Area	Band	Area	Band	Area
1	15–0	32.9	6–0	20.0	0–0	19.8
2	14–0	36.1	5–0	14.3		

differ by some 15%–20%, which we take to be indicative of the degree of precision of the present methods. Note, however, that the top row of Table I encompasses the better data, and that most of the failure of loop closures here can be blamed on the weak 5-0 band of plate 2.

Less directly, these results may be compared with measurements made using other methods. Note first that on plate 1 of Table I the adjacent W-X(6-0) and a'-X(0-0) bands have virtually the same areas and thus the same f numbers. Next, we can infer a degree of compatibility of the a'-X(0-0) value with a different type of measurement made across a progression of that system by comparing with the intensities obtained from appearance pressures as given by TB. This is done in Fig. 3. Although hardly an indicator of precise agreement, the rough extrapolation of the $v''=0$ progression in Fig. 3 suggests a reasonable consistency between the two methods.

The value of the W-X(6-0) band oscillator strength, then, is 8.5×10^{-11}. This could now be converted into the transition probability for emission, but that probability is very small relative to the values for the dipole-permitted transitions to the $B\,^3\Pi_g$ state. Accordingly, we will transfer consideration to the $v=0$ level of the $W\,^3\Delta_u$ which is the only level from which $W\rightarrow X$ transitions are able to compete effectively with those of the W-B system. Our assumption in making the transfer will have to be that the electronic transition moment does not vary appreciably among these bands, since the character of its variation, if any, is unknown. The oscillator strengths, therefore, will be said to vary according to Eq. (3), and upon

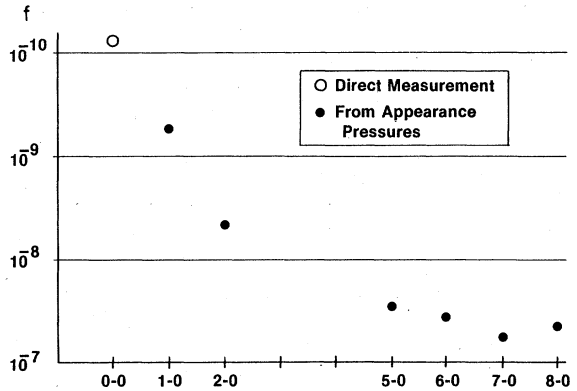

FIG. 3. Oscillator strengths for the $v''=0$ progression of the $a'\,^1\Sigma_u^-\leftarrow X\,^1\Sigma_g^+$ transition. Part of the 0-0 band of this progression (open circle) appears on Fig. 1 adjacent to the $W\,^3\Delta_u\leftarrow X\,^1\Sigma_g^+$ (6–0) band. Their projected areas are nearly the same. All other bands in the progression above (solid) have been measured by means of appearance pressures (Ref. 9) and the consistent trend of the curve here is used as a rough indicator of the compatability of the two methods of intensity determination.

inserting the data of Saum and Benesch,[8] we obtain a ratio of $f(0\text{-}0)/f(6\text{-}0)=1.49\times10^{-2}$.

So now with $f(0\text{-}0)$ in hand we should be able to proceed straightforwardly to compute a value of A, the transition probability for spontaneous emission. The relation between the two is simple to write down

$$f=g(mc/8\Pi^2e^2)\lambda^2A\,, \tag{4}$$

where λ is the wavelength and where g, the degeneracy ratio, would normally be equal to 6 for a $^3\Delta_u\rightarrow{}^1\Sigma_g^+$ transition. With regard to the present case, however, it has been suggested in conjunction with the partial rotational analysis undertaken by Saum[11] that the various spin components do not participate with equal probability in the absorption process. This was inferred both from a detailed examination of the photographs of the region and from the theoretical likelihood of a somewhat reduced transition moment connecting the F_3 component to the ground state. In order to deal with this complicated situation in a conservative manner, we will assign to g a ficticious value of 5, as representative of a case in which there is one spin component whose branches are neither fully developed ($g=6$) nor completely absent ($g=4$).

Inserting the wavelength of the 0-0 band, 1683.6 Å, into Eq. (4) with $g=5$, we obtain a value for $A_{0,0}=6.0\times10^{-4}$ sec^{-1}. In order to deduce a lifetime τ_0 for the level, we must add this transition probability to that of the other emission channels for $v'=0$. Thus

$$\tau_0=\left(\sum_{v''}A_{0,v''}\right)^{-1} \tag{5}$$

and each value of $A_{0,v''}$, the probability for emission of one of the bands in the $v=0$ progression (to one of the various vibrational levels of the ground state), can be calculated from

$$A_{0,v''}=A_{0,0}\frac{q_{0,v''}}{q_{0,0}}\frac{\lambda_{0,0}^3}{\lambda_{0,v''}^3}\,. \tag{6}$$

Again, the square of the transition moment ratio has been set equal to 1 for all bands, no data on the subject being currently available.

Table II presents eleven applications of Eq. (6) in its range of significance. The various emission channels to the ground state from the $W\,^3\Delta_u$ $v=0$ level are given on the left-hand side followed by the absolute transition probabilities and the relative transition probabilities. The summation of the center column of Table II yields a total transition probability of 0.18 sec^{-1} which corresponds to a lifetime of 5.5 sec. These values, of course, relate only to transitions to the ground state, $X\,^1\Sigma_g^+$. Insofar as transitions to the $B\,^3\Pi_g$ state compete with these, and thus enhance the depletion pro-

TABLE II. Emission channels to the ground state from the $W\,^3\Delta_u\, v' = 0$ level. The entries constitute the results of iterations of Eq. (6) to extend the measured transition probability of the 0-0 band to all members of the $v' = 0$ progression which can significantly affect the $v = 0$ lifetime. Note that the value of 0.001 sec^{-1} for the 0-0 band is not the result of normalization, but is the absolute transition probability deduced for the emission of the $W\,^3\Delta_u(0) \rightarrow X\,^1\Sigma_g^+(0)$ band.

Band $v'\ v''$	Transition probability A (10^{-4} sec^{-1})	Band contribution relative to total $v' = 0$ progression %
0–0	6.0	0.3
0–1	40.7	2.3
0–2	129.6	7.2
0–3	257.5	14.3
0–4	358.6	19.9
0–5	371.3	20.6
0–6	297.3	16.5
0–7	188.7	10.5
0–8	96.4	5.4
0–9	40.0	2.2
0–10	13.6	0.8
	0.18 sec^{-1} total	100.0%

cess, the lifetime of the level will be reduced accordingly.

To take these alternate transitions into account in refining the $v = 0$ lifetime, we again invoke Eq. (5) with the added transition probability to the $B\,^3\Pi_g$. The latter, taken from Covey *et al.*[1] is 0.06 sec^{-1} which, when summed with the $W \rightarrow X$ probability, yields a transition probability of 0.24 sec^{-1} and an effective lifetime of 4 sec (where the summed errors may exceed 1 sec).

IV. INTERPRETATION OF CALCULATED LIFETIMES

Table III and Fig. 4 give the results of all of our calculations on the $W\,^3\Delta_u$ state lifetimes to date. For the levels $v = 1$ to $v = 7$, the lifetimes are dominated by the permitted $W\,^3\Delta_u \rightarrow B\,^3\Pi_g$ transitions which were treated earlier,[1] and there is no basis for an appreciable revision in light of the present work. The $v = 0$ level, on the other hand, may be expected to channel most of its excitation to the ground state, $X\,^1\Sigma_g^+$. There is, however, nothing here approaching a simple branching ratio for the distribution of lines between the $B\,^3\Pi_g$ and $X\,^1\Sigma_g^+$. In fact, one must consider the transition probabilities almost on a line-by-line basis.

To begin with, the lifetime of 4 sec calculated for the $v = 0$ level of the $W\,^3\Delta_u$ state has been ob-

TABLE III. Lifetimes for the levels $v = 1$ through $v = 7$ have been taken directly from the table of the preceding work on the $W\,^3\Delta_u - B\,^3\pi_g$ system (Ref. 1). For those levels, virtually all radiative transitions from the W state end on the B state, producing infrared emission. From $v = 0$, ultraviolet transitions to the ground state take over. The tabulated value of 3 sec is the result of the present measurements and is dominated by the $W\,^3\Delta_u \rightarrow X\,^1\Sigma_g^+$ transition.

$W\,^3\Delta_u$ Level	Radiative lifetime
$v = 0$	4 sec, mostly $W\,^3\Delta_u \rightarrow X\,^1\Sigma_g^+$
$v = 1$	2.00 msec
$v = 2$	0.49 msec
$v = 3$	0.23 msec
$v = 4$	0.14 msec
$v = 5$	0.09 msec
$v = 6$	0.07 msec
$v = 7$	0.05 msec

mostly $W\,^3\Delta_u \rightarrow B\,^3\pi_g$

tained under the assumption that some transitions from the F_3 spin component levels will have somewhat reduced transition probabilities. It is thus implied that those levels will have somewhat longer lifetimes, although not uniformly nor, in any case, longer than those commensurate with the probabilities of transitions to the $B\,^3\Pi_g$.

As has been indicated in Table III, as far as the

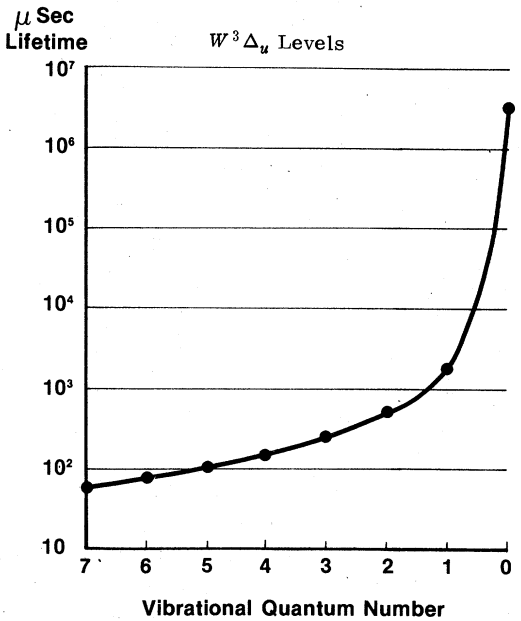

FIG. 4. Graphical representation of the numerical results of Table III. All points except the highest ($v = 0$) are lifetimes governed by $W\,^3\Delta_u \rightarrow B\,^3\Pi_g$ transition probabilities. For the $v = 0$ level, the effect of transitions to the ground state is to pull the point down from just above the 10^7 line. With that change, however, the $W\,^3\Delta_u \rightarrow X\,^1\Sigma_g^+$ transition becomes the major deactivation channel for the level.

fully participating spin components F_1 and F_2 are concerned, the quantum number of the initial $W\,^3\Delta_u$ *vibrational* level determines to a large extent the final *electronic* state to which transitions will take place. Thus, in the aurora and other low-collision environments, emission from the $W\,^3\Delta_u$ $v=0$ level should be observable in the vicinity of 2000 Å. From the point of view of the $W\,^3\Delta_u$-$B\,^3\Pi_g$ band system, all $W\rightarrow X$ radiation that appears in the ultraviolet does so at the expense of far-infrared emission from the $W\rightarrow B(0\rightarrow 0)$, its band with the largest transition moment. It is, of course, the collapse of the dipole transition ν^3 factor for the 0–0 band that directs most of the emission to the ground state rather than to the single permitted but very-long-wavelength $W\rightarrow B$ band.

The branching from the $v=0$ level to the two lower electronic states, B and W, has been calculated above to take place in a 1:3 ratio. This suggests that, in the absence of collisions, over half of the total $W\,^3\Delta_u$ $v=0$ excitation will give rise to ultraviolet photons. This conclusion is based, however, on the position of the *origin* of the $W\rightarrow B(0\rightarrow 0)$ band. Of course, the relevant frequency factor to be used in computing the spontaneous emission probability for a particular electronic-vibration-rotation line depends on the actual frequency of the line rather than on the frequency of the band origin. Accordingly, there will be an enormous range of spontaneous emission probabilities within the $W\rightarrow B(0\rightarrow 0)$ band, and a correspondingly large range of intrinsic lifetimes. That is, this particular electronic band encompasses a span of individual line frequencies from zero to some 80 cm^{-1}, so that the use of an "effective" value for ν^3 can lead to gross inaccuracies where specific line transition probabilities are required.

Quantitatively, it may be said that for most of the transitions within the $W\rightarrow B(0\rightarrow 0)$ band, the emission will be too slow to provide appreciable competition with the transitions to the ground state. Thus, the lifetime for the $W\,^3\Delta_u$ $v=0$ level, calculated on the basis of deactivation through $W\rightarrow X$ alone, yields a $v=0$ lifetime of 5.5 sec. Admitting $W\rightarrow B$ transitions also to the computation reduces the $v=0$ lifetime to 4 sec. We judge the accuracy of the present determination to be some 30%. Accordingly, the dominance of $W\rightarrow X$ over $W\rightarrow B$ for $v=0$ seems to be assured overall. By the same token, however, in the progression of bands that occurs in the ultraviolet, some portion of each will appear instead in the infrared. The part of the band most affected will be that arising from lines whose upper levels contribute to the blue end of the $W\rightarrow B(0\rightarrow 0)$ band.

V. CONCLUSION

We have studied the lifetime of the $v=0$ level of the nitrogen $W\,^3\Delta_u$ state as governed by transitions to both the $B\,^3\Pi_g$ and $X\,^1\Sigma_g$ states. The $v=0$ level is the only level from which ground-state transitions must be considered, since for $v=1$ (and above) the probability of transitions to the $B\,^3\Pi_g$ is overwhelming.

The measured lifetime of the $W\,^3\Delta_u$ $v=0$ is 4 sec, which value is subject to the condition that there are probably variations in the individual lifetimes among the three spin components of the triplet. Another anomaly derives from the competitive role of the $B\,^3\Pi_g$. Not only does the $B\,^3\Pi_g$ $v=0$ intercept radiative transitions for the infrared at the expense of the ultraviolet, but it does so selectively. This uv-ir band division manifests a dependence on rotational quantum number which comes about through the large fractional frequency variations across the $W\rightarrow B(0\rightarrow 0)$ band. In the aurora, and in other low-collision environments, the $W^3\Delta_u\rightarrow X\,^1\Sigma_g^+$ $v'=0$ progression should be emitted in the 2000-Å region with a transition probability of 0.18 sec^{-1}. Although branching to the $B\,^3\Pi_g$ will occur at the expense of all of the bands of the progression, most emitted photons will still be in the ultraviolet.

As pointed out by Cartwright *et al.*,[6] the cross sections for the direct excitation of the lower levels of the $W^3\Delta_u$ from the ground state by low-energy electrons are very large. We have found that the excitation rate for the $W^3\Delta_u$ in our discharge tubes must, indeed, be very high.[12] On the other hand, we find the distribution of population among the vibrational levels to be very much distorted from the direct electron excitation distribution. In particular, there is a heavy weighting of population toward the lower vibrational levels. We assume that the $v=0$ level attains a large population in keeping with this trend, even though there is no direct evidence bearing on the question. If so, there would arise in a pulsed discharge a time-dependent population inversion of the $W^3\Delta_u(0)$ with respect to the $B\,^3\Pi_g(0)$. Since there is a strong transition moment connecting these levels, and since the corresponding spontaneous emission is very slow, the configuration provides a favorable potential for the development of superradiance at far-infrared and microwave frequencies.

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