Comment on Paper by D. C. Cartwright, S. Trajmar, and W. Williams, 'Vibrational Population of the $A^3\Sigma_u^+$ and $B^3\Pi_g$ States of N_2 in Normal Auroras'

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Summary. Recent theoretical calculations have given rise to the declared but unobserved presence of strong auroral emissions in the N_2 $A^3\Sigma_u^+$-$B^3\Pi_g$ and $W^3\Delta_u$-$B^3\Pi_g$ systems. We suggest in the following discussion that the quantities involved are too uncertain for one to arrive at a well-defined conclusion on the basis of the theoretical calculations alone. Laboratory evidence at low pressures gives no direct indication of the presence of the systems, although this lack may be due to high radiationless deactivation rates of the $W^3\Delta_u$ and $A^3\Sigma_u^+$ states. However, the presence of the transitions at the indicated rates should be easily detectable in the measured auroral population rates of the $B^3\Pi_g$ state. According to averaged auroral measurements accumulated over the years, there is no evidence for significant contributions from the two systems in question.

Cartwright et al. [1971] propose two additional excitation modes for the N_2 $B^3\Pi_g$ state in the aurora that have not previously been considered as significant contributors. These excitation modes are the radiative transitions $A^3\Sigma_u^+$-$B^3\Pi_g$ and $W^3\Delta_u$-$B^3\Pi_g$. We suggest that the presently available quantities required for a theoretical estimate of the excitation rates due to these two systems are sufficiently uncertain that one cannot determine the significance of the transitions. The crux of the argument lies in the determination of the transition probabilities of the *A*-*B* and *W*-*B* and *B*-*W* systems relative to the *A*-*X* and *B*-*A* probabilities. The significance of the transitions in question depends critically on the values of the branching ratios for the $B^3\Pi_g$ and $A^3\Sigma_u^+$ states. These important factors are not discussed by Cartwright et al., nor are they tabulated in their work. We attempt to point out in the following discussion that the probabilities are too uncertain for one to arrive at a well-defined conclusion through theoretical estimates. The discussion results in the following additional conclusions.

1. Contrary to their claims, laboratory observations provide no evidence for or against the Cartwright et al. excitation scheme, although we can place an upper limit on the $W^3\Delta_u$ contribution by comparing lifetime and transition probability measurements on the $B^3\Pi_g$ state. The suggestion that attempts to measure the *B*-*X* electron excitation cross section optically were complicated by contributions from the *W*-*B* and *A*-*B* transitions is not confirmed by our analysis.

2. We suggest that the results of Cartwright et al. are not consistent with the quantities used in the computation. Recalculation of the contributions of the *W*-*B* and *A*-*B* system to the *B* state population rate are factors of at least 2.5 and 1.5, respectively, lower than the estimate by Cartwright et al. However, this is a side issue from our point of view, since the transition parameters themselves are highly uncertain.

3. The transitions *W*-*B* and *A*-*B* do have a significant influence on the relative population rates of the vibrational levels of the *B* state in the Cartwright et al. scheme. For this reason

these radiative sources contribute to the disagreement with the estimates by *Shemansky et al.* [1971, 1972]. However, removal of the W-B and A-B transitions still leaves the two estimates in serious disagreement. This disagreement stems from the use of very different absolute electron excitation cross sections (B-X) for the B state. The differing estimates of the B state population distribution, if W-B and A-B are neglected, are a consequence of the differences in the relative C-X and B-X electron cross sections.

4. Auroral observations provide the best opportunity for detecting the proposed transitions. Distributions of populations in the B state proposed by Cartwright et al. do not compare satisfactorily with a number of independent auroral measurements [*Shemansky et al.*, 1971; cf. *Shemansky et al.*, 1972]. On the other hand, calculations that include only a radiative contribution to the B state from the $C^3\Pi_u$ state do correlate well with the observations, including the *Sharp* [1971] rocket observations of the N_2 Vegard-Kaplan system; this result is obtained by adopting the B-X and C-X electron excitation cross sections measured by *Shemansky and Broadfoot* [1971*b*], rather than those applied by Cartwright et al.

W-B AND B-W SYSTEMS

Evidence for the presence of the $W^3\Delta_u$ state has been very carefully assessed by *Wu and Benesch* [1968], who observed 11 bands in the 2- to 4-μ region [cf. *Saum and Benesch,* 1970]. Their identification of the $W^3\Delta_u$ state was suggestive but not positive; a rotational analysis was not possible, owing to the low resolution of the observed spectra. Several uncertainties enter in the theoretical estimation of the transition probabilities of the system.

1. There remains a finite possibility that the observed transition may be the $B'^3\Sigma_u^-$-$B^3\Pi_g$ system. All of the observed bands fall at wavelength positions corresponding to B'-B transitions. These transitions with the exception of one band are associated with relatively large Franck-Condon factors. The observations were made under experimental conditions conducive to the production of $B'^3\Sigma_u^-$ molecules; a dc discharge through 2–10 torrs of flowing nitrogen would tend to be characterized by afterglow excitation of the $B^3\Pi_g$-$A^3\Sigma_u^+$ system [cf. *Noxon,* 1962] accompanied by prominent B'-B transitions [*Bayes and Kistiakowsky,* 1960].

2. Assuming the identification of $W^3\Delta_u$ is correct, we also have an uncertainty in the vibrational numbering of the state. The theoretical calculations obviously depend on the correct assignment of the vibrational quantum numbers to the observed bands. Low vibrational assignments were eliminated in the Wu and Benesch analysis on the grounds that the resultant electronic energy of the state should give rise to transitions in the visible and near infrared that were not observed in their system. Higher vibrational assignments were eliminated on the assumption that the electronic energy of the observed state must be higher than that of $B^3\Pi_g$. The assignment of vibrational levels generally requires uncertain, indirect considerations such as the above, and errors are a definite possibility.

3. The transition probabilities for the W-B and B-W transitions are theoretical estimates made by *Cartwright* [1970 and personal communication, 1971] on the basis of an assumed constant electronic transition moment. All the measured triplet N_2 states have electronic transition moments that display significant dependence on internuclear separation. There is no reason to believe the $W^3\Delta_u$ state should be an exception. A theoretical estimate that does not take into account coupling of electronic energy to the variation in internuclear separation, in our opinion, could possibly deviate from the real values by as much as an order of magnitude.

The most important factor in determining the importance of the $W^3\Delta_u$ state is the probability of the B-W transition relative to that of the B-A transition. Cartwright et al. do not provide these relative values, and, in order to clarify the discussion, we calculate the branching ratios, using the same transition moment applied by Cartwright (personal communication, 1971) and the Deslandres table given by Wu and Benesch. These numbers are given in Table 1. According to this table, the B-W transition probability varies from 0 at $v' = 0$ to 20% of the total probability (B-A) + (B-W) at $v' = 9$. Table 2 shows the approximate population rates of the $B^3\Pi_g$ state due to the various processes, taken from Figure 3 of the Cartwright et al. work. The total production rates of the $B^3\Pi_g$ levels are given in column 6. The product of these rates and the numbers given in Table 1 then give the production rates of the $W^3\Delta_u$ state (column 7) due to the B-W transitions. One other population mode of the W state was considered in the Cartwright et al. calculations, direct electron excitation. The cross section for the W-X transition has not been measured, nor has it been detected in high-resolution electron energy loss spectra [*Brinkmann and Trajmar*, 1970; *Williams and Doering*, 1969]. The peak cross section of the W state is estimated theoretically [*Cartwright*, 1970] to be about 10% of that of the B state. The electron energy distribution applied by Cartwright et al. is such that most of the excitation of the triplet systems occurs at energies in the region near the prominent peaks of the excitation functions. The relative excitation rates of the B-X (Table 2, column 2) and W-X processes should then be in roughly the same ratio as the peak values of the cross sections. The total production rate of the W state is thus estimated to be $\sim 1.9 + 2.2 = 4.1$. However, the total emission rate W-B is about 2.5 times larger according to Cartwright et al. (Table 2, column 4).

The total of 4.1 actually represents an upper limit estimate, since both components contributing to the total are larger than would be obtained from a more accurate calculation. be smaller in a more accurate estimate, since, The W-X contribution should actually be somewhat less than 10% of the B-X rate, since the peak in the W-X cross section lies at higher energy than the B-X peak, roughly 10 ev higher than the B-X peak according to *Cartwright* [1970]. The B-W contribution would

TABLE 1. Relative Probabilities of the B-W Transitions

$B^3\Pi_g$, v	$\frac{A(B\text{-}W)}{A(B\text{-}A) + A(B\text{-}W)}$
0	0
1	0.01
2	0.026
3	0.047
4	0.065
5	0.093
6	0.11
7	0.14
8	0.16
9	0.20
10	0.23
11	0.26
12	0.30

From use of B-W, W-B electronic transition moment according to *Cartwright et al.* [1971] and B-A probabilities measured by *Shemansky and Broadfoot* [1971].

TABLE 2. Population and Emission Rates (g_v, I_v) of the N_2 $B^3\Pi_g$ State

	g_v					I_v		
$B^3\Pi_{g,v}$	B-X*	C-B*	W-B*	A-B*	$\sum g_v$*	B-W†	B-A†	B-A‡
0	1.3	4.0	3.5	2.5	11.3	0	11.3	12
1	3.3	2.1	2.3	2.5	10.2	0.10	10.1	4.7
2	4.2	1.2	1.6	1.7	8.7	0.23	8.5	5.0
3	4.1	0.65	0.95	1.2	6.9	0.32	6.6	5.0
4	3.6	0.36	0.58	0.75	5.3	0.34	5.0	3.6
5	2.5	0.18	0.38	0.44	3.5	0.32	3.2	4.3
6	1.5	0.08	0.22	0.25	2.0	0.22	1.8	3.0
7	0.9	0.04	0.16	0.10	1.2	0.17	1.0	3.8
8	0.47	0.01	0.09	0.02	0.59	0.09	0.5	1.4
9	0.25		0.05		0.30	0.06	0.24	1.4
10	0.13		0.02		0.15			1.6
11	0.06				0.06			2.4
12	0.03				0.03			
$\sum g_v$	22.3	8.6	9.9	9.5	50.3	1.9	48.4	

Comparison of population and emission rate of W state: $\sum g_v = \sum I_v$; $(B\text{-}W) + (W\text{-}X) = W\text{-}B$; $1.9 + 2.2 = 4.1 = W\text{-}B \neq 9.9$.

* From *Cartwright et al.* [1971].

† Calculated from column 6 and Table 1.

‡ Relative emission rates measured by *Jeunehomme* [1966] [cf. *Shemansky and Broadfoot*, 1971*b*].

in order to obtain the equilibrium rates, one must iterate by adjusting the *W-B* rate downward from its value in Table 2. The production rate of $B^3\Pi_g$ molecules by the *A-B* transition also appears to be in excess of the maximum possible rate, within the Cartwright et al. scheme. The total production rate of N_2 $A^3\Sigma_u^+$ molecules according to Cartwright et al. on a scale relative to the numbers shown in Table 2 is 13.3. The $A^3\Sigma_u^+$ state levels below $v' = 8$ cannot contribute to the production rate of the $B^3\Pi_g$ levels. If we assume all the production of $A^3\Sigma_u^+$ $v > 8$ levels results in production of $B^3\Pi_g$ molecules, we have a maximum possible contribution rate of 6.6. The production rate according to Cartwright et al. (Table 2, column 5) is 9.5. Thus, according to these calculations, the Cartwright et al. computations appear not to be internally consistent, since the same numerical estimates of the parameters were used in the present analysis.

We note that the remarkable variation in transition probability predicted for the *B-W* system should give rise to systematic differences between the total transition probabilities of the $B^3\Pi_g$ state levels as determined by direct lifetime measurements and the measured total probabilities in the $B^3\Pi_g$-$A^3\Sigma_u^+$ system. A comparison of the measured total probabilities for *B-A* with the reciprocals of the directly measured $B^3\Pi_g$ lifetimes is provided by *Shemansky and Broadfoot* [1971*a*, Figure 8]. The directly measured values automatically include all branches of transitions from the *B* state. The lifetimes measured by *Jeunehomme* [1966] and *Hollstein et al.* [1969] show scattered but not systematic deviations of about 10% with the *B-A* values obtained by *Shemansky and Broadfoot* [1971*a*] for the $v' = 0$–12 levels. Thus, according to these measurements, the branching ratios for the higher v' levels could be 10% or less, and the numbers given in Table 1 are only marginally acceptable as possible upper limits.

A-B TRANSITION

The probabilities for this transition must be calculated from the extrapolated electronic transition moment for the *B-A* system, which displays a marked dependence on internuclear separation [cf. *Jeunehomme,* 1966; *Shemansky and Broadfoot,* 1971*a*]. The Franck-Condon factors associated with the significant probabilities are small, 10^{-3}–10^{-6} [cf. *Benesch et al.,* 1966], and especially the transitions that do not involve $v' = 0$ or $v'' = 0$ are very sensitive to small uncertainties in the shape of the potential function and the equilibrium internuclear distance. We have no direct estimate of the magnitudes of the uncertainties, but we suggest that they could be orders of magnitude. Uncertainty in the fifth figure of the equilibrium internuclear distance, which is the case with the $B^3\Pi_g$ and $A^3\Sigma_u^+$ states [cf. *Benesch et al.,* 1965], may well be sufficient to produce large uncertainties in these small Franck-Condon factors. In addition to the argument concerning the uncertain magnitudes of the Franck-Condon factors themselves, we question the validity of applying the approximation involving the separation of electronic and vibrational transition moments. The criteria [*Fraser,* 1954] for judging the validity of this approximation appear to be generally valid, although *Krupenie and Benesch* [1968] suggest the application of some additional more stringent criteria. We suggest that the combination of very small Franck-Condon factors and large vibrational quantum numbers in this case places this approximation in a region of uncertainty, according to the discussion by *Fraser* [1954]. We believe there is general agreement that the higher levels of the *A* state are populated at significant rates. The question of whether the *A-B* rates are significant in a collision free environment depends entirely on the relative *A-B, A-X* probabilities. Our own estimate of the *A-B* probabilities is in rough agreement with the statement by Cartwright et al. that the *A-B* numbers are of the same order as the *A-X* probabilities. However, the significance of the *A-B* contribution to the *B* state population depends on whether the *A-B* probabilities are significantly larger or smaller than the *A-X* probabilities. We suggest that the available information is too uncertain to determine whether the *A-B* transition makes a significant contribution.

COMPARISON WITH LABORATORY OBSERVATION

The remark in the third section of the *Cartwright et al.* [1971, p. 8371] work, 'The recent photon-emission cross sections obtained for the *B* state [*Stanton and St. John,* 1969; *McConkey and Simpson,* 1969; D. E. Shemansky and A. L.

Broadfoot, unpublished manuscript, 1971] cannot be used in the present analysis because they contain significant cascade contributions,' is an unqualified statement, and we suggest that it is in conflict with the nature of the experimental observations. The three sets of measurements referred to in this quote all indicate that the relative peak cross sections of the $B^3\Pi_g$ v = 0–5 levels follow the Frank-Condon factors for the B-X transition [cf. *Shemansky and Broadfoot,* 1971*b*]. This relative cross section distribution, as Cartwright et al. specifically point out, is very different (column 1 compared with column 6 of Table 2) from the proposed excitation scheme.

The Shemansky and Broadfoot measurements in particular are based on a combination of steady state and transient measurements. The peak cross sections of the B state lower levels fall below the threshold of the $C^3\Pi_u$ state, and lifetime measurements in the latter work at pressures of 10 μ and lower were single valued. For this reason, Shemansky and Broadfoot concluded that the observed cross section was due to the B-X process alone. It would be very difficult to explain a single-valued decay constant in any other way. We note that Shemansky and Broadfoot did observe a double lifetime at a pressure of 50 μ, but this was due to an afterglow process at least second order in [N_2] and was not detectable at 10 μ. We do not imply that the laboratory measurements rule out the presence of significant W-B and A-B contributions in a collisionless environment. It is almost a certainty that the higher A state levels are removed by a combination of homogeneous and heterogeneous collisional deactivation; it is well known that emission transitions from $v' > 2$ have never been observed in room temperature laboratory observations. The relatively long lived $W^3\Delta_u$ molecules may also be removed in the same manner in the laboratory.

The suggestion in the fifth section of the Cartwright et al. work that the *Jeunehomme* [1966] measurements support their conclusions is also in conflict with the observations, in our opinion. The three or more decay components arising in the Jeunehomme experiment are very likely afterglow processes; these processes can be first order in [N_2] if the precursor population is controlled by collisional deactivation [cf. *Shemansky and Broadfoot,* 1971*b*]. The Jeunehomme measurements are made with the use of a pulsed RF discharge in a 10:1 NO:N_2 mixture. Both NO and O are known to have large deactivation rate coefficients for N_2 $A^3\Sigma_u^+$ molecules [cf. *Young et al.,* 1969]. Atomic oxygen is also known as a catalyst for the N_2 afterglow [cf. *Oldman and Broida,* 1969]. The population rate distribution in the Jeunehomme experiment (Table 2, column 9) clearly bears no resemblance to either the optically measured relative B-X cross sections or the Cartwright et al. distribution shown in column 6. If the distribution of population in the B state did not change significantly with the use of pure N_2, as Jeunehomme claims, the N_2 $A^3\Sigma_u^+$ state must play little part in populating the B state in the A-B radiative transition in either case. The secondary results of the Jeunehomme experiment are very difficult to interpret in terms of any assumed set of excitation mechanisms [cf. *Shemansky and Broadfoot,* 1971*b*].

COMPARISON WITH AURORAL OBSERVATIONS

In contrast to the laboratory results, auroral observations of $B^3\Pi_g$ emissions should contain the effects of the longer-lived W and A states. As Cartwright et al. point out, the relative population rates of the lower $B^3\Pi_g$ levels, including the W-B and A-B transitions, should be quite different from those due only to the combined B-X, C-B processes. Table 3 shows a comparison of the averages of available auroral measurements with the predictions. This table is an extension of that given by *Shemansky et al.* [1971; cf. *Shemansky et al.,* 1972]. The predicted emission rate ratios according to Shemansky et al. were calculated from the *Shemansky and Broadfoot* [1971*b*] cross sections and include only B-X, C-B excitation processes for the $B^3\Pi_g$ state. The Shemansky and Broadfoot cross section for the B-X process is a factor of ~2.5 larger than that applied by Cartwright et al. Table 3 shows the relative emission rates for the A-X, B-A, and C-B transitions. By a remarkable coincidence the relative emission rates of the $A^3\Sigma_u^+$ v = 0 level and the second positive (0, 0) band (IV-K(0)/I2PG(0, 0)) predicted by Shemansky et al. and Cartwright et al. are identical and in good agreement with observation.

The Cartwright et al. estimate of the IV-

TABLE 3. Predicted and Observed Relative Emission Rates of N_2 Systems

	IV-K(0)/I2PG(0, 0)	I1PG(5, 2)/I2PG	I1PG(0, 0)/I1PG(5, 2)	I1PG(0, 0)/I1PG(1, 0)
Shemansky et al.	High altitude: 5.9	~110 km, increase ~10% at 200 km: 0 19	Invariant with altitude: 2.4	Invariant with altitude: 0 61
Observed	200 km, corrected for quenching: 6.6*	~110 km, average aurorae: 0.23†	~110 km, average aurorae: 2.5‡	~80 km, type B red: 0.63§
Cartwright et al.				
No quenching in W and A states	High altitude: 5.9	High altitude: 0.11	High altitude: 6.5	High altitude: 0.93
Corrected	High altitude: 4.3	High altitude: 0.10	High altitude: 5.4	High altitude: 0.89
Total quenching in W and A states	Low-altitude limit: ...	Low-altitude limit: 0.085	Low-altitude limit: 4.0	Low-altitude limit: 0.81

From *Shemansky et al.* [1971].

* *Sharp* [1971] measurements at 200 km, corrected for estimated radiationless deactivation rate of 0.2 sec^{-1}.

† From averages of measurements by *Hunten* [1955], *Petrie and Small* [1952], of N_2 2PG relative to N_2^+ 1N, and measurements on NASA rocket flights 4.163, 4.217, and 4.309 and aircraft observation by *Gattinger and Vallance Jones* [1971] of N_2 1PG(5, 2) relative to N_2^+ 1N(0, 0) [cf. *Shemansky et al.*, 1971].

‡ From averages of measurements by *Harrison* [1969] of N_2 1PG(0, 0) relative to N_2^+ 1N(0, 0) and the observations of N_2 1PG(5, 2) relative to N_2^+ 1N(0, 0) given in footnote † above.

§ From measurements of N_2 1PG(0, 0) and N_2 1PG(1, 0) by *Hunten* [1958].

K(0)/I2PG(0, 0) ratio is actually a factor of 1.5 lower than the Sharp observations if we make approximate corrections to the obvious errors in their calculation of the W-B and A-B contributions. Table 3 shows the corrected ratios for the other auroral emissions. The ratio I1PG(0, 0)/I1PG(5, 2), which represents the relative population rates of the $B^3\Pi_g$ $v = 0$ and $v = 5$ levels, predicted by Cartwright et al. differs by a factor of about 3 with average observations. The predicted relative rates using the Shemansky and Broadfoot cross sections, on the other hand, are in good agreement with all the tabulated (Table 3) observations. We note that the relative rates predicted by Cartwright et al. remain in disagreement with the observations even if total quenching of the A and W states is assumed, as is shown in the last row of Table 3. The auroral observations that contribute to the ratios shown in the table are described in detail by *Shemansky et al.* [1971, 1972]. The ratios shown in columns 2 and 3 are necessarily averaged values representing average aurorae, since the measurements were actually made relative to the N_2^+ first negative (0, 0) band. The emission rates of the triplet N_2 systems relative to the N_2^+ systems are known to vary by a factor of 2 or more [cf. *Shemansky et al.*, 1972] at any given auroral altitude, and one must depend on observations averaged over a relatively long time interval to obtain N_2/N_2^+ ratios comparable with other independent measurements. The results shown in the table omit the measurements of Vaisberg reported by *Vallance Jones* [1971]. The Vaisberg ratios I2P(0, 2)/I1N(0, 0) and I1P(1, 0)/I1N(0, 0) are factors of 1.5 and 2 larger than the averaged tabulated values, but the resulting I2P(0, 2)/I1P(1, 0) ratio is in reasonable agreement with both the Cartwright et al. and Shemansky et al. predictions. The *Sharp* [1971] measurements of the N_2^+ first negative (0, 0) emission rate relative to the N_2 second positive (0, 0) rate are ignored in the tabulation because of an order of magnitude error in the N_2^+ first negative photometer calibration, according to a private communication from Sharp.

CONCLUSION

In conclusion, we suggest that the additional excitation processes for the N_2 $B^3\Pi_g$ state introduced by Cartwright et al. involve too many uncertainties to warrant quantitative estimates on the basis of theoretical calculations. Laboratory observations show no measurable evidence of the presence of these transitions. However, this lack may not be taken as evidence against significant contributions by the proposed processes in a collision free environment; laboratory conditions would very likely never provide a collision free environment for the source states in question. Auroral evidence compiled over the years does appear to indicate (Table 3) that significant population rates in the W-B and A-B transitions do not occur.

We disagree with the suggestion that the cross section measurements by *Stanton and St.*

John [1969], *McConkey and Simpson* [1969], and *Shemansky and Broadfoot* [1971*b*] cannot be analyzed because of 'significant cascade contributions.' The evidence for the significant additional cascade processes appears only in the theoretical calculations by Cartwright et al. The relative apparent cross sections of the $B^3\Pi_g$ $v = 0$–5 levels in these measurements disagree with the Cartwright et al. predictions. The suggestion that the large sharp shoulder in the $B^3\Pi_g$ cross section near threshold is due to cascade processes is doubtful in view of the Shemansky and Broadfoot transient measurements at low energies. We suggest there is no particular reason why the cross-sectional shape should not be an intrinsic part of the *B-X* cross section. A very similar but smoother change in curvature also appears near threshold in the $C^3\Pi_u$-*X* cross section as measured by *Shemansky and Broadfoot* [1971*b*]. If the optical measurements actually did include large radiative contributions, as Cartwright et al. suggest, the apparent cross sections should be of considerable interest as further evidence of these processes. However, Cartwright et al. have chosen to disregard these results entirely. If we are to take this as a suggestion that the relative cross sections of the $B^3\Pi_g$ $v = 0$ and $v = 5$ levels as measured by Stanton and St. John, say, are accurate to within only an order of magnitude, then we must insist that the Cartwright et al. calculations can be no more accurate than this, since the measured relative cross sections are quantities that are not experimentally independent of the measured relative transition probabilities. Application of the Stanton and St. John emission rate measurements produces almost exactly the same electronic transition moment function as that obtained with the Shemansky and Broadfoot data; if the measured relative emission rates of the $B^3\Pi_g$ $v = 0$ and $v = 5$ levels are in error by an order of magnitude, as they must be if the Cartwright et al. statement is correct, complementary errors must reside in the same $B^3\Pi_g$-$A^3\Sigma_u^+$ transition probabilities used in the Cartwright et al. calculations. However, erroneous transition probabilities and hence erroneous relative emission rates are a very doubtful possibility, since the relative probabilities calculated for the emission rate measurements of *Turner and Nicholls* [1954], *Stanton and St. John* [1969], and *Shemansky and Broadfoot* [1971*a*] and from the lifetime measurements of *Jeunehomme* [1966] are all in good agreement with the exception of some transitions involving the higher vibrational levels [cf. *Shemansky and Broadfoot*, 1971*b*; *Shemansky and Vallance Jones*, 1968]. The removal of the *W-B* and *A-B* contributions (bottom row Table 3) does not bring the Cartwright et al. *B* state population distribution into agreement with either the auroral or laboratory observations because of the very low electron cross section applied to the *B-X* transition by Cartwright et al.

The fundamental factors in the determination of the significance of the proposed processes are the branching ratios. Regrettably these important quantities were not discussed or tabulated by Cartwright et al. The contents of the second paragraph of the fifth section of that work, in fact, suggest that the authors may have misunderstood the nature of the problem. We agree that the *A* state populations are about 10^5–10^6 times larger than those of the *B* state in a collision free environment. However, the population is not the determinant in the relative contribution to the *B* state. The *B* state population rate due to the *A-B* transition depends only on the *A* state population rate and the branching ratio of the *A-B* and *A-X* transitions. The *A* state population is not a relevant factor in this computation but reflects only the total transition probability of the state or level. A large population in the higher *A* state levels is simply indicative of small transition probabilities in both the *A-B* and the *A-X* branches. The same considerations apply to the *B-W*, *W-B*, and *B-A* systems. It is not clear where the factor of 2.5 and 1.5 errors arise in the Cartwright et al. calculation of the *W-B* and *A-B* contributions. However, if they found it entirely necessary to calculate excited state populations for a collision free environment at any point in their procedure, the computational method must have been erroneous.

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