Evidence for the $^3\Delta_u \rightarrow B^3\Pi_g$ Transition in N_2 †

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A dc discharge through 2 to 10 Torr of flowing nitrogen gas has been observed with an infrared spectrometer. Eleven molecular bands have been recorded, of which the 4435-, 4134-, 3830-, 3514-, 2998-, 2730-, and 2457-cm^{-1} bands have been assigned to the $^3\Delta_u \rightarrow B\ ^3\Pi_g$ system in accordance with the vibrational analysis. Vibrational quantum numbers have been assigned for the observed bands; a potential-energy curve has been computed for the $^3\Delta_u$ state; and a Deslandres and Franck-Condon table has been generated for the band system. The molecular constants calculated for the $^3\Delta_u$ state from the present analysis are: $T_e = 59738$ cm^{-1}, $\omega_e = 1539$ cm^{-1}, and $x_e\omega_e = 17$ cm^{-1}. This state is of particular interest because of its relationship with the nitrogen 1*PG* and 2*PG*, two prominent systems in most discharges containing air or nitrogen, as well as in the aurora.

This work concerns the investigation of the infrared emission spectrum of gaseous molecular nitrogen. The emission comes about as a result of a transition between two electronic states which must be very close to one another in energy, so close, in fact, that intra-system cascading becomes prevalent. Relationships of this type must be quite common among the upper states of many molecules. Unfortunately, the observability of the emission arising from even the permitted transitions is quite low as a result of the unfavorable frequency dependence of the transition probability and the prevalence of competing processes.

EXPERIMENTAL

The source of the radiation was a dc discharge through 2 to 10 Torr of flowing nitrogen gas in an inverted Π-shaped tube of Pyrex with a flattened center section. This section was, of course, observed end-on and the flattening of the tubing served to enhance the current density in the portion of the discharge under study. In addition, the choice of cross section for the constructed tube, $1\times\frac{1}{8}$ in. was made in the interest of mating the source efficiently to the spectrometer slit. The radiation was emitted from the source through a sapphire window while the electrical connections were made to two large Housekeeper seals (on the ascending legs of the Π) which were terminated in copper cups and supplied each with four radial-cooling fins. Further cooling, in the form of a surrounding bath of flowing water, was provided to the rectangular center section which otherwise would have become hot enough to melt the Pyrex. The potential across the electrodes of the source during steady discharge was about 800 V which gave a current of about $\frac{1}{4}$ A and a current density in the plasma under investigation of some $\frac{1}{3}$ A/cm^2. The brightness of the source in the infrared was never great enough to permit operation outside of the region of energy-limited resolution.

Eleven bands at 2.255 μ (4435 cm^{-1}), 2.345 μ (4264 cm^{-1}), 2.419 μ (4134 cm^{-1}), 2.511 μ (3983 cm^{-1}), 2.610 μ (3830 cm^{-1}), 2.755 μ (3630 cm^{-1}), 2.846 μ (3514 cm^{-1}), 2.995 μ (3339 cm^{-1}), 3.336 μ (2998 cm^{-1}), 3.663 μ (2730 cm^{-1}), and 4.070 μ (2457 cm^{-1}) were obtained in the present study. In the first stage of the investigation, only the first four and the last three bands of the eleven were recorded. The band at 4.070 μ was incomplete then due to the CO$_2$ absorption in the vicinity of 4.2 μ. The middle four bands and the end portion of the 4.070-μ band were obtained after pumping out the spectrometer to 10-mTorr pressure and thereby getting rid of the water and CO$_2$ absorptions. The 3.336- and 3.663-μ bands are shown in Figs. 1 and 2.

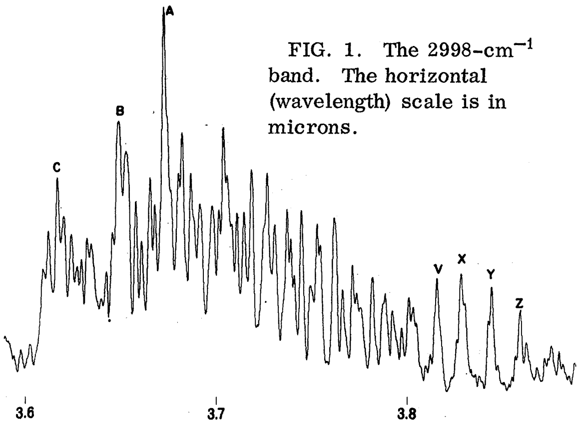

FIG. 1. The 2998-cm^{-1} band. The horizontal (wavelength) scale is in microns.

The three bands 2998 cm^{-1}, 2730 cm^{-1}, and 2457 cm^{-1} of the list of eleven seem to form a sequence; let us call it the β sequence. The three distinct band heads *A*, *B*, and *C* and the four peaks *V*, *X*, *Y*, and *Z* in the 2998-cm^{-1} band repeat themselves in the 2730-cm^{-1} and 2457-cm^{-1} bands. In fact, all the prominent peaks are reproducible and repeated in these three bands. The other eight bands from 3339 cm^{-1} to 4435 cm^{-1} appear in an overlapping of two sequences. The odd bands (in order of decreasing wave number) of these eight bands seem to form one sequence — let us call it the α se-

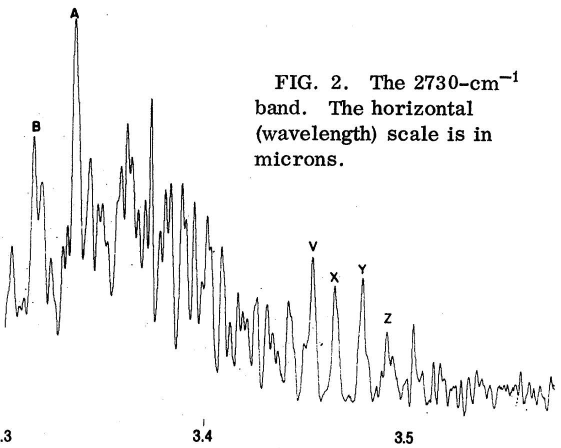

FIG. 2. The 2730-cm^{-1} band. The horizontal (wavelength) scale is in microns.

quence[1]— and the four even bands form another, the γ sequence. They are listed in Table I. The bands 4435 cm^{-1}, 4134 cm^{-1}, and 3830 cm^{-1} have the same features; i.e., they have at least three band heads, all degraded toward long wavelength, and have much the same contour. They are similar in appearance to the bands in the β sequence. The 3514-cm^{-1} band has more overlapping with the other sequence, yet it is still possible to see the similarity between this and the other three bands in the α sequence.

TABLE I. Listing of observed bands.

Preliminary name	Band extent (kaysers)	Most prominent peak
α-I	4475–4360	4435
α-II	4182–4056	4134
α-III	3891–3758	3830
α-IV	3557–3442	3514
β-I	3036–2863	2998
β-II	2768–2589	2730
β-III	2494–2330	2457
γ-I	4320–4198	4264
γ-II	4050–3927	3983
γ-III	3720–3597	3630
γ-IV	3401–3270	3339

VIBRATIONAL ANALYSIS

In view of the complicated features of the bands of the α and β sequences we believe that they are very unlikely to belong to a singlet-singlet transition. Among the known triplet-triplet transitions of N_2, the first and second positive systems are the best known. Yet the observed bands of the present study are not members of either system. This is evidently true because in the first and second positive systems the bands are degraded toward the short wavelength.

The other known permitted triplet-triplet transition emitting in the infrared region is $B^3\Sigma_u^-$ → $B\,^3\Pi_g$. A Deslandres table with the Franck-Condon factor for each band has been calculated for this system by Benesch, *et al.*[2] From the table, one finds that the $\Delta v = -1$ and $\Delta v = -2$ sequences of the $B'^3\Sigma_u^-$ → $B\,^3\Pi_g$ system fall into the 2-3- and 3-4-μ regions, respectively. If our observed bands belonged to this system then all the eight bands from 3339 to 4435 cm^{-1} should form one single sequence (i.e., $\Delta v = -1$ of $B\,^3\Sigma_u$ → $B^3\Pi_g$) instead of the two sequences as mentioned previously. However, though some overlapping occurs, one still can see from the structures of these eight bands that the 3339-cm^{-1} and 3630-cm^{-1} bands are degraded toward the blue. Hence, the observed eight bands in 2-3-μ region are more likely to belong to different sequences or even to different electronic band systems rather than to constitute a single sequence. In order to clarify this point, a low resolution spectrometer was permitted to scan the source in this spectral region.[3] The resulting spectrum indicates an overlapping of two sequences here. Furthermore, the bands of the $\Delta v = -2$ sequence of the $B'^3\Sigma_u^-$ → $B\,^3\Pi_g$ system are more closely spaced than the three bands (2998 cm^{-1}, 2730 cm^{-1}, and 2456 cm^{-1}). Expressed in wavelength scale, the three bands obtained in the present study are: 3.336 μ, 3.663 μ, and 4.070 μ. The bands of the $\Delta v = -2$ sequence of $B'^3\Sigma_u^-$ → $B\,^3\Pi_g$ system are[2] 3.16 μ (0, 2), 3.32 μ (1, 3), 3.50 μ (2, 4), 3.68μ (3, 5), 3.88μ (4, 6), and 4.09μ (5, 7). Therefore, we are reasonably well convinced that the observed bands are not part of the $B'^3\Sigma_u^-$ → $B\,^3\Pi_g$ system.

On the basis of the three bands in the β sequence and the first three bands in the α sequence, a partial Deslandres table is proposed and indicated in Table II.

TABLE II. A proposed scheme for six of the observed bands.

v'/v''	n (cm^{-1})	$n+1$ (cm^{-1})	$n+2$ (cm^{-1})
m	2998		
$m+1$	4435	2730	
$m+2$		4134	2457
$m+3$			3830

The good agreement between the $\Delta G_{1/2}$ and $\Delta G_{3/2}$ values for the lower state of this observed system and for the $B^3\Pi_g$ state (see Table III) suggests that the observed system terminates at the $B\,^3\Pi_g$ state. In addition, this fit to the data fixes the value of the vibrational number n at zero, whereupon the relevant vibrational quantum

TABLE III. Comparison of the lower state ΔG_v's of present work with those of the $B\,^3\Pi_g$.

v	$\frac{1}{2}$(cm^{-1})	$\frac{3}{2}$(cm^{-1})
ΔG_v Observed (Wu & Benesch)	1705	1677
ΔG_v Observed (Dieke & Heath[4])	1705.55	1676.32
ΔG_v Calculated	1705.53	1676.27

numbers for the $B\,^3\Pi_g$ become $v = 0, 1,$ and 2. Assuming, then, that the identity of the lower state has been established as the $B\,^3\Pi_g$ but that the $B'\,^3\Sigma_u^- \rightarrow B\,^3\Pi_g$ transition has been exonerated, there remains the matter of providing an alternative identification for the upper state of the present system.

In 1957, Mulliken[5] predicted the existence of an electronic state $^3\Delta_u$ of N_2 with $T_e = 60500$ cm^{-1} which is slightly above the $B\,^3\Pi_g$ state and has not been observed experimentally. The $^3\Delta_u$ state could account for the upper state of this new system. In fact, Carroll[6] has reported the observation of the $^3\Delta_u \rightarrow {}^3\Pi_g$ transition in CO which is isoelectronic with N_2.

Since, in Table II, n is assigned to be zero, the 2998 cm^{-1} band should be the $(m, 0)$ band of the new system, where m has not been designated yet. Using various values of m, we calculate the corresponding set of T_e' w_e' and $\chi_e\omega_e$ values of the upper state $^3\Delta_u$' and we generate the related Deslandres and Franck-Condon table.

Of all the values of m which were tried, the chosen one $m = 2$ in our assignment was arrived at for the following reasons:

(1). For $m = 0$ and $m = 1$, the calculated value of T_e for $^3\Delta_u$ state is much higher than that of the $B\,^3\Pi_g$ state. In that case, the system should be observable in the visible and near infrared region. An effort was made to look for this system with the same source in these regions; the result was negative. Only the first positive system was found in the near infrared, and the 1*PG* and 2*PG* were found in the visible. For the assignment of $m = 3$, the calculated T_e value of the $^3\Delta_u$ from the same derivation of the $^3\Delta_u \rightarrow B\,^3\Pi_g$ is lower than the T_e value of the $B\,^3\Pi_g$, which contradicts the assumption made before calculation. This inconsistent result made us discard the $m = 3$ assignment.

(2). The resultant T_e value from $m = 2$ is 59738 cm^{-1}, which is closer to Mulliken's pre-

v' \ v"	0	1	2	3	4	5	6	7	8	9
0	.2104 2 .5491 0	-.1684 4 .3553 0	-.3360 4 .8909-1	-.5008 4 .1005-1	-.6626 4 .4509-3	-.8216 4 .2396-5	-.9776 4 .1333-5	-.1131 5 .3073-5	-.1281 5 .4513-5	-.1428 5 .1094-4
1	.1526 4 .3128 0	-.1786 3 .9672-1	-.1855 4 .3762 0	-.3502 4 .1821 0	-.5121 4 .2983-1	-.6710 4 .1798-2	-.8270 4 .2607-4	-.9801 4 .2898-7	-.1130 5 .1244-5	-.1278 5 .1662-6
2	.2998 4 .1059 0	.1293 4 .2837 0	-.3835 3 .1114-2	-.2031 4 .2950 0	-.3649 4 .2531 0	-.5239 4 .5627-1	-.6799 4 .4266-2	-.8330 4 .5733-4	-.9832 4 .1641-5	-.1130 5 .9361-5
3	.4435 4 .2648-1	.2730 4 .1799 0	.1054 4 .1843 0	-.5934 3 .2037-1	-.2212 4 .1987 0	-.3801 4 .2955 0	-.5361 4 .8499-1	-.6892 4 .7804-2	-.8394 4 .1486-3	-.9866 4 .4213-6
4	.5839 4 .5121-2	.4134 4 .6581-1	.2458 4 .2090 0	.8102 3 .9784-1	-.8083 3 .6256-1	-.2398 4 .1185 0	-.3958 4 .3118 0	-.5489 4 .1153 0	-.6990 4 .1249-1	-.8463 4 .2209-3
5	.7209 4 .6902-3	.5504 4 .1611-1	.3827 4 .1043 0	.2180 4 .1983 0	.5614 3 .4219-1	-.1028 4 .9508-1	-.2588 4 .6244-1	-.4119 4 .3177 0	-.5621 4 .1449 0	-.7093 4 .1861-1
6	.8544 4 .4325-4	.6839 4 .2632-2	.5163 4 .3192-1	.3516 4 .1340 0	.1897 4 .1736 0	.3078 3 .1304-1	-.1252 4 .1129 0	-.2783 4 .2661-1	-.4285 4 .3086 0	-.5757 4 .1767 0
7	.9846 4 .4322-6	.8141 4 .1965-3	.6465 4 .5931-2	.4817 4 .5029-1	.3199 4 .1509 0	.1610 4 .1431 0	.4943 2 .1737-2	-.1482 4 .1174 0	-.2983 4 .7768-2	-.4455 4 .2972 0
8	.1111 5 .4971-5	.9409 4 .1791-5	.7733 4 .5162-3	.6085 4 .1084-1	.4467 4 .6842-1	.2878 4 .1628 0	.1317 4 .1159 0	-.2136 3 .2762-3	-.1715 4 .1130 0	-.3188 4 .3753-3
9	.1235 5 .3448-5	.1064 5 .2357-4	.8967 4 .5299-5	.7319 4 .1031-2	.5701 4 .1665-1	.4111 4 .8524-1	.2551 4 .1679 0	.1020 4 .9082-1	-.4813 3 .3643-2	-.1954 4 .1025 0

FIG. 3. A Deslandres table for the present band system. Upper entries are the band frequencies in kaysers; lower entries are Franck-Condon factors calculated from Rydberg-Klein-Rees potential curves. Each four-digit decimal is to be multiplied by the power of 10 indicated by its following single digit. Column headings give the vibrational quantum numbers for the $B\,^3\Pi_g$ state, while row designations are the vibrational quantum numbers for the $W\,^3\Delta_u$ state, Doubly underlined bands have been observed in the present work; singly underlined bands correspond to McFarlane's groups of lines. The customary Condon parabola follows the locus of maximum vibrational overlap.

dicted value of 60500 cm^{-1} than the other sets. Though this is not a really critical point, we find it most gratifying.

(3). This is the most convincing argument. The associated Deslandres and Franck-Condon table (Fig. 3), which is generated from the set of electronic and vibrational constants of the ${}^3\Delta_u$ for $m=2$, includes entries which correspond closely to groups of lines obtained by McFarlane[7] of Bell Telephone Laboratories when he used stimulated excitation of molecular nitrogen in a laser tube. The comparison between McFarlane's data and our predicted bands of the same region from the generated Deslandres table is shown in Table IV. These four groups, which we are interpreting as bands and which appear prominently in Fig. 3, were divided by McFarlane into two families. The two families fall into the two sequences, $\Delta v=+1$ and $\Delta v=-1$, of the new system with the assignment of $m=2$.

TABLE IV. Predicted bands and McFarlane's data.

	McFarlane's data (cm^{-1})	Predicted bands[a] (cm^{-1})
Group 1:	1866.89-1803.01	-1855.65
Group 2:	1692.84-1600.44	-1684.14
Group 3:	1543.82-1482.71	1526.40
Group 4:	1314.37-1239.90	1292.69

[a] The strongest head in the band.

Figure 3 is the Deslandres table for the ${}^3\Delta_u \rightarrow B\,{}^3\Pi_g$ system generated from the calculated molecular constants of the ${}^3\Delta_u$ state and the known molecular constants of the $B\,{}^3\Pi_g$ state. The upper member in each entry is the wave number and the lower one is the Franck-Condon factor for the band. The bands doubly underlined are our observed bands and those singly underlined correspond to McFarlane's "groups."

As shown in Fig. 3, almost half of the Deslandres table has a negative value. This requires an explanation. The equilibrium term value of the ${}^3\Delta_u$ state ($T_e = 59738\ \mathrm{cm}^{-1}$) is only slightly higher than that of the $B\,{}^3\Pi_g$ state ($T_e = 59619\ \mathrm{cm}^{-1}$). Therefore both transitions, ${}^3\Delta_u \rightarrow B\,{}^3\Pi_g$ and ${}^3\Delta_u \leftarrow B\,{}^3\Pi_g$, are expected. Those bands with positive sign belong to the ${}^3\Delta_u \rightarrow B\,{}^3\Pi_g$ transition and those with negative sign belong to the ${}^3\Delta_u \leftarrow B\,{}^3\Pi_g$ transition. In McFarlane's paper he suggested that "Groups 1 and 2 appear to belong to one electronic transition, and groups 3 and 4 to a second electronic transition. Oscillation in groups 1 and 2 occurs during the high-current excitation pulse and in groups 3 and 4 during the afterglow." In our proposed scheme this phenomenon can be explained as follows: groups 1 and 2 are the (1, 2) and (0, 1) bands of ${}^3\Delta_u \leftarrow B\,{}^3\Pi_g$ transition which occurs during the excitation pulse and populates the 0 and 1 (and maybe higher) vibrational levels of the ${}^3\Delta_u$ state. Groups 3 and 4 are the (1, 0) and (2, 1) bands of the ${}^3\Delta_u \rightarrow B\,{}^3\Pi_g$ transition which occurs in the afterglow. This is the phenomena of intrasystem cascading.

From the above arguments, m is assigned to be 2, and $T_e = 59738\ \mathrm{cm}^{-1}$, $\omega_e = 1539\ \mathrm{cm}^{-1}$, and $\chi_e\omega_e = 17\ \mathrm{cm}^{-1}$ are chosen to be the electronic and vibrational constants of the ${}^3\Delta_u$ state. Since the singlet Δ_u state of N_2 is designated $w\,{}^1\Delta_u$, it is our suggestion that the ${}^3\Delta_u$ state be designated W.

DISCUSSION

A delicate point in our interpretation is the decision to assign the α sequence to the positive branch of the Franck-Condon parabola rather than to the negative branch or partly to both. While we do, in fact, feel that the spacing of the bands of the new system among the remnants of the 1*PG* in the $2-3-u$ region favors assignment to the positive branch sequence, the decision necessarily calls attention to the apparent failure of the negative sequence to manifest itself in the same region. It is our suggestion that the relative weakness of the negative sequence in this case can be explained by its competitive position with respect to the 1*PG*. Note that all of the emitting $B\,{}^3\Pi_g$ states will also be the upper states of transitions to the $A\,{}^3\Sigma_u^-$ wherein the photons involved will be more energetic by a factor of more than 3 relative to those of the $W\,{}^3\Delta_u \leftarrow B\,{}^3\Pi_g$. Accordingly, the probability of 1*PG* transitions will be perhaps fifty times greater than that of transitions corresponding to the negative entries of Fig. 3. We take this interpretation to be consistent with the observation by McFarlane, which we have mentioned previously, that bands of positive sequences (in our scheme), but not of negative sequences, emit in the afterglow.

It will readily be appreciated that the principal area of difficulty in the experimental part of the present investigation arose from the weakness of the observed bands. Thus, it was necessary to resort to very wide slits and, accordingly, to work well below the level of resolution of which the spectrometer is inherently capable. The spectrometer slits were, in fact, set to a value which was judged to be optimum for the recording of the β sequence, and were maintained at that physical size throughout all of the work. This practice has led to a resolution of about 0.7 cm^{-1} in the β sequence and about 1.5 cm^{-1} in the higher-frequency α and γ sequences. In no case was the resolution great enough to permit a detailed rotational analysis. However, from the deduced electronic and vibrational constants of the $W\,{}^3\Delta_u$ state and the known molecular constants of the $B\,{}^3\Pi_g$ state, a theoretical determination can be made of the positions and intensities of the rotational lines of bands in the $W\,{}^3\Delta_u \rightarrow B\,{}^3\Pi_g$ system by treating the rotational and coupling constants of the $W\,{}^3\Delta_u$ state as parameters. Such a treatment involves 27 branches per band without taking into account Λ doubling. The goal of the calculation is to reproduce the low-resolution features of a band such as that of Fig. 1, where individual rotational details are badly overlapped, but which contains a great deal more information than would a simple band contour display. Although some results have been obtained with these procedures, they are of a preliminary nature and will be reported later.

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[1] The two bands, 4435 cm^{-1} and 4134 cm^{-1}, of the α sequence have been reported by G. Hepner and L. Herman, in Ann. Geophys. 13, 242 (1957). They have made the suggestion that these bands may belong to a $^5\Sigma \rightarrow {}^5\Sigma$ transition.

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Fully Coupled Hartree-Fock Calculations of the Refractive Index, Dynamic Polarizability, and Verdet Coefficients of Helium, Beryllium, and Neon*

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Fully coupled Hartree-Fock calculations of the refractive index, dynamic polarizability, and Verdet coefficients of He, Be, Ne, and the corresponding 2-, 4-, and 10-electron isoelectronic series are presented. The time-dependent Hartree-Fock perturbation equations are derived and solved using a variational method, in which the zero-order and the perturbed wave functions are represented by analytical functions containing adjustable parameters which are optimized according to the variational technique. The numerical results for both the refractive index and the Verdet coefficients are fitted to polynomials in even powers of $1/\lambda$, where λ is the wavelength. In this work it is found that the computed refractive indices differ from the corresponding experimental values due to Cuthbertson and Cuthbertson by a very nearly constant amount. That is, if the computed dynamic polarizabilities are adjusted so as to equal the experimental polarizability α at zero frequency, then the experimental and theoretical curves of refractive index versus frequency are nearly identical. This adjustment in α is around 5% (for He) and 10% (for Ne) of the experimental static polarizabilities. Finally, the calculated transition frequencies are around 2% too large for He, 17% too large for Ne, and 9% too small for Be.

I. INTRODUCTION

Interest in the theoretical prediction of the refractive index, the dynamic polarizability, and other related time-dependent properties of atomic systems, involving harmonic perturbations, has been revived. This is primarily because of the newly discovered techniques for solving time-dependent problems. Two of the most notable of these methods are the oscillator sum rules which have been extensively exploited by Dalgarno and his co-workers[1] and the vari-