the experimental value.

It is then hard to see how the large differences between experimental and calculated values can be removed by using a wave function which can be expanded in terms of the solutions to the HF average field. A further test of this can be afforded by measurements of the g_J factors in other members of the nitrogen isoelectronic sequence. In these, the interaction with $1s^22s\,2p^3ns$-type configurations should be different and probably smaller. We would then expect fairly constant differences between calculated and experimental values if our arguments are correct. With this possibility in mind we have calculated the g_J values in the five levels of O II, for which good HF wave functions are available.[22] The calculated values are given in Table II, and the necessary integrals computed with good HF wave functions[22] in Table I.

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PHYSICAL REVIEW A VOLUME 2, NUMBER 5 NOVEMBER 1970

$W\,^3\Delta_u$-$X\,^1\Sigma_g^+$ System of N_2 †

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(Received 20 April 1970)

Bands of $W^3\Delta_u \leftarrow X^1\Sigma_g^+$, a new system of molecular nitrogen, have been identified in absorption from their locations as predicted by the spectroscopic constants obtained in infrared emission. Three bands have been observed and measured, the (5,0), (6,0), and (7,0). A Deslandres table with Franck-Condon factors is presented, which indicates that the system will occur most readily below 2500 Å. The relevant potential energy curves for the system are given with the observed transitions displayed.

The $W\,^3\Delta_u$ state of molecular nitrogen was first identified in the course of a series of experiments which measured the infrared emission spectrum from discharges through nitrogen[1,2] and oxygen[3] 1-5-μ wavelength. A group of 15 bands of the system $W\,^3\Delta_u \rightleftarrows B\,^3\Pi_g$ have thus far been identified, comprising eight of the mode $W \leftarrow B$ and seven of the mode $W \rightarrow B$, all in emission. This array of data, developed from spectra of moderate resolution, yields a set of spectroscopic constants among which ω_e is good to 1%.

These constants form the basis for the generation of potential curves for the state in question, the $W\,^3\Delta_u$, as well as Deslandres tables and Franck-Condon factors for band systems involving all other known electronic states of the molecule. One of these tables, containing band frequencies and Franck-Condon factors, has been given previously for the group $W\,^3\Delta_u \rightleftharpoons B\,^3\Pi_g$ and another is given here for transitions between the ground state and $W\,^3\Delta_u$.

PROCEDURE

The results of the infrared work prompted an investigation of other spectral regions for transitions involving the $W\,^3\Delta_u$ state. In essence, the widening search constituted an extension of the earlier process of locating bands of ever increasing obscurity while continually improving the detection precision through the use of vibrational constants which gradually become better as more bands were in their turn inserted into the tables.

Originally, the three $W\,^3\Delta_u \rightarrow B\,^3\Pi_g$ bands now identified as the (2, 0), (3, 1), and (4, 2) in the 3–5-micron wavelength region formed the basis for a tentative set of vibrational constants. At this point, of course, neither the upper nor lower state had been established with certainty, there having been several candidates for each. The extension of the system into the 2–3-μ region, however, served to delineate several progressions of the upper and lower states, indicating the upper state to be new and the lower to be, in fact, the $B\,^3\Pi_g$.

Thus far, the analysis had been carried out using a least-squares fitting procedure involving the frequencies of prominent features of the bands (Q branch heads). The further refinement required a more definitive location of the band origins. In principle, of course, precise information concerning the frequencies of the band origins is best obtained from a complete rotational analysis of the bands. However, the complexity of a $^3\Delta - ^3\Pi$ transition is such that high resolution is required to disentangle the overlapping branches. This was not available for the infrared bands since the resolution was energy limited at about 0.5 cm^{-1}.

As an expedient, a method of attack has been adopted which is somewhat more elaborate and productive than the usual "contour analysis." It involved a computer-generated model band which contains all of the detailed features of the many branched triplet-triplet case at a resolution commensurate with that available experimentally. Molecular rotational constants for the $W\,^3\Delta_u$ state are supplied to the computer as adjustable parameters in application to the theoretical relations calculated by Kovacs and Toros[4] for the $^3\Delta - ^3\Pi$ indi-

$W\,^3\Delta_u - X\,^1\Sigma_g^+$

						V''					
V'	0	1	2	3	4	5	6	7	8	9	10
0	1683.6 .1713-2	1752.4 .1310-1	1826.0 .4721-1	1905.1 .1065 0	1990.2 .1691 0	2082.0 .2005 0	2181.4 .1846 0	2289.1 .1354 0	2406.4 .8034-1	2534.5 .3900-1	2674.9 .1559-1
1	1642.7 .8568-2	1708.1 .4711-1	1778.0 .1107 0	1852.9 .1384 0	1933.3 .8733-1	2019.9 .1401-1	2113.2 .9521-2	2214.2 .7826-1	2323.8 .1443 0	2443.0 .1520 0	2573.2 .1112 0
2	1604.4 .2295-1	1666.7 .8741-1	1733.2 .1204 0	1804.3 .5727-1	1880.4 .1253-3	1962.2 .4533-1	2050.2 .9516-1	2145.1 .5355-1	2247.7 .1094-2	2359.1 .3407-1	2480.3 .1119 0
3	1568.3 .4383-1	1627.8 .1099 0	1691.2 .7206-1	1758.8 .1040-2	1831.1 .4385-1	1908.5 .7576-1	1991.7 .1548-1	2081.1 .1425-1	2177.6 .7715-1	2282.0 .6305-1	2395.2 .4797-2
4	1534.4 .6680-1	1591.3 .1025 0	1651.8 .1818-1	1716.3 .2143-1	1785.0 .6970-1	1858.6 .1385-1	1937.3 .1912-1	2021.9 .6786-1	2112.8 .2127-1	2210.9 .9271-2	2317.0 .7073-1
5	1502.5 .8696-1	1557.0 .7284-1	1614.9 .7807-4	1676.4 .5735-1	1742.0 .3075-1	1811.9 .7809-2	1886.7 .5891-1	1966.8 .1536-1	2052.7 .1653-1	2145.2 .6249-1	2245.0 .1615-1
6	1472.3 .1003 0	1524.6 .3743-1	1580.1 .1649-1	1639.0 .5698-1	1701.6 .5108-3	1768.3 .4486-1	1839.4 .2615-1	1915.4 .8806-2	1996.9 .5382-1	2084.3 .8728-2	2178.3 .2385-1
7	1443.9 .1050 0	1494.1 .1106-1	1547.4 .4202-1	1603.8 .2820-1	1663.7 .1368-1	1727.4 .4519-1	1795.2 .2614-4	1867.5 .4465-1	1944.9 .1513-1	2027.7 .1712-1	2116.6 .4744-1
8	1416.9 .1021 0	1465.3 .3046-3	1516.5 .5511-1	1570.6 .4007-2	1628.0 .3909-1	1689.0 .1477-1	1753.7 .2141-1	1822.7 .3225-1	1896.3 .3756-2	1975.0 .4475-1	2059.2 .3523-2
9	1391.5 .9325-1	1438.1 .3737-2	1487.3 .4992-1	1539.4 .1816-2	1594.5 .4350-1	1652.9 .1630-4	1714.9 .4062-1	1780.8 .2814-2	1851.0 .3293-1	1925.8 .1525-1	2005.8 .1641-1
10	1367.3 .8129-1	1412.3 .1581-1	1459.8 .3329-1	1509.9 .1623-1	1562.8 .2659-1	1618.9 .1279-1	1678.3 .2831-1	1741.4 .6968-2	1808.5 .3377-1	1879.9 .1172-2	1956.0 .3827-1

FIG. 1. Deslandres table, with Franck-Condon factors for the $W\,^3\Delta_u - X\,^1\Sigma_g^+$ system of N_2. The top line of each entry is the wavelength in Å of the band origin, and the bottom line its Franck-Condon factor. The four-digit decimal of the Franck-Condon factor is to be multiplied by the power of 10 indicated by its following signed digit. Column headings give the vibrational quantum numbers for the $X\,^1\Sigma_g^+$ state, while row designations are the vibrational quantum numbers for the $W\,^3\Delta_u$ state. It is believed that the values of the band origins are good to 0.1 Å, as tabulated.

vidual line intensities. The molecular constants for the $B\ ^3\Pi_g$ state are well known,[5] and the appropriate values are used as input data for the several bands under study. The lines are weighted according to the relevant fractional population factors or excitation rates, distorted as by the spectrometer, and, finally, summed to generate the ordinates for a computer plot. After the generated band has been compared with the laboratory spectrometric output, the rotational constants of the $^3\Delta$ state are adjusted appropriately, and the cycle is repeated if further alteration appears warranted.

One of the products of this procedure is the specification of the position of the band origins with respect to the recognizable features of the various bands. This knowledge, of course, is of great utility in carrying out an extensive vibrational analysis, much to be preferred to relying on measured intervals between band heads. In the infrared system, the use of band origins is of special importance, since, in that wavelength region, there occur both "positive" and "negative" bands. The concept of the sign of a band arises quite simply as the required answer to the question of whether or not the upper level for the band is in the electronic state whose T_e is the larger. For the $W\ ^3\Delta_u$–$B\ ^3\Pi_g$ system, in which the difference in the T_e values is close to 0, half the bands are positive, half negative, with the dividing line running down the $\Delta v = 0$ sequence in the Deslandres table. In more conventional systems, the negative bands will be confined to a triangular area in the upper right-hand corner of the table.

Where the bands have the $W\ ^3\Delta_u$ for their initial state, they are degraded to the red, while the negative bands have $B\ ^3\Pi_g$ for their initial state and are degraded to the blue. The duality of the band shading is, clearly, a consequence of the intrasystem cascading.

When some 15 bands of the infrared $W\ ^3\Delta_u \rightleftarrows B\ ^3\Pi_g$ system had been observed and measured, a somewhat improved set of vibrational constants was generated as outlined above. Next, the vibrational and rotational $W\ ^3\Delta_u$ data were arranged as input to a computer routine which calculates the potential curve for the state in question.[6] This is an RKR curve, the use of which is now widely accepted for precision computations.[7,8] The RKR potential curve for the $B\ ^3\Pi_g$ state had been generated similarly at a somewhat earlier date,[6] and the relationship of the two potential curves as to energy and the spatial coordinate r may be observed in a juxtaposition of the two in Ref. 2.

The next step in the treatment calls for generation of a wave function for each vibrational level of the two electronic states. The wave functions are obtained as solutions to the radial Schrödinger equation which are based on the Numerov integration method for second-order differential equations.[9] Input data to the integration routine are supplied on cards as the coordinates of a series of points on a potential-energy curve. Most of the points of the potential curve are determined by the measured spectroscopic data as described above. There are, however, some portions of the potential well, those remote from the measured vibrational levels and at large values of the potential energy, which are supplied as intuitively extrapolated entries. These artificial points are required in order to carry the integration smoothly into the regions where the wave functions tend to vanish. They are not reported as part of the potential function; their actual magnitudes, if reasonable, have little effect on the computed wave functions.

The solutions are generated as a combination of two unnormalized segments propagated from point to point toward each other from the fictitious values of the potential function beyond the region of interest at large and small values of r. The solutions are rescaled at the meeting point, normalized, and stored on tape as wave functions comprising 1001 points.

The Franck-Condon program chooses the appropriate pairs of wave functions and performs the integration required for the Franck-Condon factor for each pair, as well as a series of integrals of the r-centroid type.[10]

The tabulated output of the computer routine

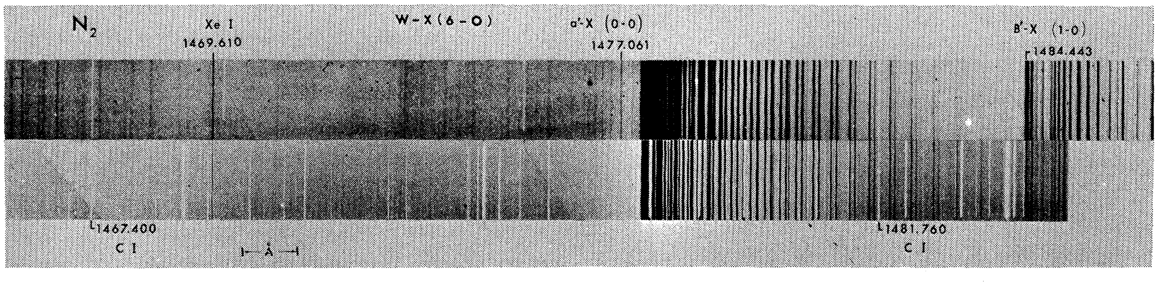

FIG. 2. (6,0) band of the $W\ ^3\Delta_u \leftarrow X\ ^1\Sigma_g^+$ system, extending from 1472 to 1475 Å. As is evident, the $W \leftarrow X$ transition is weak compared to other band systems of N_2.

consists of a Deslandres table calculated from energy differences given by the vibrational constants with associated Franck-Condon factors appended beneath each entry.

RESULTS

The Deslandres table and Franck-Condon factors generated for the transition $W\,^3\Delta_u$–$X\,^1\Sigma_g^+$ as outlined above are presented as Fig. 1. This array was used in a search of existing laboratory data. Three unanalyzed bands were found in a compendium of ultraviolet absorption spectra.[11] Reference 11 concerns the absorption of radiation by room-temperature molecular nitrogen between 1060 and 1520 Å, measured with a high-resolution vacuum spectrograph. The experimental details and methods of data reduction are discussed in Ref. 11.

Five bands of appreciable intensity appear in Fig. 1 near the vertex of the Franck-Condon "parabola" in the upper-state progression from the $v=0$ level of the ground state $X\,^1\Sigma_g^+$. The (5, 0), (6, 0), and (7, 0) bands are those found in the data of Ref. 11. The (8, 0) band is badly overlapped by other bands and the (4, 0) band is beyond the region of study of Ref. 11. The (6, 0) band of the $W\,^3\Delta_u \leftarrow X\,^1\Sigma_g^+$ system is shown in Fig. 2. This is the least overlapped of the three bands and has a more open multiplet structure than the others. Figure 2 also depicts qualitatively the strength of the $W-X$ system relative to other band systems of N_2; it absorbs very weakly, since the transition is strongly forbidden. A rotational analysis of the (5, 0) and (6, 0) bands will be presented in the future.

CONCLUSIONS

The present investigation has identified a second band system involving the nitrogen $W\,^3\Delta_u$ state, the $W\,^3\Delta_u \leftarrow X\,^1\Sigma_g^+$ transition. That the upper state is $^3\Delta_u$ can be established on the following grounds.

(*i*) $^3\Delta_u$ is the only valence state of N_2 predicted to be in this region that has not been heretofore characterized vibrationally. The fact that the constants for all other possible states in this energy region are well known allows one to rule them out as candidates for the upper state of the bands under study.

(*ii*) The constants resulting from the vibrational assignment made for the upper state here are in agreement with those obtained for the new state studied in infrared emission,[1,2] which was identified as the upper state of the permitted transition $^3\Delta_u \rightarrow B\,^3\Pi_g$.

A Deslandres table with Franck-Condon factors for this vacuum ultraviolet system is given in Fig. 1. Practically speaking, the system is restricted to the ultraviolet between 1300 and 2500 Å. The (6, 0) band is shown in Fig. 2, and the relevant potential-energy curves are presented as Fig. 3.

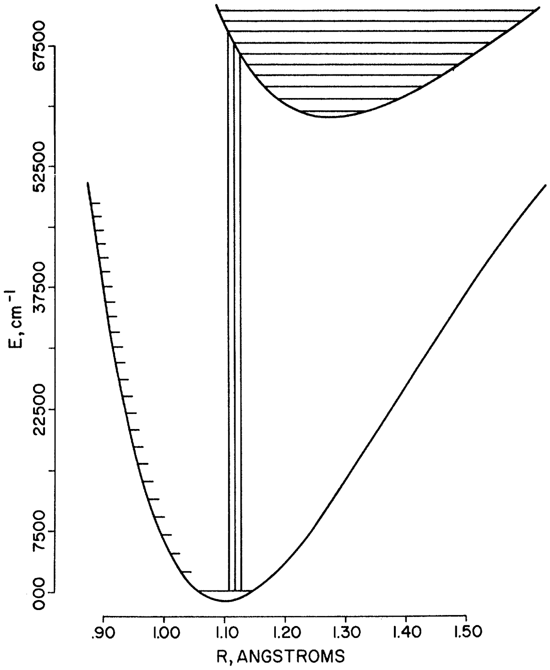

FIG. 3. Potential curve for the $W^3\Delta_u$ state relative to the $X\,^1\Sigma_g^+$ curve. Each was obtained from an independent RKR calculation. The $X\,^1\Sigma_g^+$ curve is based on constants contained in Ref. 6, the $W^3\Delta_u$ on constants derived from the infrared work (Refs. 1 and 2) and the ultraviolet bands treated here. The ultraviolet transitions discussed in this work are indicated by vertical lines. Vibrational levels for the two states are indicated.

In Ref. 2, concerning the $W\,^3\Delta_u \rightleftharpoons B\,^3\Pi_g$ system, it was clearly observed that the $W\,^3\Delta_u$ state undergoes excitation throughout a wide range of conditions, certainly including those in which emission would take place from the 1*PG*, $B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^-$ system. These combined studies suggest consideration of the $W\,^3\Delta_u \rightarrow X\,^1\Sigma_g^+$ system as an ultraviolet emission feature; a forthcoming paper will deal directly with the matter of the characteristics to be expected of such predicted emission for this forbidden system.

The present $W\,^3\Delta_u \leftarrow X\,^1\Sigma_g^+$ system, being inherently simpler and better resolved than the $W\,^3\Delta_u \rightleftharpoons B\,^3\Pi_g$, will be subjected first to a rotational analysis. Should that endeavor prove successful, the results will next be used to attempt more refined band-model iteration schemes such as the one outlined in the procedure section above.

ACKNOWLEDGMENT

The authors are grateful to Dr. Shelby Tilford for his cooperation and stimulating discussions during the course of this work.

[†] Research supported in part by the U. S. Army Research Office, Durham and by the National Science Foundation. Computer time used supported (in part) by the National Aeronautics and Space Administration under Grant No. NsG 398 to the Computer Science Center of the University of Md.

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Lower-Bound Method for Atomic Calculations*

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(Received 9 July 1970)

In the reduced-density-matrix variational method, a trial density matrix $\Gamma_t^{(2)}$ is varied subject to physical realizability conditions in order to calculate the ground-state energy $E_0=\frac{1}{2}N\min \operatorname{Tr} H^{(2)}\Gamma_t^{(2)}$. Here we expand $\Gamma_t^{(2)}$ in a finite basis of Hartree-Fock geminals and apply a number of equalities to reduce the parameter space of $\Gamma_t^{(2)}$. The method is completely general, but application is made only to the C^{++} ion, where a six-geminal expansion coupled with positivity of $\Gamma_t^{(2)}$ recovers the Hartree-Fock result.

I. INTRODUCTION

It is known that the ground-state energy $E_0(N)$ for a system of electrons with Hamiltonian

$$H=\sum_{i=1}^{N} T(i)+\sum_{i<j} V(i,j) \tag{1.1}$$

can be written in terms of a two-body reduced density matrix

$$\Gamma^{(2)}(\vec{x}_1{}',\vec{x}_2{}'|\vec{x}_1,\vec{x}_2)\equiv\int\cdots\int dx_3\cdots dx_N\sum_\alpha C_\alpha \times\psi_\alpha(\vec{x}_1{}',\vec{x}_2{}',\vec{x}_3,\ldots,\vec{x}_N)\,\psi_\alpha(\vec{x}_1,\ldots,\vec{x}_N)\,,$$

where

$$\sum_\alpha C_\alpha=1,\quad C_\alpha\geq 0 \tag{1.2}$$

via the relation

$$E_0(H)=\min_{\text{all }\Gamma^{(2)}}\ \tfrac{1}{2}N\operatorname{Tr}H^{(2)}\Gamma^{(2)}\quad, \tag{1.3}$$

where

$$H^{(2)}\equiv T(1)+T(2)+(N-1)V(1,2)\ . \tag{1.4}$$

The mechanics of carrying out the minimization required for (1.3) is, however, far from trivial.

There are a number of obvious necessary conditions which $\Gamma^{(2)}$ must satisfy – normalization, positive definiteness, antisymmetry – and a number of less obvious ones which have gradually come to light.[1] If the $\Gamma^{(2)}$ in (1.3) are taken as the set of all trial densities $\Gamma_t^{(2)}$ consistent with these conditions, without assuring that each comes from the right-hand side of (1.2) – is N realizable – then one obtains a lower bound to the energy $E_0(H)$. A lower bound is of course guaranteed only if one varies over *all* $\Gamma_t^{(2)}$; any representation of the trial $\Gamma_t^{(2)}$ by a finite expansion will result in an upper bound to the lower bound, a fact which must be borne in mind when any claims of accuracy are made.

In previous papers,[2] it was shown how an expansion of $\Gamma^{(2)}$ in terms of the lowest states of helium results in a one-particle density matrix for a series of partially ionized atoms which does not satisfy the Pauli principle, a fair indication that the restrictions employed were not very efficient. The purpose of this paper is to report on still another necessary symmetry condition for N real-

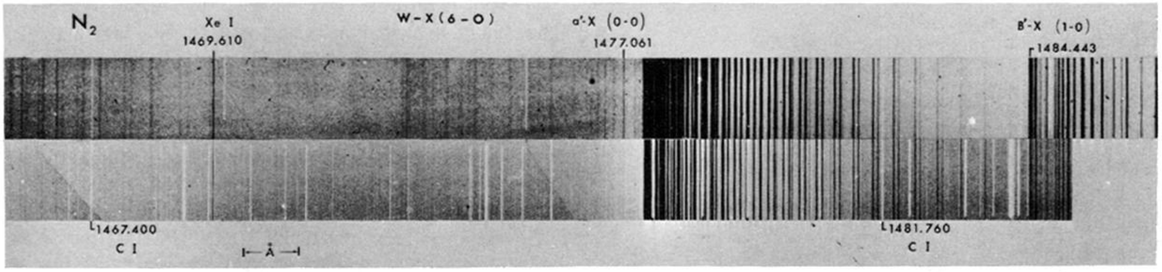

FIG. 2. (6, 0) band of the $W\,^3\Delta_u \leftarrow X\,^1\Sigma_g^+$ system, extending from 1472 to 1475 Å. As is evident, the $W \leftarrow X$ transition is weak compared to other band systems of N$_2$.