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Measurements on the $w\,^1\Delta_u \rightarrow a\,^1\Pi_g$ Transition in Molecular Nitrogen

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A new emission system of molecular nitrogen near 3.65 μ has been observed. It arises from transitions in the $0\rightarrow 0$ band of $w\,^1\Delta_u \rightarrow a\,^1\Pi_g$. The results permit a more direct determination of the electronic term value of $w\,^1\Delta_u$: $T_{00}(w\,^1\Delta_u)=71{,}698.44$ cm^{-1}. A value of the rotational constant difference $B_{0c}-B_{0d}=(1.0\pm0.3)\times10^{-4}$ cm^{-1} has been found for the $v=0$ level of $a\,^1\Pi_g$.

INTRODUCTION

A NEW emission system has been observed in molecular nitrogen arising from transitions between the $w\,^1\Delta_u$ state and the $a\,^1\Pi_g$ state. The system occurs in the near infrared around 3.65 μ and has not previously been observed using spontaneous emission sources. The present measurements were done on an oscillating optical maser with sufficient precision to show Λ doubling. Previous high-resolution measurements on the $a\,^1\Pi_g$ state[1–3] have accurately located its position with respect to the ground state. In the perturbed region at large J values Wilkinson and Houk[1] determined that the c levels lie above the d levels and with the assumption that Λ doubling in the $^1\Delta_u$ state is small, the present work indicates that this is also true at low J values. It is possible to infer the value of $T_{00}(w\,^1\Delta_u)$ by taking the observed band center for the $w\,^1\Delta_u\rightarrow a\,^1\Pi_g$ $0\rightarrow0$ transition and adding to this the known value of $T_{00}(a\,^1\Pi_g)$. Previous observations of the $w\,^1\Delta_u$ state [4] have involved transitions into the $w\,^1\Delta_u$ state from higher lying singlet levels.

THE EXPERIMENT

The experiment consisted of observing the output of a pulsed-gas-discharge optical maser[5] containing nitrogen at a pressure of 1 Torr. Similar results were obtained with flowing gas and with a static system. The pulse repetition rate was less critical than for the $a\,^1\Pi_g\rightarrow a'\,^1\Sigma_u^-$ system reported earlier[5,6] and the present observations were made at 15 pulses per sec.

Wavelength measurements were made with a Jarrell-Ash $\frac{1}{2}$-m Ebert spectrometer equipped with a 64-mm$\times$64-mm 30-lines/mm Bausch and Lomb grating blazed at 30 μ in first order. The observations of the $w\,^1\Delta_u\rightarrow a\,^1\Pi_g$ system were made in eighth order. High-order uv lines from a mercury spectral lamp were used as a calibration reference. To check on the absolute accuracy of the system, a measurement was made of the 5.4033-μ line[7] of neon[8] and it reproduced the calculated frequency to 0.014-cm^{-1}. The absolute accuracy of the $w\,^1\Delta_u\rightarrow a\,^1\Pi_g$ measurements is better than 0.04 cm^{-1} and the relative accuracy is estimated to be about 0.007 cm^{-1}.

RESULTS

A rapid scan of 12 of the lines observed is shown in Fig. 1. These have been identified as belonging to the Q_{cd} and Q_{dc} branches of the $0\rightarrow0$ transition of $w\,^1\Delta_u\rightarrow a\,^1\Pi_g$. The observed frequencies are shown in Table I

TABLE I. Observed Q branch transitions of the $0\rightarrow0$ band of $w\,^1\Delta_u \rightarrow a\,^1\Pi_g$ of nitrogen. $\nu_0=2747.29_1$ cm^{-1}, $B_{0d}'-B_{0c}''=-0.11953_1$ cm^{-1}, $B_{0c}'-B_{0d}''=-0.11945_7$ cm^{-1}.

Transition	Observed ν (cm^{-1})	Calc-Obs. $\Delta\nu$(cm^{-1})
$Q(4)$	2744.89_1	$+0.00_9$
$Q(5)$	2743.69_7	$+0.01_0$
$Q(6)$	2742.26_9	$+0.00_2$
$Q(7)$	2740.60_5	-0.00_4
$Q(8)$	2738.69_3	-0.00_9
$Q(9)$	2736.55_0	-0.01_0
$Q(10)$	2734.14_8	-0.00_6
$Q(11)$	2731.53_0	-0.00_7
$Q(12)$	2728.63_7	$+0.00_7$
$Q(13)$	2725.54_9	$+0.00_1$
$Q(14)$	2722.18_6	$+0.00_3$
$Q(15)$	2718.61_8	$+0.00_4$

with the rotational assignments. The even J lines are Q_{dc} transitions and the odd J lines are Q_{cd} transitions. The identification has assumed that only transitions between symmetric levels were observed. In spontaneous emission, transitions between symmetric levels are favored by a factor of 2 over transitions between antisymmetric levels. In stimulated emission, however, this factor of 2 appears in the single-pass optical gain

[1] P. G. Wilkinson and N. B. Houk, J. Chem. Phys. **24**, 528 (1956).
[2] J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, Astrophys. J. **141**, 395 (1965).
[3] P. G. Wilkinson, Astrophys. J. **126**, 1 (1957).
[4] A. Lofthus, Spectroscopic Report No. 2., University of Oslo, 1960 (unpublished) shows $T_{00}(w\,^1\Delta_u)=71\,697.7$ cm^{-1}. A more recent measurement of $T_{00}(a'\,^1\Sigma_u^-)$ (Ref. 12) combined with the data of Ref. 10, gives $T_{00}(w\,^1\Delta_u)=71\,698.8$ cm^{-1}.
[5] R. A. McFarlane, in *Proceedings of the Conference on the Physics of Quantum Electronics, San Juan, Puerto Rico, 1965*, edited by P. L. Kelley, B. Lax, and P. E. Tannenwald (McGraw-Hill Book Company, Inc. New York, 1965).
[6] R. A. McFarlane, Phys. Rev. **140**, A1070 (1965).
[7] W. L. Faust, R. A. McFarlane, C. K. N. Patel, and C. G. B. Garrett, Appl. Phys. Letters **1**, 85 (1962).
[8] R. A. McFarlane, W. L. Faust, C. K. N. Patel, and C. G. B. Garrett, in *Proceedings of Third International Quantum Electronics Conference, Paris, 1963*, edited by P. Grivet and N. Bloembergen (Columbia University Press, New York, 1964).

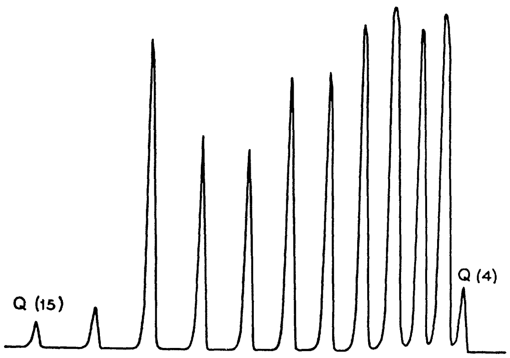

FIG. 1. A rapid scan of $Q(4)$ to $Q(15)$, $w\,^1\Delta_u \rightarrow a\,^1\Pi_g$. Some distortion of line shape apparent on the stronger lines is due to preamplifier saturation.

and makes it possible for oscillation to take place on symmetric transitions while antisymmetric transitions are below threshold and do not appear. This is clearly demonstrated in Ref. 6 where only symmetric transitions were observed. Later work on the $a\,^1\Pi_g - a'\,^1\Sigma_u^-$ transition using an increased optical path has made it possible to observe antisymmetric transitions but their intensity never exceeded 5% of adjacent symmetric transitions. The present data on $w\,^1\Delta_u \rightarrow a\,^1\Pi_g$ are believed therefore to be representative of transitions between symmetric levels. The two sets of data were fitted by the method of least squares to

$$\nu_{J\,\mathrm{even}} = \nu_0 + (B_d' - B_c'')J(J+1),$$
$$\nu_{J\,\mathrm{odd}} = \nu_0 + (B_c' - B_d'')J(J+1),$$

and the derived rotational constant differences and the band center are shown in Table I. The two values of ν_0 so determined agreed to less than half the estimated relative error and a mean value is shown. The frequencies calculated using this band center and the indicated rotational constant differences are compared in the table with the observations.

In Fig. 2 are plotted the experimental values of $\nu_{J+1} + \nu_{J-1} - 2\nu_J$ with the loci of calculated values determined from the derived constants. The straight lines represent the equations

J even:

$$\nu_{J+1} + \nu_{J-1} - 2\nu_J = 2\{B_c' - B_d' + B_c'' - B_d''\}J(J+1) + 2\{B_c' - B_d''\};$$

J odd:

$$\nu_{J+1} + \nu_{J-1} - 2\nu_J = -2\{B_c' - B_d' + B_c'' - B_d''\}J(J+1) + 2\{B_d' - B_c''\}.$$

The observations are consistent with the predicted equal and opposite slopes for the two sets of lines. It has been shown by Kronig and Van Vleck[9] that Λ doubling is negligibly small for $^1\Delta$ states and with this assumption a determination of Λ doubling in $v=0$ of $a\,^1\Pi_g$ is possible. Using all ten points for a least-squares fit to determine a representative slope in Fig. 2, we find

$$B_{0c}'' - B_{0d}'' = (1.0 \pm 0.3) \times 10^{-4}\ \mathrm{cm}^{-1},$$

where the limits are estimated.

For a specified rotational level the splitting between the c and d levels is given by[2]

$$\Delta E \approx (B_v^2/\Delta\nu)J(J+1),$$

where $\Delta\nu$ is the order of magnitude of the difference in energy between the $a\,^1\Pi_g$ state and neighboring $^1\Sigma_g$ states. Mulliken has predicted a $^1\Sigma_g^+$ state about 30 000 cm^{-1} above $a\,^1\Pi_g$. This would result in a rotational constant difference of 0.9×10^{-4} cm^{-1} if the effect of the ground state $X\,^1\Sigma_g^+$ is ignored.

The present measurements combined with recent NRL high-resolution measurements[2] on $a\,^1\Pi_g$ permit a more direct specification of the electronic term value T_{00} of $w\,^1\Delta_u$. The value of T_{00} of $a\,^1\Pi_g$ determined by Vanderslice *et al.* is 68 951.15 cm^{-1}, which is in excellent agreement with an earlier determination by Wilkinson.[3] Adding to this the band-center value from the present work,

$$T_{00}(w\,^1\Delta_u) = 71\,698.44\ \mathrm{cm}^{-1},$$

with an absolute accuracy of 0.34 cm^{-1} determined largely by the $a\,^1\Pi_g$ measurement.

The previous location of $w\,^1\Delta_u$[4] depended upon adding to T_{00} of $a'\,^1\Sigma_u^-$ the difference between the $0 \rightarrow 0$ band centers of Kaplan's first and second systems. Using the data of Lofthus and Mulliken[10] this difference is

$$T_{00}(w\,^1\Delta_u) - T_{00}(a'\,^1\Sigma_u^-) = 3959.5\ \mathrm{cm}^{-1}.$$

A determination[5,6] using an optical maser of the $0 \rightarrow 0$ band center for $a\,^1\Pi_g \rightarrow a'\,^1\Sigma_u^-$ gave a value of 1212.19 cm^{-1}. Combining this with the present data,

$$T_{00}(w\,^1\Delta_u) - T_{00}(a'\,^1\Sigma_u^-) = 3959.48\ \mathrm{cm}^{-1},$$

with an estimated absolute accuracy of 0.16 cm^{-1}. (See note added in proof.)

In Table II are shown the measured frequencies for

TABLE II. Observed R branch transitions of the $0 \rightarrow 0$ band of $w\,^1\Delta_u \rightarrow a\,^1\Pi_g$ of nitrogen. $B_{0\mathrm{av}}' + B_{0\mathrm{av}}'' = 3.0934_4$ cm^{-1}.

Transition	Observed ν(cm^{-1})	Calc. Obs.[a] $\Delta\nu$(cm^{-1})
$R(3)$	2755.50_5	-0.01_0
$R(3)$	2757.75_2	$+0.00_6$
$R(4)$	2759.76_7	$+0.00_1$

[a] Calculated with appropriate B difference assuming no Λ doubling in $^1\Delta_u$ using ν_0 from Table I and theoretical D values (Ref. 11).

[9] G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (D. van Nostrand, Inc., New York, 1950), p. 228.

[10] A. Lofthus and R. S. Mulliken, J. Chem. Phys. 26, 1010 (1957).

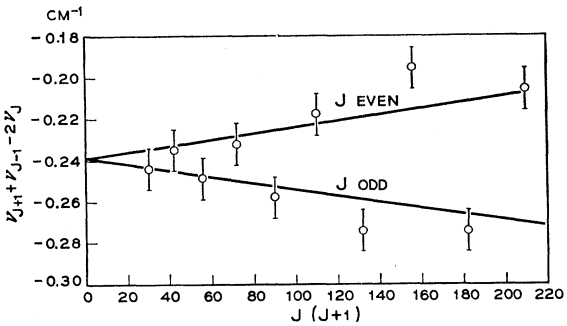

FIG. 2. A plot of $\nu_{J+1}+\nu_{J-1}-2\nu_J$ for the Q-branch transitions showing the effect of Λ doubling. The straight lines are calculated loci.

the three R branch lines observed. If one again assumes that only symmetric levels are involved because of their higher optical gain then $R(2)$ and $R(4)$ are R_c transitions and $R(3)$ is an R_d transition. The data have been analyzed to determine the sum of upper and lower state rotational constants ignoring the effect of Λ doubling on this sum only but including different rotational constants for c and d levels in $a\ ^1\Pi_g$ in difference terms. The band-center and rotational-constant differences already determined were used and since terms involving D no longer tend to cancel, theoretical values of D were included in the calculation.[11] The result of a least-squares fit to the data to determine the rotational constant sum only gives

$$B_{0\ \mathrm{av}}'+B_{0\ \mathrm{av}}''=3.0934_4\ \mathrm{cm}^{-1}.$$

A comparison between the complete theoretical result and the observed frequencies is made in Table II.

In order to compare the present results with those of other workers, it is helpful to determine an average rotational constant difference from the Q-branch data and combine this with the R-branch data to derive representative rotational constants for both states when Λ doubling is not apparent. We find

$$B_0(w\ ^1\Delta_u)=1.4870\ \mathrm{cm}^{-1},$$

$$B_0(a\ ^1\Pi_g)=1.6065\ \mathrm{cm}^{-1}.$$

[11] The values used were, for $w\ ^1\Delta_u$, $D_0'=5.61\times10^{-6}\ \mathrm{cm}^{-1}$, and for $a\ ^1\Pi_g$, $D_0''=5.89\times10^{-6}\ \mathrm{cm}^{-1}$.

Further, using the results of Ref. 6, (see note added in proof.)

$$B_0(a'\ ^1\Sigma_u^-)=1.4714\ \mathrm{cm}^{-1}.$$

These values are to be compared with the $w\ ^1\Delta_u$ data of Lofthus and Mulliken[10] who find $B_0(w\ ^1\Delta_u)=1.490$ cm^{-1}; the $a\ ^1\Pi_g$ data of Wilkinson[3] who finds $B_0(a\ ^1\Pi_g)=1.6065$ cm^{-1}, the NRL[2] result $B_0(a\ ^1\Pi_g)=1.6080$ cm^{-1}; and the NRL[12] determination $B_0(a'\ ^1\Sigma_u^-)=1.4712$ cm^{-1}.

CONCLUSION

The stimulated emission spectrum of molecular nitrogen has been extended to include transitions in the $0\rightarrow0$ band of $w\ ^1\Delta_u\rightarrow a\ ^1\Pi_g$. The results combined with previous high-resolution measurements[2,3] on $a\ ^1\Pi_g$ permit a more direct specification of the electronic term value of $w\ ^1\Delta_u$. The Λ doubling observed in $a\ ^1\Pi_g$ is in good agreement with that expected from interaction with a nearby $^1\Sigma_g^+$ state predicted by Mulliken.[13] The rotational constants in the absence of Λ doubling have been determined for the $v=0$ levels of the $w\ ^1\Delta_u$, $a\ ^1\Pi_g$ and $a'\ ^1\Sigma_u^-$ states.

[*Note added in proof.* More accurate measurements on $a\ ^1\Pi_g\rightarrow a'\ ^1\Sigma_u^-$ (R. A. McFarlane, 1966 International Quantum Electronics Conference, Phoenix, Arizona, 1966) show a $0\rightarrow0$ band center of 1212.28 ±0.02 cm^{-1}. Combining this with the present data

$$T_{00}(w\ ^1\Delta_u)-T_{00}(a'\ ^1\Sigma_u^-)=3959.57\ \mathrm{cm}^{-1}$$

with an estimated absolute accuracy of 0.06 cm^{-1}. The new data show $B_0'-B_0''=0.1361$ cm^{-1}. This leads to new $B_0(a'\ ^1\Sigma_u^-)=1.4704$ cm^{-1}.]

ACKNOWLEDGMENTS

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[12] S. G. Tilford, P. G. Wilkinson, and J. T. Vanderslice, Astrophys. J. 141, 427 (1965).