Dissociation Energy of NO and N_2*

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The vibrational levels of the $X^2\pi$ ground state of NO have been observed up to $v=23$, or an energy of 4.46 ev. In order that $D_0(NO)$ be 5.29 ev, a very sharp and sudden drop in the $\Delta G(v)$ values is necessary. No such tendency is observed, and therefore the higher value of $D_0(NO)=6.48$ ev appears most probable. This value then fixes $D_0(N_2)=9.76$ ev. A new system of NO bands in the near infrared is reported. These are probably due to a $^4\pi \rightarrow {}^4\pi$ transition.

INTRODUCTION

THE emission spectrum of NO has been studied extensively in the past.[1,2] In an attempt to establish the dissociation energy of N_2, the β bands ($B^2\pi \rightarrow X^2\pi$) of NO have been re-examined. The dissociation energy of NO is related to the dissociation energy of N_2 by[3] $N_2+O_2+1.87$ ev $\rightarrow$ 2NO. From spectroscopic studies, the value of $D_0(N_2)$ has been found to be either 7.37 ev or 9.76 ev; similarly, for the NO molecule, $D_0(NO)$ is either 5.29 ev or 6.48 ev.

The highest observed vibrational level of the ground state $X^1\Sigma$ of N_2 is $v=27$, corresponding to an energy of 6.6 ev. For NO, prior to this investigation, the highest observed vibrational level of the ground state $X^2\pi$ was $v=18$, corresponding to 3.65-ev energy. The present investigation was undertaken in the hope that the vibrational levels of the ground state of NO could be extended up to or beyond the energy of 5.29 ev. Although this extension has not been completely realized, the results are considered of sufficient interest to warrant a brief description.

EXPERIMENTAL PROCEDURE

The β bands of NO were excited by introducing a small amount of oxygen into active nitrogen. A continuous flow system was used in which the oxygen and nitrogen were mixed in the proper ratio prior to the discharge. The amount of oxygen was adjusted to just below the point at which the air afterglow (white continuum) appeared. At this stage, the nitrogen bands were very weak, and the β bands of NO very strong.

The gas was excited in a quartz tube using a vacuum tube oscillator of 1.5-kw input power operating in the frequency range 50–70 Mc/sec. The quartz discharge tube was located between the inner and outer conductor at the end of a quarter wave concentric line. The line was tuned to produce gas breakdown at the high pressures used, i.e., 15–30 mm Hg, by a variable vacuum capacitor. After passing through the discharge region the gas was drawn through a Pyrex tube 2.5 in. in diameter and 24 in. long into the vacuum pump.

Spectrograms were taken through a quartz window on one end of the Pyrex tube. The spectrograph was constructed in this laboratory by Mr. C. J. Silvernail, and consists of a 5 in.×6 in. 15 000-line/in. plane grating used in conjunction with an $f1:2$ Maksutov type camera. The camera has a 5-in. calcium fluoride corrector lens and an 8-in. diameter spherical mirror. For the present work the grating was used in the first order and gave a linear dispersion of 58 A/mm at the plate.

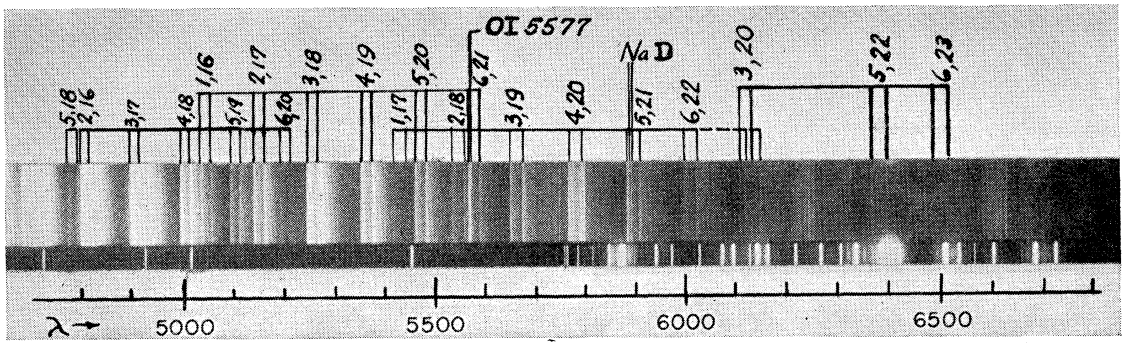

FIG. 1. New NO β bands excited in active nitrogen. Eastman 103aF plate.

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‡ Publication No. 48.
[1] Jenkins, Barten, and Mulliken, Phys. Rev. **30**, 150 (1927).
[2] A. G. Gaydon, Proc. Phys. Soc. (London) **56**, 95, 160 (1944).
[3] F. R. Bichowsky and F. D. Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Company, New York, 1936).

TABLE I. Deslandres table of new NO β bands.

v' \ v''	16	17	18	19	20	21	22	23
1	19 773 (5056.0) 19 850 (5036.3)	18 346 (5449.2) 18 431 (5424.1)						
2	20 785 (4809.9) 20 871 (4790.1)	19 360 (5163.8) 19 442 (5142.2)	17 961 (5566.1) 18 040 (5541.7)					
3		20 354 (4911.8) 20 436 (4892.1)	18 966 (5271.2) 19 038 (5250.1)	17 594 (5682.2) 17 674 (5656.5)	16 261 (6148.0) 16 338 (6118.9)			
4			19 939 (5013.8) 20 016 (4994.5)	18 577 (5381.4) 18 653 (5359.5)	17 247 (5796.4) 17 318 (5772.7)			
5			20 912 (4780.5) 20 991 (4762.7)	19 545 (5114.9) 19 620 (5095.3)	18 211 (5489.8) 18 284 (5467.6)	16 911 (5911.8) 16 982 (5887.1)	15 640 (6392.3) 15 711 (6363.4)	
6					19 169 (5215.2) 19 241 (5195.9)	17 865 (5595.9) 17 932 (5575.0)	16 597 (6023.7) 16 665 (5998.8)	15 354 (6510.9) 15 426 (6480.7)

RESULTS AND CONCLUSIONS

Figure 1 is a reproduction of the afterglow spectrum covering the region 4700–6800A taken on an Eastman 103aF plate. A total of 18 new β bands have been identified, raising the highest observed vibrational level of the ground state of NO to $v=23$. This corresponds to an energy of 4.46 ev, or 35 988 cm^{-1}. Also present on the plate are a number of weak first positive nitrogen bands as well as the forbidden atomic oxygen line λ5577. A Deslandres table of the new β bands is shown in Table I.

Figure 2 is a plot of the $\Delta G(v)$ values against the term values $G(v)$ for all the observed levels of the ground state of NO. The $\Delta G(v)$ and $G(v)$ values were computed from the present measurements and from the list of band heads given by Pearse and Gaydon.[4] As is evident from Fig. 2, the curve shows little tendency to cross the $G(v)$ axis for the value $D_0=5.29$ ev. For this lower value of D_0(NO), a very sharp and sudden drop in the $\Delta G(v)$ values is necessary. For this reason

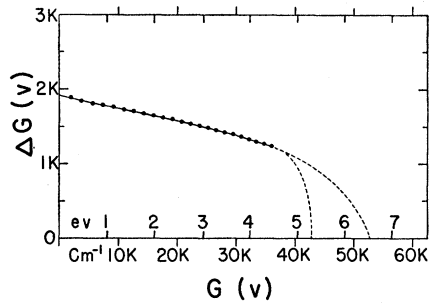


FIG. 2. Plot of $\Delta G(v)$ *vs* $G(v)$ for the observed levels of the $X^2\pi$ ground state of NO. The dashed portions of the curve represent extrapolations to the two possible values of D_0(NO).

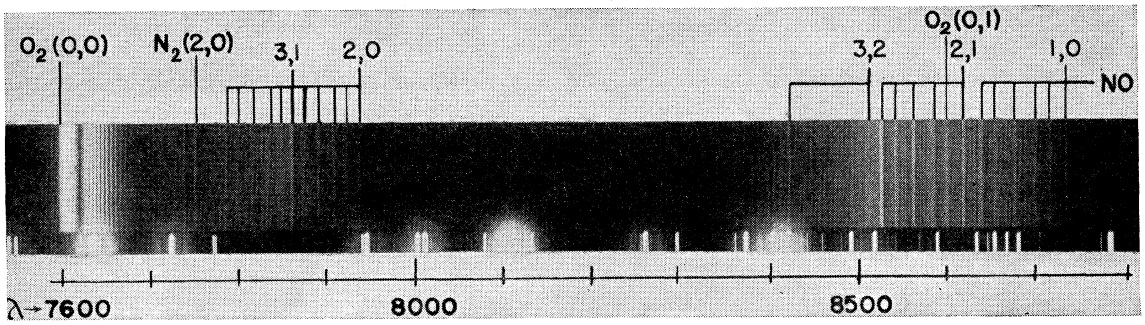


FIG. 3. Spectrogram of a new system of NO bands in the near infrared. Eastman 1—N plate.

[4] R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra* (John Wiley and Sons, Inc., New York, 1950).

TABLE II. Deslandre table of new NO β bands in the near infrared.

v' \ v''	0			1			2	
	ν	λ		ν	λ		ν	λ
0	10 272	(9732.5)						
	10 300	(9706.0)						
	10 323	(9684.4)						
	10 350	(9659.0)						
	10 375	(9636.0)						
	10 395	(9617.3)						
	1175							
	1176							
1	11 447	(8733.3)	993	10454	(9563.1)			
	11 472	(8714.4)		10 477	(9542.1)			
	11 489	(8701.8)		10 496	(9525.0)			
	11 522	(8676.5)		10 527	(9497.0)			
	11 549	(8656.1)		10 555	(9471.8)			
	11 571	(8640.3)	996	10 575	(9453.5)			
	1145			1144				
	1145			1145				
2	12 592	(7939.1)	994	11 598	(8619.8)			
	12 614	(7925.6)		...	...			
	12 636	(7912.0)		11 640	(8588.8)			
	12 667	(7892.4)		11 673	(8565.2)			
	12 693	(7876.1)		11 701	(8544.6)			
	12 716	(7861.9)	996	11 720	(8529.9)			
				1118				
				1117				
3				12 716	(7861.9)	974	11 742	(8514.2)
				...	...		...	...
				12 756	(7837.1)		...	...
				12 787	(7818.3)		...	...
				12 814	(7801.8)		...	...
				12 837	(7787.6)	972	11 865	(8425.65)

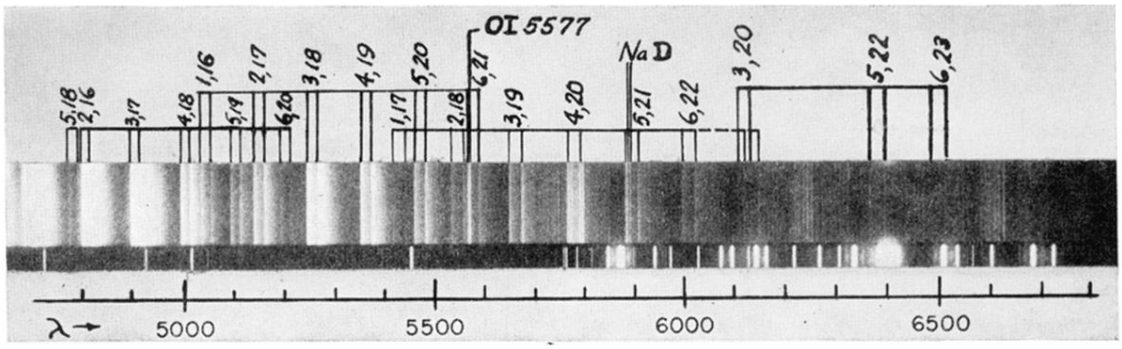
the higher value of $D_0=6.48$ ev appears more probable. This higher value would then require that $D_0(N_2)=9.76$ ev.

Figure 3 is a reproduction of the same afterglow taken on an Eastman $1-N$ plate covering the region 7500A to 9000A. The strongest feature of this spectrogram is the atmospheric O_2 (0,0) band at 7594A. The (0,1) O_2 band at 8597A is also present. The occurrence of these bands with such great intensity under conditions in which the oxygen is present only as an impurity ($\sim$3–5 percent) is rather surprising. The other prominent feature is a new system of bands belonging to the molecule NO, and probably due to a $^4\pi \rightarrow {}^4\pi$ transition. The bands show six strong heads, and are shaded to the violet. Two sequences are present in the spectrogram of Fig. 3, and another sequence was obtained by photographing the region 8500–9700A on an Eastman 1–M plate. A Deslandres table of the new system is given in Table II.

It is tempting to identify the lower state of these new bands with the upper state $B^2\pi$ of the β bands. The observed wave number differences of 994 cm^{-1} and 973 cm^{-1} agree reasonably well with the wave number differences of 996 cm^{-1} and 974 cm^{-1} between the $v=2, 3$, and 4 levels, respectively, of the $B^2\pi$ state. The presence of six strong heads, however, makes this identification improbable. A $^4\pi \rightarrow {}^4\pi$ transition would account for the six strong heads.

ACKNOWLEDGMENTS

During the course of this work we benefited greatly from a conversation with Dr. Yoshio Tanaka. He informed us that the new system of NO bands, described above, also had been found by M. Ogawa working with pure NO, and we are indebted to him for supplying us with a photograph of these bands.



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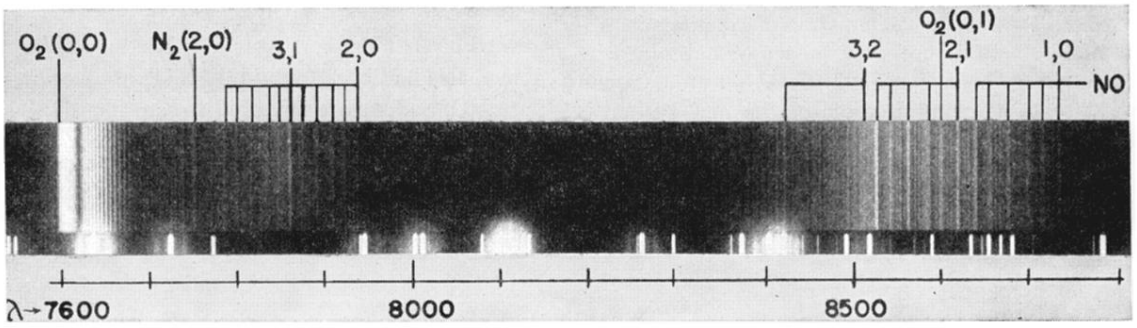

FIG. 3. Spectrogram of a new system of NO bands in the near infrared. Eastman 1—*N* plate.