Rotational Analysis of the Perturbed (13,15) $^2\Sigma-{}^2\Sigma$ N_2^+ Band

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A rotational analysis of the 13,15 $^2\Sigma-{}^2\Sigma$ N_2^+ band has been made. This analysis is of interest as a perturbation is found to occur in the upper state. The rotational analysis gives the following constants: $B_{13}'=1.54_5$ cm^{-1}, $D_{13}'=-5\times10^{-5}$ cm^{-1}, $B_{15}''=1.62$ cm^{-1} and $D_{15}''=-1\times10^{-5}$ cm^{-1}. The origin of the band is at 21044.7 cm^{-1}.

Introduction

As mentioned in the preceding paper perturbations have been found in the $v=0$, 1 and 3 levels of the upper $^2\Sigma$ state of the N_2^+ bands. These perturbations arise from an interaction of a $^2\Pi$ state with this $^2\Sigma$ state. Transitions between these two states are forbidden by selection rules and transitions of any intensity between this $^2\Pi$ state and the ground $^2\Sigma$ state lie too far out in the infrared to be observable. So what knowledge is to be obtained of the $^2\Pi$ state must be deduced from a study of the perturbations which it shares with the upper $^2\Sigma$ state.

Rotational Analysis

In the course of the investigation of the Zeeman effect for perturbed N_2^+ terms[1] already known, use was made of a discharge tube in which the N_2^+ bands were excited while the N_2 bands were not present. Hence observation of N_2^+ bands in regions ordinarily overlain with N_2 bands was possible. It was found that to the red of the $\Delta v=2$ sequence, there was a band degrading to the red and containing a perturbation. Analysis of this band gives the assignments of the lines shown in Table I. The B values of the two levels are obtained from the combination differences given in Table II. The values of the constants are

$$B_{13}'=1.54_5\text{ cm}^{-1},\qquad B_{15}''=1.62\text{ cm}^{-1},$$

$$D_{13}'=-5\times10^{-5}\text{ cm}^{-1},\qquad D_{15}''=-1\times10^{-5}\text{ cm}^{-1}.$$

Coster and Brons[2] have shown that the B values of the lower state fit a linear equation. Extrapolation by this equation to $v=15$ gives the value of B_{15}'' as 1.620 cm^{-1}. This serves to fix the vibrational quantum number of the lower state. A consideration of the B values of the upper state show that they can best be fitted by the equation

$$B_v'=B_0'(1+\alpha v+\beta v^2)$$

where $\alpha=-0.0101$ and $\beta=-0.00072$. The determination of the upper state vibrational quantum number is based on the position of the band ($\nu_0=21044.7$ cm^{-1}) and the B value of this level.

TABLE I. *Rotational assignments for the 13,15 band.*

K''	R_1		R_2	P_1		P_2
0		21,047.80				
1		50.48				
2		53.53			21,038.04	
3		56.15			34.36	
4		58.67			30.85	
5		61.02			27.15	
6		63.20			23.13	
7	65.55		65.28		18.98	
8	67.48		66.91		(15.83)	
9		68.51			10.46	
10		69.90		06.15		05.80
11				00.56		00.01
12		71.48		20,996.44		20,995.52
13		72.53		92.02		90.48
14		73.67		86.42		84.21
15		74.71			81.11	
16		75.71			75.79	
17		76.67			(69.13)	
18		77.16			64.32	
19					58.74	
20					52.34	
21					46.14	
22					39.57	
23					32.74	
24					25.82	
25					18.78	
26					11.56	

[1] A. E. Parker, Phys. Rev. **44**, 84 (1933).

[2] D. Coster and H. H. Brons, Zeits. f. Physik **73**, 747 (1932).

The point of interest in this analysis is the existence of a perturbation in the upper level. Determination of whether the perturbation occurs in the T_1 or the T_2 levels must be made by means of the intensity ratio of lines of the same K value. The ratio of intensities is as $K+1 : K$, the lines originating on the T_1 levels being the stronger. When the separation of the two sets of levels persists into the region where the spin doubling has become appreciable, this is possible as shown by Coster and Brons. This procedure is not applicable here as only the lines of low K value (inappreciable spin doubling) were excited. However, the branch in which the perturbation occurs is not detectable after the perturbation and therefore we may assume that the perturbation is in the T_2 levels. This assignment is of course open to question. In Fig. 1 the separations of the levels in the upper state are plotted against their K values.

TABLE II. *Combination differences for the 13,15 band.*

K''	$\Delta_2F''(K)$	$\Delta_2F'(K)$
1	9.76	
2	16.12	15.49
3	22.68	21.79
4	29.00	27.82
5	35.54	33.87
6	42.04	40.07
7		46.57
8	55.09	
9	61.33	58.03
10	67.95	63.75
11	73.46	
12		75.04
13	85.06	80.51
14	91.42	87.25
15	97.88	93.60
16		99.92
17	111.39	
18	117.93	112.84
19	124.82	

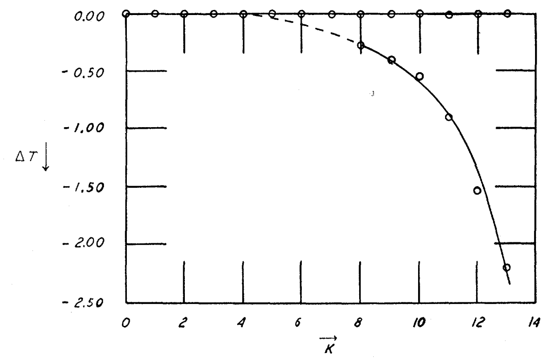

FIG. 1. Separations between the T_1 and the T_2 terms in the $v'=13$ level plotted against K, showing a perturbation in the T_2(?) levels.

We now know that the following vibrational levels of the upper $^2\Sigma$ state are perturbed: the $v=0$, 1, 3 and 13 levels. Furthermore we know that the course of the $^2\Pi$ state's levels is such that in all probability consecutive levels of it perturb the $v=0$ and 1 levels of the $^2\Sigma$ state. That there are two $^2\Pi$ levels intervening between those which perturb the $v=1$ and 3 levels of the $^2\Sigma$ state seems very likely. The spacing of the $^2\Pi$ vibrational levels is considerably smaller than that of the $^2\Sigma$ levels in question and so we need not be at all surprised at the existence of a perturbation in one of the higher vibrational levels of the $^2\Sigma$ state. In fact we might predict, by means of a level diagram, that the $^2\Sigma$ levels from nine on probably contain perturbations and that the $v=5$, 7 and 8 levels probably contain perturbation points in the region of high K values.

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