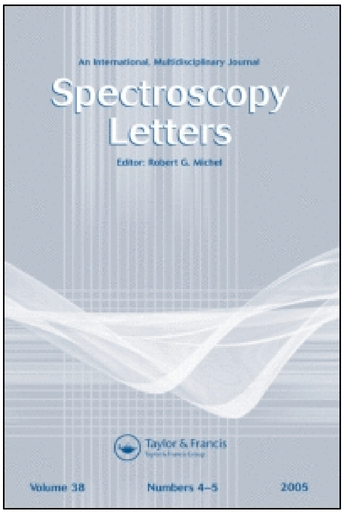

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Molecular Constants of the NbN Molecule

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MOLECULAR CONSTANTS OF THE NbN MOLECULE

Key words: intracavity laser spectroscopy,
vibrational analysis, rotational analysis,
triplet splitting, satellite components.

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ABSTRACT

Absorption spectrum of NbN has been obtained in the 560-670 nm region by intracavity laser spectroscopy. Vibrational and rotational analyses of $^3\Phi - {}^3\Delta$ transition has been caried out. Molecular constants for the upper ($^3\Phi$) and ground ($^3\Delta$) states have been determined.

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INTRODUCTION

The emission spectrum of NbN was investigated by Dunn and Rao [1]. In the red region the system consisted of only three 0,0 sub-bands was observed, which were asigned as $^3\Phi - {}^3\Delta$ transition. The $^3\Phi_3 - {}^3\Delta_2$ sub-band has been rotationally analysed. The rotational analysis of the other two sub-bands was complicated by very large nuclear hyperfine splittings at low J values. The hyperfine structure analyses of 0,0 bands was carried out by Femenias and call.[2]. Green and call[3] have analysed the IR-spectrum of NbN isolated in an argon matrix, being determined the value $G''_{1/2}$=1002.5 cm^{-1}.

In this paper the $^3\Phi - {}^3\Delta$ system of NbN recived by intracavity laser spectroscopy with the complete rotational and vibrational analyses is presented.

EXPERIMENTAL

The electronic spectrum of NbN was taken in the 550-670 nm region. The experimental equipment was described earlier [4].

The quartz cell (30 cm pathlength and 2 cm diameter) with $NbCl_5$ powder was placed in the cavity of a flash pumped dye-laser. The temperature of the cell was 250-300°C. The NbN moleculars were obtained by discharge through the $NbCl_5$ and $^{14}N_2$ ore $^{15}N_2$ mixtured vapours. The nitrogen presure was 4-5 torr.

The spectrum was recorded at grating (75 lines/mm), spectrograph DFS-3. The $^3\Phi - {}^3\Delta$ bands fotopicture was taken in the 25-27 orders of the grating at dispersion of about 1 Å/mm. The reference spectrum was provided by an iron hollow cathode lamp. The precision of the measurements for sharp unblended lines was 0.02 cm^{-1}.

VIBRATIONAL AND ROTATIONAL ANALYSIS

48 bands was obtained in the absorption spectrum of NbN. The wavenumbers of Q-heads are presented in Table 1. The $^3\Phi - {}^3\Delta$ system consists of the three sub-systems, separated by 316.13 and 390.89 cm^{-1} respectively (Fig 1). Every sub-bands degrades to the red and has two marked R and Q-heads. In the short wavelengths region two sub-systems analogous to the ones mentioned above were obtained. They were separated from the $^3\Phi_4 - {}^3\Delta_3$ subsystem by 195.75 and 554.37 cm^{-1} respectively. The assignment of these subsystems to satellite components $^3\Phi_3 - {}^3\Delta_3$ and $^3\Phi_2 - {}^3\Delta_2$ based on isotopic effects.

The triplet splittings of the $^3\Phi$ and $^3\Delta$ states were measured (see Fig.2).

Three sequences with $V=0, \pm 1$ were reviled, which allowed us to determine vibrational constants for lower and upper states. The least-squares fitting of

TABLE 1.

Deslanderes Table for $^3\Phi-^3\Delta$ System of NbN.

v'	$v''=$ 0	1	2	3	4
	*16144.36				
	16543.08	15508.10			
0	16860.20	15825.47			
	17057.72				
	17415.61	16379.61			
	17130.63	16096.84			
	17529.05	16493.00	15467.15		
1		16808.32	15780.80		
		17083.25			
		17362.56	16333.09		
		17072.37	16049.86		
		17468.49	16442.50	15424.74	
2			16754.93	15737.42	
			00000000		
			17319.17		
			17017.68	16002.09	
3			17407.93	16392.07	15386.43
				16701.85	15697.43
					15954.40
4				17348.38	16342.60
				17649.60	16648.92

TABLE 1. (continued).

v'	$v''=5$	6	7	8
5	15805.00 16290.32			
6		15856.29 16236.63		
7			15806.85 16187.62	
8				15756.49 16132.63

COMPONENTS $^3\Phi_2 - {}^3\Delta_1$, $^3\Phi_3 - {}^3\Delta_2$, $^3\Phi_4 - {}^3\Delta_3$, $^3\Phi_2 - {}^3\Delta_2$, $^3\Phi_3 - {}^3\Delta_3$ RESPECTIVLY

TABLE 2

VIBRATIONAL CONSTANTS for the NbN MOLECULAR

	$^3\Phi$	$^3\Delta$
ω_e	994.2±1.0	1043.9±1.0
$\omega_e x_e$	4.27±0.2	4.18±0.2

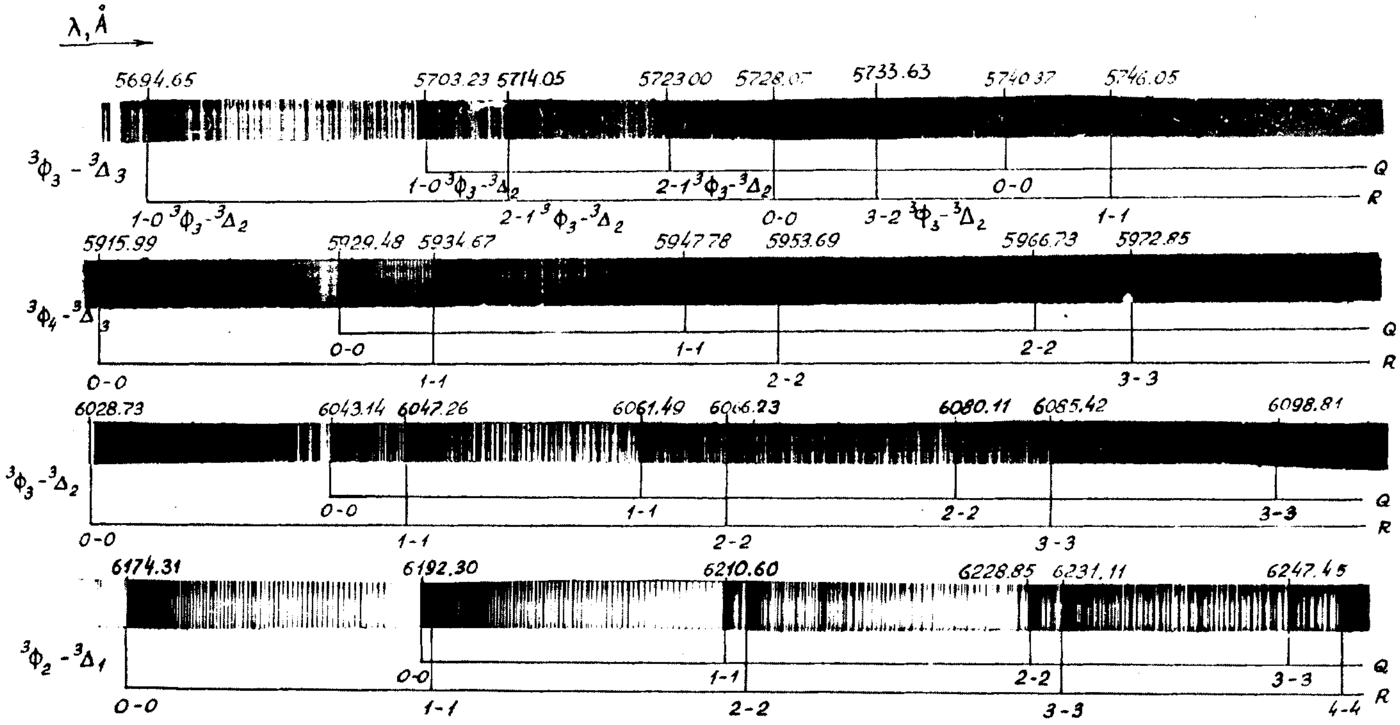

Fig. 1 A portion of the NbN electronic spectrum.

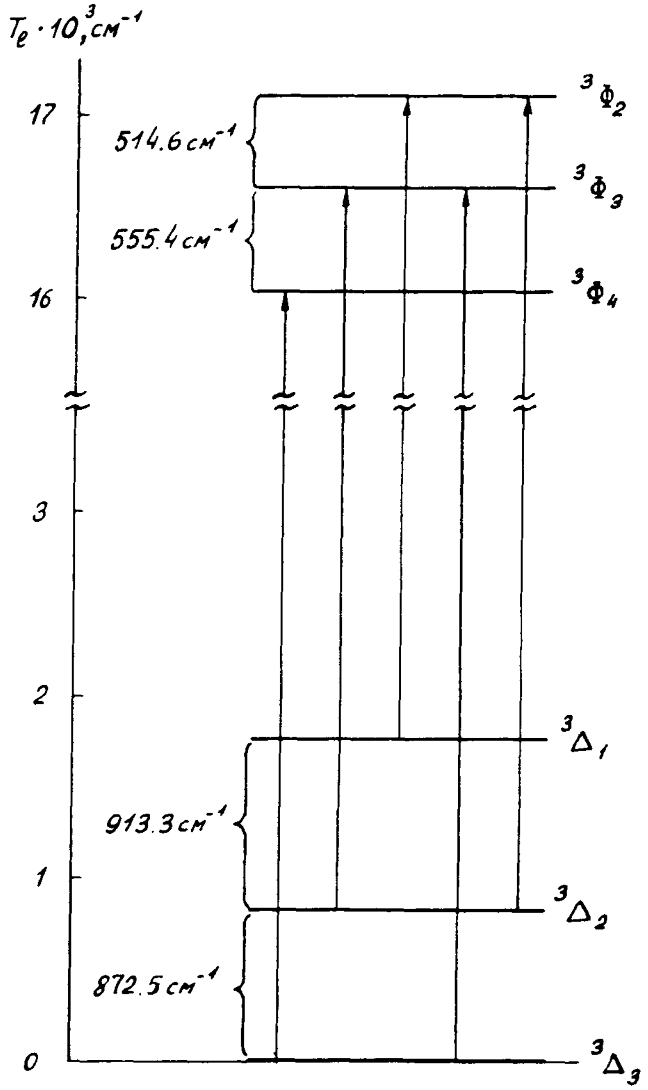

Fig. 2 Scematic energy diagram of the $^3\Delta$ and $^3\Phi$ states of NbN.

wavenumbers of Q-heads gives vibrational constants tabulated in Table 2.

The rotational structures of 0,0 bands in all sub-systems were perfectly resolved. Every band has strong Q and R-branchers as well as a weaker P-branch (see Fig 3).

We invoke the usual equations for triplet states:

$$F_1(J)=B\left\{J(J+1)-\ y_1+4J(J+1)\ ^{1/2}-\left(\frac{2}{3}\right)\frac{y_2-2J(J+1)}{y_1+4J(J+1)}\right\}-D(J-1/2)^4$$

$$F_2(J)=B\left\{J(J+1)+\left(\frac{4}{3}\right)\frac{y_2-2J(J+1)}{y_1+4J(J+1)}\right\}-D(J+1/2)^4 \qquad (1)$$

$$F_3(J)=B\left\{J(J+1)+\ y_1+4J(J+1)\ ^{1/2}-\left(\frac{2}{3}\right)\frac{y_2-2J(J+1)}{y_1+4J(J+1)}\right\}-D(J+3/2)^4$$

where $y_1= {}^2Y(Y-4)+4/3$ and $y_2= {}^2Y(Y-1)-4/9$.

As usual, from the observed branchers of band one can compute combination differences.

For the upper state:

$$\Delta_2F'_{1,2,3}(J)=F'_{1,2,3}(J+1)-F'_{1,2,3}(J)=R_{1,2,3}(J)-P_{1,2,3}(J) \qquad (2)$$

and for the ground state:

$$\Delta_2F''_{1,2,3}(J)=F''_{1,2,3}(J+1)-F''_{1,2,3}(J)=R_{1,2,3}(J-1)-P_{1,2,3}(J) \qquad (3)$$

Taking summations of the three substates, and substituting eq.(1) we have:

$$\Delta_2F_1(J)+\Delta_2F_2(J)+\Delta_2F_3(J)=B(12J+6)-D(24J^3+36J^2+90J+39) \qquad (4)$$

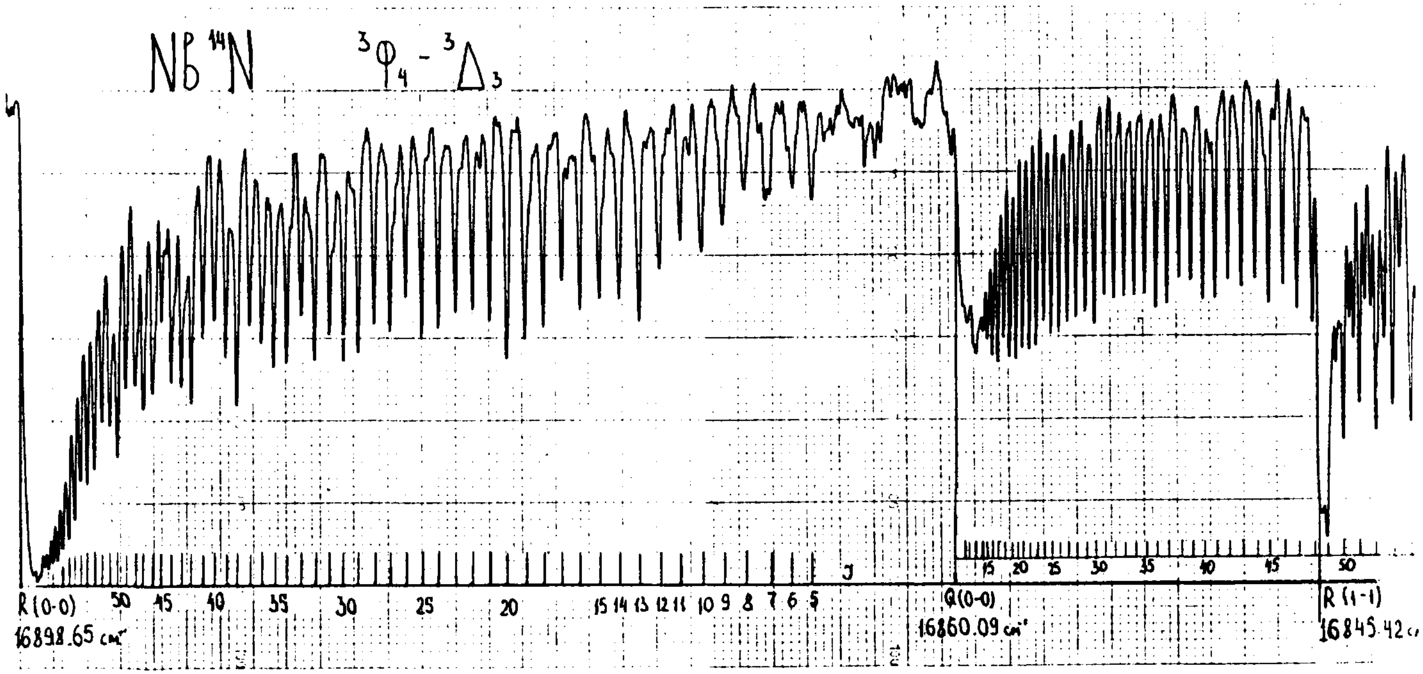

Fig. 3 Microdensitometer trace of the $^3\Phi_4 - {}^3\Delta_3$ system of NbN.

The most probable values of B'_0, D'_0, B''_0 and D''_0 were derived for all observed $J(=75)$ by least squares procedures. The results are presented in Table 3.

The rotational constants were invoked in the computation of the 0-0 band origin ν_0:

$$\nu_0(J)=1/6[P_1(J)+R_1(J)+P_2(J)+R_2(J)+P_3(J)+R_3(J)]-B'-$$
$$-(B'-B'')J-(B'-B'')J^2+(D'-D'')J^4+2(D'-D'')J^3+0.5(23D'-$$
$$-11D'')J^2+0.5(21D'-9D'')J+(\frac{1}{96})(790D'-166D'') \qquad (5)$$

From the equations (1) differences $F_3(J)-F_1(J)$ at $J=0$ becomes:

$$F_3(0)-F_1(0)=2B_0y_1^{1/2}-5D_0 \qquad (6)$$

Invoking the spin splittings of Fig.2 and ignoring the term $5D_0$, which is small, we have:

$$y_1=\left\{[F_3(0)-F_1(0)]/2B_0\right\}^2, \qquad (7)$$

that leads an estimate of triplet spliting constant Y from:

$$y_1=\Lambda^2Y(Y-4)+4/3 \qquad (8)$$

The resulting Y-values are included in Table 3.

It is known that observed bands splittings for many triptet transitions are unexpected. The additional terms taking into account spin-orbital and spin-spin interactions are necessary in the eq.(1), as was shown by Kovacs [5]. Knowing the actual splittings (Fig 2) we can thus reveal the discrepancy exhibited by indi-

TABLE 3

MOLECULAR CONSTANTS of the NBN MOLECULE (cm^{-1})

	$^3\Phi$	$^3\Delta$
B	0.4941 ± 0.0004	0.4993 ± 0.0003
$D.10^{-7}$	3.0 ± 0.2	3.1 ± 0.1
Y	358.94 ± 0.02	892.19 ± 0.02
β	1.03 ± 0.01	-38.74 ± 0.01
γ	-0.104 ± 0.001	
ν_0	16516.11 ± 0.05	

TABLE 4

COMPARISON of CALCULATED SPIN SPLITTINGS with OBSERVED SPLITTINGS

State	$F_2(0)-F_1(0)$ (cm^{-1})		$F_3(0)-F_2(0)$ (cm^{-1})	
	Cal.	Obs.	Cal.	Obs.
$^3\Phi$	529.41	555.41	528.09	514.64
$^3\Delta$	889.59	872.53	888.25	913.36

vidual electronic states. The observed differences $\Delta F_{2,1}$ and $\Delta F_{3,2}$ and computed from eq.(1) for $J=0$ are compared in the Table 4.

So it is necessary to compute spin-orbital and spin-spin corrections for the both triplet states. Following Kovacs, the true rotational terms were obtained from eq.(1) with the additional terms:

$$F_{1,t}(J)=F_1(J)-\beta/3+\beta S\Lambda_1(I-1)^2+\gamma(J+1/3)$$

$$F_{2,t}(J)=F_2(J)-\beta/3+\beta S\Lambda_1 I^2+1/3\gamma$$

$$F_{3,t}(J)=F_3(J)-\beta/3+\beta S\Lambda_1(I+1)^2-\gamma(J+2/3)$$

Using equations and adoption that γ'' for $X^3\Delta$ state was extremely small [5], the values γ', β'' and β' were found by least-squares filting. The results are presented in Table 3.

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