THE β- AND γ-BAND SYSTEMS OF ^{14}NS AND ^{15}NS

By N. A. Narasimham and K. Srikameswaran

(*Analytical Division, Atomic Energy Establishment, Trombay, Bombay*)

Received October 26, 1962

(Communicated by Dr. R. K. Asundi, F.A.SC.)

Abstract

The spectra of ^{14}NS and ^{15}NS molecules are obtained in a 2450 mc./s. microwave oscillator discharge. Vibrational assignments of the β- and γ-systems are studied in more detail. Several hitherto unrecorded bands are satisfactorily explained as belonging to higher v', v'' levels in the Deslandres schemes of both β- and γ-systems. The observed isotope shifts (^{14}NS – ^{15}NS) provide confirmatory evidence for the proposed vibrational analysis.

In the case of the γ-system, the $v' = 2$ level of the upper state appears to be strongly perturbed showing a shift of about 38 cm.$^{-1}$ from the expected position. In the β-system, the isotopic shifts in the band-heads involving the $v' = 0$ and 1 levels of the $^2\Delta_{5/2}$ of the upper state show small deviations from expected values. The reality of these small deviations is established beyond doubt by the occurrence of the effect on the 0—0 sub-band which exhibits the isotopic head in a wavelength direction opposite to the expected one.

Introduction

The spectrum of the ^{14}NS molecule was first excited by Fowler and Bakker (1932) who proposed vibrational analyses for two groups of bands called β- and γ-systems, analogous to the NO bands. From a study of the rotational structure, the γ-system was attributed by Zeeman (1951) to a $^2\Sigma$ - $^2\Pi$ and the β-system by Barrow *et al.* (1952, 1954) to a $^2\Delta$ - $^2\Pi$ transitions. There are still a number of bands originally recorded by Fowler and Bakker that remain unassigned. Four of these were tentatively grouped to form a new system (Barrow *et al.*, 1954). But as shown elsewhere (authors, 1962) Barrow's analysis is not supported by isotopic effect. Further, in the γ-system, prior to this investigation, only one progression with $v' = 0$ was known in emission. The 1—0 band was observed in absorption which locates experimentally the $v' = 1$ level (Barrow, 1952). It is, therefore, thought worthwhile to reinvestigate the spectrum of NS. Also the availability of $^{15}N_2$ samples prompted us to obtain the spectrum of ^{15}NS which provides the desired isotopic shift data to confirm some of the proposed vibrational assignments of the bands. In these investigations, we have been able to get information regarding isotopic shifts of a number of bands attributable to NS. In the present paper, we confine ourselves mainly to the β- and γ-systems and deal with the rest in a subsequent publication.

EXPERIMENTAL

The NS spectrum is excited by means of a microwave oscillator of 2450 mc./s., at 90 mA in sealed tubes, containing natural and enriched $^{15}N_2$ samples. These discharge tubes are prepared in the manner represented schematically in Fig. 1. The quartz tube of 1 cm. diameter is first baked

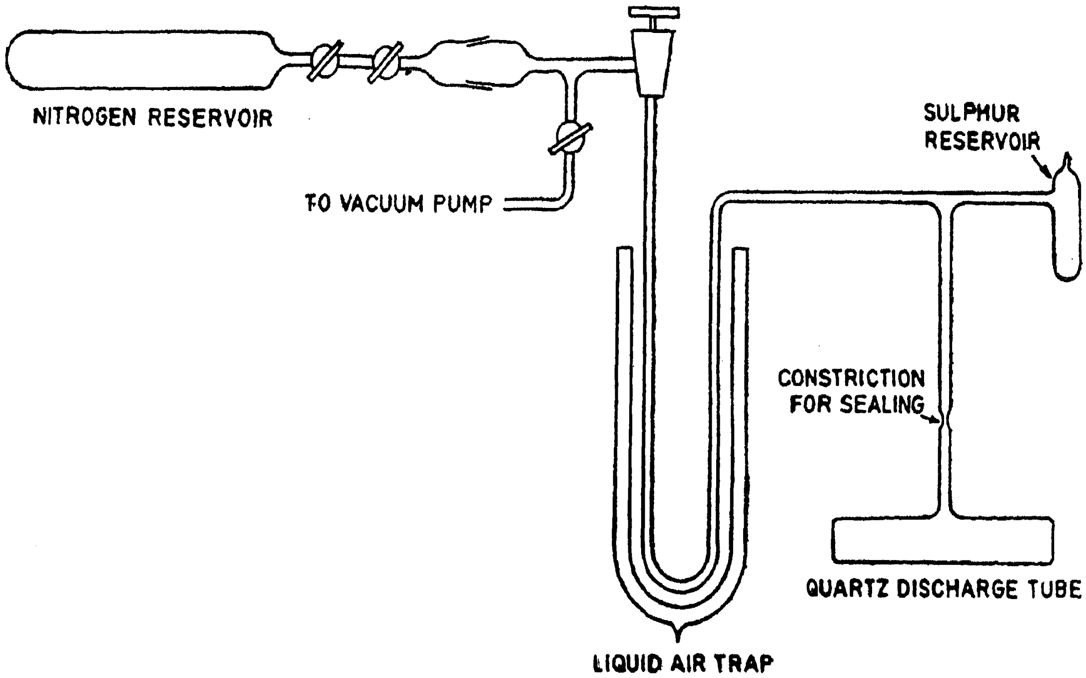

FIG. 1. Schematic diagram for preparing electrodeless discharge tubes of NS.

in a furnace at about 800° C. for two hours, simultaneously evacuating it by a rotatory pump. The tube is first flushed and evacuated with natural nitrogen several times and then filled with small quantities of nitrogen enriched in $^{15}N_2$. On excitation by microwave oscillations of 2450 mc/.s. at 90 mA, an intense orange glow of nitrogen appears. The glow turns white when sulphur vapour is introduced into the discharge by gently heating the side tube containing sulphur. These operations are repeated, if found necessary and the discharge tube is finally sealed off the vacuum line. A few such sealed discharge tubes containing natural and 50–80% enriched $^{15}N_2$ samples are prepared.

The ^{14}NS and ^{15}NS spectra are recorded on a Hilger Littrow E 492 quartz (dispersion of 2·1 Å/mm. at 2325 Å) and in the second order of a

TABLE I

Deslandres scheme for the band heads of the β-system of ^{14}NS *with horizontal and vertical differences in cm.*$^{-1}$

v' \ v''	0		1		2		3		4
0	39882·2 39697·1	1203·1 1203·7	38679·1 38493·4	1190·0 1189·1	37489·1 37304·3	(1167·6) (1170·6)	36321·5* 36133·7*		
	943·8 930·8	.. ..	.. ..	.. ..	943·2 931·2	..	(935·5) (927·8)		
1	40826·0 40627·9	..	..	..	38432·3 38235·5	1175·3 1174·0	37257·0 37061·5	(1164·8) (1155·8)	36092·2* 35905·7*
	927·5 921·0	.. ..	.. ..	.. ..	921·0 918·1	.. ..	— (921·4)	.. ..	(934·8) —
2	41753·5 41548·9	1204·6 1203·4	40848·9 40345·5	1195·6 1191·9	39353·3 39153·6	— (1170·7)	— 37982·9*	.. ..	37027·0* ..
	.. ..	.. ..	909·9 —	.. ..	(905·2) (901·6)	.. ..	.. ..	.. ..	.. ..
3	.. ..	.. ..	41458·8 —	(1200·3) —	40258·5* 40055·2*	.. ..	.. ..	.. ..	.. ..

* From plates taken on a medium quartz spectrograph.

( ) Values not used for calculation of vibrational constants.

Jarrell Ash 3·4 metre plane grating spectrographs (dispersion of 2·5 Å/mm.). Kodak B–10 plates are used to photograph the spectra. Exposures of the order of 15 minutes to 1 hour are found adequate to bring out the bands of β- and γ-systems which are shown in Fig. 2 (*b*) and (*c*).

Results

The band-head data for the β- and γ-systems (Tables I and III) represent the averages of three measurements on two different plates. The error in the wave-number values is believed to be not more than 0·8 cm.$^{-1}$ and is considerably less in more favourable cases.

The isotopic shifts are calculated from the following relation (Herzberg, 1950) and given in Tables II and IV. The respective spectra due to ^{14}NS and ^{15}NS are shown in Fig. 2 (*b*) and (*c*).

$$\nu - \nu^i = (1-\rho)\left[w_e'\left(v'+\tfrac{1}{2}\right) - w_e''\left(v''+\tfrac{1}{2}\right)\right] - (1-\rho^2)\left[w_e'x_e'\left(v'+\tfrac{1}{2}\right)^2 - w_e''x_e''\left(v''+\tfrac{1}{2}\right)^2\right]$$

where

$$\rho = \sqrt{\mu/\mu^i} = 0{\cdot}9766 \text{ for } {}^{14}\text{NS and } {}^{15}\text{NS}.$$

The superscript ^{i} refers to ^{15}NS.

μ and μ^i are reduced masses of ^{14}NS and ^{15}NS.

Table II

Isotopic displacements ($^{14}NS-{}^{15}NS$ in cm.$^{-1}$) in the band-heads of the β-system of NS

v' \ v''	0 obs.	0 cal.	1 obs.	1 cal.	2 obs.	2 cal.	3 obs.	3 cal.
0	− 2·3 + 2·4	− 3·1 − 3·2	−29·5 −25·5	−30·9 −31·1	−57·1 −53·0	−58·1 −58·3	.. ..	.. ..
1	+19·2 +20·8	+18·6 +18·3	.. ..	.. ..	−35·2 −34·1	−36·4 −36·7	−63·5 −60·8	−63·0 −63·3
2	+39·4 +37·8	+39·4 +39·2	— +11·7	+11·6 +11·4	— −15·9	−15·6 −15·8	.. ..	.. ..
3	..	..	+28·5 —	+31·7 +31·8	.. ..	.. ..	.. ..	.. ..

TABLE III

Deslandres scheme for the band-heads of the γ-system of ^{14}NS in cm.$^{-1}$ with horizontal and vertical differences

v' \ v''	0		1		2		3		4	5
0	43384·9 362·5	1204·2 00·7	42180·7 161·8	1189·7 87·8	40991·0 974·0	1175·4 73·4	39815·6* 800·6*			
	43163·1 138·4	1203·7 00·3	41959·4 938·1	1189·4 87·3	40770·0 750·8	1175·6 71·1	39594·4* 579·7*			
	1387·0 —		1389·5 —		1390·1 1378·7		1389·8 1380·4			
	1384·8 —		1388·3 —		— 1376·6		1390·2 1377·7			
1	44771·9 —	1201·7 —	43570·2 —	1189·1 —	42381·1* 352·7*	1175·7 71·7	41205·4* 181·0*	1160·3 53·0	40045·1* 028·0*	
	44547·9 —	1200·2 —	43347·7 —	— —	— 42127·4*	— 1170·0	40984·6* 957·4*	— —	— —	
	1417·9 —		1411·8 —		1410·8 —		— —		1415·5 1414·6	
	1418·9 —		1407·1 —		— —		1418·1 1403·9		— —	

2	46189·8†	1207·8	44982·0	1190·1	43791·9*	—	—	—	41460·6*	1145·3	[40315·3*
	—	—	957·5	—	—	—	42599·1*	1156·5	442·6*	40.3	302·3
	45966·8†	1212·0	44754·8	—	—	—	42388·5*	1150·6	41237·9*	—	—
	935·9†	04·5	731·4	—	—	—	—	—	—	—	—
									1328·1		1335·9
									25·4		—
									—		—
									—		—
3					—	—	43949·4*	1160·7	42788·7*	1137·3	41651·2*
					—	—	—	—	768·0*	—	—
					44899·4*	—	—	—	—	—	—
					875·6*	—	—	—	—	—	—
							1351·8				1342·6
							—				—
							—				—
							—				—
4							45301·2*				42993·8*
							—				—
											42755·0*
							—				—
							—				—

* From plates taken on medium quartz spectrograph.
† From plates taken on small quartz spectrograph.

(i) *β-system.*—Bands belonging to this system are arranged in the Deslandres scheme (Table I). The R heads are represented by:

$$\nu_h^{R_1} = 40011\cdot5 + 960\cdot3\,(v' + \tfrac{1}{2}) - 8\cdot4\,(v' + \tfrac{1}{2})^2 - 1218\cdot3\,(v'' + \tfrac{1}{2}) + 7\cdot3\,(v'' + \tfrac{1}{2})^2$$

$$\nu_h^{R_2} = 39834\cdot7 + 942\cdot4\,(v' + \tfrac{1}{2}) - 5\cdot7\,(v' + \tfrac{1}{2})^2 - 1218\cdot3\,(v'' + \tfrac{1}{2}) + 7\cdot3\,(v'' + \tfrac{1}{2})^2$$

The observed isotopic shifts (^{14}NS – ^{15}NS) agree fairly well with the expected values (Table II) and confirm the proposed vibrational assignments of the bands (Table I).

A striking feature of the isotope effect in the β-bands is that in the (0—0) band the isotope head of the component at 2506·66 Å is as expected on the shorter wave side at 2506·49 Å and the shift observed agrees with the calculated negative shift within experimental errors [*see* Fig. 2 (*a*)]. But the isotope head of the other component at 2518·35 Å clearly lies on the longer wave side at 2518·49 Å unmistakably demonstrating the reality of the positive shift which differs from the calculated shift not only in magnitude but also in sign (observed + 2·4, calculated – 3·2). A closer examination

TABLE IV

Isotopic displacements (^{14}NS – ^{15}NS in cm.$^{-1}$) in the band-heads of the γ-system of NS

v' \ v''	0 obs.	0 cal.	1 obs.	1 cal.	2 obs.	2 cal.
0	+ 2·3 —	+ 2·1	−25·6 −26·7	−25·8	−53·2 −54·2	−53·0
	+ 2·4 —	+ 2·1	−26·1 −26·7	−25·8	−53·1 —	−53·0
1	+32·1 —	+32·5				
	+31·0 —	+32·4				
2	+58·7 —	+65·6	+28·5 +31·7	+37·4		
	+61·2 —	+65·6	+30·2	+37·4		

of the isotope shift in the other two component bands of the $v' = 0$ progression shows that a difference (0—0) of about $+ 5 \cdot 6$ cm.$^{-1}$ is common to all the three sub-bands. In these sub-bands however the shift is sufficiently large to avoid the change in sign due to the common displacement of about 5 cm.$^{-1}$ which may be attributed to a perturbation. Rotational analysis of the bands is considered necessary to study the perturbation. This perturbation extends probably also in a diminished measure to the corresponding level $v' = 1$.

(ii) *γ-system.*—In the γ-system, in addition to the single progression of bands recorded earlier by Fowler and Bakker, a number of other bands are observed which could be fitted into a vibrational array as given in Table III. The vibrational constants for the lower $^2\Pi$ state agree well with those obtained from the β-bands (*see* Table V). In the upper $^2\Sigma$ state, the $\Delta G_{3/2}$ value (1412·0 cm.$^{-1}$) is larger than the $\Delta G_{1/2}$ value (1387·3 cm.$^{-1}$) which indicates that the $v' = 2$ level lies higher by about 38 cm.$^{-1}$ than expected.

TABLE V

Vibrational constants of the $C^2\Sigma$, $A^2\Delta$ and $X^2\Pi$ states of ^{14}NS and ^{15}NS in cm.$^{-1}$

	^{14}NS			^{15}NS		
State	T_0	ω_e	$\omega_e x_e$	T_0	ω_e	$\omega_e x_e$
C $^2\Sigma$	43384·9	1401·1	6·7	43382·6	1368·6	6·7[a]
A $^2\Delta_{5/2}$	39918·5[b]	942·4	5·7	39916·0	918·9	3·3
A $^2\Delta_{3/2}$	39882·2[b]	960·3	8·4	39884·5	936·3	7·2
X $^2\Pi_{3/2}$	221·4	1218·3[b]	7·3[b]	221·3	1189·8[b]	6·7[b]
X $^2\Pi_{1/2}$	0	1220·8[c]	7·9[c]	0	1186·1[c]	6·0[c]

a of ^{14}NS.
[b] Data obtained from the R heads of the $^2\Delta - {}^2\Pi$ transition.
[c] Data obtained from the Q_1 and P_2 heads of the $^2\Sigma - {}^2\Pi$ transition.

Similar observations were made by Asundi, Inn and Tanaka (unpublished results). The isotopic spectrum due to ^{15}NS [Fig. 2 (*c*)] bears out these observations. The shift of nearly 38 cm.$^{-1}$ in the $v' = 2$ level of $^2\Sigma$ state is probably brought about by a strong perturbation. Probably just this perturbation, explains the difference between O—C values of isotope heads of bands with $v' = 2$ which is outside experimental errors. Rotational analysis of the bands involving this level should provide more information on the nature of this perturbation.

The isotopic shifts observed in the other γ-bands agree closely with the calculated ones, thus confirming the proposed vibrational assignments of the bands, shown in Table IV.

Finally the vibrational constants of the electronic states $^2\Sigma$, $^2\Delta$ and $^2\Pi$ involved in the γ- and β-band systems are given in Table V for ^{14}NS and ^{15}NS.

ACKNOWLEDGEMENTS

The authors are indebted to Professor R. K. Asundi for many helpful discussions during the course of this work. They had also the benefit of going through Professor Asundi's unpublished work on the β- and β-band systems of ^{14}NS which agrees well with the present investigation. Thanks are due to Drs. D. Gupta and S. D. Paul of the Chemical Engineering Division for supply of the $^{15}N_2$ samples used in these investigations.

REFERENCES

1. Fowler, A. and Bakker, C. J. *Proc. Roy. Soc.*, 1932, **136**, 28.
2. Herzberg, G. .. *Molecular Spectra and Molecular Structure*, Vol. I (New York: Van Nostrand), 1950.
3. Zeeman, P. B. .. *Can. J. Phys.*, 1951, **29**, 174.
4. Barrow, R. F., Downie, A. R. and Laird, R. K. *Proc. Phys. Soc.*, 1952, **65 A**, 70.
5. ———, Drummond, G. and Zeeman, P. B. *Ibid.*, 1954, **67 A**, 365.
6. Asundi, R. K., Inn and Tanaka, Y. Private Communication.
7. Narasimham, N. A. and Srikameswaran, K. *Proc. Ind. Acad. Sci.*, 1962, 325.

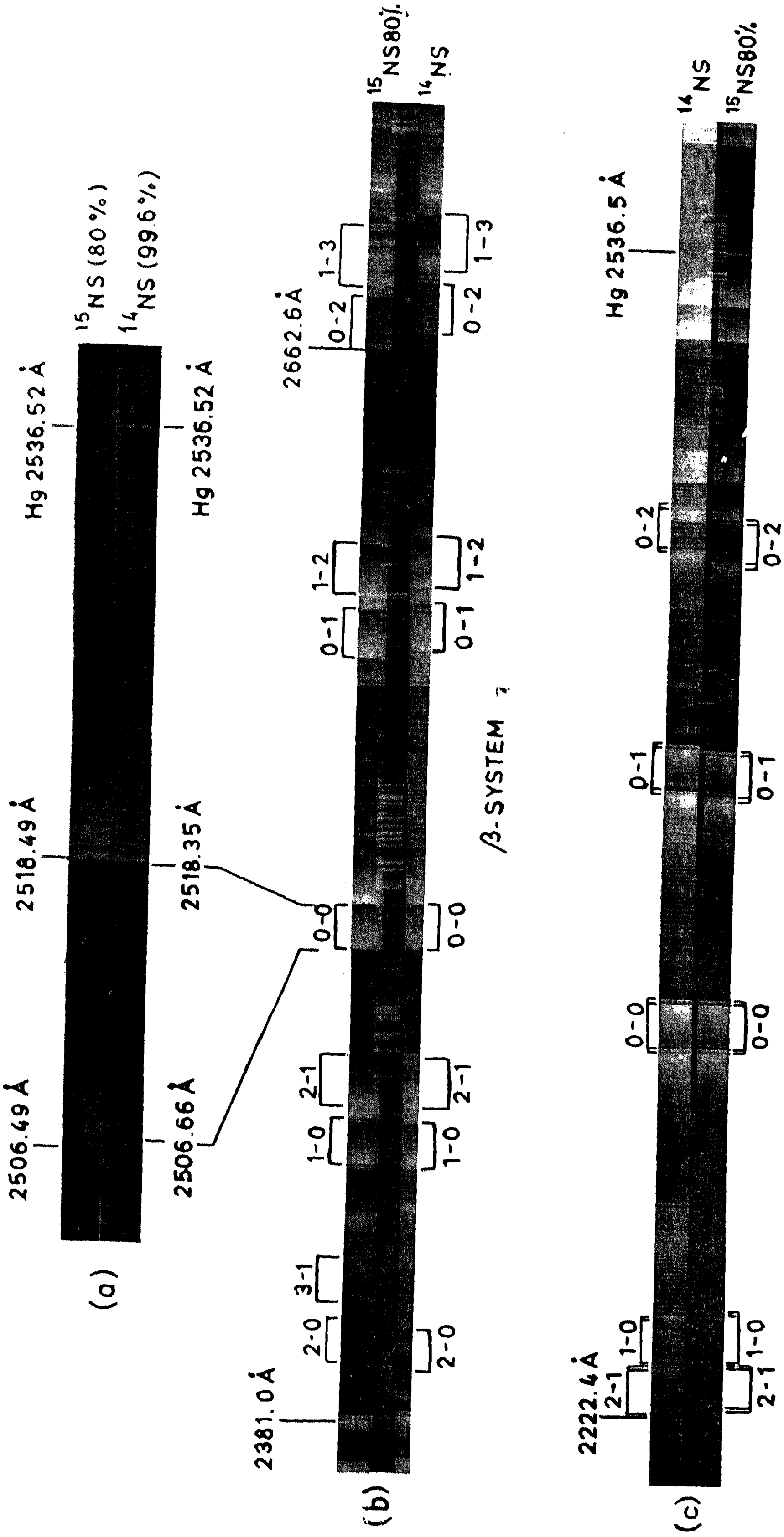

FIG. 2. The β-and γ-bands of NS containing natural and 80% enriched ^{15}N. (*a*) is an enlargement of the 0—0 β-band in (*b*) showing the sub-band-heads due to ^{14}NS and ^{15}NS. (*c*) γ-band system.

N. A. Narasimham and
K. Srikameswaran

Proc. Ind. Acad. Sci., A, Vol. LVI, Pl. IX

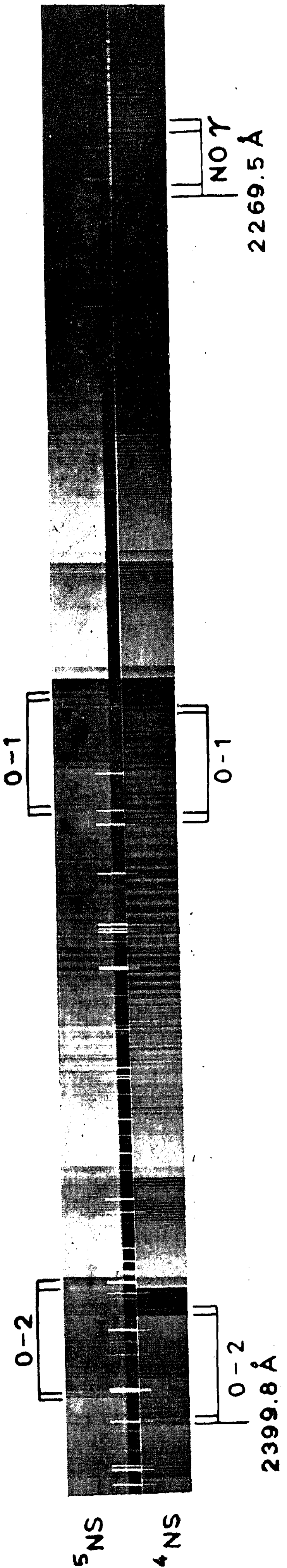

FIG. 1. The 0—1 and 0—2 bands of the new $^2\Sigma$ - X $^2\Pi$-system. The band-heads due to ^{15}NS and ^{14}NS are shown by leading lines at the top and bottom of the spectrogram. ^{15}N concentration is 80%.