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A New $^2\Pi_i$–$X^2\Pi_r$ Band System of NS

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Vibrational and rotational analysis of four bands of NS lying in the region 2550–2665 Å is reported. They form a new band system involving a $^2\Pi_i$–$^2\Pi_r$ transition and arise from a common initial vibrational level $v' = 0$ to $v'' = 4$ and 5 levels of the ground state. The assignment of v', v'' quantum numbers is supported by isotope shift data from N ^{34}S and Δ_2F (J) values of the $v = 4$ and 5 levels of the $X^2\,\Pi$ state.

INTRODUCTION

Four red-degraded bands at 2556.89, 2583.02, 2634.09, and 2661.82 Å were excited in a microwave (2450 MHz) discharge through trace amounts of nitrogen and sulphur vapor contained in a carrier gas of neon at 5 mm of Hg pressure. These were reported earlier in the literature (*1*) but were attributed to different systems of N ^{32}S (*2*). Isotope shift studies of these bands with respect to N ^{34}S [Fig. 1 (a)] and an analysis of their rotational structure [Fig. 1(b), (c) and (d)] photographed at a dispersion of 0.73 Å/mm in the third order of an Ebert 3.4-m grating spectrograph showed that they belonged to a single new system involving $^2\Pi_i$–$X^2\Pi_r$ transition.

RESULTS AND DISCUSSION

(*i*) *Vibrational Analysis and Isotope Shift*

The four bands form two sets of doublets, 2556.89, 2583.02 Å, and 2634.09, 2661.82 Å, with a doublet separation of 395.4 cm^{-1}. The two sets of doublets are 1146 cm^{-1} apart. This separation corresponds to the $\Delta G_{4+1/2}$ value of 1146.5 cm^{-1} of the $X\ ^2\Pi_r$ state of NS as observed by Smith and Meyer (*3*). In Fig. 1 (a) the bands due to the isotopic molecule N^{34}S are shown below those of N^{32}S. The subbands at 2556.89 and 2583.02Å show a shift of −43 cm^{-1} while the subbands at 2634.09 and 2661.82 Å show a shift of −52.7 cm^{-1}. Taking these isotope shifts the value of v' could be fixed in the following manner. In the expression for isotope shifts, v' was assumed to have successive values of 0, 1, 2, etc and, for each such value, the upper state frequency ω_e' was determined. For $v' = 0$, a value 820 cm^{-1} for ω_e' was obtained whereas with $v' = 1$, ω_e' was found to be 273 cm^{-1} which is too low for NS. Higher values of v' gave still smaller values for ω_e'. The observed bands were hence assigned as the

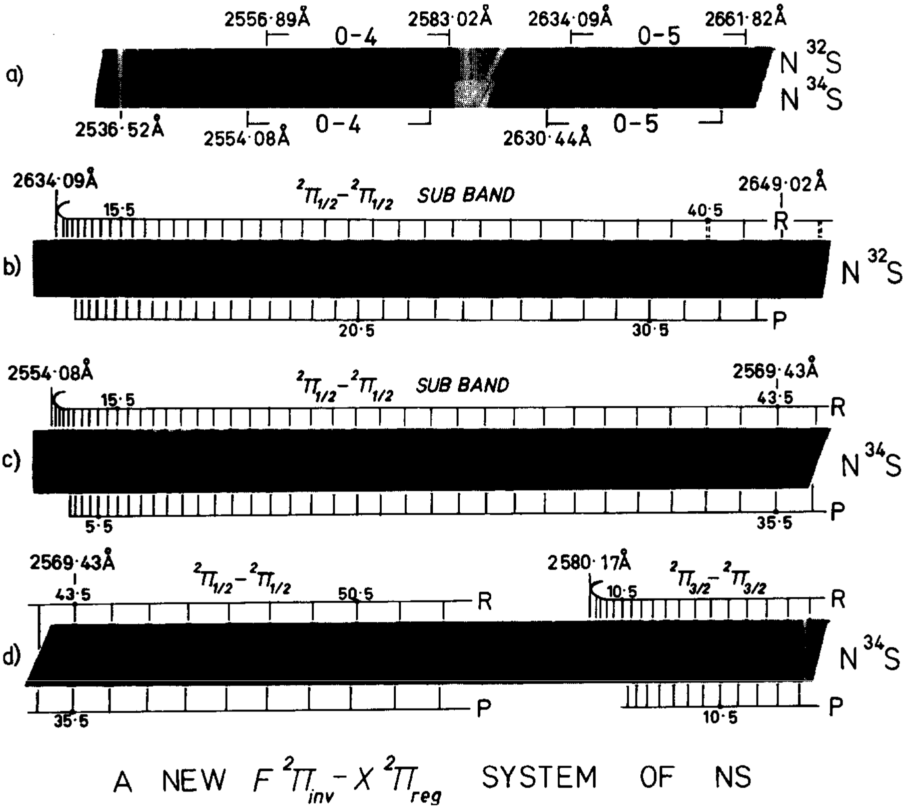

Fig. 1. A new $F\ ^2\Pi_i - X\ ^2\Pi_r$ system of NS. (a) Isotope shifts of $N\ ^{34}S$ bands relative to $N\ ^{32}S$, (b) Rotational structure of $^2\Pi_{1/2}$–$^2\Pi_{1/2}$ subband of the 0–5 band belonging to $N\ ^{32}S$, (c), (d) Rotational structure of $^2\Pi_{1/2}$–$^2\Pi_{1/2}$ and part of $^2\Pi_{3/2}$–$^2\Pi_{3/2}$ subbands of the 0–4 band of $N\ ^{34}S$.

0–4 and 0–5 bands. Since the expected positions of the other members of the progression are found to fall in regions of stronger band systems of NS, they could not be identified with certainty.

(*ii*) *Rotational Analysis and Identification of the Transition*

The subbands at 2556.89 and 2634.09 Å and the corresponding isotopic bands could be completely analysed. The subbands at 2583.02 and 2661.82 Å and the corresponding isotopic band could not be analysed as they are severely overlapped. The band at 2580.17 Å belonging to N ^{34}S was free from overlap near the head and hence a partial analysis of this band could be carried out. The final rotational assignments of the lines of the 0–4 and 0–5 bands are given in Tables I and II.

As may be seen from Fig. 1 (b), (c) and (d) each band consists of single *P* and *R* branches (with no obvious *Q* branch) showing that the transition is of the type $\Delta\Lambda = 0$. Two sets of combination differences $\Delta_2F'(J) = R(J) - P(J)$ one from the band at 2556.89Å and the second from the band at 2634.09 Å

TABLE I

Vacuum wavenumbers (in cm^{-1}) of the rotational lines of the new bands of ^{14}N ^{32}S

$^2\pi_{1/2}$ - $^2\pi_{1/2}$

	0-4 Band			0-5 Band		
J-1/2	R(J)	P(J)	R(J)-P(J)	R(J)	P(J)	R(J)-P(J)
0	39097.02b			37951.28b		
1	97.72b	39093.24b	4.48	51.76b		
2	98.35h	91.18b	7.17	52.40h	37945.20	7.20
3	98.35h	89.10b	9.25	52.40h	42.74	9.66
4	98.35h	86.32	12.03	52.40h	40.39	12.01
5	97.72b	83.64b	14.08	51.76b	37.76	14.00
6	97.02b	80.56b	16.46	51.28b	34.61	16.67
7	95.92	77.20b	18.72	50.33	31.34	18.99
8	94.72	73.47b	21.25	49.28	27.77	21.51
9	93.24b	69.35	23.89	47.72	23.90	23.82
10	91.18b	65.00	26.18	45.84	19.63	26.21
11	89.10b	60.34	28.76	43.85	15.30	28.55
12	86.58	55.49	31.09	41.57	10.41	31.16
13	83.64b	50.38	33.26	38.95	05.55	33.40
14	80.56b	44.84	35.72	35.94	00.22	35.72
15	77.20b	39.14	38.06	32.91	37894.69	38.22
16	73.47b	32.97	40.50	29.38	88.82	40.56
17	69.62	26.66	42.96	25.61	82.64	42.97
18	65.33	20.02	45.31	21.58	76.23	45.35
19	60.83	13.06	47.77	17.12	69.53	47.59
20	55.92	05.85	50.07	12.61	62.50	50.11
21	50.64	38998.30	52.34	07.71	55.26	52.45
22	45.22	90.56b	54.66	02.46	47.82	54.64
23	39.48	82.39b	57.09	37897.02	39.87	57.15
24	33.40	73.90b	59.50	91.27	31.76	59.51
25	27.03	65.12b	61.91	85.23	23.35	61.88
26	20.34	56.10b	64.24	78.88	14.64	64.24

contd ....

TABLE I (continued)

J-1/2	R(J)	P(J)	R(J)-P(J)	R(J)	P(J)	R(J)-P(J)
27	13.35	46.71b	66.64	72.28	05.69	66.59
28	06.07	37.11b	68.96	65.35	37796.43	68.92
29	38998.54	27.13b	71.41	58.16	86.84	71.32
30	90.50b	16.95b	73.61	50.66	76.99	73.67
31	82.39b	06.38b	76.01	42.85	66.90	75.95
32	73.90b	38895.61b	78.29	34.82	56.53	78.29
33	65.12b	84.50	80.62	26.50	45.83	80.67
34	56.10b	73.05	83.05	17.80	34.83	82.97
35	46.71b	61.40b	85.31	08.97	23.52	85.45
36	37.11b	49.40	87.71	37799.70	12.00	87.70
37	27.13b	37.13	90.00	90.18	00.12	90.06
38	16.95b	24.43	92.52	80.47	37688.08	92.39
39	06.38b	11.59	94.79	70.52	75.64	94.88
40	38895.61b 94.92	38798.36		60.05 59.44	62.93	
41	84.10	84.87		49.30		
42	72.57			38.52		
43	61.40b 60.60			27.54 26.81		
44	48.67			15.47		
45	36.24			03.68		
46	23.46			37691.50		
47	10.63			79.10		
48	38797.08			66.36		

b - blended lines

h - band head

are found to agree for all the *J* values observed, thus confirming that they arise out of the same initial level. The lower-state combination differences for $v'' = 4$ and 5 levels could be calculated from the known rotational constants of the ground state $X\ ^2\Pi$. These values are found to be in good agreement with the observed $\Delta_2F''(J)$ values of the bands at 2556.89 and 2634.09 Å, thus lending further support to the earlier conclusion based on vibrational and isotope shift data that they involve transitions to $v'' = 4$ and 5 levels of $X\ ^2\Pi_r$.

The doublet separation observed for these bands if 395.4 cm^{-1}. Since the ground state, which is a regular state, is known to have a spin–splitting of 223 cm^{-1} the upper $^2\Pi$ state of these bands must be an inverted one with a splitting of 172.4 cm^{-1}. Rotational analysis of the 0–4 band belonging to N ^{34}S, wherein both the subbands could be analysed, provides further support to this conclusion. It was found that for the upper $^2\Pi$ state, the $B_{\mathrm{eff}}\ (\Pi_{1/2}) > B_{\mathrm{eff}}\ (\Pi_{3/2})$. This clearly shows that the $^2\Pi_{1/2}$ set of levels are to be correlated with the $F_2(J)$ term series of the Hill–Van Vleck expression while the $^2\Pi_{3/2}$ set of levels goes with the $F_1(J)$ series. For $^2\Pi$ states approximating to Hund's case (a) such a correlation holds only if the $^2\Pi$ state is inverted. For the lower state, the reverse

TABLE II

Vacuum wavenumbers (in cm^{-1}) of the rotational lines of the new bands of $^{14}N\ ^{34}S$

	$^2\pi_{1/2}$ - $^2\pi_{1/2}$ 0-4 Band			$^2\pi_{1/2}$ - $^2\pi_{1/2}$ 0-5 Band			$^2\pi_{3/2}$ - $^2\pi_{3/2}$ 0-4 Band	
J-1/2	R(J)	P(J)	R(J)-P(J)	R(J)	P(J)	R(J)-P(J)	R(J)	P(J)
0	39140.07b			38003.97b				
1	40.78b	39136.21b	4.57	04.51b			38744.95b	
2	41.32h	34.42b	6.90	05.00b	37997.68	7.32	45.44b	
3	41.32h	32.12b	9.20	05.11h	95.84	9.27	45.70h	38736.22
4	41.32h	29.64	11.68	05.00b	93.28	11.72	45.44b	33.86
5	40.78b	26.87b	13.91	04.51b	90.70	13.81	44.95b	30.95
6	40.07b	23.89b	16.18	03.97b	87.61	16.36	44.08	27.83
7	39.20	20.52b	18.68	03.20	84.47	18.73	42.94	24.40
8	37.84	16.87b	20.97	01.84	80.77	21.07	41.47	20.60
9	36.21b	12.76	23.45	00.36	76.93	23.43	39.70	16.40
10	34.42b	08.82b	25.60	37998.64	72.87	25.77	37.69	12.07
11	32.12b	04.17	27.95	96.72	68.52	28.20	35.21	07.35
12	29.79	39099.28	30.51	94.31	63.83	30.48	32.51	02.33
13	26.87b	94.27	32.60	91.75	58.89	32.86	29.51	38697.00
14	23.89b	88.78	35.11	88.92	53.72	35.20	26.16	91.30
15	20.52b	83.14	37.38	85.74	48.24	37.50	22.53	
16	16.87b	77.15	39.72	82.31	42.44	39.87	18.62	
17	13.02	70.94	42.08	78.56	36.46	42.10	14.27	
18	08.82b	64.33	44.49	74.61	30.17	44.44	09.73	
19	04.27	57.50	46.77	70.35	23.54	46.81	04.78	
20	39099.43	50.43b	49.00	65.75	16.64	49.11	38699.65	
21	94.40	42.92	51.48	60.95	09.55	51.40	94.13	
22	89.08	35.29b	53.79	55.86	02.02	53.84		
23	83.40	27.24b	56.16	50.50	37894.36	56.14		
24	77.46	18.89b	58.57	44.86	86.33	58.53		
25	71.06	10.30b	60.76	38.84	77.99	60.85		
26	64.48	01.39b	63.09	32.56	69.50	63.06		

contd ....

TABLE II (continued)

J-1/2	R(J)	P(J)	R(J)-P(J)	R(J)	P(J)	R(J)-P(J)
27	57.67	38992.38	65.29	26.07	60.67	65.40
28	50.43b	82.88	67.55	19.30	51.58	67.72
29	43.08	73.09	69.99	12.25	42.17	70.08
30	35.29b	62.99	72.30	04.82	32.47	72.35
31	27.24b	52.61	74.63	37897.13	22.48	74.65
32	18.89b	41.97	76.92	89.19	12.30	76.89
33	10.30b	31.07	79.23	80.99	01.83	79.16
34	01.39b	19.83	81.56	72.48	37790.94	81.54
35	38992.17	08.24	83.93	63.69	79.86	83.83
36	82.56	38896.49	86.07	54.54	68.50	86.04
37	72.79	84.39	88.40	45.23	56.85	88.38
38	62.70	72.02	90.68	35.60	44.89	90.71
39	52.32	59.32	93.00	25.71	32.72	92.99
40	41.76	46.19	95.57	15.66	20.22	95.44
41	30.50	32.99	97.51	04.92	07.42	97.50
42	19.17	19.59	99.58	37794.11	37694.51	99.60
43	07.48	05.46	102.02	82.96	80.94	102.02
44	38895.48	38791.18	104.30	71.58	67.30	104.28
45	83.39	76.83	106.56	60.00	53.44	106.56
46	70.90	61.93	108.97	48.09	39.08	109.01
47	58.06	47.01	111.05	35.84	24.70	111.14
48	44.91	31.46	113.45	23.42	09.85	113.57
49	31.57			10.50		

b - blended lines

h - band head

situation applies, i.e., the B_{eff} ($\Pi_{1/2}$) $<$ B_{eff} ($\Pi_{3/2}$). This is indeed expected since it is a regular $^2\Pi$ state.

Evaluation of Vibrational and Rotational Constants

The initial as well as the final $^2\Pi$ states have large spin-splittings and thus belong to Hund's coupling case (a). The rotational constants B_{eff} and D_{eff} are evaluated from the relation

$$\Delta_2F_k(J) = (4B_{v\,\mathrm{eff}}^{(k)} - 6D_{v\,\mathrm{eff}}^{(k)})(J + \tfrac{1}{2}) - 8D_{v\,\mathrm{eff}}^{(k)}(J + \tfrac{1}{2})^3 \qquad (k = 1 \text{ or } 2).$$

The quantum $\Delta G_{4+1/2}$ was evaluated making use of the R and P lines. Differences between R or P lines of the same J value corresponding to the 0–4 and 0–5 bands (the branches referring to same subband) give

$$\Delta G^{(k)}_{4+1/2} - (B^{(k)}_{4\,\text{eff}} - B^{(k)}_{5\,\text{eff}})J(J+1) \qquad (k = 1 \text{ or } 2).$$

A plot of this difference against $J(J+1)$ is a straight line with intercept giving the $\Delta G^{(k)}_{4+1/2}$ value and the slope giving $B^{(k)}_{4\,\text{eff}} - B^{(k)}_{5\,\text{eff}}$. The value of $B^{(1)}_{4\,\text{eff}} - B^{(1)}_{5\,\text{eff}}$ was found to be 0.00638 cm^{-1} which is slightly higher than the value of $B^{(1)}_{0\,\text{eff}} - B^{(1)}_{1\,\text{eff}} = 0.00614$ cm^{-1} for the $X\ ^2\Pi$ state obtained from γ-band analysis (*4*). The discrepancy is outside experimental errors and may be attributed to the fact that the relation between $B^{(1)}_{v\,\text{eff}}$ and v for the ground state is not just linear but has a nonvanishing $(v + \frac{1}{2})^2$ term. Using the $B^{(1)}_{4\,\text{eff}}$ and $B^{(1)}_{5\,\text{eff}}$ values one obtains, on extrapolation, a value of $B^{(1)}_{0\,\text{eff}}$ which is in good agreement with that obtained from microwave data (*5*).

From a knowledge of the lower-state coupling constant A_4'', the upper state coupling constant A_0' was determined, using the R-branch lines of the two subbands of the 0–4 band of N ^{34}S.

Finally, the band origins of the individual subbands were determined from a plot of $R\ (J-1) + P\ (J)$ against J^2, which incidentally, gave precise values for $(B''_{v\,\text{eff}} - B'_{v\,\text{eff}})$ and $(D''_{v\,\text{eff}} - D'_{v\,\text{eff}})$.

All the constants thus determined are listed in Tables III and IV.

Λ *Doubling*

No Λ doubling was observed even in the $^2\Pi_{1/2}$–$^2\Pi_{1/2}$ subbands of both the isotopic molecules, N ^{32}S and N ^{34}S. Since the $\Pi_{1/2}$ component of the $X\ ^2\Pi$ state is known to have appreciable Λ doubling ($p = 0.013$ cm^{-1}) one would have normally

TABLE III

VIBRATIONAL AND ROTATIONAL CONSTANTS (IN cm^{-1}) OF THE NEW $^2\Pi_{\text{inv}}$ AND $X^2\Pi_{\text{reg}}$ STATES OF ^{14}N^{32}S

Upper $^2\Pi_{\text{inv}}$ state	Lower $X^2\Pi_{\text{reg}}$ state
$\Pi_{1/2}$ substate	$\Pi_{1/2}$ substate
$\omega_e = 813 \pm 10$[a]	$\Delta G_{4+1/2} = 1146.10$
$B_{0\,\text{eff}} = 0.5971_3$	$\omega_e = 1218.60$[b]
$D_{0\,\text{eff}} = 1.7_0 \times 10^{-6}$	$\omega_e x_e = 7.25$[b]
	$B_{4\,\text{eff}} = 0.7447_4$
	$B_{5\,\text{eff}} = 0.7383_6$
	$D_{4\,\text{eff}} = D_{5\,\text{eff}} = 1.3_0 \times 10^{-6}$
	$B^{(1)}_{v\,\text{eff}} = 0.7727_0 - 0.00608(v + \frac{1}{2}) - 0.000030(v + \frac{1}{2})^2$
Band origins	
$^2\Pi_{1/2}$–$^2\Pi_{1/2}$ subband:	$\nu_0(0\text{–}4) = 39095.41$ cm^{-1} $\nu_0(0\text{–}5) = 37949.30$ cm^{-1}

[a] Calculated using isotope shifts obtained from band origins.

[b] Derived from present $\Delta G^{(1)}_{4+1/2}$ and Zeeman's $\Delta G^{(1)}_{1/2} = 1204.10$ cm^{-1} from γ-band analysis (**4**).

TABLE IV

VIBRATIONAL AND ROTATIONAL CONSTANTS (IN cm^{-1}) OF THE NEW $^2\Pi_{\mathrm{inv}}$ AND $X^2\Pi_{\mathrm{reg}}$ STATES OF $^{14}N^{34}S$

Upper $^2\Pi_{\mathrm{inv}}$ state		Lower $X^2\Pi_{\mathrm{reg}}$ state	
$\Pi_{1/2}$ substate		$\Pi_{1/2}$ substate	
Obsd	Calcd from $^{14}N^{32}S$	Obsd	Calcd from $^{14}N^{32}S$
$B_{0\,\mathrm{eff}} = 0.5864_0$	0.5864_6	$B_{4\,\mathrm{eff}} = 0.7316_4$	0.7316_7
$D_{0\,\mathrm{eff}} = 1.6_4 \times 10^{-6}$	$1.6_4 \times 10^{-6}$	$B_{5\,\mathrm{eff}} = 0.7254_3$	0.7254_6
		$D_{4\,\mathrm{eff}} = 1.2_7 \times 10^{-6}$	$1.2_5 \times 10^{-6}$
		$D_{5\,\mathrm{eff}} = 1.2_7 \times 10^{-6}$	$1.2_5 \times 10^{-6}$
		$\Delta G_{4+1/2} = 1136.46$	1136.45
$\Pi_{3/2}$ substate		$\Pi_{3/2}$ substate	
$B_{0\,\mathrm{eff}} = 0.582_2$		$B_{4\,\mathrm{eff}} = 0.736_6$	
Coupling Constant $A_0 = -172._4$			
Band origins			
	$^2\Pi_{1/2}$–$^2\Pi_{1/2}$ subband:	$\nu_0(0\text{–}4) = 39138.43\ \mathrm{cm}^{-1}$	
		$\nu_0(0\text{–}5) = 38001.98\ \mathrm{cm}^{-1}$	

expected some Λ doubling in the observed bands. Since no doubling is perceptible in the series, one has to assume that the Λ doubling of the upper $\Pi_{1/2}$ component is of the same magnitude as the lower state and that their relative symmetries are such that the Λ-components of the branch lines fall on top of each other.

Some of the lines, however, show a doubling, as for example, the $R(40.5)$ and $R(43.5)$ lines of the 0–4 and 0–5 bands belonging to the $^2\Pi_{1/2}$–$^2\Pi_{1/2}$ transition of N ^{32}S. These were also noticed in the bands of the isotopic molecule N ^{34}S. These are perhaps due to some perturbation which seems to affect the upper $\Pi_{1/2}$ state. Since both the Λ components are affected, the perturbing state is a degenerate $^2\Delta$ or $^2\Pi$ state. Neither of the known $^2\Delta$ or $^2\Pi$ state of NS seems to cause the observed perturbations.

The new $^2\Pi$ state lies at $T_e = 43941 \pm 5\ \mathrm{cm}^{-1}$ with a spin–splitting constant $A_0 = -172.4\ \mathrm{cm}^{-1}$, $r_0 = 1.705$ Å and $\omega_e = 813 \pm 10\ \mathrm{cm}^{-1}$. This could be assigned to one of the states arising out of the electron configuration $K\ K\ L\ (z\sigma)^2\ (y\sigma)^2\ (x\sigma)^2\ (w\pi)^3\ (v\pi)^2 \cdots {}^2\Pi_i,\ {}^2\Pi_r,\ {}^2\Pi,\ {}^4\Pi_i,\ {}^2\Phi_i$. The same configuration also gives rise to a $^2\Pi_r$ state which is indeed the initial state of the known $^2\Pi$–$X\ ^2\Pi$ system and lies at $T_e = 30328.5\ \mathrm{cm}^{-1}$ with $A_e = 72.8\ \mathrm{cm}^{-1}$, $r_e = 1.703$ Å, and $\omega_e = 800\ \mathrm{cm}^{-1}$.

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