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Berkeley, California

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CHARACTERIZATION OF THE B$^2\Pi$ STATE OF NS IN THE EMISSION FROM ACTIVE NITROGEN-SULFUR FLAMES

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CHARACTERIZATION OF THE $B^2\Pi$ STATE OF NS IN THE EMISSION FROM ACTIVE NITROGEN-SULFUR FLAMES

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Abstract:

The emission spectrum of NS has been excited in active nitrogen-sulfur compound flames in three different ways. Photographs in low and in high dispersion, in the 34000-20000 cm^{-1} region, show some 80 new bands which are all believed to be part of a new $B^2\Pi \rightarrow X^2\Pi$ system. The value T_o = 30100 cm^{-1} has been confirmed with N^{15} and S^{34} isotopes. ω_e = 800 cm^{-1} and B_e =0.612 cm^{-1} correspond closely to the values expected from the related NO molecule.

Introduction

Lord Rayleigh[1] observed that blue light is emitted from the low

pressure reaction of active nitrogen with several sulfur compounds, and

observed 30 bands which he did not assign to any molecule. Pannetier[2]

recently studied the hydrogen sulfide-active nitrogen flame and found

several red degraded bands which he attributed to NS. The purpose of

the present investigation was to identify conclusively the emitting

species from several such flames. We also hoped to learn more about

the excitation of the molecules which are intermediates in the production

of sulfur nitrogen compounds.[3] Two molecules in point are S_2 and NS.

For the first, one transition from a low lying energy level, the $^3\Sigma_u^- - {}^3\Sigma_g^-$,

is known and it would be very valuable to find excitation conditions under

which other transitions, such as the $^1\Sigma - {}^1\Sigma$, which has been proposed

by Haranath[4], would be preferably excited. In the case of NS two

transitions,[5,6] the $A^2\Delta \rightarrow X^2\Pi$ and the $C^2\Sigma \rightarrow X^2\Pi$, have been carefully

analyzed. Several more low lying energy levels should be present, and

three recent reports deal with bands attributed to a transition from a

$^2\Pi$ state which, in analogy to NO, was called $B^2\Pi$ [5,7,8].

Experimental

Flames of active nitrogen with disulfur dichloride and with hydrogen

sulfide were produced by combining the reagents in the quartz cell

shown in Figure 1. This cell was connected to a conventional flow

system. H.P. dry nitrogen was passed over magnesium perchlorate, hot

activated copper, and through a trap at -78°C. Active nitrogen was produced

using two methods: with an electrodeless discharge from a 2450 mc/s microwave

generator and with a 2.5 kV 500W pulsed discharge using tungsten
electrodes. H.P. disulfur dichloride and hydrogen sulfide (Matheson)
were both distilled under vacuum into the storage vessel. The reactant
flow rates were adjusted to maximize the flame intensities. For nitrogen
they varied from 2.5 to 25 mmol per min., corresponding to about 50 to
500 μmol of nitrogen atoms, and for the sulfur compounds they were
between 5 and 50 μmol per min. The pressure in the reaction cell was
kept within0.5 - 5 mm Hg. For experiments with enriched isotopes 5 mg
of a 1:1 mixture of isotope 32 and 34 of elemental sulfur were converted
to disulfur dichloride. For nitrogen experiments 94% N_2^{15} was used. For
quantitative recovery of this isotope the flow system was modified and
the mechanical pump was replaced by a trap which was cooled with liquid
hydrogen.

The reaction flame was mounted, without lenses, in front of the
spectrometer slit. For low dispersion studies a Jarell Ash f = 6.3
Czerny-Turner spectrograph was used with a 1250 lines per mm grating
blazed for 3000A. The dispersion was 5A/mm. High dispersion plates were
made in the second order of a 21 ft Paschen Runge concave grating spec-
trograph with a dispersion of0.6A/mm. All spectra were recorded on
103a-O Kodak plates which were developed for 15 minutes to give highest
sensitivity.

Results and Interpretation

A. Low dispersion survey:

1. <u>Disulfur dichloride and microwave-excited active nitrogen</u>: The
predominant emission in the 2828-3400 A region is due to the S_2 molecule.
The bands correspond to the (9,0) to (0,10) levels of the $^3\Sigma_u^- \rightarrow {}^3\Sigma_g^-$

transition. V" levels higher than 10 are not observed and even the strongest band, the (9,0), is at least four orders of magnitude weaker than in the emission from an electrodeless discharge through a S_2-Ar tube. In the 3,200-5000 A region of the reaction flame other bands are observed. They are red degraded, occur in pairs and form at least two progressions.

The spectrum of the S^{34} enriched disulfur dichloride flame was recorded in the 3900-4800 region. All bands are doubled. The new heads are located towards the blue from the S^{32} heads, and the isotopic spacing increases towards the red. The doubling indicates that the emitting species contains one sulfur atom, and the spacing shows that the origin of the system observed is in the direction of higher energies. Spectra of a flame with disulfur-32 dichloride and N^{15} are similar to spectra of the reaction of natural isotopes, but all the band heads are shifted towards the blue. This shows that the emitting species also contains nitrogen. It seems, therefore, that the bands under observation are due to NS.

2. <u>Hydrogen sulfide and microwave-excited active nitrogen</u>: The same spectrum is observed as in case 1., but with only about half the intensity. The band heads in the 4300-5000 A region are now the strongest features, and at low pressures the S_2 emission is very weak. The strongest NS heads in this region have been described by Pannetier et al.[2] who, because of low sensitivity, believed that the S_2 emission was absent.

3. <u>Disulfur dichloride and pulsed active nitrogen</u>: Again strong red degraded bands occur in pairs. In this flame they cover the whole 3000-4500 A region forming long progressions. No S_2 is observed.

The emission is still weaker than in the hydrogen sulfide flame. The region of highest intensity is around 3100 A.

The band pairs of all three flames have overlapping spectral regions and seem to be due to different excitation of one single system of the NS molecule.

B. Vibrational analysis:

All band heads of medium or high intensity can be fitted in a vibrational scheme. (Table I.) The different excitation of the three spectra makes it possible to record a rather extended part of the new system: In flames with pulsed discharged nitrogen, v' progressions are well developed. The highest emission intensity is found for high v' values. The band heads are broad because of high rotational excitation. In the hydrogen sulfide flame the strongest bands have high v'' and low v' values. The microwave excited disulfur dichloride flame represents an intermediate case and is, in excitation, closest to an equilibrium source. In some parts of the spectrum the bands overlap considerably. In this case they are marked with b. Due to the different rotational excitation in high v' and high v'', and due to different excitation in different light sources, the limiting factor in the precision of band head readings is the accuracy in estimating the head location. The energy values for the band heads in Table I. are the average of measurements on different plates and are believed to be accurate within $\pm 2 cm^{-1}$. The $\Pi_{1/2}$ and the $\Pi_{3/2}$ component have in the origin region the same vibrational separation. The spacing of the band heads decreases, however, slowly for high v' and increases for v''. This indicates that $\omega''_{1/2}$ is slightly greater than $\omega''_{3/2}$ and $\omega'_{3/2}$ is greater than $\omega'_{1/2}$. Averaged vibrational data is listed in Table II. The lower state vibrational constant,

ω_o'', is 1206 cm^{-1} and corresponds closely to the value for the ground state of NS. This state is a $^2\Pi$ state with a sublevel splitting of 220 cm^{-1}. The average separation of a band pair in the observed transition is 135 cm^{-1}. If the lower state of the newly observed system corresponds to the $X^2\Pi$ state in NS, then the average head separation indicates that the upper observed state corresponds to a $^2\Pi$, Hund's case a, with a sub level splitting of 85 cm^{-1}. It is interesting to note that in the v" progressions the $\Pi_{3/2}$ transition is consistently stronger than the $\Pi_{1/2}$. For higher v' the reverse is true.

Table III lists the calculated and observed isotopic shifts for some band heads of N^{15} and S^{34}. The close agreement between observed and calculated shifts indicates that this system is really due to NS and that the vibrational numbering is correct.

C. Rotational analysis:

For further confirmation of the correct assignment of the new system, and for correlation of it with already known states of NS, a rotational analysis was planned. Forty and seventy hour exposures were necessary to obtain plates which were suitable for analysis of the strongest bands. The heads at 4128 A and 3946 A were selected because they showed the least overlap with neighboring bands. They correspond to the $\Pi_{1/2}$ - $\Pi_{1/2}$ (0,5) and $\Pi_{1/2}$ - $\Pi_{1/2}$ (0,4) transition. A densitometer recording of the 4128 A head is shown in Figure 2. The band head and the origin are not completely resolved. Strong P and R branches can be recognized. A closer observation shows that both branches have λ doubling. Since the transition is case a, $^2\Pi$ - $^2\Pi$, the Q branches are expected to be weak, and indeed, no Q branches were observed. Table IV lists the position of

the R and P lines, and Table V gives a summary of the calculated constants. The B values were computed by the $\Delta_2 F$ technique[9]. The B" values of both bands correspond reasonably well with the data predicted by Barrow et al.[5] which is based upon analysis of 3 heads around the origin of the $A^2\Delta \rightarrow X^2\Pi$ transition. It seems, therefore, beyond doubt that the lower state is identical with the X-state of NS. The difference of the r_e values for the upper and the lower state indicates that the Franck-Condon curve should have a maximum around v' = 5. This is in excellent agreement with the intensities observed for this transition and explains the occurrence of well developed v" progressions. The $\Delta_2 F$ values for J = 11 indicate that this level is perturbed.
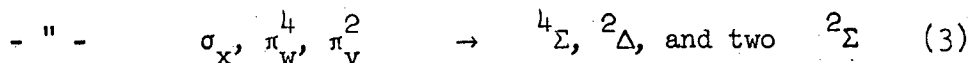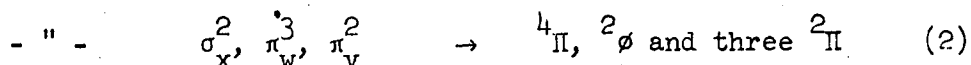
Discussion

As a result of this work a new $^2\Pi$ state of NS has been identified. It lies 30100 cm^{-1} above the ground state. The 16 band heads observed by Pannetier et al.[2] and attributed by him to a $D^2\Sigma - C^2\Pi$ transition, between two new and high lying energy levels, were found to be part of the newly discovered $^2\Pi$ system. Furthermore, seven UV-bands analyzed by Narasimham[8] probably also fit into this system, although only one was observed during the present work. Their band head position and B value would correspond to their being the (7,0), (8,0), (9,0), (10,0) heads. Barrow tentatively attributed four unassigned bands in the 2300 A region to a transition from a $^2\Pi$ state to the ground state. Patel[7] later assigned several other bands to this system which he called the B-system in analogy to NO. Narasimham[10] showed, however, using N^{15} isotopes, that this assignment must be wrong and that the bands observed by Barrow are rather part of a new $^2\Sigma$ state. Since several other bands of the so-called B system can be

attributed to other transitions of NS and NS^+ it is doubtful whether a

transition occurs in this energy region. It is here proposed that the

newly discovered $^2\Pi$ state with $T_o \sim 30100$ cm^{-1} is the B-state. For com-

parison, Figure 3 shows some of the low lying energy levels of NS and

NO. Both molecules have eleven valence electrons and the same electron

configuration for the outer electrons. The ground state configuration

of NS gives rise to only one $^2\Pi$ state:

$$\text{KKL, } \sigma_z^2, \sigma_y^2, \sigma_x^2, \pi_w^4, \pi_v^1 \qquad \rightarrow \qquad ^2\Pi \qquad\qquad (1)$$
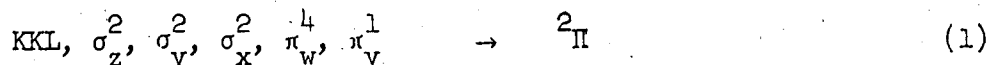
The first two excited electronic configurations lead to the following

states:

$$- \text{ " } - \qquad \sigma_x^2, \pi_w^3, \pi_v^2 \qquad \rightarrow \qquad ^4\Pi, \, ^2\phi \text{ and three } ^2\Pi \qquad (2)$$

$$- \text{ " } - \qquad \sigma_x, \pi_w^4, \pi_v^2 \qquad \rightarrow \qquad ^4\Sigma, \, ^2\Delta, \text{ and two } \quad ^2\Sigma \qquad (3)$$

In absorption several Rydberg states are observed for NO, for example:

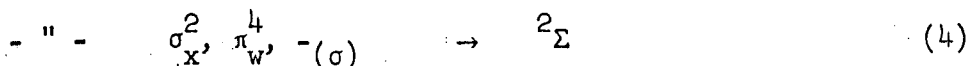$$- \text{ " } - \qquad \sigma_x^2, \pi_w^4, -(\sigma) \qquad \rightarrow \qquad ^2\Sigma \qquad\qquad (4)$$

Figure 3 shows the location of some of these states as observed

for NO. Due to its larger size, one would expect that the energy levels

of the heavier NS would lie slightly lower than in NO. If the states in

the two molecules could be clearly correlated, the "shrinkage rate" could

be determined. Since one expects only one low lying $^2\Delta$ state, the cor-

relation between NO and NS for the A $^2\Delta$ configuration can be computed

unambiguously. Since there is also only one low lying $^2\Pi$ state in NO, the new

$^2\Pi$ state in NS can be clearly assigned to this B state of NO. The shrinkage for

configurations 2 and 3 is given in Table VII. A different situation

exists in the case of the C $^2\Sigma$ state of NS. The small r_e value indicates

that this is a Rydberg state for which the shrinkage might be considerably

different than for the other state.   In addition
there are too many neighboring Rydberg states conceivable to allow a
conclusive correlation.

The data in Table VII indicates that both excited electron configura-
tions 2 and 3 undergo a similar energy change from NO to NS. If one
assumes an analogous behavior of the other states belonging to the same
electron configuration, one can predict approximately some additional
energy levels for NS: (Table VIII).

Figure 3 also contains the energy diagram observed for PO, which
is isoelectronic with NS. It is interesting to note that the states so
far observed for PO are different from the ones known for NS. This
might be due to different excitation conditions or different observation
conditions such as created through the presence of the P_2 molecule. All
the reported states are, however, close to states predicted (see Table
VIII) for NS.

It would be interesting to verify the relation between NO, NS and
PO by direct observation.

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Captions to Figures:

Figure 1.   Quartz reaction cell. The light emission

from this cell is greater than from a

multiple jet or any other design so far

used.

Figure 2.   Densitometer tracing of the (0,5).

$\Pi_{1/2} \rightarrow \Pi_{1/2}$ head.

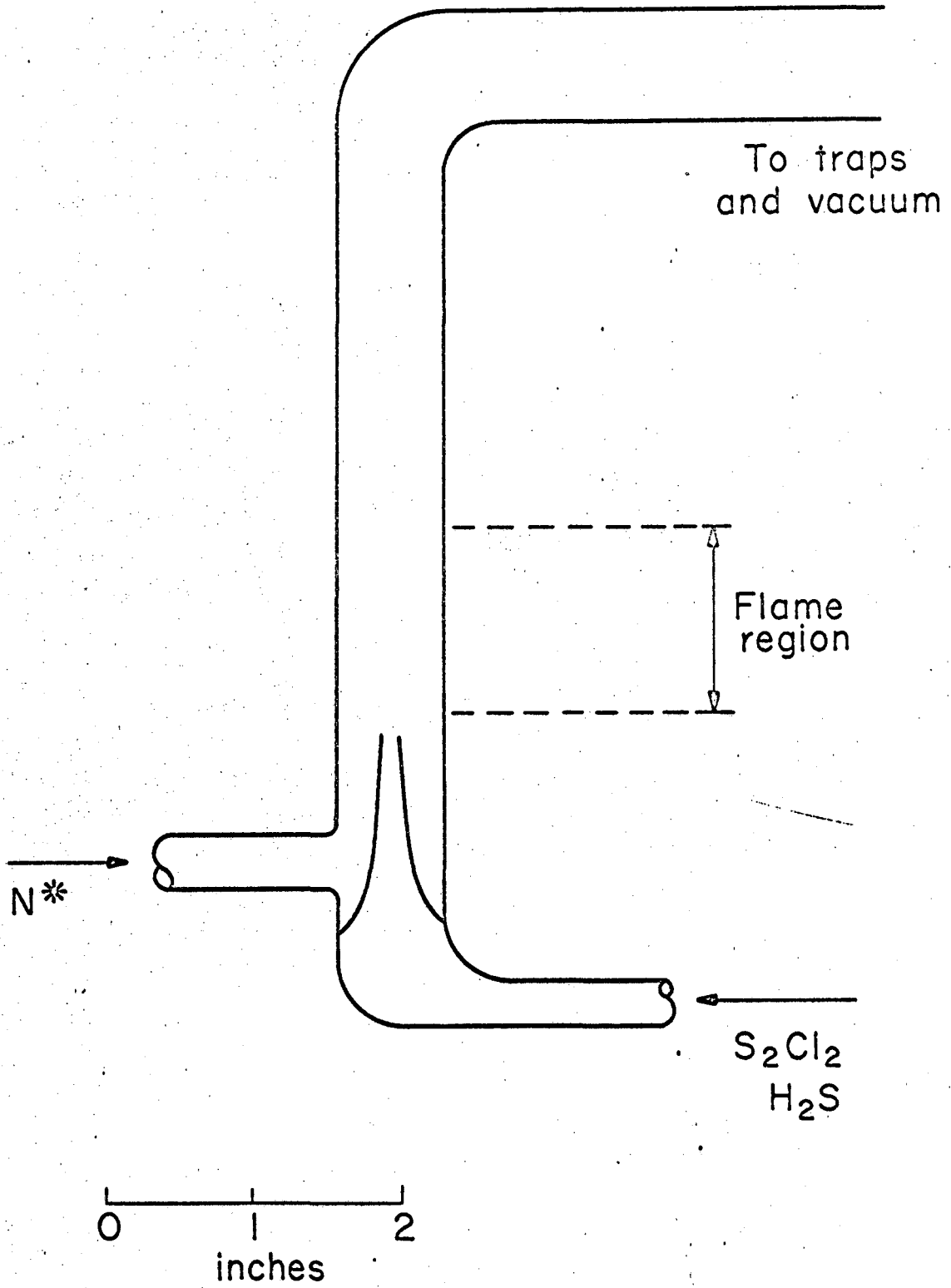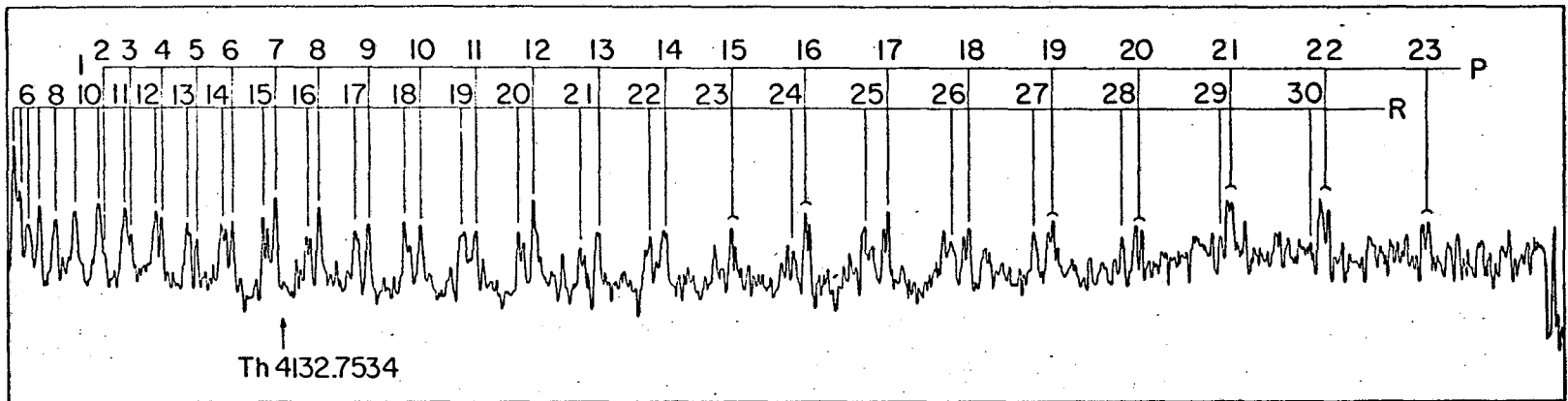Figure 3.   Energy levels of NO, NS and PO.

Data for NO from Ref. ($\underline{11}$, $\underline{12}$); for

PO from Ref. ($\underline{13}$, $\underline{14}$).

To traps
and vacuum

Flame
region

N*

S_2Cl_2
H_2S

0   1   2

inches

Fig. 1

MU-33262

Th 4132.7534

Fig. 2
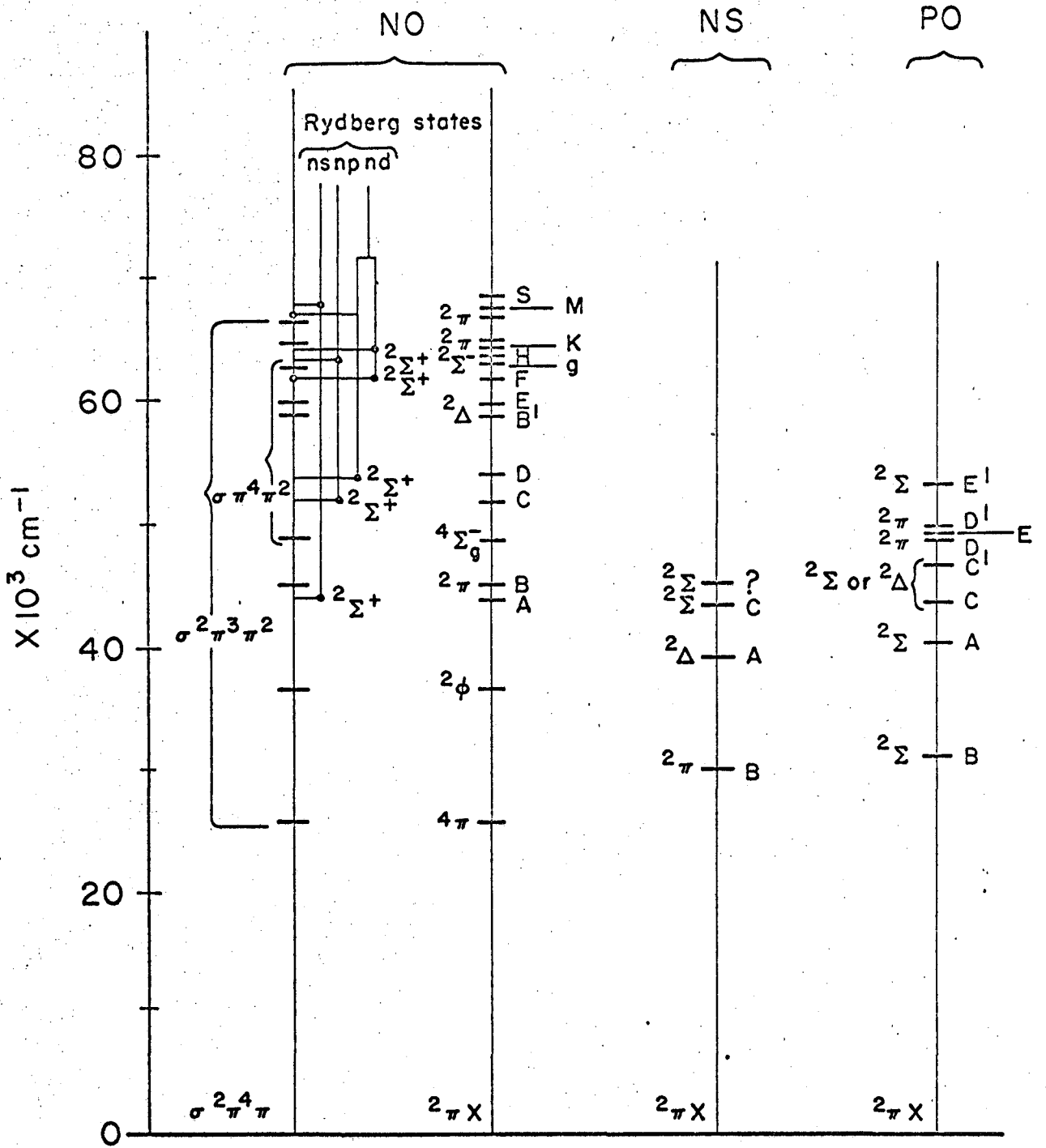
Fig. 3

MU-33263

Table I

Deslandres Scheme for the Band Heads of NS.

v" \ v'	0	1	2	3	4	5	6	7
0				32440pc 32314pc	33204p (33091p	33963p	34712p	35456p
1		29673c 29540c	30458pc 30317pc	31231pc ( )p	31995pc	32759pc		34251p
2	27708hc 27572hc	28476hc 28342hc	29269c 29140b	30056pc 29930c				
3	26518hc 26383hc	27310hc 27178hc	b b					
4	25358hc 25224hc	26150hcb 26018hcb	b b					
5	24212hc 24077hc	(25000)hcb (24870)hcb	25803c 25669c	26279pc				
6	23087h 22954h	(23850)hcb (23720)hcb	24633c 24501c	25140pc				
7	- 21875h	22760 (22564)	23400	24212c				
8	- 20820h	21717h 21562hc	22487hc 22337hc	(23210)c 23087c				
9		20650h						

b) Blended;   c) S_2Cl_2 -flame;   h) H_2S -flame;   p) Pulsed discharge.

Table II

Vibrational Data for the New $^2\Pi - ^2\Pi$ System of NS in cm^{-1}

(0.0) head	$\Pi_{1/2} = 30104$		T_o a)	$\Pi_{3/2} \rightarrow 30190$
	$\Pi_{3/2} = 29968$			$\Pi_{1/2} \rightarrow 30105$
	$\bar{\omega}_o'' = 1206$		$\bar{\omega}_o' = 795$	
	$\omega_o X_o'' \sim 7$		$\omega_o X_o' \sim 3$	
	separation of band pairs		~ 135	
	$\Pi_{3/2}'' - \Pi_{1/2}'' = 220$ a)		$\Pi_{3/2}' - \Pi_{1/2}' = 85$	

a) Computed from the assumption that the lower state observed is identical with the $X^2\Pi$ State.

Table III

Isotope Shifts for N^{15} and S^{34} Flames

Band	$N^{14}S^{34}$		$N^{15}S^{32}$	
	Measured	Calculated	Measured	Calculated
(0.3)	31	33	88	87
	33	33	90	87
(1.4)	35	36		
(0.4)	42	40	113	105
	43	41	115	
(0.5)	53	51	137	130
	53	51	138	130
(0.6)	60	59	141	151
	62	59	155	151
(1.6)			128	128
(2.6)	46	48		
(3.6)			118	110

Table IV

Rotational Lines of the 4129 and 3946 Bands:[a]

	(0.5)			(0.4)	
J	R	P		R	P
2		24204.08			
3		2.57[b]		25357.81	
4	24212.14	0.13		57.16	25345.72
5	211.68	197.67		56.52	42.87
6	10.24	4.36		55.42	39.72
7	9.43	0.99		54.10	36.27
8	8.71	87.29		53.06[b]	32.45
9	7.18	3.16		51.53[b]	28.42
10	5.43	79.28		49.16	24.03[b]
11	3.40	74.90		48.27	19.68
12	00.85[b]	69.98		45.28[b]	14.69
13	198.18	65.17		41.28	9.28
14	95.30	59.34		39.38[b]	4.02
15	92.16	53.96		35.67[b]	298.17
16	88.52	48.11		31.45[b]	91.55
17	84.31	41.79		27.82[b]	85.28
18	80.10	35.18		23.60[b]	78.84
19	75.92	28.34		18.80[b]	71.58
20	71.01	21.28		13.85	
21	66.12	14.03		08.61[b]	
22	60.50	06.70			
23	55.36	098.26			
24	48.70				
25	43.38				

a) The line positions listed represent the average of the λ-components and are measured to ± 0.01 cm^{-1} against thorium standards.

b) Blended line.

Table V

Rotational Data for the B $^2\Pi$ -X$^2\Pi$ Transition: in cm^{-1}

(0.4):   B' ~0.610   B" =0.764 $\Delta\lambda$ ~0.3

(0.5):   B' =0.6136   B" =0.7622

calculated for (0.0):

B' = 0.612   D' = 1.4 x 10^{-6} r$_e$' = 1.68 A.

B' = 0.7732   D" = 1.25 α" = 0.0022

Table VI

Summary of Spectroscopic Constants for
the NS Molecule

State		T_o	ω_e	$x_e\omega_e$	B	α	$D_e \times 10^6$	r_e
(D)	$^2\Sigma$	44280						
C	$^2\Sigma$	43385	1401	6.7	0.8267		1.1	1.447
	$^2\Pi_{3/2}$	30190						
B			800	4	0.612		1.4	1.68
	$^2\Pi_{1/2}$	30105						
	$^2\Delta_{5/2}$	39918	942	5.7				
A					0.6960	0.0069	1.5	1.577
	$^2\Delta_{3/2}$	39882	960	8.4				
	$^2\Pi_{3/2}$	223						
X			1219	7.5	0.7736	0.0061	1.3	1.496
	$^2\Pi_{1/2}$	0						

The D values are calculated from Kratzer's relation, $D_e = 4B_e^3/\omega_e^2$
cm^{-1} for all quantities except A for r_e.

Table VII

Ratios of Spectroscopic Constants for NO and NS.

	A $^2\Delta$	B $^2\Pi$	$X^2\Pi$
T_e	1.5	1.5	--
ω_e	1.3	1.3	1.6
r_e	0.84	0.82	0.76
k_e	1.3	1.3	1.9
B_e	1.9	1.9	2.2
$\Pi_{3/2} - \Pi_{1/2}$	--	0.35	0.55

Table VIII

Predicted Data For Not Yet Observed Energy Levels Of NS
(Rydberg States not included)

$$T_e$$

two	$^2\Pi$	~43000 cm^{-1}
two	$^2\Sigma$	~43000
	$^4\Sigma$	~32000
	$^2\phi$	~24000
	$^4\Pi$	~18000