

New band systems of NiBr molecule in visible region

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Abstract. Thermal emission spectrum of NiBr molecule excited by vacuum graphite tube furnace revealed the existence of ten new band sub-systems in the region $\lambda\lambda$ 5540–4720 Å which were attributed to $A \rightarrow X$, $B \rightarrow X$, $C \rightarrow X$ and $D \rightarrow X$ transitions. Vibrational analysis was carried out for each of the systems mentioned above. $A^2\Delta$ has been suggested as the ground state of NiBr molecule with an electronic interval of about 533 cm^{-1} . Transitions responsible for NiBr spectrum appear to be of the type ${}^2\Pi - {}^3\Delta$ and ${}^3\Delta - {}^3\Delta$.

Keywords. Thermal emission; molecular spectra; spectra of inorganic diatomic molecule; transition elements.

1. Introduction

The early study of the emission spectrum of nickel bromide was made by Mesnage (1939) using high frequency discharge technique and later by Krishnamurty (1952) using heavy current discharge. Reddy and Rao (1960) photographed 62 emission bands in discharge in the region $\lambda\lambda$ 4700–4050 Å and classified them into six systems. Sundarachary (1962) obtained few additional bands in the region $\lambda\lambda$ 4525–4050 Å and tried to reassign them into four groups.

The previous workers had photographed the emission spectrum excited by various discharge techniques and were consequently confronted with a large number of atomic lines which had made the measurement and identification of bands quite uncertain. The molecular constants even for the ground state reported by them were not consistent. In thermal emission the chances of involvement of ground state are higher and the spectrum is almost free from atomic lines. It was therefore decided to examine the thermal emission spectrum of NiBr molecule.

2. Experimental

The vacuum graphite tube furnace of this laboratory was used for these studies. A small quantity of anhydrous nickel bromide (B.D.H.) mixed with spec-pure nickel powder (Johnson Mathey) was placed inside the graphite tube of 10 cm length and internal diameter of 8 mm. After making necessary routine adjustments and evacuation of the furnace chamber nitrogen gas was introduced at a pressure of 45 cm of mercury. The most favourable temperature for the proper development of bands

was found to be about 2300°C and an exposure time of 10 min. was sufficient to photograph the spectrum. These bands failed to appear when nickel powder was vapourised under the same conditions. The spectra were photographed on Ilford R-40 and HP-3 panchromatic plates with a Hilger E-492 large quartz spectrograph. Copper arc spectrum served as the comparison standard. The measurements were made on C.Z. Abbe comparator with a least count of 0.0001 mm.

3. Results

Thermal emission spectrum of NiBr molecule lying in the region $\lambda\lambda$ 5540-4720 Å has been obtained for the first time and is reproduced in figure 1. A total of 128 bands have been photographed and analysed into ten new sub-systems. All the bands are red-degraded and line-like in structure. It was found that all the prominent bands reported by earlier workers also appeared on the plate along with these new band systems. A few additional bands lying at about λ 4720 Å have been recorded and tentatively attributed to the systems *E* and *F*. The spectrum is almost free from atomic lines of nickel. Following are the vibrational assignments proposed by the authors for various systems.

3.1 System *A* → *X* ($\lambda\lambda$ 5540-5270 Å)

This system contains 37 single headed bands in all, out of which eleven bands have been attributed to sub-system $A_2 \rightarrow X_2$ and another eleven bands to sub-system $A_1 \rightarrow X_1$. The remaining 15 bands have been assigned to the sub-system $A_2 \rightarrow X_1$. The bands in this system have poor contrast because the graphite tube which becomes incandescent white, emits a continuum in the red region which was difficult to eliminate. The wave numbers and visual estimates of intensities together with assignments have been presented in table 1. Table 2 incorporates the vibrational constants determined for all the three sub-systems.

3.2 System *B* → *X* ($\lambda\lambda$ 5270-5000 Å)

Thirty three single headed bands have been assigned to this system. All these bands have been analysed and fitted into three groups $B_2 \rightarrow X_2$, $B_1 \rightarrow X_1$ and $B_2 \rightarrow X_1$. The relevant band-head data, their classification and visually estimated intensities are listed in table 1. The calculated vibrational constants for all the sub-systems are given in table 2.

3.3 System *C* → *X* ($\lambda\lambda$ 5085-4895 Å)

Out of sixteen single headed bands recorded, 7 have been attributed to $C_2 \rightarrow X_2$ sub-system and the remaining nine bands have been classified in the sub-system $C_1 \rightarrow X_1$. Table 1 contains the wave numbers, their classification and visually estimated intensities. The vibrational constants for the sub-systems are displayed in table 2.

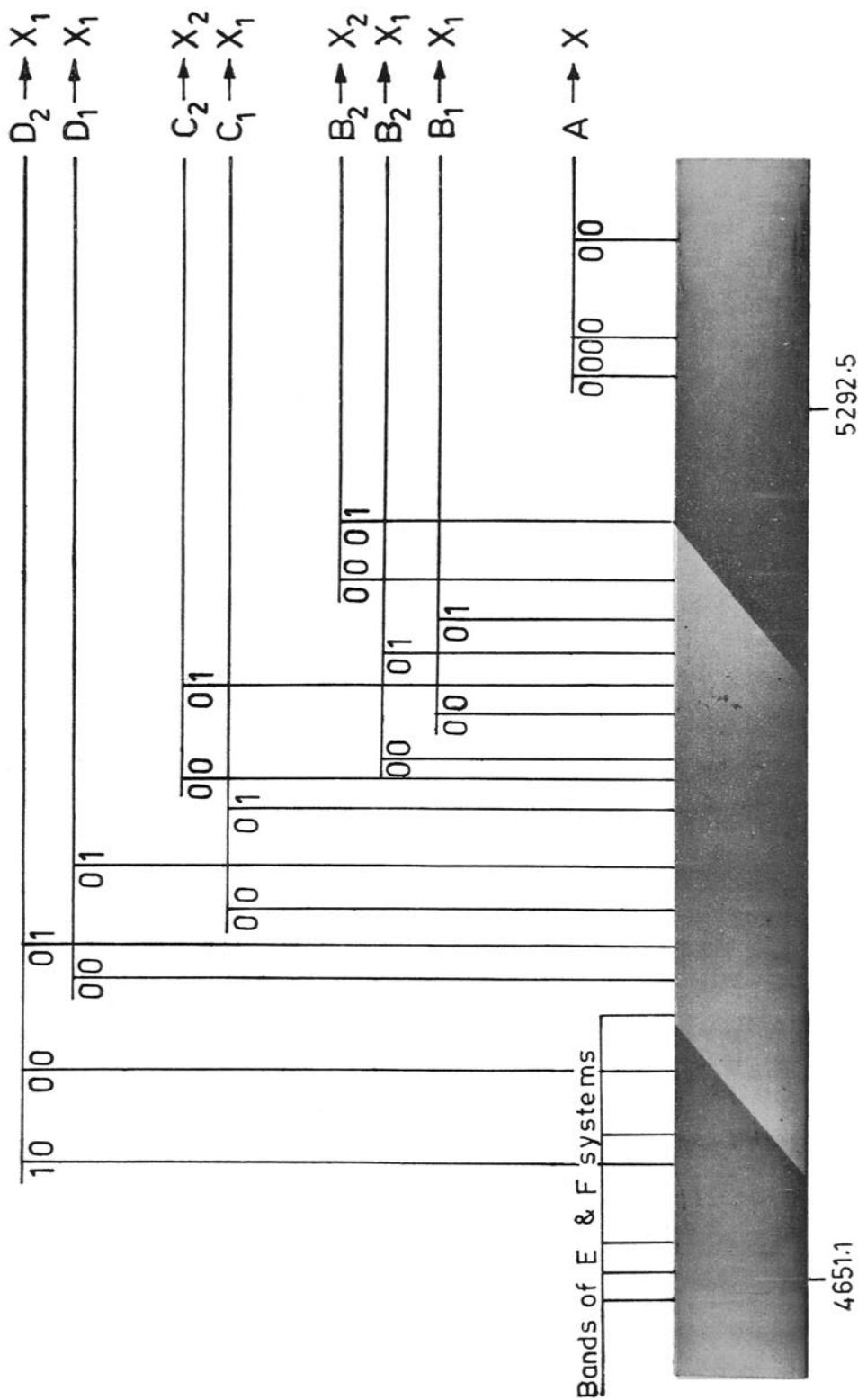


Figure 1. A → X, B → X, C → X and D → X systems of the NiBr molecule in thermal emission.

Table 1. Band head data of the ten new sub-systems of NiBr

$\nu_{\text{vac}} \text{ cm}^{-1}$	Int.	(v', v'')	$\nu_{\text{vac}} \text{ cm}^{-1}$	Int.	$(v' v'')$
<i>System A₂→X₂</i>			<i>System A₁→X₁</i>		
18427	3	1,0	18825	3	1,0
18410	2	2,1	18791	2	2,1
18392	2	3,2	18753	1	3,2
18374	1	4,3	18715	1	4,3
18350	1	5,4	18537	3	0,0
18132	3	0,0	18505	3	1,1
18119	3	1,1	18471	2	2,2
18104	2	2,2	18438	1	3,3
18088	2	3,3	18216	2	0,1
18071	1	4,4	18188	1	1,2
18051	1	5,5	18156	1	2,3
<i>System A₂→X₁</i>			<i>System B₂→X₂</i>		
18960	3	1,0	19445	4	0,0
18929	2	2,1	19421	4	1,1
18897	2	3,2	19398	3	2,2
18865	1	4,3	19368	2	3,3
18831	1	5,4	19340	2	4,4
18665	4	0,0	19308	1	5,5
18640	3	1,1	19269	1	6,6
18612	2	2,2	19136	3	0,1
18584	2	3,3	19116	3	1,2
18552	1	4,4	19093	2	2,3
18344	3	0,1	19068	2	3,4
18322	2	1,2	19043	1	4,5
18296	2	2,3	19009	1	5,6
18268	1	3,4	18978	1	6,7
18240	1	4,5			
<i>System B₁→X₁</i>			<i>System C₁→X₁</i>		
19833	4	0,0	20421	5	0,0
19815	3	1,1	20396	4	1,1
19798	3	2,2	20371	3	2,2
19779	2	3,3	20358	2	3,3
19763	2	4,4	20332	2	4,4
19746	1	5,5	20102	4	0,1
19511	3	0,1	20080	3	1,2
19496	3	1,2	20065	3	2,3
19480	2	2,3	20042	2	3,4
19467	2	3,4			
19453	1	4,5			
<i>System B₂→X₁</i>			<i>System C₂→X₂</i>		
19978	5	0,0	20026	5	0,0
19945	4	1,1	20008	4	1,1
19908	3	2,2	19990	3	2,2
19870	2	3,3	19717	3	0,1
19658	3	0,1	19703	3	1,2
19628	3	1,2	19688	2	2,3
19592	2	2,3	19668	2	3,4
19556	1	3,4			

Table 1. (contd.)

$\nu_{\text{vac}} \text{ cm}^{-1}$	Int.	(ν' , ν'')	$\nu_{\text{vac}} \text{ cm}^{-1}$	Int.	(ν' , ν'')
<i>System D₁ → X₁</i>			<i>System D₂ → X₁</i>		
20651	4	0,0 R	21163	3	1,0 R
20636	5	0,0 Q	21155	3	1,0 Q
20622	3	1,1 R	21127	2	2,1 R
20606	4	1,1 Q	21116	2	2,1 Q
20590	3	2,2 R	21088	1	3,2 R
20575	3	2,2 Q	21081	2	3,2 Q
20558	2	3,3 R	20875	5	0,0 R
20540	3	3,3 Q	20865	6	0,0 Q
20332	3	0,1 R	20843	4	1,1 R
20316	4	0,1 Q	20833	5	1,1 Q
20304	3	1,2 R	20811	3	2,2 R
20287	3	1,2 Q	20799	3	2,2 Q
20272	2	2,3 R	20775	2	3,3 R
20257	3	2,3 Q	20762	2	3,3 Q
20243	2	3,4 R	20554	3	0,1 R
20228	2	3,4 Q	20543	4	0,1 Q
20213	2	4,5 R	20527	2	1,2 R
20199	2	4,5 Q	20517	3	1,2 Q
20182	1	5,6 R	20494	2	2,3 R
20166	2	5,6 Q	20481	2	2,3 Q
			20460	1	3,4 R
			20447	2	3,4 Q

Table 2. Vibrational constants determined for various band systems of NiBr

System	$\nu_{0,0}$ in cm^{-1}	ω'_e	$\omega'_e x'_e$	ω''_e	$\omega''_e x''_e$
$A_2 \rightarrow X_2$	18132	299.0	2.00	310.0	1.20
$A_2 \rightarrow X_1$	18665	299.0	2.00	322.8	1.10
$A_1 \rightarrow X_1$	18537	293.0	2.00	322.8	1.10
$B_2 \rightarrow X_2$	19445	290.0	2.50	310.0	1.20
$B_2 \rightarrow X_1$	19978	290.5	2.40	322.5	1.20
$B_1 \rightarrow X_1$	19833	305.0	1.00	322.8	1.10
$C_2 \rightarrow X_2$	20026	296.0	2.50	310.0	1.20
$C_1 \rightarrow X_1$	20421	300.0	1.50	322.8	1.10
$D_2 \rightarrow X_1$	20875/65	293.5	2.25	322.8	1.10
$D_1 \rightarrow X_1$	20651/36	293.0	1.50	322.8	1.10

3.4 System $D \rightarrow X$ ($\lambda\lambda 4960\text{-}4720\text{\AA}$)

This system comprises of 21 double-headed bands interpreted as *R* and *Q*. The *Q* heads are found to be stronger than *R* heads. All these bands have been fitted into two groups $D_1 \rightarrow X_1$ and $D_2 \rightarrow X_1$. It cannot be said unambiguously that D_1 and D_2 are the components of the same upper state. The band head data, visual estimates of the intensities and quantum assignments have been incorporated in table 1. The vibrational constants determined by the authors for all these sub-systems are presented in table 2.

4. Discussion

The vibrational frequencies for the ground state components X_1 and X_2 evaluated in the present study are 322.8 cm^{-1} and 310.0 cm^{-1} respectively. The values for the two low lying states of NiBr suggested by Reddy and Rao (1960) are 322.8 and 311.6 cm^{-1} , and 322.82 and 309.5 cm^{-1} as suggested by Sundarachary (1962). Thus the vibrational frequencies of the ground state components for NiBr molecule determined by the present authors and previous workers are in close agreement. The new bands obtained from thermal emission and arranged in the ten sub-systems referred to above have therefore rightly been assigned to the diatomic NiBr.

The rotational studies of NiH molecule by Heimer (1934), Gaydon and Pearse (1935) and Andersen *et al* (1963) reveal that the ground state of NiH is a $^2\Delta$. Rao and Rao (1969) had suggested on the basis of rotational analyses that the ground state for NiCl molecule to be a $^2\Delta$. Recently Gopal (1978) had studied the thermal emission spectra of NiF and suggested that the electronic term for the ground state is also a $^2\Delta$ arising from an electronic configuration $(u\delta)(t\sigma)^2$. Therefore a $^2\Delta$ may also be accepted as the ground state for NiBr molecule. And the probable electronic transitions responsible for NiBr spectrum for the systems would be $^2\Pi-^2\Delta$, $^2\Delta-^2\Delta$ and $^2\Phi-^2\Delta$.

In the systems $A \rightarrow X$, $B \rightarrow X$ and $C \rightarrow X$ only a single-headed bands have been recorded, which appear to be the R heads. Therefore the excited states A , B and C may be a $^2\Delta$. In the system $D \rightarrow X$, the Q heads were found to be stronger than the R heads. One would therefore be justified to attribute it to a $^2\Pi-^2\Delta$ transition. The intensity consideration of $D_2 \rightarrow X_1$ and $D_1 \rightarrow X_1$ reveals that D_1 and D_2 may not necessarily be the components of the same upper state. However in the absence of rotational analyses or any other evidence, the excited states of all these systems could not be decided unambiguously. The bands are in general diffused which may presumably be due to bromine isotopes.

The present investigations reveal the presence of two pairs of band sub-systems $A_2 \rightarrow X_1$ and $A_2 \rightarrow X_2$ and $B_2 \rightarrow X_1$ and $B_2 \rightarrow X_2$ in which an electronic interval of about 533 cm^{-1} exists for each pair. The vibrational frequency of the components of the excited states involved in the different pairs is nearly the same. This leads to suggest that an electronic interval of about 533 cm^{-1} is associated with the two components of the $^2\Delta$ ground state. Moreover, our extensive study of NiF and NiCl molecules under thermal emission by Gopal (1978) shows that there exists an electronic separation of 370 cm^{-1} and 484 cm^{-1} for the ground state $^2\Delta$ of NiF and NiCl respectively. Hence an electronic separation of about 533 cm^{-1} attributed to the ground state $^2\Delta$ of NiBr is quite justified.

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