

LETTERS TO THE EDITOR

NEW BAND SYSTEMS OF THE NiF MOLECULE

R. GOPAL AND M. M. JOSHI

Department of Physics
University of Allahabad
Allahabad 211 002, India

A SURVEY of existing literature reveals that the spectroscopic information about the NiF molecule is inadequate. Krishnamurty¹ recorded four groups of thirteen diffused bands in the region $\lambda\lambda$ 4860-4518 Å and attributed them to NiF. However rotational analysis of two of these bands by Pinchemel *et al.*² reveals that the bands belong to a transition of the type ${}^2\Pi-{}^2\Delta$ or ${}^2\Delta-{}^2\Pi$. The present investigations have been carried out with a view to have more detailed spectroscopic information regarding the NiF molecule using thermal excitation technique.

A small quantity of anhydrous nickel fluoride of high purity mixed with spectro-pure nickel metal powder kept in graphite tube of high temperature vacuum furnace was heated electrically at about 2300°C in the atmosphere of argon at about 60 torr. Exposure of about six minutes was found sufficient to obtain good spectrogram on Ilford HP-3 plates using Hilger E-492 large quartz spectrograph. Measurements were done on C. Z. Abbe comparator with a least count 0.0001 mm.

Thermal emission spectrum of the NiF molecule has been recorded for the first time in the region $\lambda\lambda$ 5125-4650 Å. A total of 88 bands have been photographed and analysed into six new sub-systems, viz., $A_2 \rightarrow X_2$, $A_1 \rightarrow X_1$, $B \rightarrow X_1$, $B \rightarrow X_2$, $C \rightarrow X_1$ and $C \rightarrow X_2$. All the prominent bands reported by previous workers^{1,2} have also appeared on the plate in addition to present bands. The systems $A \rightarrow X$ and $C \rightarrow X$ consist of 22 and 26 red degraded bands respectively, in which Q heads have been found to be stronger than the R heads. In the system $B \rightarrow X$, forty violet degraded bands have been classified and the B heads have been found to be stronger than the Q heads. The vibrational frequency for the ground state determined by the authors is in close agreement with that suggested by Krishnamurty¹. The vibrational constants for the various electronic states of the NiF determined by the authors have been incorporated in Table I.

Gaydon and Pearse³ and Anderson *et al.*⁴ on the basis of rotational studies have established that the

TABLE I

Vibrational constants of various electronic states of NiF

State	T_0 , cm ⁻¹	ω_0	$\omega_0 x_0$	Deg.
C	20681	705.5	5.25	R } V
B	20340	766.0	1.50	
A_2	20006	701.0	3.25	
A_1	19930	704.5	3.25	P
X_2	370	738.5	2.25	
X_1	0	738.5	2.25	

ground state of the NiH is a ${}^2\Delta$. Pinchemel *et al.*² on the basis of rotational analyses have proposed that the transition responsible for the NiF spectrum is either a ${}^2\Pi-{}^2\Delta$ or a ${}^2\Delta-{}^2\Pi$ while Rao and Rao⁵ on similar basis have suggested that the ground state of the NiCl is a ${}^2\Delta$. Therefore it is quite reasonable to assume that the ground state of the NiF is a ${}^2\Delta$ and transitions responsible for NiF spectra are ${}^2\Phi-{}^2\Delta$, ${}^2\Delta-{}^2\Delta$ and ${}^2\Pi-{}^2\Delta$.

It has been found that in the systems $A \rightarrow X$ and $C \rightarrow X$, the Q heads are stronger than the R heads, which is expected in a ${}^2\Pi-{}^2\Delta$ transition. Hence these systems may be attributed to a ${}^2\Pi \rightarrow {}^2\Delta$ transition. It is well known that in ${}^2\Delta \rightarrow {}^2\Delta$ and ${}^2\Phi \rightarrow {}^2\Delta$ transitions the Q heads are expected to be weak and the same has been observed in $B \rightarrow X$ system. Thus the excited state of the $B \rightarrow X$ system is either a ${}^2\Phi$ or a ${}^2\Delta$. Since the transitions involving ${}^2\Phi$ state have scarcely been observed, the probability of upper state being a ${}^2\Delta$ is higher. However in the absence of rotational analyses the excited states of these systems could not be decided unambiguously.

According to present analyses, there are two pairs of band subsystems, viz., $B \rightarrow X_1$ and $B \rightarrow X_2$ and $C \rightarrow X_1$ and $C \rightarrow X_2$ in which an electronic interval of about 370 cm⁻¹ exists for each of them. Since the upper state vibrational frequencies in each pair are almost the same, one may associate the separation 370 cm⁻¹ with common lower state components identified as the ground state ${}^2\Delta$. In case of NiCl and NiBr molecules Gopal⁶ has found that an electronic separation of 484 cm⁻¹ and 533 cm⁻¹ respectively has been associated with their ground state ${}^2\Delta$.

Therefore an electronic separation of 370 cm^{-1} attributed to the ground state ${}^2\Delta$ of the NiF molecule is justified.

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SPECTROPHOTOMETRIC DETERMINATION OF IRON(II) WITH BIACETYL MONOXIME

M. ZARINA AND P. RIYAZUDDIN

Department of Analytical Chemistry
University of Madras
Guindy Campus, Madras 600 025, India

BIACETYL MONOXIME (BAM) has been reported as a photometric reagent for palladium¹, rhenium², molybdenum³, cobalt⁴, copper and nickel⁵. Literature survey shows that this compound has never been used as an analytical reagent for iron. However, as early as 1926, Taylor *et al.*⁶ reported that BAM forms a blue coloured water soluble complex with iron(II) in the presence of dilute sodium hydroxide which can be extracted into benzene and the colouration of the aqueous solution was unstable and completely destroyed on heating. In the course of our investigation we found that sodium hydroxide concentration should be critically maintained and it has a marked effect on the colour, intensity and extractibility of the complex. Thus BAM was not considered as a suitable reagent for iron. However, we found that when sodium hydroxide was replaced with ammonia, or methylamine in the presence of ascorbic acid as an anti-oxidant, a red coloured solution resulted whose intensity increased with rise in temperature. This iron complex could not be extracted into benzene. In this paper the characteristics and properties of iron(II)-BAM complex in the presence of ascorbic acid in ammonia or methylamine medium is described and a sensitive photometric method for determining iron in microgram level is proposed.

Procedure

To an aliquot of the solution containing 50 to 175 μg $(\text{NH}_3)/22$ to 80 μg (methyl amine) of iron(II) was added 2 ml of ascorbic acid (0.1 M) followed by 2.5 ml of BAM solution (0.1 M) and 5 ml of ammonia ($\sim 7\text{M}$) or 3 ml of methyl amine (40%). The solution was heated to 80–85° C for 5–10 min, cooled and the volume made up to 25 ml with distilled water. Absorbance was measured at 505 nm with NH_3 or 510 nm with methyl amine against a reagent blank.

Results and Discussion

A pH study of the complexation of BAM with iron(II) showed that the red complex gives a constant absorbance above pH 9.0 in ammonia or methyl amine medium. Excess of the amine did not effect the intensity of the colour.

The complexation between iron(II) and BAM in ammonia or methyl amine solution is slow and takes about 3 hours to reach equilibrium at room temperature ($27 \pm 1^\circ\text{C}$). The rate of the reaction can be increased by heating. A time-temperature study was made with solution containing 2.5 ml of 0.1 M reagent and 100 μg of iron(II). At various time intervals, the solutions were removed from the water bath, cooled and diluted to 25 ml with water and the absorbance was measured from 325 to 600 nm against water as reference. The results showed that the complex exhibited maximum absorbance at 495–515 nm with ammonia and 510 nm with methylamine after 5 min heating at 80–85° C. The colour produced in the reaction was stable for more than 10 hours. These conditions were therefore chosen for subsequent work. Reagent blanks prepared in a similar way did not show any absorption at 495–515 nm.

During the complexation between BAM and iron(II) which requires ammonia or methylamine, it is probable that the primary step is the reaction between the carbonyl group of BAM and amine resulting in the formation of an 'imine-oxime' compound.

Anti-oxidant

The red colour of the complex diminished in intensity on exposure to air but was stable on adding ascorbic acid. Several anti-oxidants were tested (sodium sulphite, hydroxylamine hydrochloride, hydrazine hydrochloride, sodium nitrite and ascorbic acid). Only ascorbic acid gave reproducible results.

Composition of the complex

The mole ratio method and the method of continuous variation were employed to determine the composition of the complex. These two methods showed conclusively that the complex contained one atom of iron to two molecules of the reagent. However, for complete complexation 5 and 10 fold excess of BAM is required in the methylamine and ammoniacal media respectively.