

Thermal emission spectra of the NiF molecule in the region $\lambda\lambda$ 4500 – 4850 Å

R Gopal, K N Uttam and M M Joshi

Physics Department, University of Allahabad, Allahabad-211 002, India

Received 6 February 1990, accepted 21 August 1990

Abstract: Thermal emission spectra of the NiF molecule have been photographed in the wavelength region $\lambda\lambda$ 4500-4850 Å on a reciprocal linear dispersion of 3.5 Å/mm. Out of 60 bands recorded 45 are new ones. These bands have been classified into four systems viz. λ 4518 Å, λ 4675 Å, λ 4700 Å and λ 4550 Å. The vibrational constants have been obtained for the first three systems and the vibrational analysis of the system λ 4518 Å has been confirmed by observed isotopic shift due to nickel.

Keywords: NiF molecule, thermal emission, optical spectra, vibrational constants.

PACS No : 33.20. kf

1. Introduction

The band spectra of NiF molecule was first photographed by Krishnamurty (1953) on low resolution using high frequency discharge in the region $\lambda\lambda$ 4578-4860 Å. He reported three groups of bands, each consisting of 4, 5 and 4 bands lying at λ 4518 Å, λ 4675 Å and λ 4700 Å respectively and assigned all these bands to a single system. Pinchemel *et al* (1979) on the basis of rotational analyses of bands at λ 4518 Å and λ 4700 Å attributed them to the $^3\Pi-^3\Delta$ transition. Later Pinchemel (1981), on the basis of rotational analysis, suggested that the band λ 4675 Å belongs to the transition $^3\Pi-^3\Sigma^+$ and the ground state of NiF is $^3\Sigma^+$. Gopal and coworkers (Gopal and Joshi 1981, Gopal *et al* 1981) have studied thermal emission spectra of NiF at low resolution and obtained 4 and 5 new sub-systems in the regions $\lambda\lambda$ 4650-5125 Å and $\lambda\lambda$ 4100-4430 Å respectively. Recently Bai and Hilborn (1986) on the basis of L. I. F. studies suggested that the ground state of NiF molecule is $^3\Delta$.

Present investigations have been carried out with a view to have more detailed spectroscopic information regarding the NiF molecule using thermal emission technique.

2. Experimental

A small quantity of anhydrous nickel fluoride (Alfa-Ventron) mixed with spec-pure nickel metal powder kept in experimental tube of Saha's high temperature furnace (Saha et al 1927) was heated electrically at about 2400°C in an atmosphere of argon at about 60 torr. Exposure of about 5 and 10 minutes was found sufficient to record good spectrogram on ORWO-400 ASA film on a Carl Zeiss Ebert Plane Grating Spectrograph PGS-2 with grating blazed at λ 5600 Å and total lines 45600 on a reciprocal linear dispersion of about 7 Å/mm and 3.5 Å/mm respectively. Spectrum of Cu was used for comparison. Measurements were done on Carl Zeiss Abbe comparator with a least count of 0.0001 mm.

3. Results

Thermal emission spectrum of NiF molecule has been reproduced in Figure 1. While intense part of the spectrum lies in the region $\lambda\lambda$ 4500-4700 Å, a group

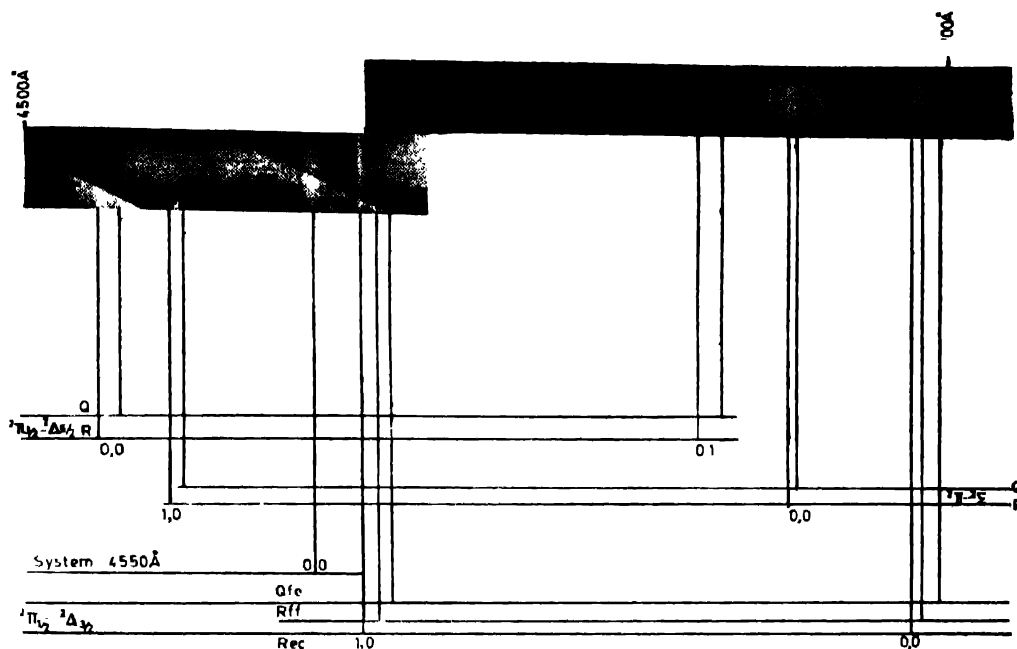


Figure 1. Thermal emission spectrum of the NiF molecule in the region $\lambda\lambda$ 4500-4700 Å.

of weaker bands also lies on $\lambda\lambda$ 4841 Å. Following are vibrational analyses suggested by the authors :

3.1. System λ 4518 Å (${}^2\Pi_{3/2} - {}^2\Delta_{5/2}$ transition) :

Two groups of bands lying at λ 4518 Å and λ 4662 Å consisting of 15 and 13 bands have been classified as $\Delta v = 0$ and $\Delta v = -1$ sequences respectively. The

bands are red degraded and Q heads are found to be stronger than the R heads. Isotopic shift due to nickel observed in case of 7 bands of $\Delta v = -1$ sequence justify our analysis. Out of these 28 bands 22 are new ones. The vibrational constants obtained for this system are as follows :

$$\nu_{0,0} = \begin{matrix} 22141 \text{ R} \\ 22125 \text{ Q} \end{matrix} \text{ cm}^{-1}, \omega_e'' = 692.98, \omega_e'x_e'' = -3.99, \omega_e' = 696.20$$

$$\text{and } \omega_e'x_e' = 3.85.$$

Table 1 is the collection of the band head data, visual estimates of intensities and

Table 1. Band-head data for the system λ 4518 Å.

ν_{obs}	ν_{int} in cm^{-1}	Int.	(v', v'')	ν_{obs}	ν_{cal} in cm^{-1}	Int.	(v', v'')
22125.5	22125.0	7	0, 0 Q*	21491.0	21491.3	3	3, 4 R
22128.5	22128.5	6	1, 1 Q*	21493.9		1	3, 4 R ¹
22132.0	22132.3	4	2, 2 Q*	21504.0	21503.6	2	4, 5 R
22141.0	22141.0	6	0, 0 R*	21506.7		1	4, 5 R ¹
22144.5	22144.5	5	1, 1 R*	21517.0	21516.2	2	5, 6 R
22148.2	22148.3	4	2, 2 R*	21519.6		1	5, 6 R ¹
22152.0	22152.4	4	3, 3 R	21529.8	21529.1	2	6, 7 R
22157.0	22156.7	3	4, 4 R	21543.2	21542.3	2	7, 8 R
22161.6	22161.2	3	5, 5 R	21556.0	21555.7	1	8, 9 R
22166.6	22166.2	3	6, 6 R	21570.0	21569.4	1	9, 10 R
22171.5	22171.4	2	7, 7 R	21584.3	21583.4	1	10, 11 R
22176.5	22176.9	2	8, 8 R				
22181.9	22182.6	2	9, 9 R				
22187.7	22188.6	1	10, 10 R				
22193.0	22194.9	1	11, 11 R				
				Nickel Isotope Effect			
				v', v''	$\Delta\nu_{\text{cal}}$ in cm^{-1}		$\Delta\nu_{\text{obs}}$ in cm^{-1}
21440.7	21440.0	5	0, 1 Q	0, 1 Q	2.95		3.3
21444.0		2	0, 1 Q ¹	0, 1 R	2.95		3.4
21451.5	21451.5	4	1, 2 Q	1, 2 R	2.90		3.1
21456.0	21456.0	4	0, 1 R	2, 3 R	2.84		3.0
21459.4		2	0, 1 R ¹	3, 4 R	2.78		2.9
21467.2	21467.5	3	1, 2 R	4, 5 R	2.73		2.7
21470.3		2	1, 2 R ¹	5, 6 R	2.68		2.6
21479.0	21479.3	3	2, 3 R				
21482		2	2, 3 R ¹				

¹Denotes bands due to $^{60}\text{Ni } ^{19}\text{F}$ molecule.

*Bands reported by Pinchemel et al (1979).

their classifications. A comparison of isotopic shift with those of calculated is also shown in Table 1.

3.2. System λ 4700 Å (${}^2\Pi_{1/2} - {}^2\Delta_{5/2}$ transition) :

Three groups of 12 bands lying at about λ 4557 Å, λ 4700 Å and λ 4841 Å have been analysed as $\Delta v = +1, 0$ and -1 sequences of the system. It includes 6 band heads lying at λ 4700 Å attributed to $\Delta v = 0$ sequence by Pinchemel et al (1979). In this case also the Q heads are found to be stronger than the R heads. The vibrational constants for the system are as below,

$$\nu_{0,0} = 21288.2 \text{ R}_{rr} \text{ cm}^{-1}, \Delta G''_{1/2} = 644.7 \text{ cm}^{-1} \text{ and } \Delta G'_{1/2} = 642 \text{ cm}^{-1}.$$

$$\begin{matrix} 21294.5 \text{ R}_{ee} \\ 21274.7 \text{ Q}_{re} \end{matrix}$$

Table 2 displays the band head data along with visual estimates of their intensities and classifications.

Table 2. Band-head data.

ν_{obs}	ν_{cal} in cm^{-1}	Int.	(v', v'')	ν_{cal} in cm^{-1}	Int.	(v', v'')	
System 4700 Å				System 4675 Å			
20630.0	20630.0	2	0, 1 Q _{re}	21384.6	21384.6	4 0, 0 Q*	
20643.4	20643.5	1	0, 1 R _{rr}	21388.7	21388.7	6 0, 0 R*	
20650.0	20649.8	1	0, 1 R _{ee} ⊕	21390.4	21390.9	3 1, 1 Q	
21274.7	21274.7	7	0, 0 Q _{re}	21394.5	21395.0	5 1, 1 R	
21288.2	21288.2	5	0, 0 R _{rr} ⊕	21403.0	21403.0	4 2, 2 R	
21294.6	21294.5	5	0, 0 R _{ee} ⊕	21413.1	21412.7	4 3, 3 R	
21273.6	21272.0	6	1, 1 Q _{re} ⊕	21423.5	21423.0	4 4, 4 R	
21286.7	21285.5	4	1, 1 R _{rr} ⊕	21434.2	21436.1	4 5, 5 R	
21291.8	21291.8	4	1, 1 R _{ee}	22073.1	22073.1	1 1, 0 Q	
21916.5	21916.7	2	1, 0 Q _{re}	22077.2	22077.2	2 1, 0 R	
21930.3	21930.2	1	1, 0 R _{rr}				
21936.4	21936.5	1	1, 0 R _{ee}				
				Unclassified bands			
				21935.0		3	
				21943.0		3	
21972.1		6	0, 0	21951.6		2	
21976.7		5	1, 1	21954.0		2	
21980.0		4	2, 2	21985.6		2	
				21995.1		1	

*Bands reported by Pinchemel et al (1979, 1981).

3.3. System λ 4675 Å (${}^2\Pi_{3/2} - {}^2\Sigma^+$ transition) :

A group of 8 strong bands lying at λ 4675 Å has been classified as $\Delta v = 0$ sequence. It includes three bands reported as (0, 1) by Krishnamurty (1953) which later on was classified as $\Delta v = 0$ sequence by Pinchemel (1981). A faint band lying at

λ 4528 Å has been attributed to this system as (1, 0). In this case R heads are found to be stronger than the Q heads. The vibrational constants obtained for the system are as below.

$$\nu_{0,0} = \frac{21388.7 \text{ R}}{21385.0 \text{ Q}} \text{ cm}^{-1} \quad \omega''_e = 691.6, \quad \omega''_e x''_e = 4.7, \quad \omega'_e = 696.2 \quad \text{and} \quad \omega'_e x'_e = 3.85$$

The band head data along with visual estimates of their intensities have been collected in Table 2.

3.4. System λ 4550 Å :

It consists of three strong bands attributed to $\Delta v=0$ sequence along with few weaker bands lying both the sides of these bands and are left unclassified. The band-head data has been mentioned in Table 2.

4. Discussion

The earlier workers on the basis of low resolution studies of NiF spectra, classified the two group of bands lying at λ 4518 Å and λ 4675 Å as $\Delta v=0$ and $\Delta v=-1$ sequences respectively and the vibrational frequency for ground state had been found to be 740 cm^{-1} . Recently Pinchemel (1981) on the basis of rotational analysis reassigned the group of bands lying at λ 4675 Å as $\Delta v=0$ sequence of a new system. A comparison between the vibrational frequencies ω obtained from present vibrational analyses and an approximate value of vibrational frequencies (Herzberg 1950) calculated from the rotational constants B and D using relation $D = \frac{4B^3}{\omega^3}$ has been compiled in Table 3. It is clear from the table that the order of magnitude of ω_e determined from vibrational and rotational data are almost the same for various electronic states. The comparison of ω''_e for NiF, NiCl and NiBr also justify the ground state vibrational frequency of the NiF molecule. This value is also consistent with those observed in the ground state of similar molecules (for example : 640 cm^{-1} in the $X^2\Pi$ state of CuO).

Pinchemel *et al* (1979) on the basis of rotational studies proposed that the transition responsible for the bands λ 4518 Å and λ 4700 Å are $^2\Pi_{3/2} - ^2\Delta_{5/2}$ and $^2\Pi_{1/2} - ^2\Delta_{3/2}$ respectively. Later on Pinchemel (1981) attributed the band λ 4675 Å to $^2\Pi - ^2\Sigma^+$ transition and suggested $^2\Sigma^+$ as the ground state of NiF molecule. Recently Bai and Hilborn (1986) on the basis of L.I.F. study and measurement of decay time of fluorescence of bands λ 4518 Å and λ 4675 Å of NiF molecule proposed that both the bands arise from the same upper state $^2\Pi_{3/2}$ and $^2\Sigma^+$ lies about 740 cm^{-1} above the ground state $^2\Delta_{5/2}$, which is contrary to Pinchemel's suggestion (1981). In present observations authors have found that the first vibrational quanta in the upper state of the two band system λ 4518 Å and

λ 4675 Å are of the same order. Thus authors' observations are in support of Bai and Hilborn's suggestion (Bai and Hilborn 1986).

Table 3. Spectral data of NiF molecule.

State	To in cm^{-1}	B_r	$D_0 \times 10^7$	cm^{-1}	Present ω_e in cm^{-1}
$^1\pi_{3/2}$	22125	0.3792	3.7	768	696
$^3\pi_{1/2}$	21645	0.3772	4.0	733	≈ 646
$^2\Sigma^+$	740	0.38567	4.9	684	691.6
$^2\Delta_{3/2} (X_2)$	370	0.3861	4.6	707	≈ 650
$^2\Delta_{5/2} (X_1)$	0	0.3886	3.5	819	693
Molecule		NiF	NiCl		NiBr
ω_e^a in $\text{cm}^{-1} (X_2)$		650	433.9		310.0
(X_1)		693	427.1		322.7
Doublet separation (ΔX) in cm^{-1}		370	484		533

*An approximate value of calculated from rotational constants (Herzberg 1950).

The rotational studies of NiH reveal that the ground state of NiH molecule is $^2\Delta$ (Huber and Herzberg 1979). Rao and Rao (1969), Darji and Suresh Kumar (1989) and Darji (1989) on the basis of rotational studies found that ground state of NiCl is $^2\Delta$. Considering the analogous case of NiF, in light of above facts, it is reasonable to assume $^2\Delta$ as the ground state of NiF molecule as suggested by Bai and Hilborn (1986).

Acknowledgments

The authors are thankful to late Prof B K Agarwal and Prof S K Kor for their keen interest in this work. RG is also grateful to UGC, New Delhi for the financial support.

References

- Bai J and Hilborn R C 1986 *Chem. Phys. Letters* **128** 133
 Darji A B and Suresh Kumar 1989 *Indian J. Pure Appl. Phys.* (In press)
 Darji A B 1989 *Second IPA/DST Symposium on Lasers and Applications*, (B. H. U., Varanasi) p 197
 Gopal A and Joshi M M 1981 *Curr. Sci.* **50** 530
 Gopal R, Singh L K and Joshi M M 1981 *Indian J. Phys.* **55B** 507
 Herzberg G 1950 *Molecular Spectra and Molecular Structure Vol 1. Spectra of Diatomic Molecules* (New York: Von-Nostrand) p 105
 Huber K P and Herzberg G 1979 *Constants of Diatomic Molecules* (New York: Van Nostrand Reinhold)

Krishnamurty V G 1953 *Indian J. Phys.* 27 354

Pinchemel B, Lefebvre Y and Schamps J 1979 *J. Mol. Spectrosc.* 77 29

Pinchemel B 1981 *J. Phys. B : At. Mol. Phys.* 14 2569

Rao N V K and Rao P T 1969 *Curr. Sci. (Ind.)* 38 589

Saha M N, Sur N K and Majumdar K 1927 *Z. Phys.* 40 648